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*"Photopolymers–Principles,
Processes & Materials"*

NOVEMBER 6-7, 1967
The Nevele Country Club
Ellenville, N. Y.

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"PHOTOPOLYMERS - PRINCIPLES, PROCESSES & MATERIALS"

Regional Technical Conference

Sponsored by

Mid-Hudson Section

Society of Plastics Engineers, Inc.

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TABLE OF CONTENTS

TABLE OF CONTENTS (Cont'd.)

PAGE

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ULTRAVIOLET LIGHT SOURCES FOR PHOTOPOLYMERIZATION

Dr. H. R. Day and E. T. Leppelmeier

Lighting Research Laboratory

General Electric Co.

Cleveland, Ohio

ABSTRACT

A large number of lamp types having significant ultraviolet emission is presently available. The variety of spectral characteristics is great and is increasing. The spectral distribution of the emission from incandescent, gas-discharge, and fluorescent lamps can all be adjusted by varying the lamp construction, by changing the constituents or using various additives, and by altering the operating parameters.

This paper discusses the factors influencing the selection of lamps for ultraviolet photopolymerization, the characteristics of presently available lamps, and the possibility of new lamps with different characteristics. Also ~~discussed~~ ~~will be~~ some non-standard modes of operation which alter the spectral distribution as well as increasing the emitted energy. are also discussed. (AUTHOR modified

Although not available commercially, lamps are described which are being developed to match the spectral sensitivity of several specific reactions.

* * * * *

A plastics engineer who requires an ultraviolet lamp can very well find it much easier to describe the lamp's task in chemical terms than to relate these needs to the technical performance details he finds in the catalogs and to identify the specific lamp type that is best for the job.

The scientist or engineer isn't necessarily most interested in getting a lamp exactly optimized for the job. He simply wants one that emits a lot of radiation, at least some of it in the right place, and he wants it quickly. Often price and cost of operation are not vital factors.

Later, if the process finds regular commercial use, optimization becomes a concern. Selective radiation at effective wavelengths, price, cost of operation, simplicity and reliability all become important.

It is the purpose of this paper to review the kinds of lamps which can serve as sources of ultraviolet energy for photopolymerization, to point out a few good general purpose lamps, discuss the relative effectiveness of some typical lamps for a few typical photosensitive systems, and to indicate some of the things that can be done to optimize a source for a specific reaction.

I should point out that I work in a Lighting Research Laboratory and view this subject through the eyes of a physicist-turned-engineer. I will be speaking about general lamp categories, including some experimental ones that are not yet available. I won't discuss lamp numbers or specific application details, but Mr. Leppelmeier and I will be pleased to answer later questions of an application engineering nature.

The effectiveness of a given lamp for an application in photopolymerization depends largely upon the degree to which the spectral distribution of its emission matches the spectral sensitivity of the polymer system - the energy has to be radiated at the wavelengths where the chemicals like to have it.

To illustrate, consider the Kodak series of photo-resist materials. The Kodak series has been chosen for illustration as a matter of convenience, since these materials are fairly representative and information about their spectral sensitivities is readily available.

Figure 1 shows the curve for Kodak Metal Etch Resist and Kodak Thin Film Resist. It peaks at 400nm and drops to 10% at 330 and 470nm. The sensitivity of other resists, such as fish glue, albumen, chromated colloids, have curves very similar to this one, except that they are sometimes a little broader, reaching a little farther (perhaps 10 or 20nm) on both ends - and shifted slightly to short wavelengths, peaking at 370 or 380.

It is clear that to be effective lamps must have significant radiation in this region, the nearer to the maximum the better - and to be efficient, should have most of their radiation there.

In Figure 2 the curve for Kodak Photo Resist is shown. This one has two peaks, and a hole right where the previously mentioned ones are most sensitive. It wouldn't be surprising if a light source optimized for the other system turned out not to be too good for this one. It is interesting that this hole coincides with the 365 line in which, under certain conditions, mercury radiates most of its energy.

Figure 3 is the curve for Kodak Ortho Resist. The hole is shifted somewhat to the longer wavelengths, just enough to allow the 365 line to be fairly efficient. Also, while the previous ones were down to 10 per cent at 460 or so, this one is still rising, and holds up for another 100nm, clear to 550nm. This is important since it permits selection from a wider variety of lamps - on the other hand, since it extends quite far into the visible, it requires the use of more severely restricted safelights.

Now let's look at the emission spectra of several kinds of lamps. In this series of illustrations of emission spectra, the ordinates are marked in units of relative energy in order to avoid some pitfalls that absolute units always present. However, so that one lamp may be compared to the next, the same nameless units have been used for all the illustrations.

First, one that shouldn't be overlooked is the old reliable incandescent lamp (Figure 4). With the advent of halogen-filled regenerative cycle incandescent lamps it has become possible to operate tungsten filaments at higher temperatures than previously would have been consistent with good lamp life.

You will recall that the Kodak Ortho Resist had its peak sensitivity at 470nm and dropped 10 per cent at 550nm. This illustration does not indicate absolute values but it does illustrate that a really significant part of the radiation of a halogen incandescent lamp is effective in exposing certain photoresists, and because of its simplicity, it shouldn't be overlooked for less demanding applications.

In Figure 5 are shown the curves for some standard Daylight and Blue fluorescent lamps. As with the tungsten, a significant part of their radiation is effective for exposing Kodak Ortho Resist. The mercury lines have been omitted for the sake of clarity.

Figure 6 shows the curves of several fluorescent lamps which were designed especially for UV work. The one labeled "Blacklight" is typical of the emission of the older UV phosphors which are Sr, Ba and/or Mg silicate-lead activated. The other two curves indicate what can be done to optimize a source for a particular application.

Since most photocopy papers have their maximum sensitivity between 350 and 450nm, they fall between the emission of the blacklight phosphor and the blue one in Figure 5. Several "improved" phosphors have been developed recently. They are alkaline earth phosphates activated with divalent europium. The spectral emissions of two of them are represented by the curves labeled "Deep Blue" and "Diazo". To prevent confusion, the mercury lines have been eliminated.

Although fluorescent lamps are relatively very efficient, cool sources, they are sometimes unsuitable because higher power or a more compact source is required.

A well-known source for photopolymerization is the open carbon arc (Figure 7). It is efficient and bright and can be doped to emphasize a number of different areas of the spectrum. The one shown here is cerium cored and has a very nice peak near 390nm.

Figure 8 is a picture of a very common mercury lamp. The discharge is contained in the quartz tube that you see inside the lamp. This tube is surrounded by an atmosphere of inert gas contained by a hard glass outer bulb. One of the purposes of the outer bulb is to insure that the temperature builds up enough to provide adequate mercury pressure when the lamp is used outdoors. For laboratory work under more controlled conditions, it is possible to omit the outer jacket. The lamp on the right has been color corrected by the use of a phosphor on the outer jacket. Although this lamp was designed for the visible, the same kind of thing can be done in the ultraviolet if desired.

Without the outer jacket they look like this (see Figure 9). These are rated at 400 and 750 watts.

Figure 10 is an assortment of some of the mercury lamps now commercially available. They range from 100 watts to 1500 watts. Mercury lamps are often categorized according to their operating pressure. There are roughly four categories. The first is the very low pressure, well below an atmosphere, which are glow discharge lamps. The emission consists of a few sharp lines and they are often low power lamps. The lamps on this slide are all in the next range, from 2 to 8 atmospheres.

Figure 11 is a helical mercury lamp, rated at 1550 watts, which is used extensively in the printing industry. It operates at approximately one atmosphere.

Figure 12 is a compact mercury arc which falls in the next range, around 20 to 30 atmospheres.

The high pressure range is 100 to 130 atmospheres. Figure 13 is one of those. This lamp is 3" long and is rated at 900 watts. Its light emitting area is 1.5mm x 25mm.

Figure 14 is the emission from a mercury lamp in the 2 to 8 atmosphere range. The lines are shown as bars as a way to indicate the energy they contain relative to the continuum. Also shown is the effect of the transmission of the envelope material.

A number of tricks are available to the lamp designer to modify the spectral distribution of a mercury lamp. I call your attention to the principal mercury lines at 365, 406, 435, 546, 578.

One of the tricks is to dope the discharge with other metal vapors (Figure 15). A number of such lamps are on the market. Here is the curve for one of them. Notice that the mercury lines are suppressed and replaced by other major lines at 415, 456, 538 and 589. In this example, the designers were shooting for a better white lamp but it is possible to do the same kind of optimization in the ultraviolet.

It is also possible to alter the emission from standard lamps by non-standard operation.

Figure 16 shows what happens when a mercury lamp is flashed repetitively rather than operated continuously. All the shorter wavelength lines are reduced and the energy appears in the 365 line. This could be very useful if the reaction of interest is sensitive at 365.

As I mentioned earlier, the pressure of the mercury is also a factor.

Figure 17 illustrates the curves for two lamps of about the same power but different pressures. In general, as the pressure increases, the radiation shifts toward longer wavelengths. Notice that below 320nm the lower pressure lamp is a better performer at 750W than the 900W high pressure lamp.

The portion of the spectrum below 300nm can be very important for photopolymerization. The photoresists mentioned earlier are photosensitive materials in which the light produces crosslinking of one kind or another, growing short chains into longer ones. This can be accomplished with low energy photons. One really isn't making the polymers, but rather, crosslinking them. To really make a polymer, it is necessary to break carbon-carbon, or equivalent, bonds. To do this requires something like 100 kilocalories and, therefore, wavelengths of 280nm or less.

Dr. A. N. Wright will describe at this conference his work in surface photopolymerization in which hydrocarbon and other polymers are formed right on the spot by photons. The spectral sensitivity of these reactions is extremely narrow. The one for hexachlorobutadiene for example, is only 20 to 30nm wide, located at approximately 230nm. The one for TFE is probably even narrower.

Looking at this chart, one can see that the medium pressure lamp would be about ten times as effective for the hexachlorobutadiene reaction as would the high pressure lamp.

Here is a 2000-watt xenon lamp (Figure 18).

Figure 19 is a 4000-watt pulsed xenon lamp which is used extensively in the graphic arts industry. Important advantages are its "instant on" operation and accurately controllable exposure.

Figure 20 is the emission from the high pressure xenon which is a very bright compact arc. The curve shape is about the same for linear and pulsed lamps.

A number of questions have been received concerning the usefulness of the new high pressure sodium lamps for photopolymerization (Figure 21).

We have included it here for completeness, but as you can see from the curve (Figure 22), it's a fine visible light source but it does not emit much ultraviolet. As a matter of fact, that's part of the reason it is such a good visible source. It can be very useful for reactions dye-sensitized to visible light. This lamp is also interesting in that its envelope is made from translucent aluminum oxide which can withstand the attack of the high pressure sodium hundreds of times better than quartz. The availability of this new envelope material (which has good ultraviolet transmission) would permit consideration of discharge materials which would be completely incompatible with quartz.

To illustrate how different lamps can be optimum for different systems we have rated the performance of a number of lamps mentioned for exposing the various photo resists (Figure 23). This is how it's done. The effectiveness of a carbon arc is taken as reference and the other sources compared to that. The incremental emission of the source is multiplied by the sensitivity of the material at each wavelength and the product is integrated from 300 to 550nm. The integral is the effectiveness of the source is exposing that material. If the source is more effective than carbon, the exposure time ratio will be less than unity. If it is less effective than carbon, the ratio is greater than unity and a longer exposure is required.

These values are shown in Figure 24 for equal lamp watts for comparison, but it should be kept in mind that the geometries of the sources are quite different. A thousand watts of fluorescent lamps take up more space than a thousand watt arc. Nevertheless, phosphors are often more effective than arcs where an extended source is required or where heat is a serious consideration.

In cases where large areas must be uniformly irradiated, fluorescent lamps are a natural choice. To achieve uniform large area irradiation from concentrated sources requires long throw distances and the inverse square law soon dilutes their efficiency.

In the case of Kodak Ortho Resist, the Diazo, Blue and Daylight fluorescents are about equally effective but a ratio of as high as 5:1 is found for these lamps on other materials.

It is evident that incandescent lamps are less effective but they are also inexpensive and very simple to operate.

All the numbers in Figure 25 are based upon a system which includes 4mm of glass between the source and the material, to account for hold-down plates, lenses, covers, etc. If one would go all out and use an all quartz system, the improvement would range from negligible for the Kodak Metal Etch Resist to 15% improvement for the Kodak Ortho Resist (which extends farthest into the ultraviolet) exposed by a mercury lamp.

The exposure efficiency of mercury sources is affected by lamp operating pressure and envelope material. All-quartz lamps in the 2-8 atmosphere range are from 10 to 35% more effective in exposing these materials than lamps operating at 20 to 30 atmospheres. The lower pressure sources also offer 3 to 4 times the useful life of the medium pressure lamps and are usually less expensive for equal lamp watts. The most efficient mercury source for the 300 to 400nm range is the one at 100 atmospheres. Another advantage is its short warm-up time of 10 seconds and lamp cost is moderate. The penalty for these advantages is a relatively short life of 50 to 300 hours.

Comparing the second line from the top and the second line from the bottom, we see that the use of a hard glass outer jacket reduces speed by 20 to 50%. Offsetting this disadvantage is the longer life - 10 to 20 times longer - that results.

Comparing the bottom two lines we see that present mercury sources with metallic additives can be from 25 to 60% faster than comparable plain mercury lamps. This advantage is partially offset by short life - 1/3 to 1/4 that of plain mercury - and higher cost.

Xenon sources are 2 to 3 times less effective for these materials than equivalent mercury sources, but they do have the advantage of instant starting with no warm-up time.

It is possible to selectively enhance portions of the emission spectra (Figure 26). This slide shows how the energy in part of the Xenon spectrum can be boosted with additives to improve its effectiveness for a certain reaction.

Figure 27 is the curve for a lamp designed to match a reaction with a narrow band at 330nm.

Figure 28 is one for a reaction 20nm wide at 210nm. Of course, it would not be possible to tailor-make special lamps for each customer, but the variety of materials available to the lamp designer is now fairly large and, with aluminum oxide and other new envelope materials being developed, many new discharge media can be considered. As new photochemical processes become commercially important, chances are excellent that new lamps can be developed to optimumly satisfy their requirements.

LIGHTS

In summary:

1. Fluorescent lamps are very efficient sources of ultraviolet light and produce a minimum of heat. They are useful where extended sources of medium power are required but are restricted to wavelengths longer than 300nm.

2. Xenon and mercury compact arcs have high brightness and approximate point sources. Xenon systems are considerably more expensive than mercury but have the advantage of instant starting.

3. High pressure mercury capillary lamps are the most efficient emitters of ultraviolet energy between 300 and 400nm. They are

compact and can be apertured to approximate point sources. They have medium cost but relatively short life. Their start-up time is ten seconds or less; faster than other mercury lamps.

4. Low and medium pressure mercury arc lamps are convenient, efficient ultraviolet sources which are useful as general purpose photochemical lamps where medium compactness and medium to high power is required. They provide useful radiation at wavelengths longer than 200nm and are the most efficient ones in the 200 to 300nm range.

5. Halogen regenerative cycle tungsten lamps can be used for materials such as Kodak Ortho Resist. While they are less efficient, their simplicity and availability in high wattage compact sizes makes them useful in some applications.

6. And finally - experience teaches us that the spectral characteristics of high intensity discharges may be optimized for specific photopolymerization applications by adjusting doping, pressure, electrical loading, envelope materials, envelope size, pulsing and other parameters.

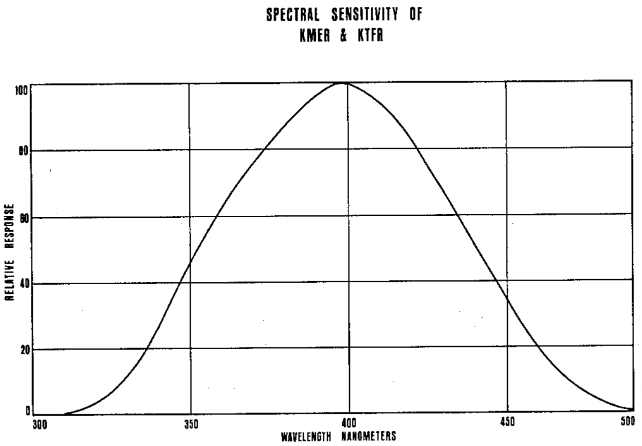
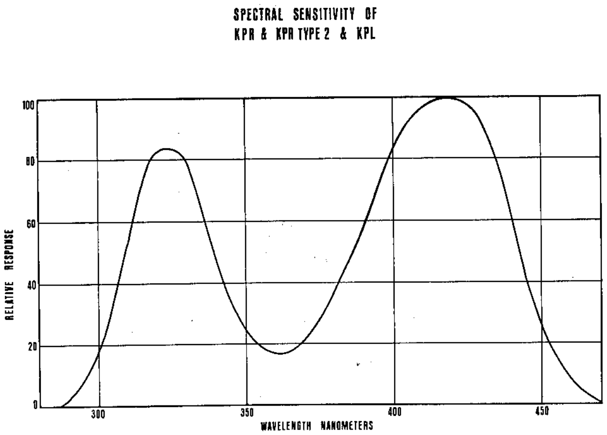


FIGURE 1



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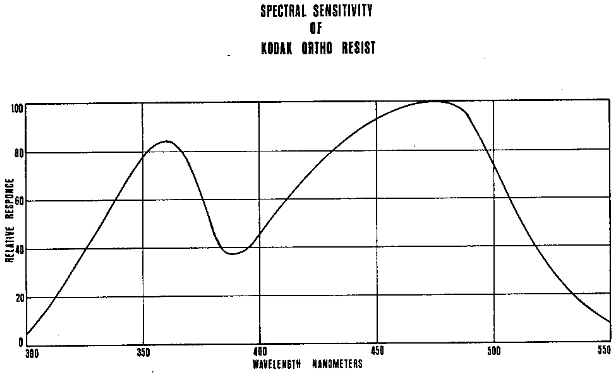

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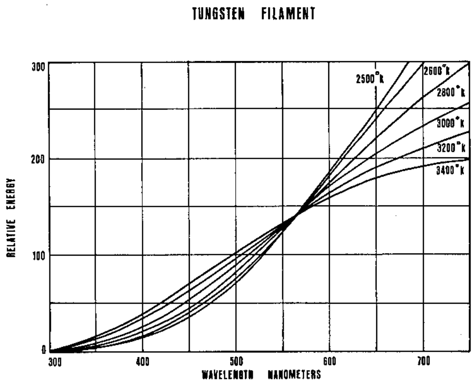

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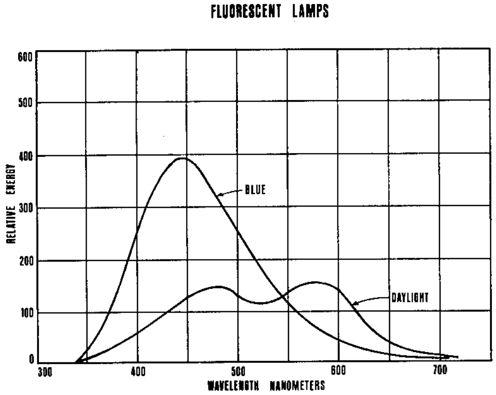

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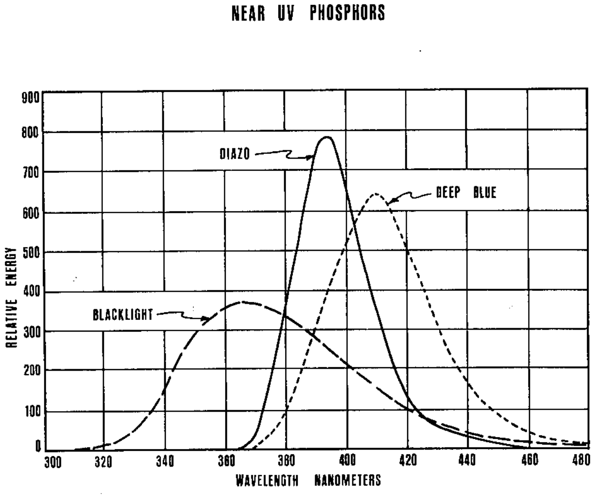

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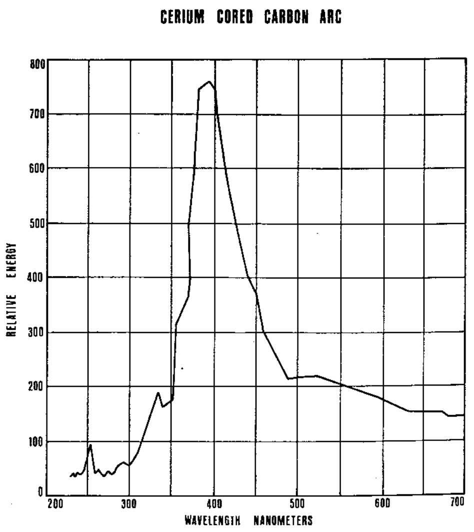

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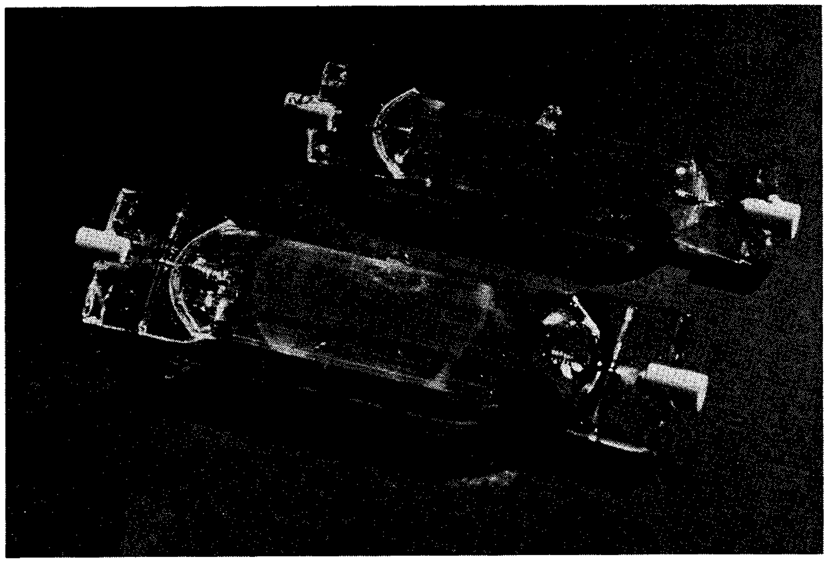

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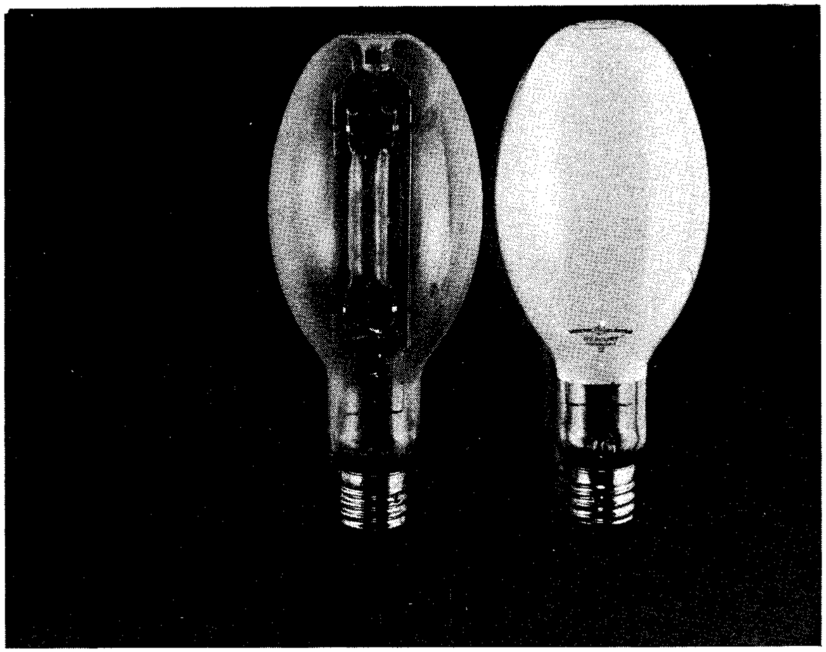

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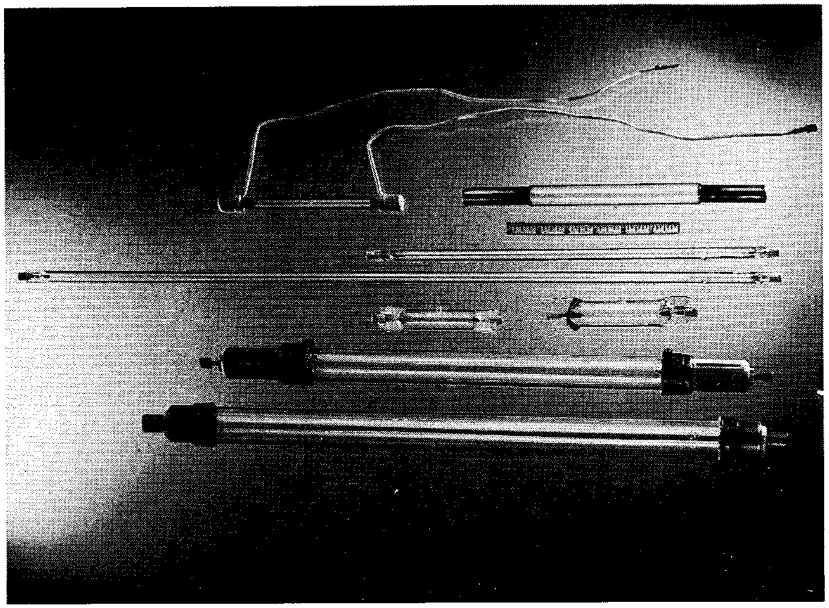

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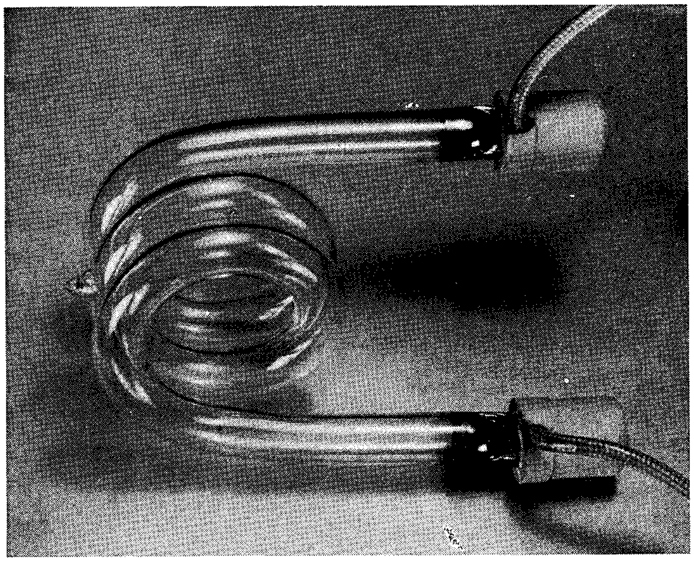

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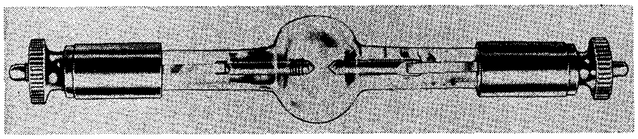

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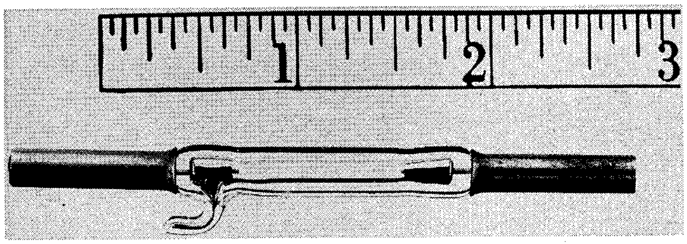

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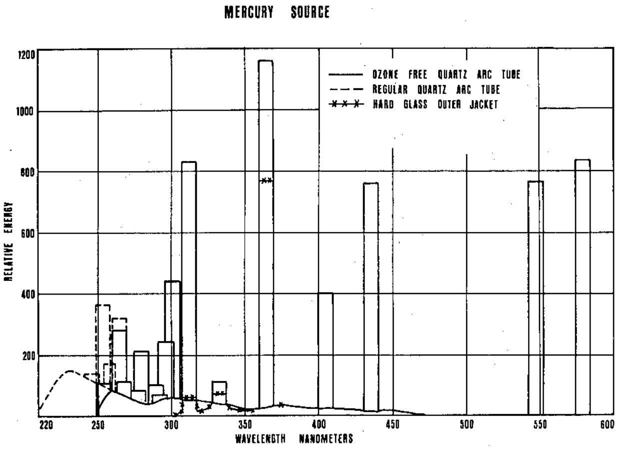

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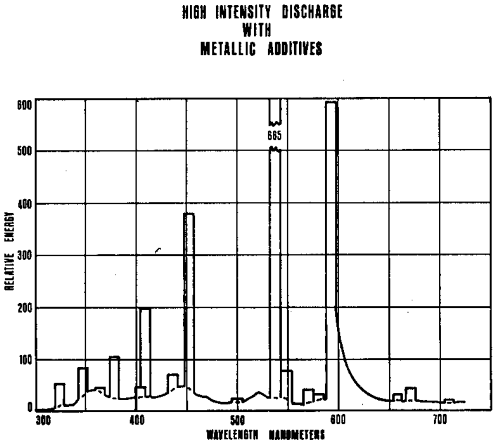

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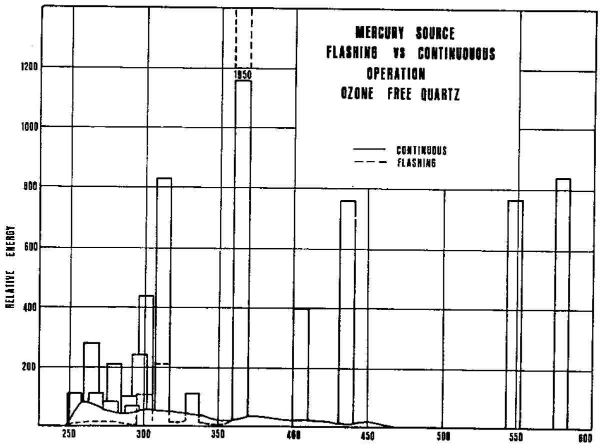

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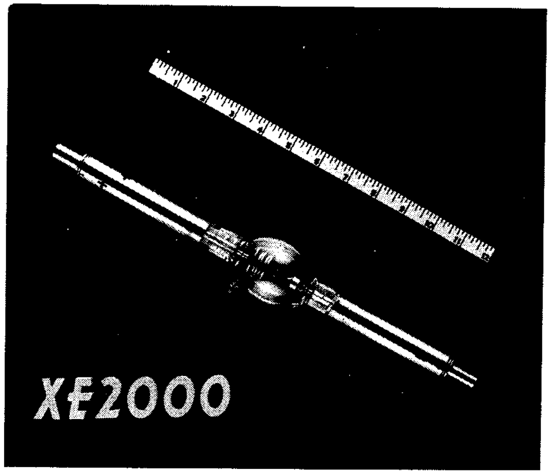

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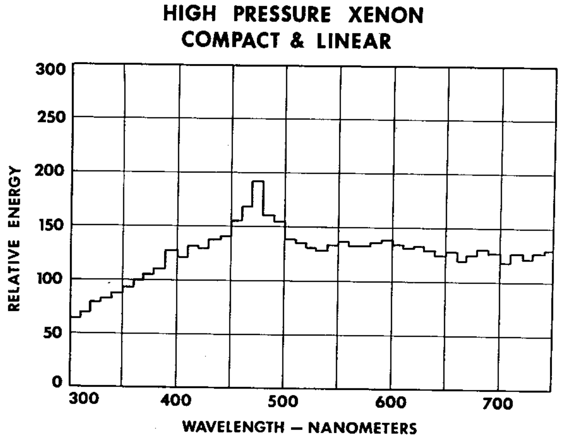

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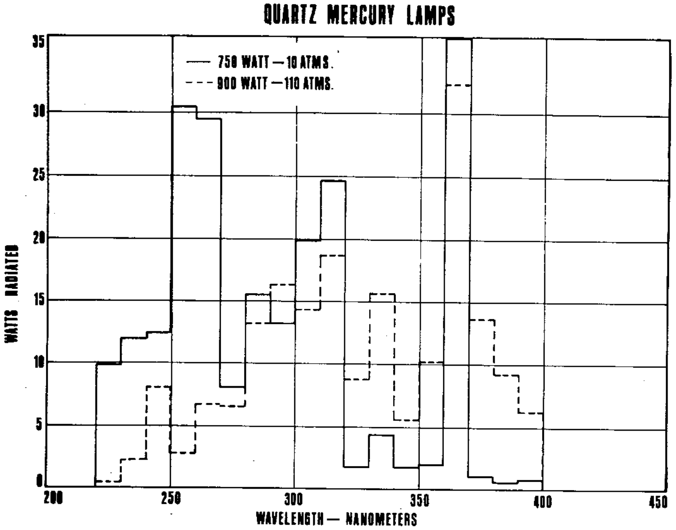

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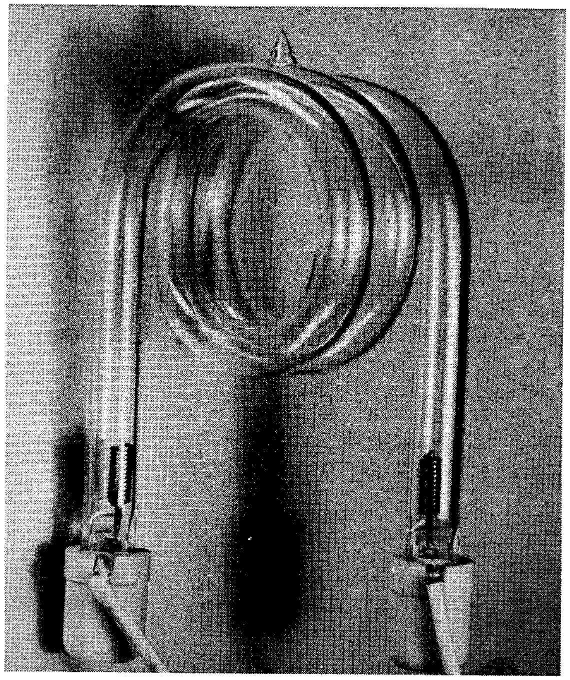

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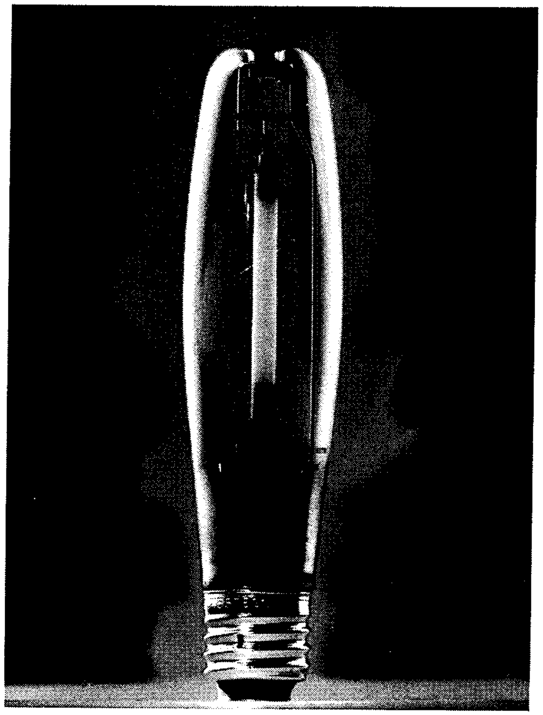

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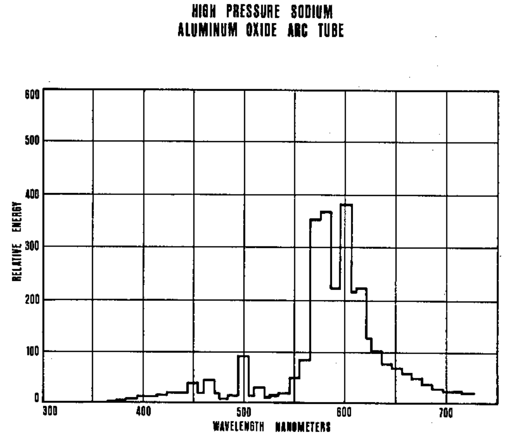

FIGURE 22

$$\text{RELATIVE EXPOSURE} = \frac{\int_{3000\lambda}^{5500\lambda} PR_{\lambda} C_{\lambda} d_{\lambda}}{\int_{3000\lambda}^{5500\lambda} PR_{\lambda} S_{\lambda} d_{\lambda}}$$

PR = PHOTORESIST SENSITIVITY FOR WAVELENGTH λ.

C = CARBON ARC RADIANT ENERGY FOR WAVELENGTH λ.

S = SOURCE RADIANT ENERGY FOR WAVELENGTH λ.

FIGURE 23

RELATIVE EXPOSURE TIMES
(EQUAL LAMPS WATTS)

SOURCE	$(NH_4)_2Cr_2O_7$ IN PVA	KMER KTFR	KPR KPL	KOR
CARBON ARC	1.00	1.00	1.00	1.00
TUNGSTEN – 3200°K	12.30	12.70	12.30	5.20
BLACKLIGHT	.50	.65	.80	.80
DIAZO	.55	.45	.60	1.05
BLUE	1.80	1.50	1.35	1.00
DAYLIGHT	2.45	2.05	1.75	1.10
HI PRESS. Na.	14.90	12.80	12.10	7.80

FIGURE 24

RELATIVE EXPOSURE TIMES
(EQUAL LAMP WATTS)

SOURCE	$(NH_4)_2Cr_2O_7$ IN PVA	KMER KTER	KPR KPL	KOR
CARBON ARC	1.00	1.00	1.00	1.00
QUARTZ MERCURY (2-8 ATMS)	1.00	1.35	1.00	1.20
QUARTZ MERCURY (20-30 ATMS)	1.35	1.60	1.35	1.30
QUARTZ MERCURY (100-130 ATMS)	.60	.70	.60	.60
XENON COMPACT & LINEAR	3.75	2.40	3.90	2.50
FLASHING MERCURY	.90	1.20	1.20	1.15
MERCURY (HARD GLASS) (2-8 ATMS)	1.40	1.60	1.50	1.50
H. I. D. HARD GLASS (METALLIC ADDITIVES)	1.10–1.65	1.15–1.70	1.20–1.80	.95–1.40

FIGURE 25

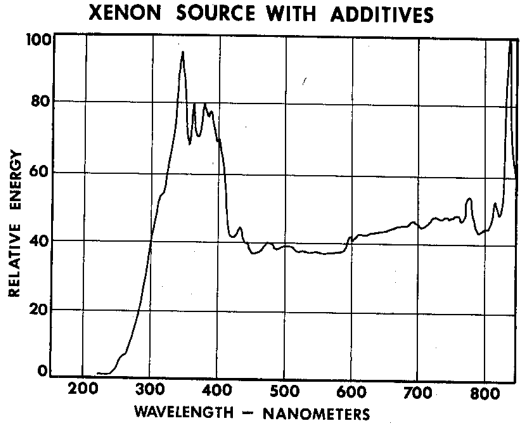

FIGURE 26

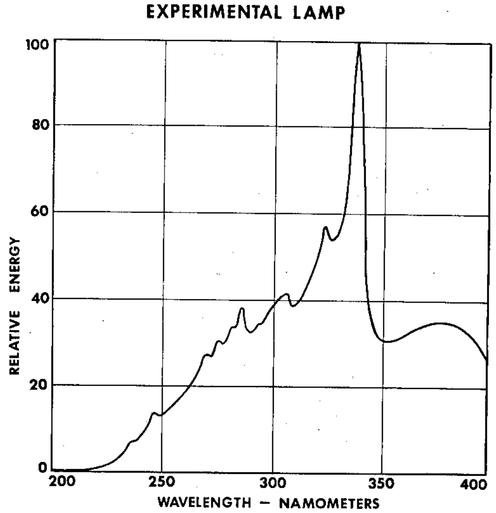

FIGURE 27

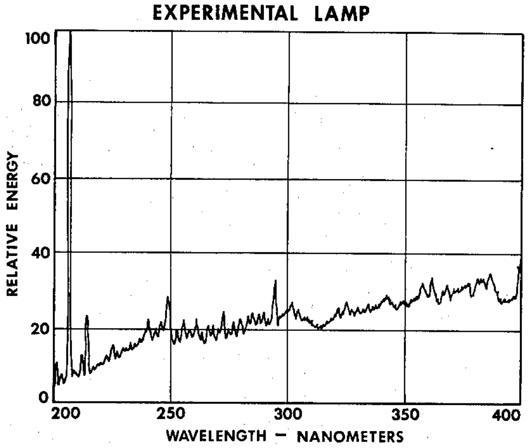

FIGURE 28

RECIPROCITY FAILURE IN FILMS OF FLASH EXPOSED DICHROMATE SENSITIZED POLYVINYL ALCOHOL

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ABSTRACT

The validity of the Bunsen-Roscoe reciprocity law in flash exposed dichromate sensitized polyvinyl alcohol (PVA) films was investigated. It was found that the The flashlamp operating conditions ~~were~~ are an important parameter in an exposure system, since a spectral distribution shift of the lamp output ~~could~~ can be obtained by changing the pulse duration from 0.3 to 2.0 msec. The apparent reciprocity failure obtained by varying the pulse duration while maintaining the energy stored in the capacitor bank fixed ~~was~~ is consistent with the spectral distribution shift in the lamp output. When this shift ~~was~~ is accounted for, there ~~was~~ is only a negligible reciprocity failure found over the range of these flash exposures; ~~however, comparison with a steady~~ mercury arc lamp showed that the flash exposure crosslinked the PVA about 200 times more efficiently.

(1) minor, mod [illegible]

INTRODUCTION

The application of dichromate sensitized polyvinyl alcohol (PVA) as a photoresist material is well known[1] and even though better materials, such as the Kodak photoresists, are now available, this system is still used in some applications. Traditionally, the usual light sources for exposure of resists have been carbon arcs; however, now that other high intensity light sources are available, carbon arcs can be replaced by more reliable and convenient sources such as the xenon flashlamp. This source has the advantage of supplying a large amount of actinic radiation in a single flash; therefore, the exposure of the resist can be accomplished in a fraction of a second rather than several minutes. Since one of the problems encountered with many photographic systems[2] is the failure of reciprocity, at either long or short exposure times, it was thought significant that the effect of flash exposure be investigated. The definition of the reciprocity law used in this work is based on the original law of Bunsen and Roscoe[2] and means that the mass of photoproduct produced is dependent upon the product of the intensity and time, and is independent of these two factors separately. It was not possible to find a reference to any reciprocity study for this system in the published literature; however, in his book on "Light Sensitive Systems",[1] J. Kosar mentions that it is not certain if the dichromated colloids follow the

the reciprocity law. The flash system was operated with values of inductance, capacitance and lamp loading compatible with a long lamp lifetime and a high energy output. The inductance was varied to achieve a desired intensity and to obtain pulse durations between about 0.3 and 2.0 msec.

EXPERIMENTAL

In the usual experimental determination of reciprocity failure,[2] a steady light source is used and the light sensitive material is exposed for an appropriate time yielding the preselected image density. It is possible to vary both the intensity, I, or the time, t, to achieve the same image density. Usually the intensity is increased in steps and the results are plotted as exposure for a predetermined density, i.e., It, versus intensity, I. The reciprocity law is considered to hold when this plot shows a line parallel to the intensity axis and is said to fail when there is a change of slope. With a steady source the shape of the intensity versus time curve is really a step function, but the output from a flashlamp in normal use is close to a Gaussian curve with a small tail. With the flashlamp the total exposure is the area under the curve as before, but the intensity varies with time. Since our objective was to study the effect of a standard flash system, we chose the average intensity, obtained by dividing the area under the curve by the time of the flash at 1/3 peak height, as the appropriate intensity of the flash.

A. Flashlamp System and Output Calibration

The exposure light source was a 3" arc length xenon filled flashlamp (PEK Laboratories, XE16-3) mounted in a box containing a parabolic reflector and a 2" round hole. A schematic circuit diagram of the lamp power supply is shown in Figure 1. The clamping diodes were used to prevent voltage reversal across the capacitors and to limit the radiation output to one pulse. The experiments were usually conducted with 300, 400 or 600 joules of energy stored in the capacitor bank and the variable choke was used to change the pulse duration and the average intensity of the lamp output. The box with the lamp was mounted on an optical bench and an EG&G Lite Mike was used to determine the shape of the relative radiant energy curve as a function of distance from the lamp showing the deviation from the inverse square law at short distances. The relative output of the lamp in the actinic ultraviolet at each choke setting and stored energy was obtained by using an RCA IP28 photomultiplier tube fitted with a Corning 7-54 glass filter (as well as several screens for a neutral density filter). The peak current through the lamp was measured with a Power Designs current proble and the current density was obtained by dividing this current by the area of the flashtube bore. It was found that there was an appreciable spectral distribution shift with a change in pulse duration and current density and some typical results are shown in Table I. The spectral distribution shift towards the ultraviolet[3] results from an increase in the current density through the flashlamp as the pulse duration is changed by adding inductance to the circuit. The calibration curves for the relative total actinic energy radiated as a function of distance from the lamp were obtained by using the Lite Mike derived curves to determine the general shape of the curve at short distances and the filtered photomultiplier results to determine the spacing between the curves.

B. Sample Preparation

The sensitized polyvinyl alcohol samples were prepared fresh for each run. A 5% solution of Baker PVA (99-100% hydrolyzed having an indicated viscosity of 28-32cp at 20°C for a 4% solution) was prepared in quantity and used to make the individual sensitized coating solutions by adding 0.25ml of a 0.2M ammonium dichromate solution for every 5ml of the 5% PVA solution. Microscope slides were dip-coated with the sensitized PVA solution, dried in an oven maintained at 40°C for thirty minutes, and cooled at room temperature (20-21°C) for ten minutes. The age of any of the sensitized solutions did not exceed 90 minutes from the time of preparation until the final use of the dried slide. The dried coating resulting from this preparation procedure was about 1.8μ thick in the useful area of the slide.

C. Exposure Procedure

For exposure, the coated slides were contacted to a test pattern formed on a suprasil quartz square with a Corning 7-54 filter between the flashlamp and the test pattern and mounted on the optical bench in alignment with the flashlamp as shown on Figure 2. The useful radiation actually received by the resist sample can be seen from Figure 3, which contains the absorption curve of sensitized PVA obtained from Duncalf and Dunn,[4] a typical flashlamp output[3] and the transmission of the 7-54 filter.

A series of coated slides were exposed at each fixed total stored energy and at each inductor setting by varying the lamp to PVA coated slide distance in centimeter steps. The series of slides at different distances from the lamp at fixed energy and fixed inductance produced a set of images that progressed from no image to an obviously overexposed image. For a fixed stored energy the total relative energy delivered to the sample at each distance and inductor setting could be obtained by using the Lite Mike derived calibration curve adjusted for the output variation expected at the different pulse durations. The relative intensity for this same distance could be obtained by dividing the relative energy by the pulse duration at one-third peak height.

After exposure, the slide was dipped into a beaker of running water maintained at 30°C for a thirty second wash. Immediately after the wash step, the slide was dipped for two seconds into a solution of Rhodamine B dye to stain the remaining PVA and was air dried.

D. Image Evaluation

The images were evaluated to determine the energy needed for exposure to the preselected "density" which was chosen as the image that was just marginally acceptable. The acceptability did not depend on whether the image could be used to produce a useful product such as an etched printing plate, but simply depended upon whether the target was successfully reproduced without being washed away. Ideally, the slide taken one centimeter closer to the lamp had a better image and the slide taken one centimeter further away yielded an image that was starting to be washed away badly. This criterion seemed reasonable since a large difference in image quality was expected between an image that had PVA crosslinked at the glass-PVA interface compared to one at which the crosslinking reaction had not progressed to this interface. The exposed slides were all evaluated on this basis by viewing a series of exposures at different distances for a constant total stored energy and pulse duration. Since this evaluation method depends on a subjective estimate of image quality, all the slides were evaluated independently by two observers. Although there were differences between the two observers, the trends of the results were the same since differences resulted essentially from a different choice of image quality as a basis for decision. About 4-6 series of images were made at each total stored energy and pulse duration at appropriate distances and after evaluation the results were averaged to obtain the distance required to achieve the desired image quality. For a given observer, the distance from the lamp required to achieve the desired image could be reproduced by ± one centimeter which is about ± 7% in total energy delivered to the sample film. The total range of distances needed to cover the results for a given run was only about 8-10 centimeters; therefore, an error of ± one centimeter at each point was quite significant. Nevertheless, the trends of the results were always distinguishable from any random variation in data.

After selecting the appropriate image at each pulse duration for a fixed stored energy, the distance from the lamp could be used to obtain the relative energy and the relative intensity for the exposure by using the calibration curves. For each total stored energy, the intensity and energy required for the desired image at different pulse durations was normalized to the values at the shortest pulse duration (highest intensity) producing a relative comparison of the exposure required for the same image density at various flash intensities and flash energies.

RESULTS AND DISCUSSION

A. Effect of Spectral Distribution Shift

Since the sensitized PVA is ultraviolet sensitive, the spectral distribution shift of the flashlamp output can be an important parameter in an exposure system. For example, on Figure 4 the results of some crosslinking experiments are shown in which the data were obtained without using the Corning 7-54 filter. (The line drawn on the figure only represents a trend and is not meant to be the best line through the points). For the same total stored energy, the intensity and the current density through the flashlamp are both high when the pulse duration is short and at long pulse durations the current density and intensity are low. These results clearly show that the exposure needed with a high current density flash (high radiant intensity) is about a factor of three less than with the lowest current density flash, consistent with the trend expected on the basis of a spectral distribution shift in the lamp output as shown in Table I. The practical importance of this result is that in any flash exposure system designed for ultraviolet sensitive resists, the flashlamp should be operated at the highest current density, assuming reciprocity holds, to achieve the greatest shift of the lamp output into the ultraviolet region of the spectrum. Unfortunately, the lifetime and size of the components of the exposure system are affected at high current densities and a compromise would have to be made.

B. Filtered Flash Results

The results of experiments using the filtered flash are shown on Figure 5. This illustration contains all the results at 300, 400 and 600 Joules stored energy and pulse duration between 0.3 to 2.0 msec obtained by the two observers. There were no discernible trends in the data showing a specific effect of total energy or in the evaluation by the observers; therefore, no such distinction has been made in the data points on the Figure. When the spectral distribution shift of the flashlamp is taken into account by using the 7-54 filter, only a small reciprocity failure seems to occur over the range of these experiments. There is at most only about a 20% difference in exposure required at low intensity compared to a high intensity flash; however, because of the scatter in the points, the data really could indicate that there is a negligible reciprocity failure. These results indicate that if a flash exposure system is desired, there is little need to worry about reciprocity failure effects; however, to take advantage of the spectral distribution shift it is desirable to operate the lamp with intense, short pulses.

C. Tentative Comparison of Steady Source Versus Flashlamp Exposure

No complete attempt has been made to relate these results for flash exposure to exposures with steady sources; however, to establish a general idea of the effectiveness of a steady source compared to the flashlamp a 100 watt S4 General Electric Mercury Arc lamp was used as an exposure source. The experiment was carried out as before at a distance of 30cm from the lamp and it was found that an exposure of 35 sec. was required to produce a good image. Based on this information and the measured relative intensity of the flashlamp versus the mercury lamp, it seems that crosslinking of the polymer occurs about 200 times more efficiently with a flash than with a steady source as indicated by the slope of the line on Figure 5. By analogy with the oxygen sensitive Kodak resists (KPR, KMER, KTER) it may be possible that oxygen affects the dichromate-PVA system at low intensity exposures by removing the reactive intermediates before crosslinking can take place. With either a flash or other very high intensity exposure a large number of intermediates are formed very quickly and some of these may react with the locally present oxygen while the remainder can react to produce crosslinking before any more oxygen can diffuse into this area and remove the active species. This technique could be applicable to all oxygen sensitive resist materials and not just PVA.

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1. Kosar, J., "Light Sensitive Systems", Wiley, New York, 1965, Chapt. 2.
2. Mees, C.E.K. and James, T. H., "The Theory of the Photographic Process, The MacMillan Co., New York, 3rd Ed., 1966, Chapt. 7.
3. Goncz, J. and Newell, P. B., J. Opt. Soc. Am. 56, 87 (1966).
4. Duncalf, B. and Dunn, A.S., J. App. Polymer Sci. 8, 1763 (1964).

TABLE I

SPECTRAL DISTRIBUTION SHIFT OF FLASH OUTPUT

Pulse Duration, msec	Relative Energy (with 7-54 filter)	Current Density (300 J) (PEK XE16-3 lamp), amp/cm^2
0.29	1.00	2800
0.46	0.950	1720
0.76	0.738	1160
0.95	0.703	918
1.35	0.547	714

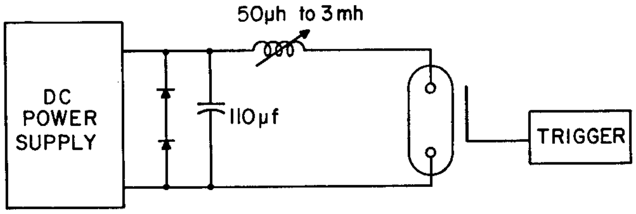

FIGURE 1: Flashlamp discharge circuit

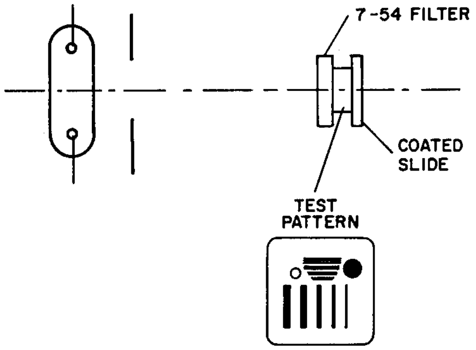

FIGURE 2: Typical exposure arrangement and test pattern design

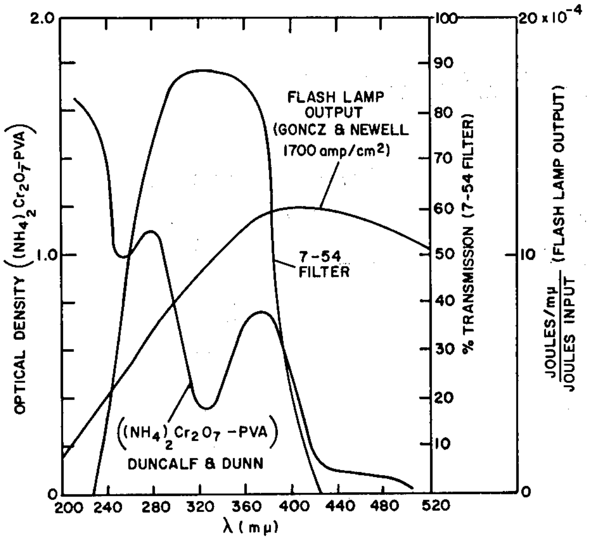

FIGURE 3: Comparison of polyvinyl alcohol-$(NH_4)_2Cr_2O_7$ absorption with the filter transmission and flashlamp output

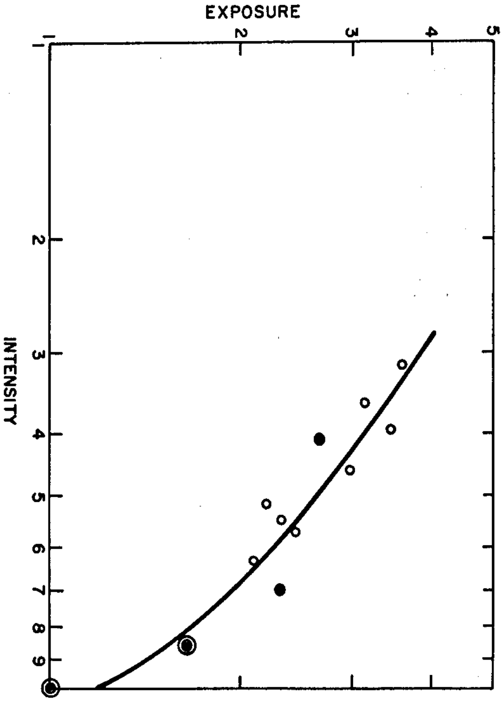

FIGURE 4:

Reciprocity relationship in sensitized polyvinyl alcohol using an unfiltered flash for exposure. (Concentric circles indicate more than one point at the same coordinates).

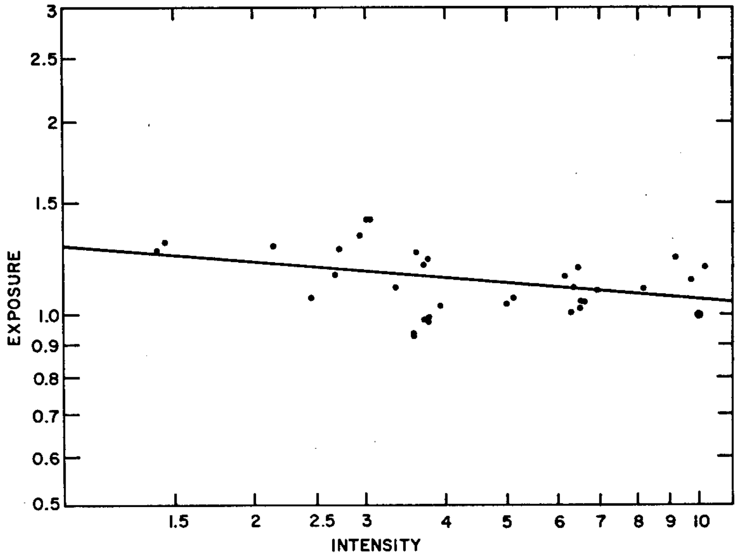

FIGURE 5: Reciprocity relationship in sensitized polyvinyl alcohol using a filtered flash for exposure

SENSITOMETRIC MEASUREMENTS ON KODAK ORTHO RESIST AT MICROSECOND EXPOSURE TIMES

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Within the past few years, a number of systems have been developed which permit high-speed, computer-controlled electronic photocomposition of high quality. Nearly all of these depend on conventional silver halide-based photosensitive materials as the printout medium. This requirement dictates that one or more steps of stripping and re-photographing of the output of such photocomposition equipment must intervene before plate-making can begin.

With the availability of appropriate electronic signals from computer memory on the one hand, and high-intensity laser light sources and means to modulate and deflect them on the other, the ability to expose directly photosensitive plate-making materials under computer control appears to be an attractive time and cost-saving possibility.

One of the light sources which is most promising for an application of this kind is the ionized argon laser. It can be constructed at reasonable cost to produce up to 10 watts of light at several wave lengths (i.e., 4545Å, 4580Å, 4880Å and 5145Å) in the visible spectrum with long life and high reliability.

Kodak Ortho Resist (KOR) is a negative-working resist (hardened by light) which has a useful spectral sensitivity extending from about 270-530 mμ. Because this region includes the wave lengths emitted by the argon laser (Figure 1), KOR would appear to be a material of potential value for the generation of printing plates using laser radiation.

Inquiries directed to Kodak established that they had performed no quantitative measurements of the absolute sensitivity ("speed") of this material, partly because of the difficulties in defining what a "correct exposure" really is, this being a parameter which depends both on the end use of the image and on a personal judgment. Another difficulty which limits the utility of such measurements is the fact that, for a given result, the integrated exposure required is a non-linear function of the resist thickness.

~~It was our goal~~ In this paper (the author) ~~work to~~ determines a "bench mark" figure for exposure needed which INDICATES ~~would permit us to~~ judge the usefulness of KOR in applications where an exposure of 1-10 μsec/spot is contemplated.

MEASUREMENTS AT "NORMAL" LIGHT INTENSITY

Coatings of KOR 3-4μ thick were applied to copper and glass substrates. The samples were exposed through a mask carrying a resolution test pattern to the light from a xenon arc lamp, filtered through infrared-absorbing filters and then through 5mμ-half-bandwidth interference filters at 4600, 4900 and 5200Å. The light intensity was measured with a calibrated thermopile and was in the range of 1-2 mwatt/cm^2. Exposure required to obtain "satisfactory" images (those producing raised images obtained after development, etching and stripping, whose dimensions approximated those of the mask) were ca. 40 mwatt-sec/cm^2 at 4900Å, ca. 50 mwatt-sec/cm^2 at 4600Å, and ca. 100 mwatt-sec/cm^2 at 5200Å. Images obtained using 5200Å light were not very satisfactory, showing considerable spreading and reticulation. We believe that the photochemical reaction which occurs at this wave length may be qualitatively different from the one operating at shorter wave lengths, which suggests that the 5145Å line from the argon laser may not be as useful for this material as those of higher energy. The results are summarized in Table I.

MEASUREMENTS AT HIGH LIGHT INTENSITY-SHORT EXPOSURE TIMES

Glass slides bearing 3-4μ thick layers of KOR were dropped through a 4880Å light beam brought from an argon laser. The beam was focused to a diameter of ca. 5μ and was reflected off a mirror which was deflected sinusoidally through a small angle at a rate of 7.8 kc. The amplitude of the mirror was damped during the passage of the slide through the beam (Figure 2). Because the integrated light exposure is inversely related to the amplitude of the sinusoidal trace obtained in this way, an image such as shown in Figure 3 was expected. The "peaks" of such a trace were always exposed because the linear motion of the light beam was slowest (greatest integrated exposure) at these points.

Measurement of the amplitude and line width associated with those portions of the traces in which the center, nearly linear, portion showed the correct hardening of the resist allowed the calculation of the corresponding exposure time, as shown in Figure 4.

The measured intensity of the beam at the surface of the resist in our experiments was of the order of 10-35mwatt, corresponding to power densities of 0.5-2 x 10^8 mwatt/cm^2. Photographs of actual traces obtained are shown in Figure 5. The technique was found to be a sensitive measure of exposure times required for a given light flux inasmuch as the change from a ragged, broken center trace to a satisfactorily hardened one was associated with a rather small change in trace amplitude. The experimental conditions used in the laser exposure are summarized in Table II.

Analysis of the results for the exposure needed for satisfactory hardening of KOR by 4880Å light showed that 25 mwatt-sec/cm^2 at an exposure time of 0.5 μsec. was just too low while exposures of 80 mwatt-sec/cm^2 at both 0.4 and 1.3 μsec gave satisfactory traces. Thus, essentially no "reciprocity law failure" was observed for KOR down to less than a μsec at 4880Å.

These figures suggest that, in order to obtain a satisfactory exposure of a spot 0.002" in diameter in 1 μsec on a KOR layer 4μ thick, ≈1.5 watts of radiation at 4880Å would be adequate. The corresponding power for a 10 sec exposure would, of course, be 0.15 watt. Another way of stating these results is that, with appropriate means of deflection and modulation, a 1 watt laser could completely harden an area of KOR corresponding to a 14 x 22" newspaper page (1960 cm^2) in 100 seconds. Inasmuch as the proportion of the plate which actually transfers ink to a typical page of print is considerably less than the full area, the time involved for high-speed "dotwise" plate composition would be considerably less.

TABLE I

SENSITOMETRIC DATA FOR KOR AT "CONVENTIONAL" LIGHT LEVELS

Wave Length, mμ	Exposure Required, millijoules/cm^2
460	50
490	40
520	100

Samples were 3-4 microns thick on copper or glass slides. Incident light intensity was 1-2 milliwatt/cm^2.

TABLE II

EXPERIMENTAL PARAMETERS FOR LASER EXPOSURE OF KODAK ORTHO RESIST

Substrate: Glass slides

Coating thickness: 3-4 microns

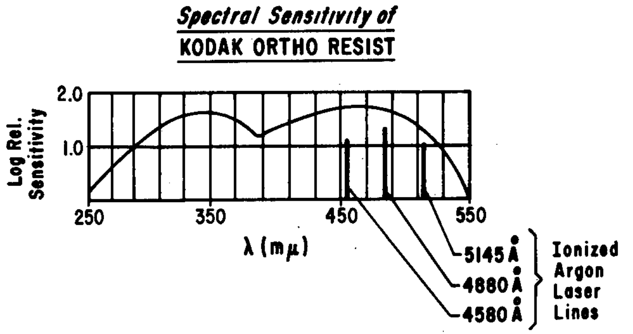
Wave length: 4880Å

Power in Laser beam: 10-30 milliwatts

Spot diameter: ca. 5 microns

Power density at surface $0.5 - 2 \times 10^8$ mwatt/cm^2

Exposure times: 0.4 - 1.3 μsec.



Spectral Sensitivity of KODAK ORTHO RESIST

FIGURE 1: Sensitivity vs wavelength curve for Kodak Ortho Resist showing the wavelengths of argon laser lines.

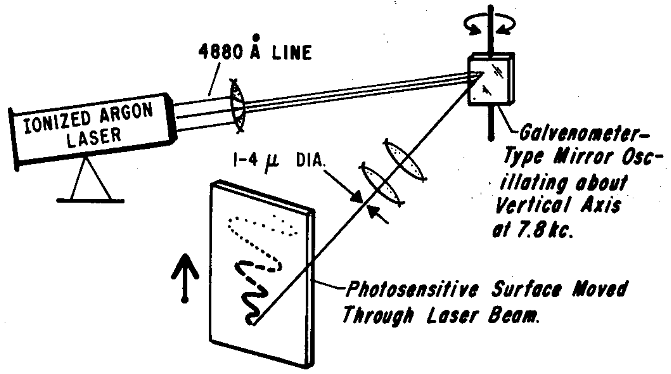


FIGURE 2: Schematic description of the experimental apparatus for high-intensity, short-time exposure of KOR. The amplitude of the mirror oscillation was damped as the slide was moved through the beam.

EXPECTED TRACE

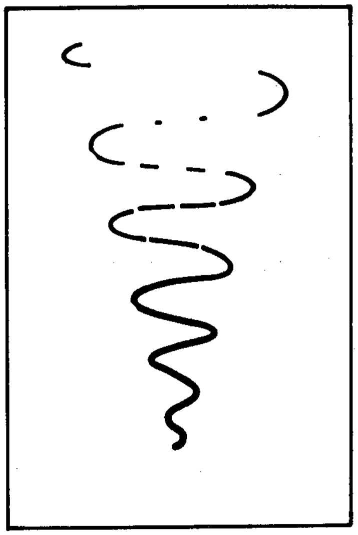
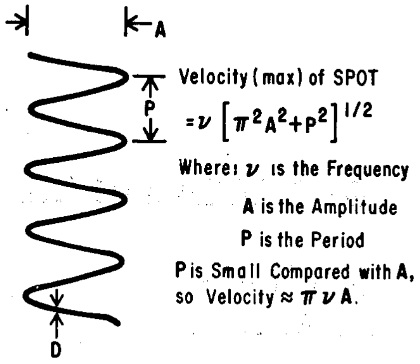


FIGURE 3: Idealized trace of hardened resist obtained from experiment shown in Figure 2.

ANALYSIS OF TRACE



If D is SPOT Diameter, the Exposure Time is D/Velocity. thus

$$\boxed{\text{Exposure Time} \cong D/\pi\nu A}$$

FIGURE 4: Showing how the equivalent exposure time may be calculated for the center portion of the trace of hardened resist. The Frequency, ν, is the frequency of the oscillating mirror shown in Figure 2. The Period, P, depends on the rate with which the slide is passed through the beam of light.

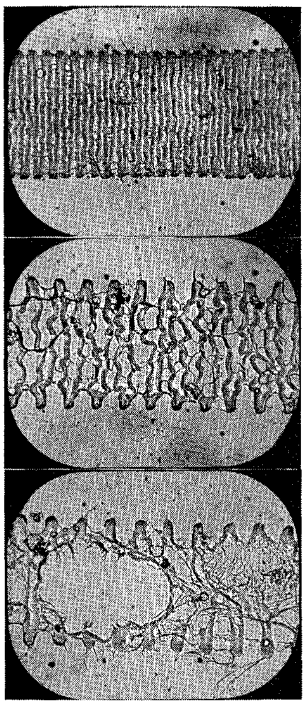


FIGURE 5: Photomicrographs of traces of hardened KOR on glass slides.

CHARACTERISTICS OF IMAGES FORMED IN KODAK THIN FILM RESIST BY PROJECTION EXPOSURES

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Eastman Kodak

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ABSTRACT

The speed of Kodak Thin Film Resist (KTFR) is such that it is normally recommended for use as a contact-print material. Furthermore, thin layers of this resist, such as are required for high resolution, essentially cannot be exposed in the presence of oxygen. Thus, the normal procedure for using this material is to make contact prints in a vacuum frame. However, KTFR can also be exposed conveniently in a camera, by simply flooding the surface with nitrogen during exposure. Experiments are reported in which the Kodak Photosensitive Metal-Clad Plate, which is coated with KTFR, has been exposed in CAMERA ~~this fashion~~. The equipment, optics and light sources used, as well as the exposure levels required, are described. Submicron imagery in the final etched pattern has been obtained, and is illustrated. The characteristics of the images formed, and the exposure latitude of the process, are discussed. (A with modified)

* * * * *

The purpose of this paper is to describe a method for making direct in-camera exposures on Kodak Thin Film Resist (KTFR), and also to describe the results of various image-structure tests made on that resist by means of such projection exposures. The use of the projection technique is interesting because it allows the resists to be tested at higher spatial-frequency ranges than is possible by contact-printing. This is so because if the resist is to be tested by printing, it becomes necessary to prepare suitable contact test-objects, and to devise an adequate printing procedure. However, because the potential resolution of almost any resist is very high, the preparation of test objects and the printing procedure become very difficult. At the resolution levels required, optical projection is a much more manageable technique.

In the course of the work to be described here, direct exposures were produced not only on KTFR, but also on all three types of Kodak Photo Resist. However, Barowsky,[1] of Spectra-Physics, has already reported camera exposures of KPR. In addition, it is well known that the sensitometric and image-forming properties of resist layers vary significantly with the thickness of the layer. For these reasons, we shall restrict ourselves here to reporting the results obtained with the Kodak Photosensitive Metal-Clad Plate, which is a uniform material of known and constant characteristics, and which is conveniently available. This plate is coated with a layer of KTFR about 0.6 micron thick.

In the particular case of KTFR, a special problem must be overcome before in-camera exposures are convenient. The problem is the oxygen-sensitivity of the material. This term is used to describe the fact that the photographic speed of KTFR is seriously reduced if oxygen is present during the time of exposure.[2] The exact magnitude of the speed loss caused by the presence of oxygen depends to some extent on the thickness of the resist layer; for an 0.6μ layer it is of the order of 60 times.

Nevertheless, there is a simple way to avoid this speed loss, and that is to flood the resist with nitrogen while the exposure is being made. This is particularly convenient in our camera, which uses pneumatic gauging for control of focus. Such gauges operate by blowing compressed air through a jet at the surface to be gauged. The jet is placed close to, but not touching, the surface, as a result of which pressure builds up in the line. The pressure level varies with the distance from the jet to the surface, and thus provides a measure of the distance.

To use such a device for focus control, the jet is fixed to the camera objective, and the airstream is directed toward the plate being exposed. The pressure corresponding to the position of best focus is established by trial and error, and can thereafter be reset quickly and accurately. It has been found that such a gauge gives the same results with an input of compressed nitrogen as it does with compressed air. Therefore, the only modification required to expose KTFR is to change the supply.

The equipment installed in our camera consists of a commercially available air gauge with a specially designed probe. The probe, which is shown in Figure 1, consists of a hollow circular chamber which fits around the microscope objective, with the input at one side. The actual gauging jets are above and below the objective. This jet configuration is used to help balance out any departure from flatness in the surface of the plate, and it should be noted in passing that it may not be optimum for the purpose of flooding the resist surface with nitrogen. The consumption of gas by the gauge system is 1.5 cubic feet per minute, so that the cost of full operation with nitrogen is about one dollar per hour. However, if for some reason the supply of nitrogen is limited, equally good results can be obtained by adjusting the focus with air, turning off the air, and flooding the plate surface from a secondary supply of nitrogen during the actual exposure.

The complete optical system of the camera is shown in Figure 2. The source is a General Electric AH-4 mercury arc, which is used unfiltered. Therefore, resists such as KPR and KTFR are exposed with the 436, 404 and 365 mμ lines of the mercury spectrum.

The light from the mercury arc is focused on the entrance pupil of a complete compound microscope by a condenser lens. Condenser illumination is used because for a given source it puts considerably more light in the reduced image than would a diffuser system. The test object or other original to be reduced is placed immediately in front of the condenser lens.

The reduced image is formed by the compound microscope, worked backwards, as described in many publications.[3] Apochromatic microscope objectives are used because a very high degree of correction for blue light is required. In the work to be described, two objectives having numerical apertures of 0.32 and 0.65, respectively, were used.

The sample to be exposed is placed in the focal plane of the objective, and the exposures are timed by a simple shutter. In the present work, direct one-stage reductions ranging from 200 to 400 times were made. The pattern which was reduced was a standard three-bar resolution test object, of which exposure series were made. The plates were processed as recommended.

The energy required to expose the plates was measured by placing a thermopile behind the focal plane of the camera. For optimum exposures with the three wave lengths indicated, the required energy was about 0.1 joule/centimeter.^{2} This value compares favorably with that reported by Barowsky for KPR. The actual times of exposure required in our camera with the AH-4 arc as a source were of the order of 1/2 sec.

The results can be illustrated by micrographs made from the images which were obtained. These micrographs show the final etched image and not the resist image. Figure 3 shows a sample made with the 0.32 N.A. objective. The spatial frequency of the last resolved group is 1000 lines/mm, corresponding to lines and spaces whose width is 0.5 microns. This last group is clearly resolved in accordance with the classical definition, which states essentially that a pattern is considered resolved so long as any line structure can be detected visually. However, the group is somewhat degraded, and might not be usable for the manufacture of integrated circuits. The next larger group, whose spatial frequency is 900 lines/mm, is reproduced fully and with no loss in modulation, and is, therefore, judged to be operationally useful. In this case, the element width is 0.55 . It is interesting to compare this image with that produced by a High Resolution Plate and the 0.32 N.A. objective. Such an image is shown in Figure 4. It can be seen that, although the limiting resolution is actually higher, the modulation is decreasing as the spatial frequency increases. As a result, the higher-frequency images, although resolved by definition, are not operationally useful for micro-electronics. Thus, the limiting resolution of the HR plate, when exposed with the 0.32 objective, is 1100 lines/mm, while what we may term the "maximum useful resolution" is about 600 lines/mm. The comparable values for the Metal-Clad Plate, as given above, are 1000 and 900 lines/mm, respectively.

It is interesting to speculate on the modulation transfer function of a system which reproduces 900 lines/mm at full modulation. However, the system is so nonlinear that transfer-function concepts cannot be applied in the usual way. Therefore, only the resolution values can be reported at this time.

Actually the limiting resolution of the 0.32 N.A.objective itself is only about 1250 lines/mm, and it was, therefore, considered probable that the objective was limiting plate performance. Accordingly, similar tests were made with an objective whose numerical aperture was 0.65; the resolution of this objective is about 2500 lines/mm. Using this lens, we have observed images whose limiting resolution was 1800 lines/mm, and whose maximum useful resolution level was 1400 lines/mm. The corresponding line width is 0.36μ. However, it should be added that in order to achieve such imagery, the adjustment of such parameters as focus and exposure is exceedingly critical. A High Resolution Plate exposed with the 0.65 N.A. objective records a limiting resolving power of about 2000 lines/mm, but the maximum useful resolution is only about 1000 lines/mm.

The property of the resist-chrome system which permits such small images to be made at full modulation is the extremely sharp sensitometric toe, which results in very nearly a "go-no-go" system. That is, below the critical exposure threshold, the resist does not polymerize, and the chromium is completely removed by the etchant. On the other hand, once the exposure threshold is exceeded even slightly, enough resist is polymerized to protect the chrome, and a complete image results. There is essentially no intermediate exposure range in which transmittance is proportional to exposure; this is what was meant by the term "nonlinear".

The go-no-go property is one of the principal factors which determines the image-forming characteristics of the chrome plate. It has already been shown that it permits the production of very fine patterns at full modulation. In addition, for the same reason, chrome-resist systems are very sensitive to small exposure variations, and exposure levels must be controlled accurately.

This may be especially troublesome when a range of image sizes is to be reproduced in a single picture. It is well known from optical theory that in the size range of importance in microelectronics, the actual amount of energy present in an element of a micro-image depends upon the size of that element. If diffraction-limited lenses and a specific wave length of exposing light are assumed, the variation of illuminance can be calculated as a function of image size, and the results of such calculations have been published in the literature. The matter is discussed, for example, in the Kodak Data Book "Techniques of Microphotography", in which curves are shown for the case of an isolated fine line of varying width.[4] Figure 5, which is taken from that book, shows that the decrease of exposure for fine lines can be very significant compared to wide lines which have received the same input exposure.

In a practical sense, if both wide and narrow lines are to be reproduced in the same pattern, and if the exposure is adjusted to be correct for the wide lines, the narrow lines may disappear entirely. Furthermore, an additional problem may be encountered in such a case. As can be seen from Figure 5, there will be a continual decrease of actual exposure from the proper level in the wider lines to the effective zero-exposure level in the fine lines. Between these endpoints, a region may be encountered in which the resist at the surface of the layer has received enough exposure to polymerize, while that at the bottom of the layer is still not properly exposed. Under these conditions, bits of polymerized resist may pull free from the chrome during the processing and settle elsewhere. If they remain on the plate through the processing cycle, and dry down on the chrome, they will then protect that particular area from the etchant. The result is unwanted microscopic dense areas in the plate. If this problem is encountered, it can be ameliorated by careful balancing of the effective exposure in the variously sized lines. This procedure is called "masking", and it is also discussed in "Techniques of Microphotography". It may also be desirable to use a stronger developer, such as xylene, to ensure that all loose resist is removed from the plate.

Another characteristic of the chrome plate which should be noted is the manner in which the image spreads as exposure increases. This has been evaluated by filar-micrometer measurements on an exposure series, and the results are shown in Figure 6. The center line of a triad of 2.5-μ lines was measured. Similar measurements made on a High Resolution Plate exposed in green light are also plotted in this figure. It can be seen that the rate of change of image width with exposure is significantly greater for a chrome plate than for a High Resolution Plate. For this reason, also, the exposure levels for chrome plates are very critical. In addition, it is evident that when wide lines and narrow lines are present in the same pattern, the wider lines may spread objectionably if the exposure is adjusted for the very narrow lines.

Finally, the question has been raised in a number of resist applications as to the density difference required in the original for a good image to be formed in the resist. This was evaluated for the projection case by preparing a series of low-contrast test objects similar to the standard high-contrast pattern. The density differences in these test objects varied from 0.5 to 1.3, whereas the density difference in the standard test object is greater than 3.0. Exposure series were made of these special test objects, and the resulting images were studied to determine the minimum usable contrast. From this standpoint, the go-no-go characteristic of resists is an advantage, and exceedingly high contrast in the original is not necessary to produce a good reduction. Good images were formed when the density difference in the test object was only about 1.0, and in fact, it was found that in certain cases where the exposure could be adjusted very exactly, even lower density differences could be used. However, the minimum useful contrast level for our camera may be different from that of other cameras having different optical properties. In any case, it should not be difficult to maintain density differences in the original which are well above the minimum useful amount.

In summary then, procedures have been described for making direct in-camera exposures on chrome plates overcoated with resist. By such techniques it is easy to produce finer images than can be made by contact-printing from other masters; this allows some of the image-forming characteristics of resist systems to be studied. Usable line pairs have been produced having widths of the order of 0.5μ. This corresponds to a spatial frequency of 1000 lines/mm. The images have low exposure latitude, and, therefore, the exposure must be adjusted exactly to avoid unreasonable image spread, and problems with bits of polymerized resist which do not adhere to the chromium substrate. Under some conditions, masking of the original may be required. The chrome-plate system possesses what would be termed in ordinary photographic technology a very sharp sensitometric toe and a very high gamma. Therefore, the density difference required in the original to produce a satisfactory final etched image is relatively low, being of the order of 1.0.

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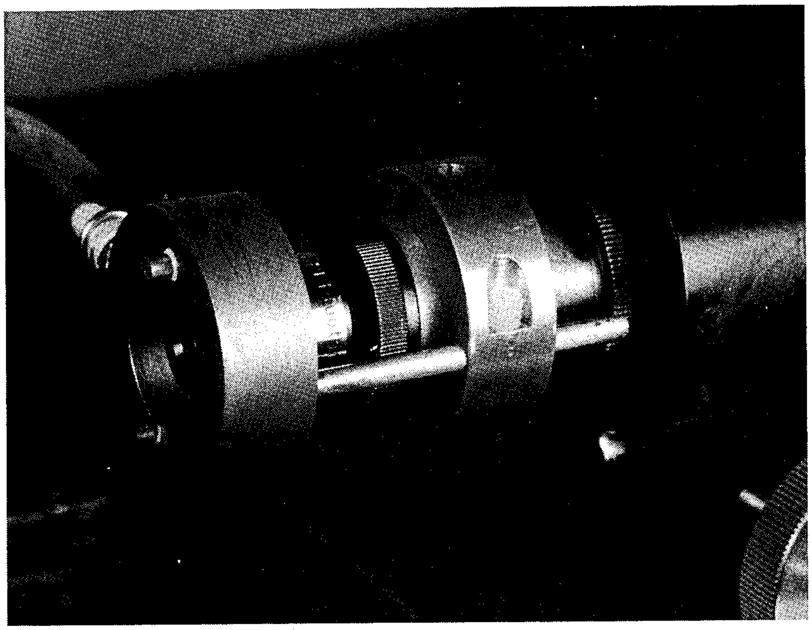
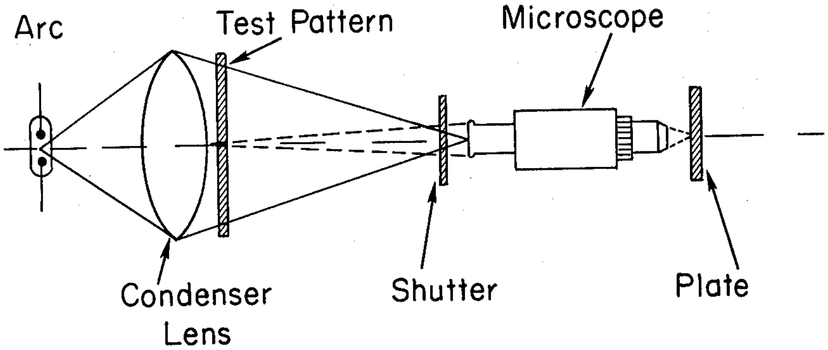


FIGURE 1:
Probe of pneumatic gauge used for control of focus. The actual head is the circular chamber at the left; the jets can be seen above and below the microscope objective.

FIGURE 2:
Optical diagram of the camera used to make direct exposures on Kodak Thin Film Resist



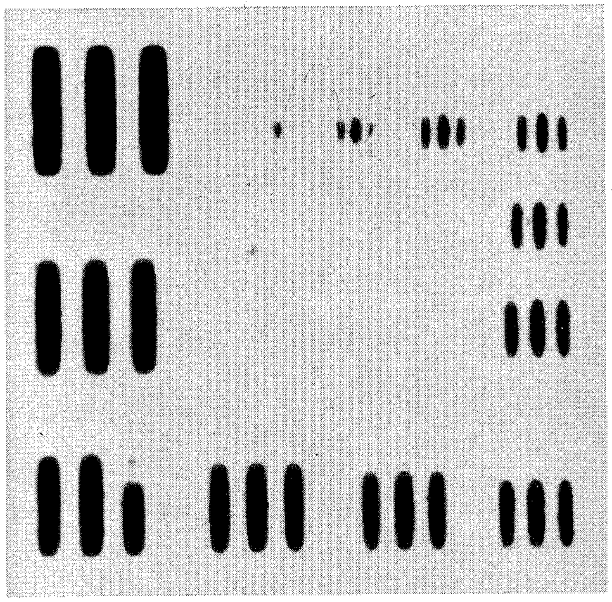


FIGURE 3: Micrograph of etched image on a Kodak Photosensitive Metal-Clad Plate, made with an objective whose numerical aperture was 0.32. The width of a line in the largest group is approximately 1.6μ, decreasing in successive groups by a factor of $\sqrt[6]{2}$.

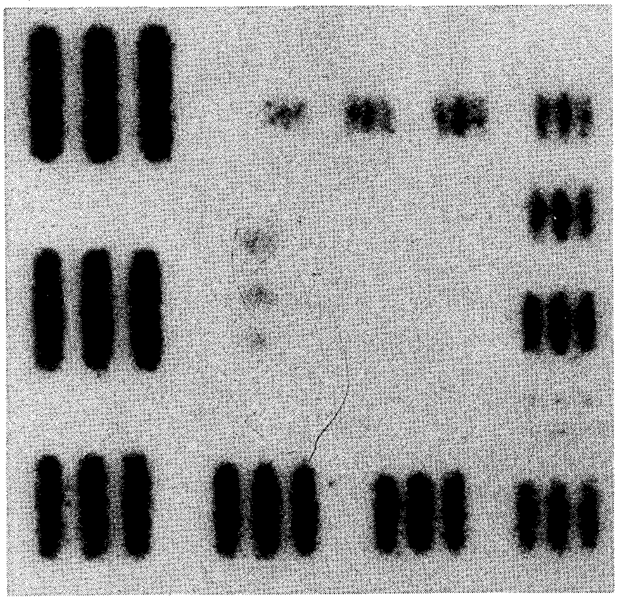


FIGURE 4: Micrograph of an image on a Kodak High Resolution Plate, made with the same objective as used for Figure 3. Dimensions, same as Figure 3.

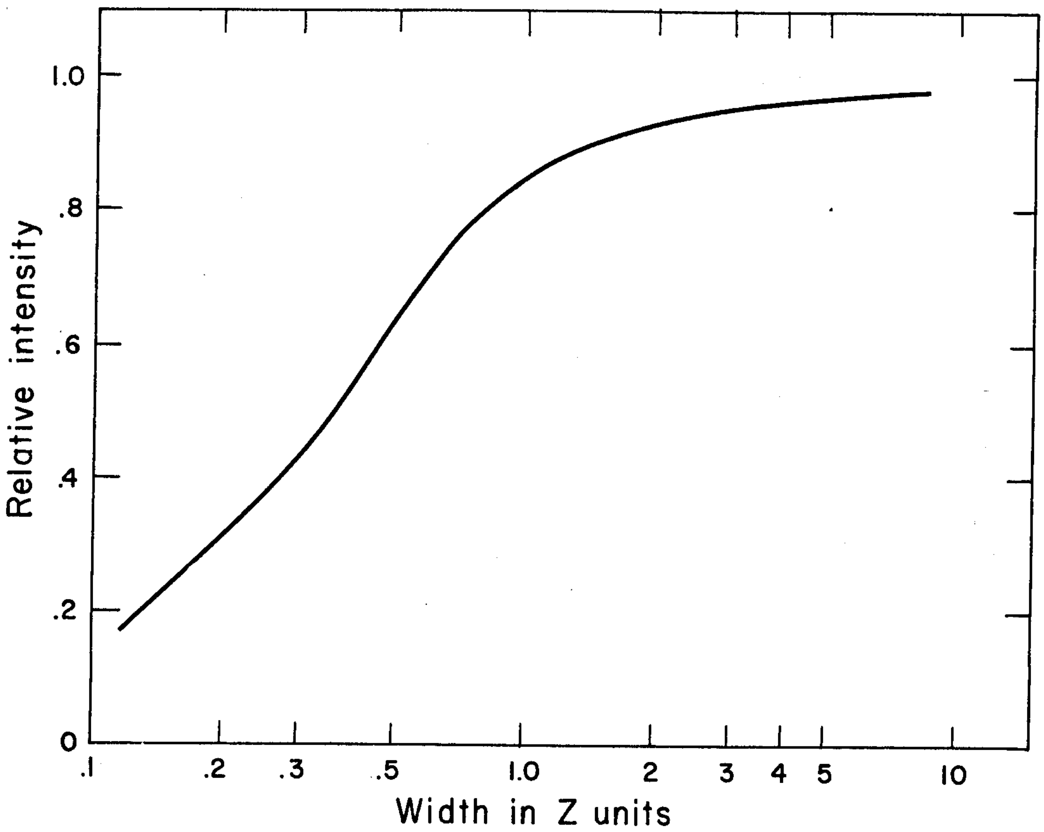


FIGURE 5: Variation of maximum slip illuminance for a lens of given aperture as a function of relative slip width.

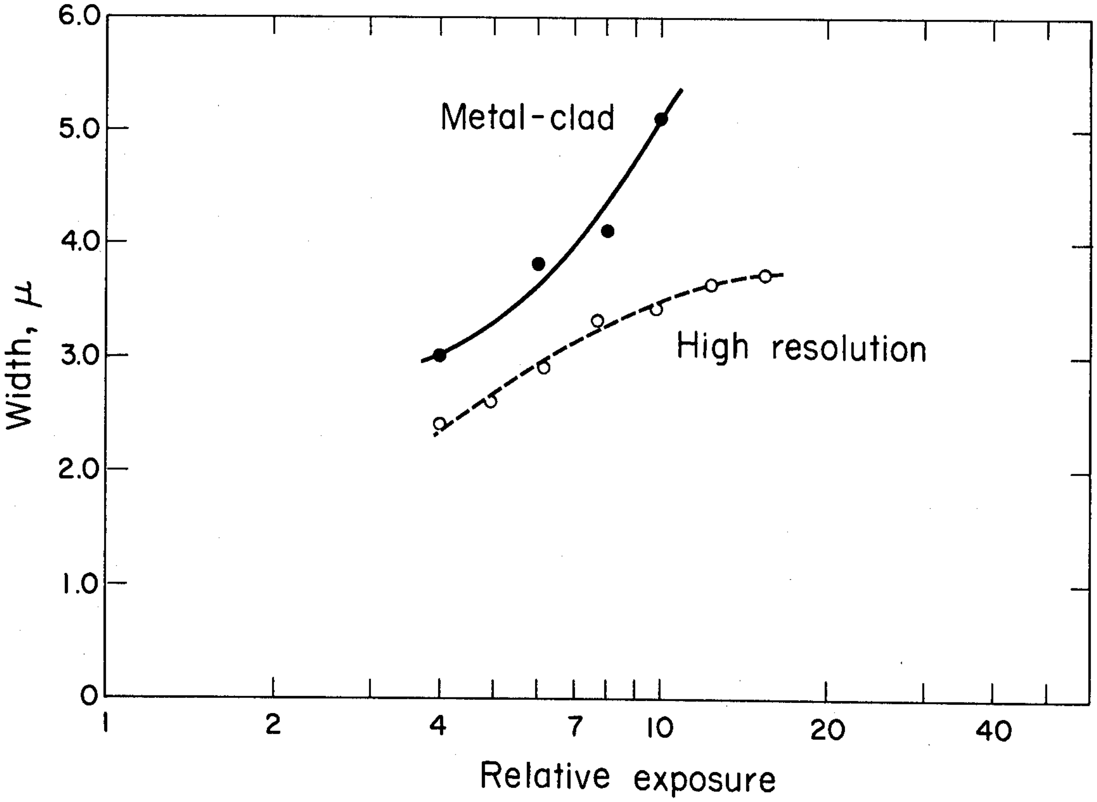


FIGURE 6: Increase in width of images etched in a Kodak High Resolution Plate, as a function of exposure.

PHOTOPOLYMERS FROM MONOMERS - GENERAL SURVEY OF RECENT DEVELOPMENTS

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PHOTOPOLYMERIZATION VERSUS PHOTOCROSSLINKING

The photochemical polymerization of monomers and the photocrosslinking of polymers are usually considered to fall under the general subject of photopolymerization processes. However, this is an oversimplification since the only common denominators between these two subjects are the use of light as a means of initiating a reaction and polymeric materials as the objects of interest, albeit in photochemical polymerization they are the end products of the process, while in photocrosslinking, they are both the starting and end materials.

Many of the handling and product requirements in the use of polymerization for the preparation of polymers are distinctly different from those where photocrosslinking is utilized, e.g., in the fields of photography and microelectronics. Whereas, polymerization involves the conversion of simple monomeric compounds into higher molecular weight products by a successive, multistep process, photocrosslinking for the most part converts preformed polymers into higher molecular weight products by a number of independent, single steps, generally dimerization rather than polymerization. Thus, premature termination of chain growth by impurities or oxygen may yield a low molecular weight polymer, which is undesirable as a coating or as a molding compound. On the other hand, photocrosslinking is not concerned with extensive propagation since it involves independent individual dimerization steps. The major effect of impurities is not to terminate chain growth but rather to absorb light selectively and prevent it from catalyzing the dimerization process.

In addition, photocrosslinking, as indicated by its name, has as its major objective the rapid formation of an insoluble, generally infusible, substrate upon exposure to light. Polymerization per se has as its objective the conversion of a monomer into a polymer. Photopolymerization simply describes the method of initiation of polymerization. If the polymer so produced is later to be processed or fabricated into a shaped object, whether it be a thick molded profile or a thin coating, it is mandatory that it be a soluble or fusible product. If insolubility is desired in the final product it is necessary that the monomer be placed in the final shape or form and that a polyfunctional crosslinking monomer be incorporated into the mixture of monomers exposed to the polymerization initiating light.

PHOTOINITIATED POLYMERIZATION

Having indicated the differences between photoinitiated polymerization and photocrosslinking, it should be noted that the former process is utilized in the field of photography as well as in the preparation of polymers. Although both photography and polymer synthesis utilize light as an initiating species, in photography in contrast to synthetic applications it is an imagewise process generally restricted to thin films. In both cases, however, it is possible to carry out reactions at lower than usual temperatures in a controlled manner.

Light, as utilized in polymerization processes, generally means ultraviolet light. The major advantages of ultraviolet radiation is its ability to excite a molecule to a state in which it can participate in reactions other than those which one would find in a normal environment. In photography, the concern is with making substrates sensitive to visible light. In polymerization it is preferable to have materials quite stable in visible light, as it is seldom practical to handle materials in the dark as is done in photography.

The addition of a photosensitizer to a photographic system has as its objective an increase in the range of effective wave lengths of light. In other words, the photosensitizer increases the amount of energy which is absorbed from a given quantity of light. The photosensitizer in the polymerization field has a different significance in that most of the materials that are used as so-called photosensitizers are radical precursors. In other words, the effect of light is to generate from the sensitizer a species which is capable of initiating polymerization directly or through attack on another molecule.

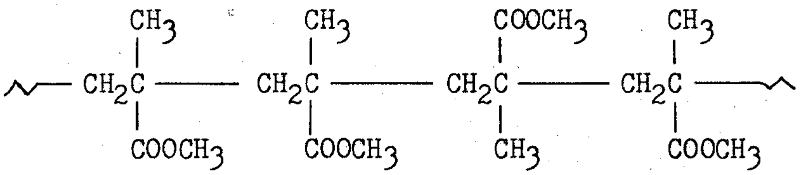
There are two separate aspects of light catalyzed reactions in polymerization. On the one hand, there is activation of molecules resulting in a light catalyzed in contrast to a chemically catalyzed polymerization. Such a process was known almost 120 years ago. As early as 1840, compounds were found to polymerize when put on a window sill exposed to ultraviolet light from the sun. This is an activation process, apparently with no added sensitizer. Subsequent study has indicated, however, that in many instances even such reactions are actually chemically initiated due to the fact that the action of UV has been to abstract a hydrogen atom and the resultant free radical reacts with oxygen in the air to produce hydroperoxides or peroxides which then cleave to yield an initiating species for polymerization.

The amount of work in the polymer field that has actually been done with photoinitiation is rather limited insofar as any intensive study is concerned, and much of it has resulted from the interest in photography. This results from the major shortcomings of ultraviolet light, i.e., low degree of penetration of UV range and the scattering of light by precipitated or insoluble polymer.

The second aspect when ultraviolet light is considered in connection with the initiation of polymerization, generally, is as a means of generating free radicals. The generation of radicals per se is not necessarily a step in the right direction in that stable radicals which may be produced under the influence of UV light may not be very good initiators.

An advantage of light in polymerization is the opportunity to carry out reactions at low temperatures. Normal polymerization procedures are thermally activated, either per se without any added catalyst or else are thermally activated by virtue of the input of heat decomposing a free radical catalyst or precursor to generate a polymerization initiator. With light, it becomes possible to carry our reactions at temperatures as low as -60°C., where one can change the nature of a polymer.

At low temperatures, side reactions such as chain transfer and chain termination are minimized, and higher molecular weight polymers are obtainable. Recently low temperatures have become important as a means of providing control of the structure of a polymer through stereo control, i.e., the change in the mode of addition of a monomer to a growing chain from one conformation to another will result in a structure which will have different properties. Normal free radical polymerization of methyl methacrylate at 50-150°C. yields an atactic polymer (I) in which the substituents are randomly distributed on both sides of the backbone.

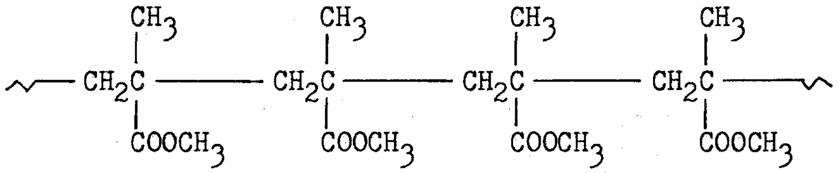


$$\sim CH_2\underset{COOCH_3}{\overset{CH_3}{C}} - CH_2\underset{COOCH_3}{\overset{CH_3}{C}} - CH_2\underset{CH_3}{\overset{COOCH_3}{C}} - CH_2\underset{COOCH_3}{\overset{CH_3}{C}} \sim$$

(I)

atactic

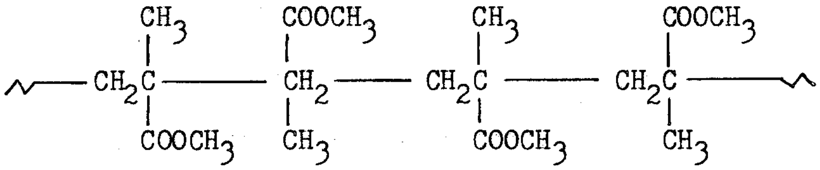
An organometallic-catalyzed polymerization of the methacrylate monomer yields an isotactic structure (II) in which all of the substituents are on the same side of the backbone. A free radical reaction carried out below 0°C. yields a syndiotactic structure (III) with alternating substituents. The lower the temperatures, the greater the degree of stereoregularity and it is possible to obtain a virtually completely syndiotactic poly(methyl methacrylate) at -60°C.



$$\sim CH_2\underset{COOCH_3}{\overset{CH_3}{C}} - CH_2\underset{COOCH_3}{\overset{CH_3}{C}} - CH_2\underset{COOCH_3}{\overset{CH_3}{C}} - CH_2\underset{COOCH_3}{\overset{CH_3}{C}} \sim$$

(II)

isotactic



$$\sim CH_2\underset{COOCH_3}{\overset{CH_3}{C}} - \underset{CH_3}{\overset{COOCH_3}{CH_2}} - CH_2\underset{COOCH_3}{\overset{CH_3}{C}} - CH_2\underset{CH_3}{\overset{COOCH_3}{C}} \sim$$

(III)

syndiotactic

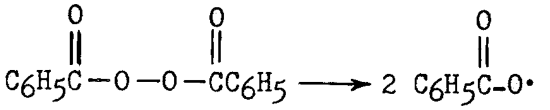
A. Photosensitized Radical Initiated Polymerization

Numerous compounds have been utilized as photosensitizers in polymerization in order to permit low temperature reactions. Representative types are shown in Table I.

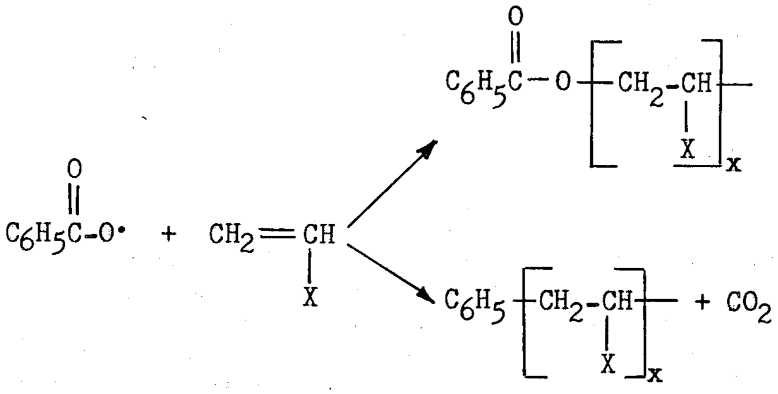
Many photosensitizers are actually polymerization initiators. Thus, when biacetyl is used in a photoinitiated polymerization the acetyl radicals are generally found in the polymer structure. however, a major use of biacetyl in photopolymerization is as a sensitizer for the decomposition of azobisisobutyronitrile at low temperatures.

There are differences among the types of carbonyl compounds, specifically the wave length of light to which they are sensitive and their efficiency. α-Halocarbonyl compounds are much more sensitive and decompose into radicals upon exposure to light more readily than compounds such as acetone. On the other hand, compounds such as benzophenone, in lieu of decomposing into radical species, act to absorb light at a particular wave length and then emit such light at a different energy level. Benzophenone, excited to a higher energy level by light, thus acts as an activator rather than as an initiating species.

Peroxides represent an interesting class of photosensitizers. Benzoyl peroxide will decompose under the influence of light to give benzoyloxy radicals. Depending upon the temperature, the ultimate species found in the polymer are phenyl radicals or benzoyloxy radicals. It has not been determined whether the decarboxylation occurs prior to or at the time of interaction with a substrate such as a monomer.



$$C_6H_5\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}C_6H_5 \longrightarrow 2\ C_6H_5\overset{\overset{O}{\|}}{C}-O\cdot \qquad (1)$$



$$C_6H_5\overset{\overset{O}{\|}}{C}-O\cdot + CH_2{=}\underset{\underset{X}{|}}{CH} \longrightarrow C_6H_5\overset{\overset{O}{\|}}{C}-O\left[CH_2-\underset{\underset{X}{|}}{CH}\right]_x- \qquad (2)$$

$$\longrightarrow C_6H_5\left[CH_2-\underset{\underset{X}{|}}{CH}\right]_x- + CO_2 \qquad (3)$$

Di-tertiary-butyl peroxide is a far less effective catalyst for photosensitized initiation than for thermal initiation. Thermal decomposition results in cleavage of the oxygen-oxygen bond and yields reactive tertiary-butoxy radicals.

$$(CH_3)_3C-O-O-C(CH_3)_3 \xrightarrow{\Delta} 2\ (CH_3)_3C-O\cdot \qquad (4)$$

Under the influence of light, cleavage occurs at the carbon-oxygen bond.

$$(CH_3)_3C-O-O-C(CH_3)_3 \xrightarrow{h\nu} 2\ (CH_3)_3C\cdot \ + O_2 \qquad (5)$$

The result is the formation of the less reactive tertiary butyl radicals and, at the same time, the generated oxygen inhibits polymerization. Consequently one has to be selective in the choice of initiators since not all peroxides are going to be desirable.

Hydrogen peroxide under the influence of light is effective in iniating polymerization and presents the opportunity to carry out reactions in an aqueous system. While this is valuable for water-soluble polymers, when the polymer is insoluble in the aqueous phase, it precipitates from the reaction mixture. The efficiency decreases as a result of light scattering and the maxumum conversion may be less than 5%, unless the polymer in the system settles and additional monomer can be polymerized. These are the types of processes which would work most efficiently only on a continuous basis where the polymer is removed as it is formed and the reaction mixture is recycled. In this manner it is possible to avoid the scattering of light and advantage may be taken of the function of the light, namely, low temperature initiation.

Sulfur-containing compounds such as disulfides are analogous to the peroxides and are also used as photosensitizers. Here another problem arises in that while the sulfur-sulfur linkage cleaves under the influence of light to yield radicals for the initiation of polymerization, such radicals are also very effective as far as coupling is concerned and may act to lower the molecular weight of the polymer produced.

Azobisisobutyronitrile is one of the most widely used initiators in polymerizations carried out at low temperatures under the influence of light. While the azo compound is light sensitive, it is generally used in conjunction with a photosensitizer such as biacetyl for polymerizations at temperatures in the range of -60 to -20°C.

In addition, the α-halo carbonyl compounds which are photosensitizers, halogens per se, e.g., chlorine, are effective polymerization initiators. Under the influence of light a chlorine molecule cleaves into chlorine radicals.

$$Cl_2 \xrightarrow{h\nu} 2\ Cl\cdot \qquad (6)$$

Acrylonitrile has been polymerized in an atmosphere containing a small amount of chlorine under the influence of light. The chlorine radicals initiated the polymerization which was carried out in water. The polymer precipitated and the reaction stopped at 3% conversion. However, when the reaction was carried out in aqueous calcium thiocyanate or calcium chloride solutions which are solvents for polyacrylonitrile, it was possible to carry out a light catalyzed reaction using chlorine, as the entire system remained homogeneous and there were no light scattering effects. Thus, it may be necessary to modify environments in order to carry out light initiated polymerization reactions.

Metal carbonyls such as manganese carbonyl $Mn_2(CO)_{10}$ are effective photosensitizers in the presence of carbon tetrachloride. There is apparently an interaction between the metal carbonyl, CCl_4 and the monomer with the result that a $CCl_3\cdot$ radical is generated from this system. The $CCl_3\cdot$ radical is the initiator for the polymerization of a monomer such as methyl methacrylate and styrene.

The trichloromethyl group is apparently the reactive precursor. Thus, poly(vinyl trichloroacetate) may be utilized in lieu of carbon tetrachloride as the radical source. In this case, the photolysis of a mixture of poly (vinyl trichloroacetate), a vinyl monomer such as methyl methacrylate and a metal carbonyl results in the generation of radicals on the polymer backbone and a graft copolymer is produced. If the monomer is styrene, which terminates predominantly by coupling at temperatures below 60°C., crosslinking occurs.

The use of zinc oxide as a photosensitive material has been known for many years. It has also been shown to initiate vinyl polymerization under the influence of light in the presence of water and oxygen.

Among the metal compounds, there are several salts which are effective in initiating a two-step process which leads to polymerization. Thus, under the influence of light ferric oxalate and ferric citrate are reduced to ferrous ions. While the oxalate and citrate ions are converted to radical species which may initiate vinyl polymerization, a more significant fact is that the formation of ferrous ions is the basis of a latent photographic image. The ferrous ion, generated within a substrate containing a vinyl monomer such as acrylamide, is not capable of initiating polymerization but can act as a reducing agent in a redox system. Thus, exposure to light in an imagewise manner results in the formation of ferrous ions in the exposed areas. If a peroxide or hydroperoxide is present, radicals are generated and the vinyl monomer may be polymerized in the area where the ferrous ion-peroxide reaction occurs, i.e., in the areas where the ferrous ion was generated. Alternatively, since the exposed, ferrous-ion containing areas represent a latent image, it is possible to expose the substrate containing the vinyl monomer to an oxidizing agent such as hydrogen peroxide, at a later time.

Dye-sensitization has been the subject of considerable investigation in recent years. Since it is the subject of several papers in this conference, it is adequate at this point to briefly note that, in general, dye-sensitized photopolymerizations involve a photoreduction of the dye and the formation of a radical species. Oxygen appears to be a necessary component of the system and may be the precursor of the radical which results from its reaction with the photoreduced dye. However, the role of oxygen in dye-sensitized photopolymerization is still an unresolved matter.

B. Photosensitized Ion-Radical Initiated Polymerization

Photosensitized or photoactivated free radical polymerization is obviously limited to those monomers which are susceptible to free radical attack. In the field of photography, there are additional limitations, namely, the need to use non-volatile, generally, solid monomers and the inhibiting effect of oxygen on the polymerization reaction. This latter effect becomes significant when, as a result of oxygen interaction, amplification of the light input is reduced or, low molecular weight soluble polymer is formed in the exposed area and is removable along with the unpolymerized monomer in the unexposed areas.

The generation of species under the influence of light, capable of initiating the polymerization of monomers insensitive to radical polymerization but susceptible to ionic polymerization, would broaden the scope of photopolymerization. Saturated monomers such as lactones, epoxides and acetals as well as unsaturated monomers such as α-methylstyrene and vinyl ethers could be added to the number of photopolymerizable monomers.

A further valuable asset would be the insensitivity of the polymerization reactions to oxygen inhibition. Activation by oxygen would obviously be even more significant, particularly, in photographic applications where the presence of an air atmosphere is unavoidable.

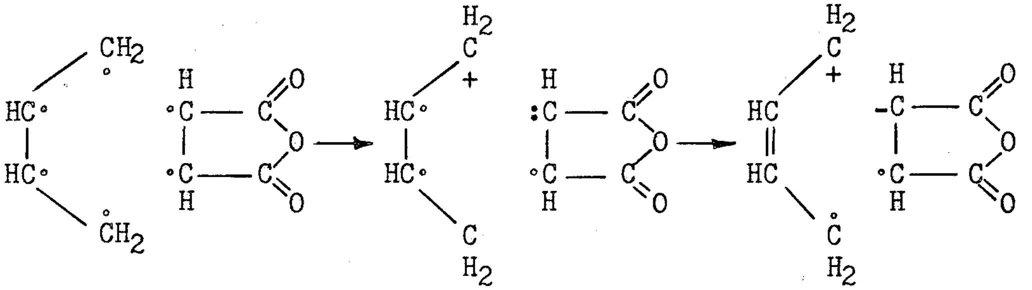
As a result of investigations within the past few years, these goals can be met, although at present, only to a limited extent. However, as our understanding of the phenomena involved increases, the scope will also increase.

The basic feature of these new light activated polymerizations involving ionic species is the formation of a complex between the monomer and an additive. The latter is not a catalyst per se. However, upon exposure of the complex to light an electron-transfer reaction occurs and a polymerization-initiating species is formed. The complex, generally termed a charge-transfer complex, results from the interaction of an electron donor and an electron acceptor. The polymerizable monomer may be either the donor or the acceptor. The co-reactant in the formation of the complex may be an inorganic or an organic compound or even a polymerizable monomer. The complex itself, resulting from a one electron transfer reaction, is an ion-radical species, ie., it consists of a paired anion-radical and cation-radical.

The ion-radical species may polymerize by a radical or an ionic mechanism, depending upon the nature of the monomer and the environment. Reactions involving ion-radical intermediates are extremely solvent dependent. It should be noted that charge transfer interactions may occur spontaneously or under the influence of some form of energy such as heat, light, gamma radiation or chemical catalysts including free radicals.

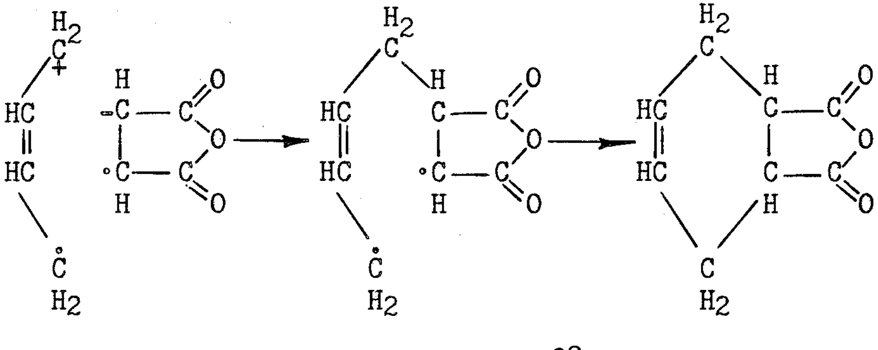
A brief review of charge transfer reactions will illustrate the scope and limitations.

The classical example of a reaction involving charge transfer intermediates is the Diels-Alder reaction in which a one electron transfer between an electron donor and an electron acceptor results in the formation of the complex.



(7)

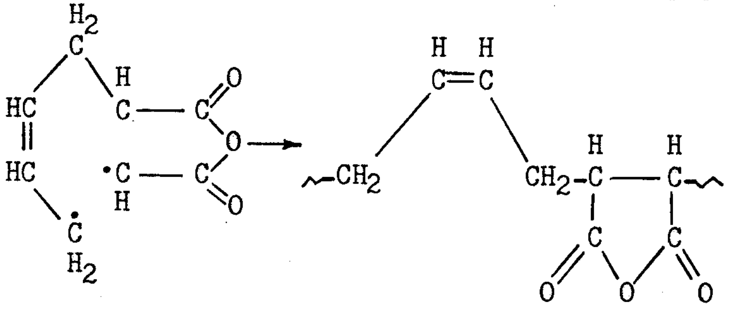
For the sake of illustration, the electron donor, butadiene, and the electron acceptor, maleic anhydride, are shown with electrons on the carbon atoms in lieu of the double bonds. The one electron transfer reaction converts the donor to a cation-radical and the acceptor to an anion-radical. The resulting charge transfer complex is actually a diradical species which couples to yield the adduct, tetrahydrophthalic anhydride.



(8)

The reaction occurs slowly at room temperature but is accelerated at elevated temperatures. It has recently been found that Lewis acids such as aluminum chloride catalyze sluggish Diels-Alder reactions. The Lewis acid is an electron acceptor and as a result of complexation with the carbonyl group of the electron acceptor converts it to an even better electron acceptor. The formation of the charge transfer complex occurs more readily and the reaction is thereby catalyzed.

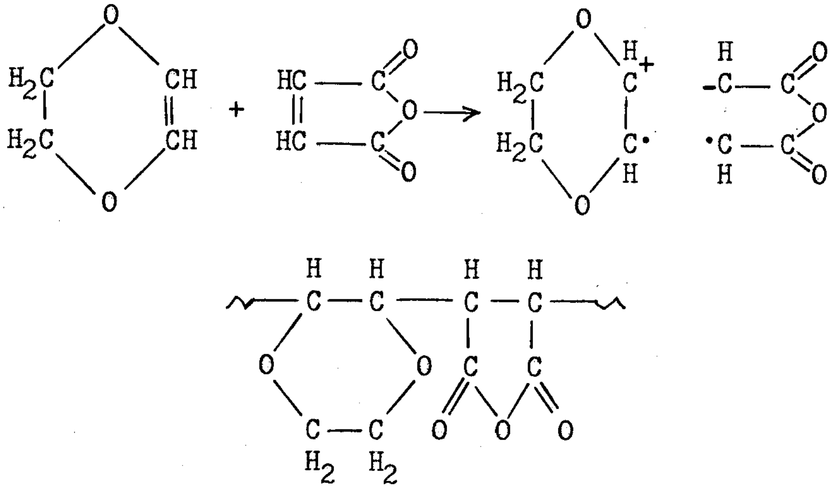
Although this reaction has been known for more than 30 years, it was found only recently that under the influence of high energy species such as gamma radiation from a Co-60 source or chemical catalysts it is possible to open the diradical transition state, i.e., the charge transfer complex, and produce alternating copolymers through a diradical propagation step.



(9)

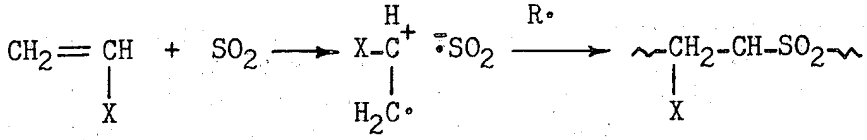
This is an example of a charge transfer complex which normally undergoes intramolecular coupling but opens under the influence of high energy forces.

The reaction of p-dioxene with maleic anhydride is an example of a charge transfer intermediate which does not couple to form an adduct but is extremely stable. However, in the presence of a free radical generated under normal conditions from azobisisobutyronitrile an alternating copolymer is formed through a diradical mechanism.

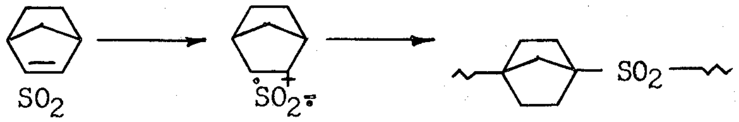


(10)

An extremely reactive charge transfer complex which opens spontaneously is formed in the reaction of bicycloheptene with sulfur dioxide. Whereas the complex between an olefin such as 1-butene or cyclohexene and sulfur dioxide requires free radicals in order to initiate copolymerization, a spontaneous copolymerization occurs when SO_2 is passed into a toluene solution of bicycloheptene at -40°C.



$$\underset{X}{\underset{|}{CH_2{=}CH}} + SO_2 \longrightarrow X\text{-}\overset{H}{\underset{H_2C\cdot}{C^{+}}}\ {}^{\cdot -}SO_2 \xrightarrow{R\cdot} \sim CH_2\text{-}\underset{X}{\underset{|}{CH}}\text{-}SO_2\sim \qquad (11)$$

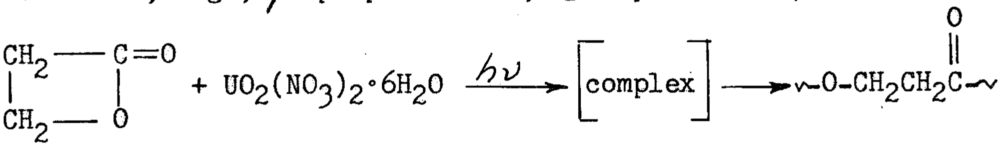


(12)

Sulfur dioxide is an extremely strong electron acceptor and the bicycloheptene is apparently a strong electron donor. The one electron transfer reaction occurs readily and the complex opens spontaneously to yield a copolymer with a molecular weight in the millions within a few minutes.

The objective in presenting these reactions has been to demonstrate that charge transfer complexes have varying degrees of stability. Since the complexes are ion-radical species, ionic polymerizations are possible. Thus, the polysulfone formed by the free radical induced opening of the styrene-sulfur dioxide complex is accompanied by polystyrene which results from the cationic polymerization of styrene monomer initiated by the styrene cation-radical. Similarly, the polymerization of N-vinylcarbazole under the influence of an electron acceptor such as chloranil, tetracyanoethylene, chlorine or maleic anhydride results in the formation of poly(N-vinylcarbazole) through a cationic mechanism. In some cases, the reaction is photosensitive, i.e.,the reaction occurs only to a small extent, if at all, in the dark.

A number of ionic polymerizations have recently been reported to occur under the influence of light. Uranyl nitrate is well known as a photosensitizer for radical reactions such as the chlorination of toluene. However, under the influence of ultraviolet light, uranyl nitrate catalyzes the polymerization of a number of monomers which are only polymerizable through a cationic mechanism, e.g., β-propiolactone, ε-caprolactone, diketene, trioxane, etc.



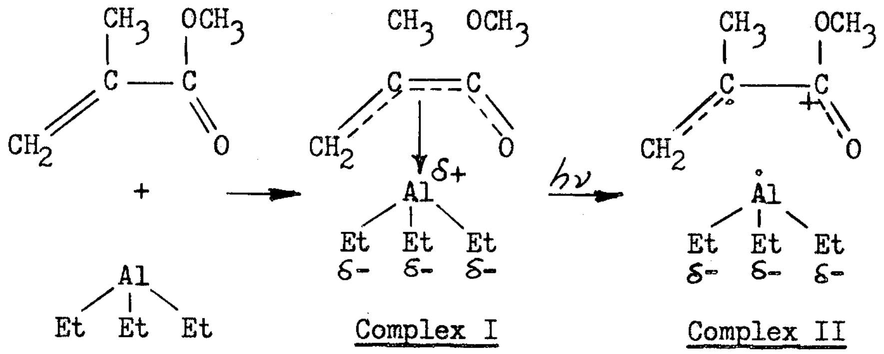
$$\begin{array}{l} CH_2 - C{=}O \\ \ |\qquad\ \ | \\ CH_2 - O \end{array} + UO_2(NO_3)_2\cdot 6H_2O \xrightarrow{h\nu} \left[\text{complex}\right] \longrightarrow \sim O\text{-}CH_2CH_2\overset{O}{\overset{\|}{C}}\sim \qquad (13)$$

These ring-opening polymerizations are actually activated rather than inhibited by oxygen. On the other hand, they are inhibited by diphenylpicrylhydrazyl and benzoquinone as well as ethanol, acetone and diethyl ether. This illustrates a major factor in polymerizations which proceed through a charge transfer complex, i.e., they are not sensitive to some of the normal inhibitors but are inhibited by presumably inert materials such as simple solvents. The inhibition is not the usual interference with the propagation reaction but rather interference with the formation of the complex. Thus, examination of the ultraviolet spectrum of a mixture of β-propiolactone and uranyl nitrate reveals a maximum indicative of complex formation. However, in the presence of ethanol, acetone or ether there is no evidence of complex formation and no polymerization occurs on exposure to ultraviolet light.

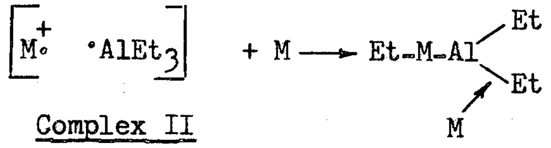
Although the photopolymerization of β-propiolactone in the presence of uranyl nitrate is a cationic reaction, the polymerization and copolymerization of methyl methacrylate under the same conditions is a free radical reaction. Thus, the nature of the monomer determines whether the ion-radical resulting from the one electron transfer reaction initiates a radical or an ionic polymerization.

Another example of a photopolymerization involving a charge transfer complex is the triethylaluminum catalyzed polymerization of methyl methacrylate or methyl acrylate. Although it was reported many years ago that aluminum alkyls catalyze the polymerization of methyl methacrylate to a stereoregular polymer, it was only recently found to be a photochemical reaction.

It has been proposed that the reaction of the acrylic monomer with triethylaluminum at -20°C. in toluene forms a yellow complex. Upon exposure to light one electron transfer generates a cation radical from the monomer and an anion radical from the organoaluminum compound. The initial and the ionradical complexes are considered the lower and higher energy forms of a charge transfer complex. Interaction of the ionradical complex with additional monomer results in polymerization through an anionic insertion mechanism.

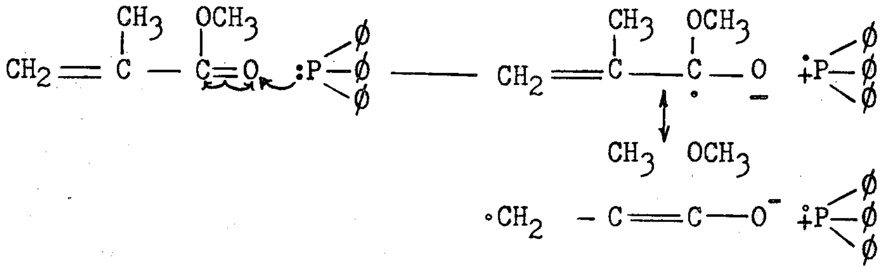


(14)



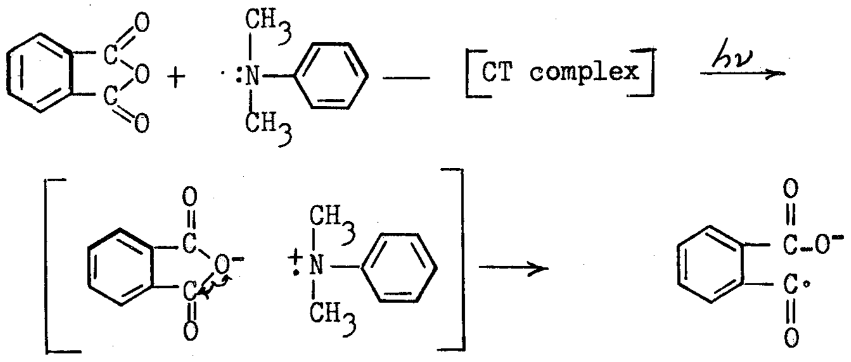
(15)

A photoinitiated free radical polymerization of methyl methacrylate has recently been reported to occur through a charge transfer complex involving triphenylarsine, triphenylstibene and triphenylphosphine. The organometallic compounds each have an ultraviolet absorption spectrum with a different maximum. However, in the presence of methyl methacrylate they all have the same maximum resulting from complex formation. When the monomer and an organometallic compound such as triphenylphosphine are exposed to light a complex is formed, a one-electron transfer occurs converting the phosphine to a cation-radical and the monomer to an anion-radical. As a result of resonance, a terminal free radical is produced and initiates free radical polymerization.

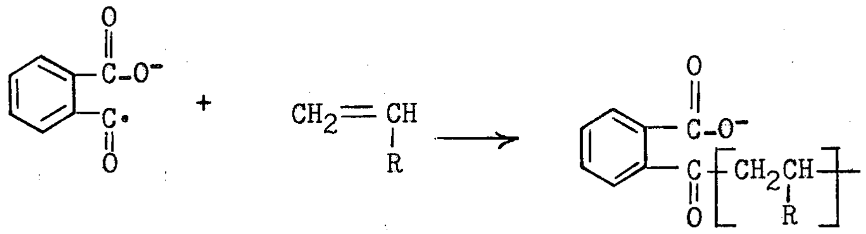


(16)

A charge transfer complex may be formed under the influence of light, without involvement of a monomer, and generate a species capable of initiating the polymerization of a monomer. Thus, the interaction of phthalic anhydride and dimethylaniline forms a charge transfer complex. Under the influence of light, a one electron transfer from the nitrogen atom converts the anhydride to an anion-radical through the cleavage of the oxygen-carbon bond. The resultant radical species initiates the polymerization of methyl methacrylate and acrylonitrile.



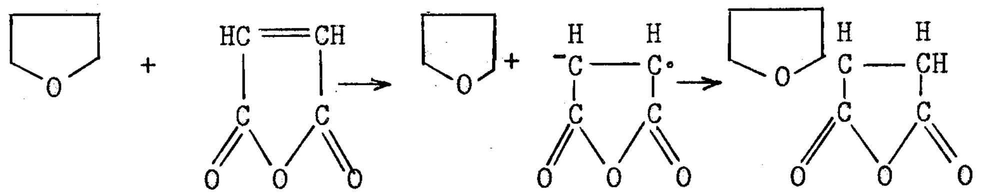
(17)



(18)

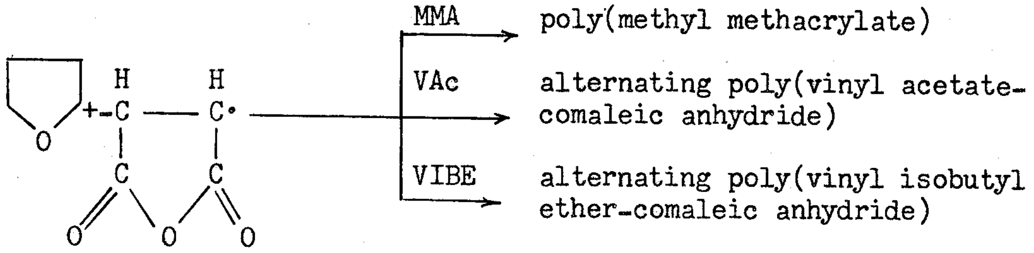
Although benzoic anhydride yields the same results as phthalic anhydride, pyromellitic dianhydride fails to yield a polymerization initiating species under these conditions.

Another interesting case involves the formation of a charge transfer complex between tetrahydrofuran and maleic anhydride. The complex is yellow since its absorption extends to the visible part of the spectrum. The complex is stable in the dark. However, in the presence of light, an adduct is formed.



(19)

If a monomer is present during the irradiation, free radical initiated polymerization occurs. Thus, methyl methacrylate is polymerized to poly(methyl methacrylate). However, vinyl acetate yields a vinyl acetate-maleic anhydride alternating copolymer and vinyl isobutyl ether yields a vinyl isobutyl ether-maleic anhydride alternating copolymer. The failure to incorporate maleic anhydride in the methyl methacrylate polymer results from the poor copolymerizability of these monomers as they are both electron acceptors. The formation of the alternating copolymer from the electron donor vinyl isobutyl ether is not polymerizable by an anionic mechanism, yields homopolymer through a cationic mechanism and yields a copolymer in the presence of a free radical source.

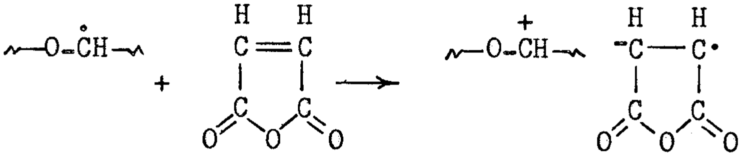


(20)

In contrast to the photoinduced free radical reactions resulting from the interaction of tetrahydrofuran and maleic anhydride, dioxane and maleic anhydride initiate cationic reactions in the presence of light and other sources of energy.

The reaction was originally discovered as a result of the exposure of a mixture of trioxane and maleic anhydride to gamma radiation. The formation of polyformaldehyde indicated the occurrence of a cationic reaction. It was further found that bis(chloromethyl)oxacyclobutane was also polymerized in the presence of maleic anhydride and that ultraviolet radiation was an equally effective initiator. However, the reaction was dependent upon the presence of oxygen. Since this was unusual for a simple cationic initiation process, it was concluded that radical species might be involved. This was confirmed by the successful polymerization of trioxane and the oxacyclobutane in the presence of maleic anhydride under the influence of free radicals thermally generated from benzoyl peroxide. The proposed mechanism involved hydrogen abstraction from the methylene group adjacent to the ethereal oxygen under the influence of free radicals or irradiation in the presence of oxygen. A one electron transfer from the resultant free radical to the electron acceptor maleic anhydride yields a cationic species capable of initiating cationic polymerizations.

$$\sim\!O\!-\!CH_2\!-\!\sim \;\longrightarrow\; \sim\!O\!-\!\overset{\circ}{C}H\!-\!\sim \qquad (21)$$



(22)

It was further reported that exposure of a solution of maleic anhydride in dioxane to gamma or ultraviolet radiation in the presence of oxygen or heating the solution containing benzoyl peroxide gave a solution which was conductive and, upon addition to vinyl isobutyl ether or N-vinylcarbazole, initiated the cationic polymerization of these monomers. The cationic nature of this reaction is confirmed by the formation of poly(vinyl isobutyl ether) since radical species would have resulted in the formation of a vinyl isobutyl ether-maleic anhydride copolymer, as demonstrated in the tetrahydrofuran-maleic anhydride system.

The same results have recently been shown in the peroxide or radiation induced homopolymerization of vinyl isobutyl ether in the presence of a carbonyl compound such as propionaldehyde, benzaldehyde, acetone or methyl ethyl ketone and an electron acceptor such as maleic anhydride, chloranil or tetracyanoethylene. Here again, a radical generated on the carbonyl compound is converted to a cation by one electron transfer to the electron acceptor.

The influence of solvents is a recurrent theme throughout the chemistry of polymerization reactions which proceed through a one electron transfer step. The solvent may inhibit the formation of the charge transfer complex, may compete with the electron acceptor in the transfer reaction, or may participate in the reaction as the source of the initiating species.

SUMMARY

Photopolymerization, under the influence of ultraviolet light, may proceed through radical or ionic mechanisms. The use of photosensitizers permits the low temperature polymerization of vinyl monomers through the generation of free radicals which are capable of initiating polymerization. Ion-radical species are produced through donor-acceptor interactions, generally involving the formation of charge transfer complexes. In some cases, the one electron transfer reaction occurs prior to the exposure to light and the latter serves as an energy source to open the resultant complex. In other cases, the one electron transfer occurs as a result of the exposure to light. Ion-radical initiated polymerizations may proceed through radical or ionic mechanisms depending upon the nature of the monomer, the solvent and the presence of co-reactants. The photoinduced formation of ionic species broadens the scope of photopolymerization to include saturated as well as unsaturated monomers which are not subject to free radical initiated polymerization.

TABLE I

REPRESENTATIVE PHOTOSENSITIZERS

Type	Examples
Carbonyl compounds	acetone, cyclohexanone, biacetyl, benzophenone, benzoin, 2-halocarbonyl compounds
Peroxides	benzoyl peroxide, di-tertiary-butyl peroxide, hydrogen peroxide
Sulfur compounds	benzyl disulfide, thiobenzoic acid, ethyl thiocarbamate
Nitrogen compounds	azobisisobutyronitrile, diazonium salts, azoxybenzene
Halogen compounds	chlorine, bromine, iodine, carbon tetrachloride, carbon tetrabromide
Metal carbonyls	manganese carbonyl
Inorganic compounds	zinc oxide, mercurous bromide, silver chloride, ferrous oxalate, cerous nitrate, uranyl nitrate
Dyes	methylene blue, eosin

PHOTOELECTROLYTIC POLYMERIZATION PROCESSES

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and

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Fort Monmouth, N. J.

ABSTRACT

Many ways of initiating polymerization electrolytically have been reported. Most of these techniques require the passage of current for relatively long times. We are specifically interested in forming polymer for image recording; light intelligence is converted to an image-wise conductivity pattern via a photoconductor. Time, for this purpose, is of considerable importance.

Three techniques ~~will be~~ are described which are capable of initiating polymerization quickly and which require modest amounts of current. Mixtures of acid and hydrogen peroxide are capable of initiating polymerization at the cathode as rapidly as desired, depending on the current passed. The resulting uniform polymer that coats the cathode has good adhesion and dye receptivity. Soluble zinc salts under carefully controlled conditions, also initiate polymerization at the cathode upon passage of current. A third technique described involves processing of metal ions introduced into the polymerizable media from the metal anode itself. ([illegible])

INTRODUCTION

Since the problems of military air reconnaissance have not been completely solved by silver halide photography, military laboratories have had considerable interest in novel techniques of image recording.[1,2] One of the most attractive new image recording techniques has been photopolymerization or polymerization iniated by light. Unlike silver halide photography which owes its success to the large amplification step obtained through post exposure chemical development,[3] amplification is obtained through a free radical initiated chain reaction in this technique. As presently constituted, however, photopolymerization has several defects. The most serious defect, unfortunately, is that a light sensitivity cannot be obtained which is comparable to that found in conventional silver halide photography. Another defect in some photo-initiated systems is that the coated films degrade on standing, either through autopolymerization or through decomposition of the initiating species.

In an effort to improve on the sensitivity obtained in photopolymerization,

E. Cerwonka, A. S. Deutsch and S. Levinos, began investigating photoelectrolytically initiated polymerization.[4] This work is now being continued internally by the Photo Optics Technical Area of the Combat Surveillance & Target Acquisition Laboratory at Fort Monmouth, New Jersey.

Photoelectrolytic-polymerization differs from photopolymerization in that the chain reaction is initiated and sustained by the passage of an electric current. If the current density is made proportional to the available incident light an image-recording system similar to that of photopolymerization results. In practice a sandwich arrangement is used as shown in Figure 1. The image recording layer, or monomer coating, is sandwiched between two conductive supports, one of which, in this case a Nesa coating, is light transparent. This transparent electrode allows light to strike a photoconductive layer in contact with the monomer coating. The two possible configurations with the image recording layer either below or above the photoconductor layer are shown in the figure. In the dark, and with an applied voltage, little current flows through the photoconductor. When given an image-wise exposure, however, an image-wise conductivity pattern forms.[5] The amount of current which flows is proportional to the intensity of light striking the photoconductor. This flow of current is used to produce free radicals through electrolysis of materials contained in the monomer coating. Polymerization is controlled by the electrolytic production of these free radicals. Since photoconductors can be fabricated such that one photon of light results in the flow of many electrons, one photon can lead to the production of many electrolytically formed free radicals, yielding an additional amplification in the final imaging system. Indeed, photoconductors of quantum yields of tens, hundreds and even thousands of electrons per photon have been devised and offer a great opportunity to improve upon the "photo-sensitivity" of polymerization schemes used in image formation.

The problem of finding a suitable photoelectrolytic-polymer system readily breaks down into two parts; that of finding an effective photo-conductive layer having a large quantum yield and capable of converting light into a proportional amountof current when a potential is applied, and that of finding the components of an image recording layer sensitive to electrolysis.

A great deal of work has been done in fabricating and examining photoconductive layers in many laboratories. Suffice here to say that photoconductor systems which are inert to the otheringredients of the imaging system have been made with good quantum yields and rapid light response. Polymerization, efficiently and rapidly initiated through electrolysis, is a relatively infant field of investigation and we would now like to focus our attention on image recording layers sensitive to the passage of current. Progress on photoconductive layers used in conjunction with electrolytically initiated polymerization for imaging purposes will be reported later.

THE IMAGE RECORDING LAYER

The image recording layer generally contains the monomer or monomers, the initiating species which react upon electrolysis, electrolytes which aid the passage of current, binders or gelling agents, humectants, stabilizers and other ingredients necessary for the functioning of the particular system of interest.

Polymerization using aqueous solutions of monomers seems to be the most promising to date, although other polar solvents containing electrolytes which enable them to conduct current have been used. Emulsions of slightly water soluble monomers, as acrylonitrile in aqueous systems, have also been successful with some initiating techniques, although we have not pursued such systems in depth. Aqueous systems have an important advantage in that they are compatible with gelatin and agar binding materials. With glycerine or other humectants, and with carefully chosen electrolytes, gels of polymerizable systems can be made using gelatin or agar that readily conduct current. A "dry" image recording layer, as pictured in Figure 1, is a desirable goal in any convenient photographic system, a consideration which will permeate much of the work, and a point to which we will repeatedly return.

N,N'-methylenebisacrylamide is easier than most water soluble monomers to polymerize, and is commercially available. However, its limited water solubility (4gms/100gms H_2O) limits its utility somewhat. N,N'-trimethylenebisacrylamide is much more water soluble (50gms/100gms H_2O) and is even more easily polymerized. Most of our exploratory work has been made with mixtures of N,N'-trimethylenebisacrylamide and the very soluble acrylamide, which yields a tough solid copolymer.

Before going on to a discussion of the initiating mechanisms, an additional point might be mentioned. In an imaging system it is desirable to have an opaque or colored polymer which stands out from a clear or differently colored monomer. The opacity of a copolymer of N,N'-trimethylenebisacrylamide and acrylamide, very dependent on the relative concentrations of the two, is not opaque enough for this purpose.[6] For these monomers it is necessary to include a dye or pigment in the layer and then follow the polymerization step with a washing which dissolves the unpolymerized monomer, leaving behind the insoluble copolymer and trapped coloration. However, inclusion of heavy metal acrylates, such as calcium, barium or lead acrylate, gives a very opaque polymer, eliminating the need for dyes and washing.[6] α-Chloracrylamide appears to be more easily polymerized than the unsubstituted acrylamide, and also gives a very opaque polymer. There is no end to the types of monomers which could be used. We have barely begun research in this area.

ELECTROLYTIC INITIATION

The very heart of the photoelectrolytic polymerization system is the initiation mechanism. An immediate advantage of electrolytically initiated systems over photo-initiated systems, is of course, that in the absence of current the film in the electrolytically initiated system is insensitive to light. There are many electrolytical methods available to initiate polymerization. Unfortunately, most of these are quite slow. In the following discussion we will focus our attention on three general schemes which show promise of rapidly and efficiently initiating polymerization.

The first scheme is quite simple. Mixtures of water soluble monomers with acid and hydrogen peroxide yield flawless polymer at the cathode.[7] Considering, for example, a 1N solution of HCl containing 10% acrylamide, 1% N,N'-trimethylenebisacrylamide and 0.1% H_2O_2, all percentages by weight, uniform polymer is formed on a steel cathode in less than 10-3 seconds upon the application of 3 volts between two electrodes one cm. apart. The resulting polymer has excellent adherence and dye receptivity. The nature of the mechanism believed to be effective in this reaction is given in equation 1.

1. A $H_2O_2 + H^+ \rightarrow H_3O_2^+$

B $H_3O_2^+ + e \rightarrow H_2O + HO\cdot$

This mechanism involves reduction of protonated hydrogen peroxide to yield hydroxyl free radicals. Stainless steel cathodes seem to give the most uniform polymer in the shortest time. Many electrode materials, especially those known to interfere with peroxide reactions, such as lead, copper and manganese, yield no polymer. Because steel is so much more effective with this system, we have not quite given up the idea that ferrous oxidation by peroxide aids in the formation of polymer by a co-reaction. The presence of ferrous or ferric ions, however, is not essential for polymer formation.

The speed of this reaction and the fact that polymeric images are formed with no post development are encouraging. Unfortunately the strong acid concentrations necessary for this system to work efficiently are sufficient to destroy some photoconductors with which the mixture is placed in contact.[8] Although the mixture containing acid and peroxide is quite stable as a liquid for long periods of time, "dry" emulsions coated on metal substrates appear to autopolymerize upon standing several days.

Carefully buffered emulsions containing stabilizers such as sodium fluoride, sodium pyrophosphate, and phenacetin, on silver-coated substrates would probably solve much of the problem of instability, a facet which we have not yet investigated.

A more promising technique of initiating polymerization electrolytically which shows none of the tendencies of autopolymerization that the acid peroxide system shows, is a system of metal ion initiation. The image recording layer is coated on a metal substrate, which is made the anode. Upon electrolysis, the anode is partially oxidized and metal ions are ejected into the emulsion upon passage of current. Equation 2A shows this for an iron anode.

$$\begin{array}{lll} 2. & A & Fe \rightarrow Fe^{+3} + 3e \\ & B & Fe^{+3} + R \rightarrow Fe^{+2} + R^{+} \\ & C & Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + HO^{-} + HO\cdot \\ & D & H_2O_2 + R \xrightarrow{Fe^{+3}} R^{+} + HO^{-} + HO\cdot \end{array}$$

Many other materials work; this particular example is typical for a metal which dissolves primarily in the higher of two readily available valence states. Certain anions, such as chlorides in the case of a steel anode, or nitrates in the case of a copper anode, aid this process of metal oxidation. Reducing agents, such as hydroxylamine hydrochloride or diphenylcarbazide, present in the solution or emulsion, then reduce the metal ions to their lower valence state, equation 2B. The developing step then involves adding hydrogen peroxide or washing the exposed emulsion in dilute hydrogen peroxide solution to yield the hydroxyl free radicals capable of initiating polymerization. Equation 2D, obtained by the addition of 2B and 2C, suggests that the overall reaction is one catalyzed by dissolved metal ions. This suggests that one metal ion can be used to form many free radicals, another source of amplification in the final image forming process. Careful studies of the concentrations of reducing agents and metal ions in 10% acrylamide, 1% N,N'-trimethylenebisacrylamide solutions indicate that, at least in the case of iron, an amplification factor of ten or greater can be expected; that is, reaction 2D occurs ten or more times before the metal ion is so trapped by polymer that it can react no more.

The amplification demonstrated in equation 2D is somewhat counteracted by a loss of efficiency in 2A, representing the conversion of current to oxidized metal ions. Table I shows the efficiencies of stainless steel electrode dissolution under various conditions. The maximum efficiency that could be expected is 0.33 since three electrons are required for the formation of a single ferric ion. The first group of figures demonstrates that efficiency is a function of the nature of the electrolyte. Potassium chloride and sodium chloride are the most efficient, giving the highest yield of ferric ion, about 0.13, for each electron passed. The second group of figures show that efficiency increases greatly with increasing strength of the electrolyte. Higher oxidation efficiencies can be obtained with soft iron electrodes.

Equation 3 shows that the metal ion initiating system works as well in principle if the anode dissolves in the lower of two available valence states. In this case, a silver anode dissolves in its common +1 valence. Persulfate oxidizes the silver ion, as shown in equation 3B, and forms free radicals capable of initiating vinyl polymerization. Mild reducing agents, reduce the Ag^{+2} back to Ag^{+1}. Equation 3D again demonstrates that the silver ions act much as a catalyst for the direct reaction of persulfate with the reducing agent. In this manner one silver ion is capable of initiating more than one polymer chain.

3. A $Ag \rightarrow Ag^+ + e$

B $Ag^+ + S_2O_8^{-2} \longrightarrow Ag^{+2} + SO_4^{-2} + (SO_4^-)\cdot$

C $Ag^{+2} + R \rightarrow Ag^+ + R^+$

D $S_2O_8^{-2} + R \xrightarrow{Ag^+} SO_4^{-2} + R^+ + (SO_4^-)\cdot$

Some careful studies have been made on the metal ion initiating system. On a steel plate in which the monomer and initiating materials[9] are incorporated in a "dry" gelatin coating, polymer can uniformly be deposited over 1cm.^{2} area upon the passage of 50 milliamps of current for 1/100 of a second. The actual current sensitivity, however, appears somewhat dependent on the type of binder used. Using the same mixture in liquid experiments, without the gelatin, it is apparent that differential polymerization occurs for solutions containing as little as 10^{-5} molar ferric ion.[10] Electrolysis experiments using steel electrodes demonstrates that the passage of 10^{-6} coulombs is sufficient to generate enough ferric ion to polymerize a disc 1cm.^{2} and 0.1mm thick. As the solution efficiencies of Table I indicate, the exact amount of current which converts metallic iron to ferric ions is a function of the potential. The passage of between 0.1 to 1.0 milliamps for 1/100 of a second might thus be considered a limit to the sensitivity of this system for image formation. Comparing these figures with the figures given previously for polymerization on a gelatin plate makes it apparent that a great deal of current sensitivity is lost in going from liquid systems to gelled layers. We are presently extensively investigating different binders to minimize this loss of sensitivity. Gelatin is one of the poorest binders. Since acrylamide and acrylates seem to affect the gelling strength of gelatin, high concentrations of this binder are required. There is also evidence that gelatin copolymerizes, shortening the polymer chains. The use of agar as a binding material seems to hold much promise, eliminating the two difficulties just mentioned. Preliminary experiments show that agar layers have a current sensitivity almost ten times greater than that of gelatin.[11]

A third technique for initiating vinyl polymerization that we would like to discuss utilizes aqueous solutions of zinc salts. The mechanism we believe to be active is that given in equation 4, which reminds one of the mechanisms often associated with the photoconduction of zinc oxide.[12] Zinc ions complex with oxygen dissolved in the media.

4. A $Zn^{+2} + O_2 \rightarrow ZnO_2^{+2}$

B $ZnO_2^{+2} + e \rightarrow ZnO_2^{+}$

$ZnO_2^{+} \rightarrow Zn^{+2} + O_2^{-}$

or

B' $ZnO_2^{+2} + 3e \rightarrow ZnO_2^{-}$

C $O^{-}_2 + H_3O^{+} \rightarrow H_2O + HO_2\cdot$

D $H_2O + HO_2\cdot \rightarrow H_2O_2 + HO\cdot$

E $Zn + 2H_3O^{+} + 2H_2O_2 \rightarrow Zn^{+2} + 4H_2O + 2HO\cdot$

Upon electrolysis this charged complex migrates to the cathode where it is reduced, releasing O_2^- according to reaction 4B or 4B'. O_2^- then reacts to yield perhydroxyl free radicals, equation 4C, or these radicals further react to form hydroxyl radicals, equation 4D. Either perhydroxyl or hydroxyl radicals can initiate polymerization. Equation 4E is added to demonstrate that in slightly acidic media any zinc deposited according to equation 4B' can be used to reduce the H_2O_2 formed, again resulting in hydroxyl-free radicals.

The polymer formed by zinc salt initiation adheres well to the cathode. The system works equally well with steel, aluminum and lead electrodes; initiation on copper seems to be somewhat more efficient.

An immediate advantage of the zinc salt initiating technique over that of metal ion injection is that polymer is formed immediately, with no post processing. It also gives us, of course, some flexibility in examining photoconductors which have rectifying properties that make cathodic initiation desirable. Agar layers utilizing the zinc salt initiation system have been made which show the formation of polymer with about the same current sensitivity as that demonstrated in the metal ion injection system; that is, the passage of 50 milliamps for 1/100 of a second, will leave a readily observable 1cm.^{2} polymer image in an agar bound layer coated on steel.

DISCUSSION

Vinyl polymerization involves between 10^3 and 10^6 monomers, although it is certainly doubtful that we can easily obtain the latter figure. Considering 100 per cent conversion of light to electricity, one photon could thus cause between 10^3 and 10^6 events. Since photoconductors with efficiencies of tens, hundreds and even thousands, have been devised, additional amplification can be obtained above that provided by the polymerization itself. Silver halide is generally quoted to have an amplification upon development of between 10^6 and 10^9, and there are occasional reports of greater amplification. On this basis, imaging systems based on photoelectrolytic polymerization might compete. But whether one electron can lead to the formation of a chemical species that will initiate polymerization is a question as yet not answered. Such a sensitivity would be the theoretical limit of the acid-peroxide system, and, under favorable conditions, the zinc salt initiating systems. Although moderated by the fact that metal anode solution is a process with an efficiency less than one, the fact that under favorable conditions one metal ion could lead to the formation of many free radicals, each capable of initiating polymerization, gives the metal ion injection scheme the promise of efficiencies greater than one.

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6. This opacity is due to light scattering from the colloidal nature of the copolymer. In some cases, this opacity is lost as the copolymer dries with age and the particles coalesce.

7. Other per-compounds, such as persulfates, perborates and even water soluble peroxides and hydroperoxides work equally as well.

8. This fact, in itself, does not seriously put this initiating scheme at a disadvantage. The photoconductor can be isolated from the polymerization system by any intermediate layer which conducts current greater in a direction perpendicular to its surface than parallel, Figure 1. An example of such an intermediate might be Corning's "microlead" glass, a glass containing small wires imbedded to carry current only perpendicular to its major surfaces.

9. These results are for 0.1 N KCl solution of 10% acrylamide and 1% N,N'-trimethylenebisacrylamide, using 0.6% hydroxylamine hydrochloride as the reducing agent, all percentages by weight. It might be expected that greater concentrations of monomers would give greater current sensitivities, which is true in liquid experiments. Greater acrylamide concentrations, however, require higher concentrations of gelatin to prevent crystallization, and little additional sensitivity is obtained in the final "dry" layer.

10. Depending on the reducing agent used, there may be a slow reaction between the reducing agent and the per-compounds used, releasing free radicals and initiating polymerization even in the absence of metal ions. For a given concentration of per-compound the rate of this

direct oxidation-reduction reaction is directly proportional to the concentration of the reducing agent. If it takes X time for this direct reaction to initiate polymerization, then we say "differential polymerization" occurs with sufficient metal ion concentration to iniate polymerization in less than X/4.

11. In evaluating the sensitivity of layers using gelatin as a binder, it is necessary to exercise some care, if only for the sake of completeness, in discriminating between polymerization and gelatin tanning. The injection of some metal ions, as, for example, those of Cr from steel, can be very effective in rendering gelating insoluble.

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TABLE I

STAINLESS STEEL ANODE OXIDATION EFFICIENCY[a]

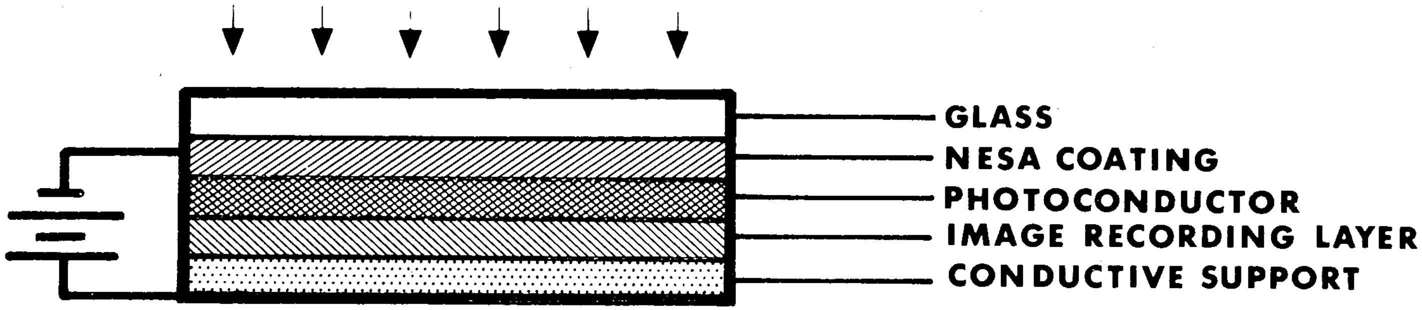
Two Electrodes 1cm. Apart

Electrolyte	Potential, Volts/cm.	Efficiency, Fe^{+3}/electron
0.1N KF	71	0.04
0.1N KCl	71	0.12
0.1N KBr	71	0.01
0.1N KNO_3	71	0.02
0.1N K_2SO_4	71	0.02
0.1N K_2CO_3	71	0.005
0.1N NaCl	71	0.13
0.1N KCl	71	0.12
0.1N KCl	48	0.07
0.1N KCl	24	0.05
1.00N KCl	71	0.19
0.10N KCl	71	0.12
0.01N KCl	71	0.06

---

[a] Type 304 steel: 0.08% C max, 2.0% Mn Max, 1.0% Si max, 18-20% Cr, 8-11% Ni, and the remainder Fe.

1-PHOTOCONDUCTOR BETWEEN LIGHT SOURCE & IMAGE RECORDING LAYER



2-PHOTOCONDUCTOR BETWEEN IMAGE RECORDING LAYER & CONDUCTIVE SUPPORT

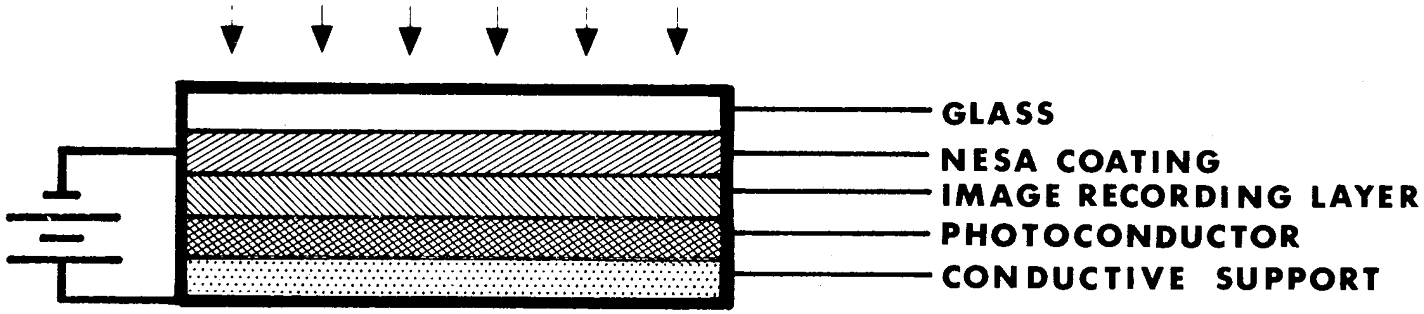


FIGURE 1: Sandwich arrangement of component parts in photoelectrolytic imaging systems

PHOTOPOLYMERIZATION STUDIES:

I. POLYMERS FROM NEW PHOTOREDOX CATALYST SYSTEM[1]

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ABSTRACT

A new photoredox catalyst is described wherein a phenothiazine dye in its excited state oxidizes a catalyst to a free radical. This free radical efficiently initiates the polymerization of metal acrylates giving ~~rise to~~ polymers ~~which are~~ insoluble in the monomer containing medium. The polymers precipitate as insoluble colloidal particles. Optical transmission measurements are used to follow the polymerization and to calculate the number and size of the polymer particles. ~~The effect of various factors such as~~ the nature of the catalyst and the photooxidant, the pH and the temperature of the medium on photopolymerization are described. ~~It is indicated that this new system may be useful for rapid photographic imaging and display applications.~~ (Author)

* * * * *

Dye-sensitized photopolymerization of acrylic and vinyl monomers has been studied by many investigators.[2-22] It has been suggested that the use of visible radiation in photochemical sequences leading to polymerization required the presence of an electron donor and oxygen.[2,15,23-26] Most investigators have not recognized the importance of direct photochemical generation of the free radical initiator. Usually, studies have centered around initiator systems which required multiple reactions or whose free radicals were very inefficient for initiating polymerization.

Dyes of certain classes, in particular, the phenothiazine dyes, are strong oxidants in their photoexcited state (probably the triplet state). Redox catalyst initiation of polymerization[27] has been shown to be a very efficient means of polymerizing vinyl and acrylic monomers. Photochemically induced redox catalysis, referred to here as "photoredox catalysis", has proved useful to initiate polymerization directly, and with efficiencies which are greater than any heretofore reported for dye-sensitized photopolymerization. The present paper deals with a photoredox catalyst system consisting of a phenothiazine dye photooxidant, such as methylene blue and thionine, and an organic sulfinic compound, such as p-toluenesulfinic acid. The system does not require oxygen to function efficiently, but on the other hand, it is not particularly adversely affected by the presence of oxygen. Organic sulfinic acids, particularly when activated by aromatic amines, have been proposed and studied for initating the polymerization of vinyl and acrylic monomers.[28,29] The system described in this paper, along with results presented in other papers of this series,[1] have led to dry processed photographic techniques and information storage and retrieval systems.

EXPERIMENTAL MATERIALS AND METHODS

Barium diacrylate was prepared by neutralizing distilled acrylic acid with a distilled water solution of barium hydroxide octahydrate. The pH was usually adjusted to 5.0 to 7.0 with excess acrylic acid and the solution filtered. In some preparations the solution was concentrated under vacuum, and in other preparations undistilled acrylic acid was used, followed by treatment with activated carbon and filtration. Generally, the concentration of the solutions were kept at from 35% to 46% by weight. The refractive index of a 40% by weight solution at pH = 6.25 was 1.399.

Methylene blue (Harleco, Methylene blue chloride, 90% dye content, C.I. No. 52015), and thionine (Matheson, Coleman and Bell, Biological stain, C.I. No. 52000) were used without further purification.

Sodium p-toluenesulfinate monohydrate (Distillation Products Industries 90%+) was used without further purification.

A. Apparatus and Procedure

The photopolymerization of barium diacrylate was studied in a unique manner. Barium diacrylate monomer is very soluble in water, but the polymer is very insoluble. As barium diacrylate polymerizes, it precipitates from solution as colloidal particles which scatter light. The light which passes completely through the polymerizing medium is monitored by the photomultiplier and the signal is recorded on the strip chart recorder. The signal is compared to that obtained when the sample cell is filled with distilled water. The radiation incident on the sample cell was measured with an Eppley thermopile and micro-voltmeter. The sample cell consisted of two 5 cm x 5 cm glass plates 0.69 mm thick and separated by a peripheral plastics shim 0.15 mm thick. The cells were loaded in the dark and clamped together.

The apparatus used in the present study is shown in Figure 1. It essentially consists of a light source (500-watt projector) a; a filter holder for neutral density or bandpass interference filters b; a sample holder for thin films of monomer-catalyst compositions under study c; another filter holder for neutral density filters to attenuate the light which is transmitted through the compositions under study d; a photomultiplier assembly e; and a strip chart recorder f. Items b, c, d and e were secured to a conventional optical bench.

Typical photocatalyst solutions were prepared by dissolving 2.14 g of sodium p-toluenesulfinate monohydrate and 0.03 g of methylene blue (or 0.0227 g of thionine) in about 90 ml of distilled water by stirring for 24 hours at room temperature. The volume of the solution was made up to 100 ml with distilled water and the solution filtered.

Typical photosensitive solutions were prepared in the dark by mixing 4.0 ml of barium diacrylate solution with 1.0 ml of photocatalyst solution.

RESULTS AND DISCUSSION

A. Light Scattering Phenomenon

It can be shown that, at least in the region of low monomer conversion, the number of colloidal particles precipitated per unit volume is such that each polymer particle may be treated independently as a single scattering entity. The evidence for this is that the curve of optical density versus reciprocal wave length can be fit closely to the Mie scattering curve which was developed theoretically for single scattering. Undoubtedly at higher values of optical density where monomer conversion is very high, multiple scattering could play an increasingly important role.

For single scattering, the light transmitted through a thickness d of scattering medium will be:

$$I = I_0 \ \exp. (-d\gamma)$$

Where I_0 is the intensity of the incident beam and γ is the extinction coefficient. The extinction coefficient is given by:

$$\gamma = N \pi a^2 Q$$

where a is the radius of each colloidal particle, N is the number of colloidal particles per unit volume and Q is the extinction cross-section. In Mie scattering theory for spherical particles, the extinction cross-section is given by:

$$Q = 2 - \frac{4}{p} \sin p + \frac{4}{p^2} (1 - \cos p)$$

where $$p = \frac{4\pi a (m - 1)}{\lambda}$$

γ is the wave length of the incident radiation, and m is the ration of the refractive index of the particle to the refractive index of the medium. By definition, the optical density D is: $D = \log (I_0/I)$ or from the above: $D = 0.434d\ N.\ a^2Q$

It is, therefore, apparent that the mass of polymer formed will be directly proportional to the optical density rather than to transmitted light. Figure 2 gives a curve for optical density versus reciprocal wave length in microns. The solid curve is a portion of the Mie curve and the circled points are data secured in the following manner:

A photosensitive solution 1.25m in barium diacrylate, 2 x 10^{-2} M in sodium p-toluenesulfinate and 2 x 10^{-4} M in thionine was adjusted to a pH of 6.1 and placed in a sample cell, giving a film 0.15 mm thick. The film was polymerized with uniform white light of arbitrary intensity to give a film having an optical density of about 0.45 to 0.55. The film was fixed* and the optical density measured as a function of wave length over a range of 0.4 to 0.8 on a Coleman, Model 14, spectrophotometer. From this data and from the Mie light scattering equation, Figure 2 was drawn. This data was also used to calculate the particle radius and the number of particles per cubic centimeter N, with m estimated to be about 1.101. This gives a = 3.36 x 10-5 cm and N = 3.85 x 10^{10} particles/cc.

The relationship between optical density and mass of precipitated polymer may be established in still another manner. If photosensitive solutions containing various initial monomer concentrations are uniformly and completely polymerized in film form in the above described apparatus and the optical density of the films measured with a densitometer, the optical density measured will be due to the colloidal polymer particles resulting from the total conversion of the various initial monomer concentrations.

Several solutions were prepared having a pH of 5.65 which were 2 x 10^{-2} M in sodium p-toluenesulfinate and 2 x 10^{-4} M in methylene blue and contained barium diacrylate in varying concentrations of 0.129 M, 0.258 M, 0.8M and 1.29M, respectively. The solutions were each placed in a sample cell to form a uniform film 0.15 mm thick. The films were illuminated with white light of arbitrary intensity for a sufficient length of time to insure complete polymerization as evidenced by no further change in optical density measured with white light. In this manner a "limiting" or saturation optical density was achieved. The initial monomer concentration was plotted against saturation optical density in Figure 3. A very high degree of linearity is shown by the curve up to an optical density of about 2. Above this value there is deviation which is probably due to multiple scattering effects from the increasing number of particles and shadowing effects. Particles in the foreground shadow particles in the background resulting in less average effective scattering per particle as the number increases.

B. Polymerization

As photoinitiated polymerization occurs in the apparatus of Figure 1, light is scattered by the colloidal particles formed. The light that passes through is suitably attenuated by filters and converted to a signal which is directly proportional to the intensity of the transmitted light. The optical density is calculated, based on the intensity transmitted by a cell filled with water.

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*Thermal fixing or desensitization will be the subject of a subsequent paper in this series. For optical fixing, see Ref. (1).

For purposes of comparison, the recorded signal and the optical density curves are shown in Figure 4. The photosensitive solution was 1.25 M in barium diacrylate, 2×10^{-2} M in sodium p-toluenesulfinate, and 6.3×10^{-3} M in methylene blue and had a pH of 6.0. The intensity of the light incident on the sample cell was 8.8×10^{-4} watts/cm^2 after passing through a red filter having 1% transmission at 550 mm, 31% at 650 mm and 70% transmission at $750 M\mu$.

C. Comparison of Polymerization Initiators

The photosensitive solution that was used in this study was prepared in the dark to contain concentrations of 1.25 M barium diacrylate, 10^{-1} M of initiator shown in Table I, and 2×10^{-4} M methylene blue. The pH of the solution was adjusted to 6.5 and sample cells were filled with solution as previously described. Each cell was illuminated with white light of the same, but arbitrary, intensity. The time was recorded to give 50% transmission of the incident light. Table I gives the results and demonstrates the superior reactivity of the sulfinic radicals in initiating the photopolymerizations.

D. Induction Period

In most polymerizations, a short period of time usually elapses before the polymerization can be observed. If oxygen is carefully removed from the solution and then excluded from redissolving, the induction period is materially shortened, but not eliminated. This indicates that there are inhibitors present other than gaseous inhibitors (probably oxygen).

The reactions involved in free radical generation and annihilation can be written in the following manner:

$$\begin{array}{llllll}
D^{+} & + & h\nu & \longrightarrow D^{+*} & ; & I_{abs}. \\
D^{+*} & + & RSO_2^{-} & \longrightarrow D^{\circ} + RSO_2^{\circ} & ; & k_c \\
RSO_2^{\circ} & + & M & \longrightarrow RSO_2M^{\circ} & ; & k_i \\
RSO_2^{\circ} & + & N & \longrightarrow RSO_2N \text{ (Inactive)} & ; & k_n
\end{array}$$

In the first equation, light is absorbed by the dye cation D^+ to produce the excited state D^{+*}. This reacts with the sulfinic anion to form a sulfinic-free radical and a dye-free radical. The sulfinic-free radical initiates polymerization by reacting with a monomer molecule. However, in the presence of an inhibitor N it will react to form inactive species. The rate of formation of the excited dye (triplet) molecule is dependent upon the intensity of absorbed light and the quantum yield of the intersystem crossover, ϕ.

$$D^{+*} = \phi \, I_{abs}.$$

The excited dye reacts with sulfinic ion to form the free radical polymerization iniator RSO_2°. By assuming a steady state condition for the formation and use of the free radical, the following equation can be derived:

$$dN = -K\,dt$$

where M can be eliminated from the equation because during the disappearance of the inhibitor the free radical will react preferentially with the inhibitor and not with the monomer and the monomer concentration will not substantially change but will remain the same as the initial concentration, and where:

$$K = k_c I_{abs.} \phi S$$ (S is the concentration of sulfinic acid catalyst)

The solution to this equation is:

$$N_o - N = Kt$$

An induction period may be defined as that time period t_I after which the concentration of inhibitor becomes negligibly small and $N \rightarrow 0$.

Placing N = 0 in the above equation, the induction period is:

$$t_I = \frac{N_o}{K}$$

or $$I_{abs.}\, t_I = \frac{N_o}{kc\, \phi S}$$

This last equation indicates that the induction period should be proportional to the reciprocal of the intensity.

A photosensitive solution was used which was 1.25M in barium diacrylate, 2×10^{-2} M in sodium p-toluenesulfinate and 2×10^{-4}M in methylene blue. The pH of the solution was adjusted to 7.0. Sample cells were filled with the solution to give films 0.15mm thick and exposed to white light of various intensities which were measured in arbitrary units with a photometer. The intensity of the light was controlled by using neutral density filters and an iris diaphragm in the filter holder b of Figure 1. The induction period was measured as that length of time from the start of illumination until an optical density of 0.01 above background was observed on the photomultiplier assembly. Figure 5 is a plot of this data and shows that the induction period does indeed vary as the reciprocal of light intensity over a very wide range of intensities.

E. Comparison of Photooxidant Dyes

In order to be useful as a photooxidant in the photoredox catalyst system under study, a dye must be a stronger oxidizing agent in the excited state than in its ground state. A fairly wide variety of water-soluble dyes were tested for the ability to function as a photooxidant using p-toluenesulfinate ion as the catalyst.

A photosensitive solution which was adjusted to $pH = 6.0$ was prepared containing 1.25 M barium diacrylate, 2×10^{-2} M sodium p-toluenesulfinate and 10^{-4} M of the dyestuff under study. The The transmittance of the sample cell was measured and the time in seconds for the transmittance to fall to 0.5 was recorded for each dye. The results are given in Table II in which light from a quartz high pressure mercury arc lamp was used to illuminate the sample cell. Since there is a considerable variation in spectral intensity of this light and the results of Table II should only be considered as qualitative.

F. Extent of Polymerization

An inspection of the optical density versus time curve of Figure 4 shows that at least a part of this slowly curving toe is due to competitive inhibitor and initiation reactions. We have seen that there is a linear relationship (Figure 3) between extent of polymerization and optical density. Mathematically, this linear relationship can be expressed by:

$$\frac{M_o - M}{M_o} = \frac{D}{D_S}$$

or

$$M = \frac{M_o}{D_S} (D_S - D)$$

where D_S is the saturation optical density. M_o is the initial monomer concentration and M is the concentration of the monomer remaining in the polymerizing solution at any given time.

Photopolymerizations are usually first order in monomer concentration. If we assume this is true in this case also, then the rate of disappearance of monomer is given by:

$$-\frac{dM}{dt} = k\,M$$

Substituting the above equation in this differential equation there is obtained:

$$\frac{d\,D}{dt} = k\,(D_S - D)$$

Solving this, we get:

$$\log \left[\frac{D_S - D}{D_S}\right] = -kt$$

A photosensitive solution which was adjusted to $pH = 5.0$ was prepared which was 1.29 M in barium diacrylate, 2×10^{-2} M in sodium p-toluene sulfinate, and 2×10^{-4} M in methylene blue. Sample cells were filled with the solution and heated to various temperatures for three minutes, then held at the particular temperature while photopolymerization was occurring and the optical density was being monitored. Figure 6 shows the data plotted as time in seconds versus logarithm of relative optical density according to the above equation. The curves are linear at each temperature. In preparing these curves, a saturation optical density of $D_S = 2.78$ was used as determined from long time exposure of this solution.

G. Effect of Temperature and Polymerization and the Activation Energy

According to Figure 6 and the above equation, it is possible to calculate the logarithm of the rate constant for each temperature. A representation of this data is given in Figure 7 where the logarithm of the rate constant is plotted against reciprocal absolute temperature using the above data.

The rate constant can be expressed as:

$$k = A \exp. - \left[\frac{\Delta E}{RT}\right]$$

$$\log k = \log A - \frac{0.434 \Delta E}{RT}$$

From Figure 7 and the above equation, the activation energy can be calculated as

$$\Delta E = 4.8\text{k cal./mole}$$

This activation energy is for the overall photopolymerization process and is of a value which is not inconsistent with low energy photoprocesses.[30, 31]

H. Effect of pH on Photopolymerization

The effect of pH on the rate of photopolymerization is illustrated in Figures 8 and 9. It must be noted that the pH values plotted along the abscissa are the pH of the monomer solution, and that the addition of a photocatalyst solution lowered the values somewhat from those indicated above a pH of 8. While the induction period is shortest at relatively low pHs, the rate of polymerization after the end of the induction period is fastest in approximately neutral solutions. Thus, if a method of eliminating the induction period is employed, the rate will be greatest in a solution with a pH of about 7. The advantage of an approximately neutral solution becomes greater as the light intensity is increased.

Several factors are known to be involved in the relationship between rate and pH. First of all, the oxidative strength of the dye is inversely proportional to the pH, and presumably the potential of the dye in the excited state follows suit. The rapid decrease in polymerization rate with increasing pH above 8 may be due to this change in the oxidation potential of the dye and a resulting diminished efficiency in the oxidation of the catalyst. Second, the composition of the monomer is pH dependent, the ratio of free acrylic acid to barium diacrylateincreasing rapidly as the pH is decreased in the region of pH 5. The reactivity of the acid is probably less than that of the salt. Moreover, the oncorporation of free acid in the polymer tends to render the polymer more compatible with the solvent, so that solvent remains associated with the polymer particles and their light-scattering power is diminished. Therefore, the apparent rate of polymerization, as determined by the optical density of the polymer film, is less than the actual rate of polymerization based on the number of monomer units incorporated in the polymer. These factors reduce the apparent rate of photopolymerization at low pHs. Since none of these factors explain the variation in the induction period, still other factors are involved.

As the monomer is changed from virtually all barium diacrylate to include substantial amounts of acrylic acid, a point is reached at which photopolymerization first forms an opaque, light-scattering polymer which is then converted to clear gel upon continued polymerization. This will occur at a pH of 2.3, for example. Such behavior indicates the barium diacrylate is incorporated into the polymer more rapidly than the free acid.

I. Effect of Wave Length of Light on Photopolymerization

Photopolymerization rate activity follows very closely the absorption curve of the photooxidant dye which in this case is methylene blue or thionine. Figure 10 is an absorption curve for methylene blue and sodium p-toluenesulfinate solution where the sodium p-toluenesulfinate concentration is one hundred times that of the methylene blue.

Several sample cells were filled with a photosensitive solution with concentrations of 2 M barium diacrylate, 2 x 10^{-2} M sodium p-toluenesulfinate, and 2 x 10^{-4} M methylene blue at a pH of 6.9. The cells were exposed to light through several filters. The transmission characteristics of each filter was measured and found to vary as follows: no filter, 2.5 x 10^{-5} watts cm^{-2}; red filter, 2.45 x 10^{-6} watts cm^{-2}; green filter, 1.4 x 10^{-6} watts cm^{-2}; and blue filter, 7.45 x 10^{-6} watts cm^{-2}. Because several different power levels of light of different frequency bands were used, the light power was multiplied by the illumination time for each optical density data point to give the energy used per square centimeter to secure the given optical density. Because of the large range of energies used in this experiment, the logarithm of the energy for each color band was plotted against optical density for a given photopolymerization. Figure 12 shows that the photosensitive solution is most sensitive to blue light. A curve showing the polymerization with white light from an incandescent bulb is given for comparison.

J. Termination Mechanism

The polymerization of barium diacrylate and other metal acrylates can be thought of as involving the polymerization of a tetrafunctional monomer $(CH_2 = CHCOO)_2$ Ba. On the other hand, the polymerization can be conceived as involving the polymerization of acrylic acid anion $CH_2 = CHCOO^-$ to form a polyelectrolyte which combines with barium cation to become crosslinked. Regardless of the validity of either concept, the polymer which results is highly crosslinked and becomes insoluble at a relatively low degree of polymerization. Because of this, a growing polymer chain ceases to grow and add monomer upon becoming insoluble and precipitating from solution. Precipitation from solution can, therefore, be conceived as a termination mechanism. There is, undoubtedly, some continued addition of monomer in the precipitated colloidal particle but this addition is very sluggish in comparison to the polymerization rate in solution.

We have observed that there is substantial radical trapping in the precipitated colloidal particles because it is possible to induce continued polymerization and increase in optical density in the polymer particles. The increase in optical density occurs only in the precipitated polymer particles and is roughly proportional to the mass of polymer already precipitated.

K. Photographic Application

Figure 12 gives the optical density of a film of photosensitive composition in terms of the logarithm of the energy per unit area required to achieve that optical density. In photographic terms, the curves of Figure 13 are the characteristic curves of a photographic material, also called H and D curves. The energy per unit area is the exposure. Usually the unit employed is the meter-candle-second. If these units are used then the slope of the straight line portion of the characteristic curve is called the gamma of the composition. The authors have utilized the photoinitiated polymerization process and compositions described above and in another paper[1] to develop a dry processed photographic method which at the present time is capable of achieving a sensitivity equivalent to about ASA = 10^{-2}.

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TABLE I

COMPARISON OF VARIOUS COMPOUNDS AS CATALYSTS

Catalyst	Illumination time (sec) required to achieve 50% T
Sodium benzenesulfinate	10
5-salicylsulfinic acid	11
p-acetamidobenzenesulfinic acid	13
sodium p-toluenesulfinate	14
2,4-pentanedione	24
thiosinamine	200
hydrazine	247
thiourea	330
triethanolamine	500
ethylenediaminetetraacetic acid	no polymer
hydroxylamine	no polymer
hexamethylenetetramine	no polymer
diethylaminoethyl alcohol	no polymer
sodium oxalate	no polymer

TABLE II

COMPARISON OF PHOTOOXIDANT DYES

Dye (10^{-4} M)	Time (seconds) for transmittance to drop to 0.5
thionine	3
azure C	4
azure B	5
methylene blue	5
toluidine blue O	5
azure A	6
proflavine	6
new methylene blue N	9
acridine yellow (sat'd. dye solution)	11
phenosafranine	20
methylene green	20

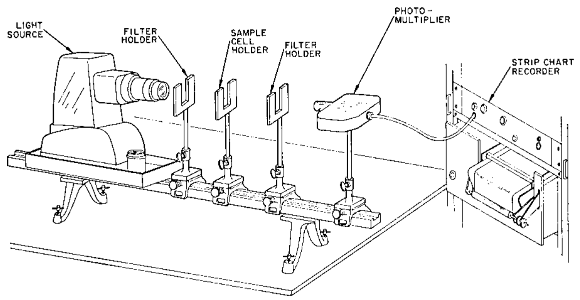

FIGURE 1: Photopolymerization apparatus

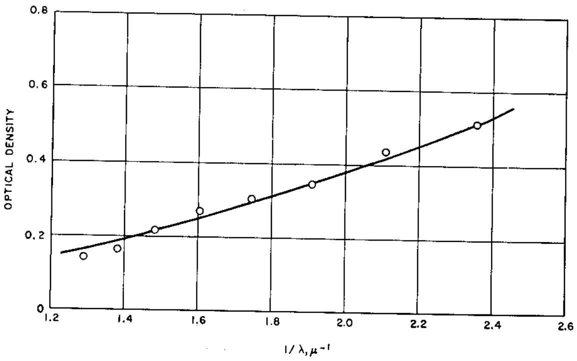

FIGURE 2: Optical density of light-scattering polymer particles versus reciprocal wavelength. Solid line is a portion of Mie curve

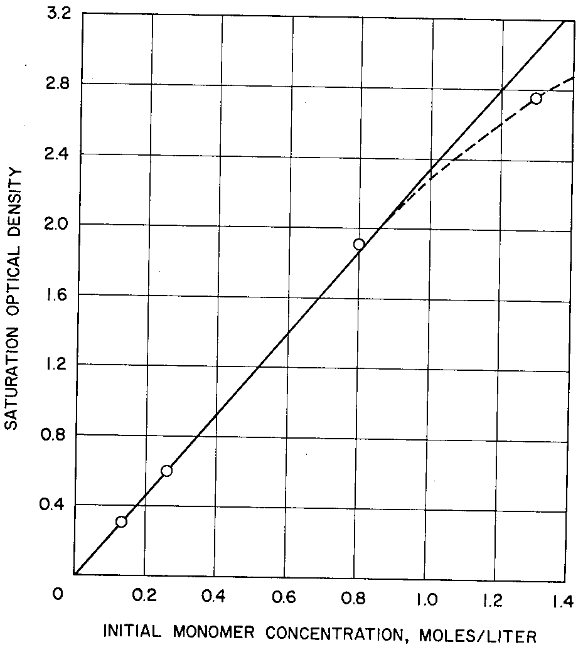

FIGURE 3: Relationship of optical density to mass of light-scattering polymer particles

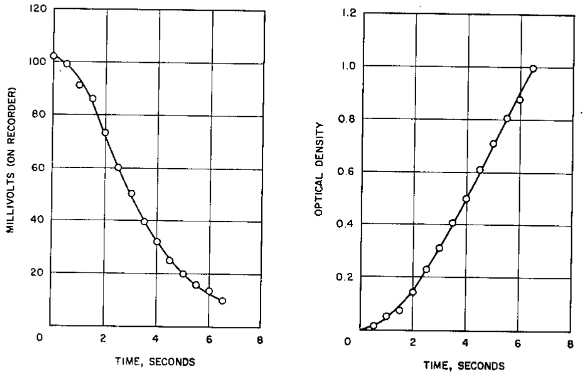

FIGURE 4: Left curve – Variation of photomultiplier signal with polymerization time. Right curve – Derived curve of variation of optical density with polymerization time

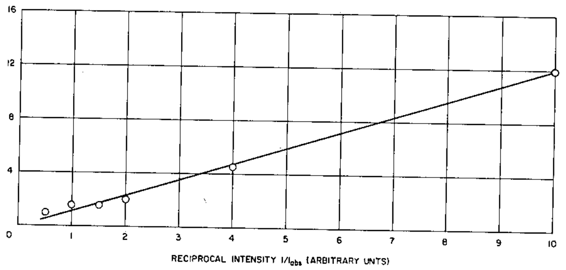

FIGURE 5: Dependence of induction period of reciprocal of light intensity

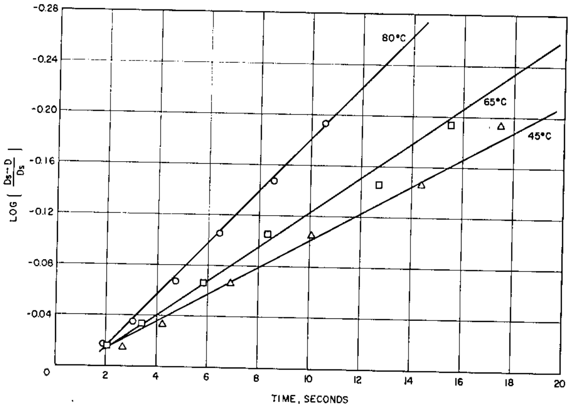

FIGURE 6: Polymerization time versus logarithm of relative optical density showing dependence of polymerization to be first order in monomer concentration

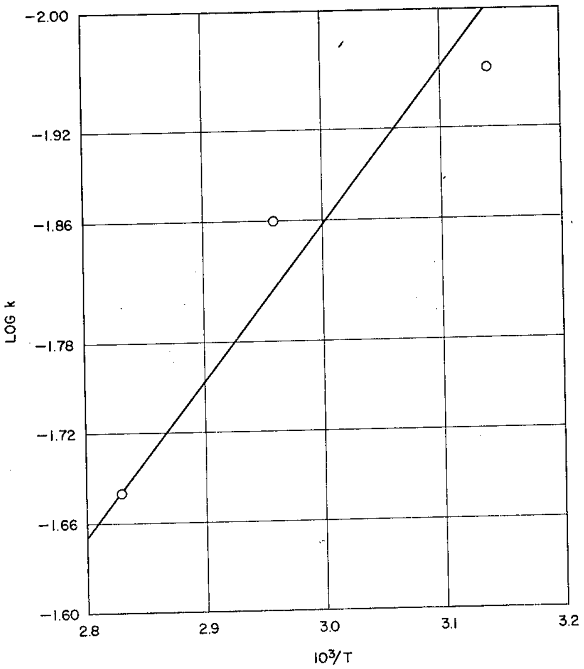

FIGURE 7: Arrhenius plot for photoredox initiated metal acrylate polymerization

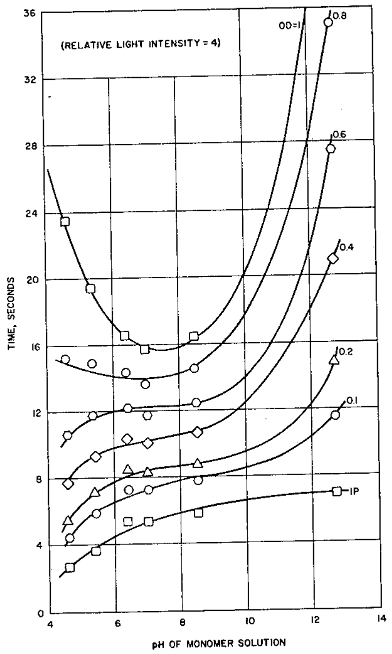

FIGURE 8: Effect of pH on rate of polymerization

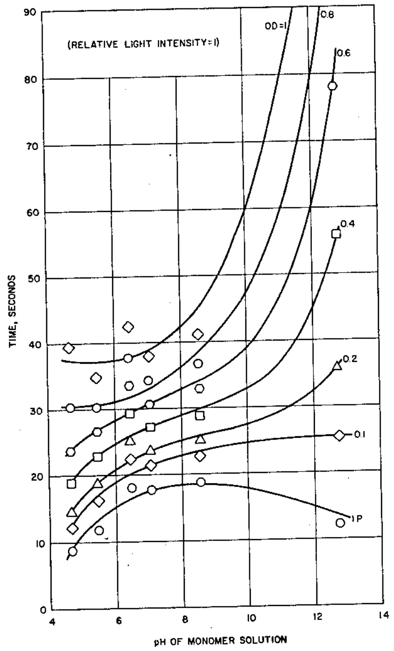

FIGURE 9: Effect of pH on rate of polymerization

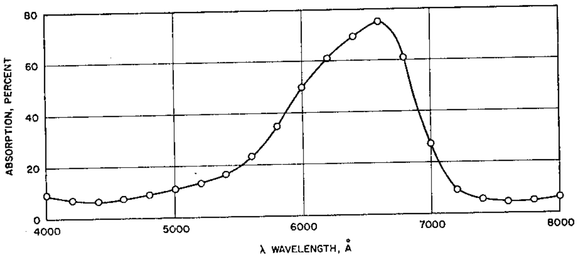

FIGURE 10: Spectral absorption curve of methylene blue and sodium p-toluene sulfinate aqueous solution

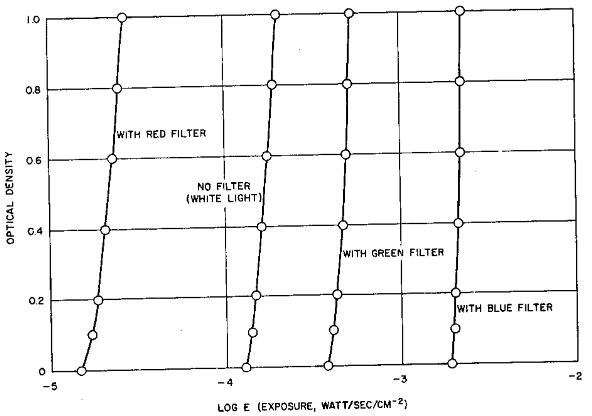

FIGURE 12: Extent of polymerization as optical density versus logarithm of energy input for different ranges of light frequency

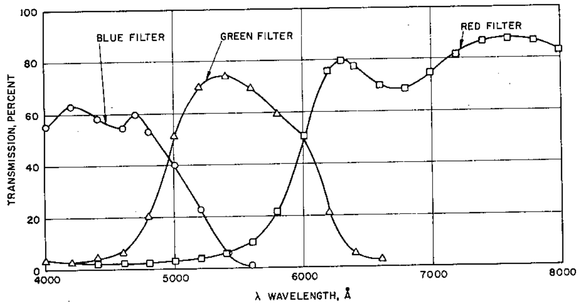

FIGURE 11: Spectral transmission of light filters

PHOTOPOLYMERIZATION OF ACRYLAMIDE AND ITS DERIVATIVES BY LIGHT-SENSITIVE METAL SALTS

Edward Cerwonka

General Aniline and Film Corp.

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This review ~~will be~~ is concerned with the properties of photopolymerizable compositions in the form of coated layers, the treatment being limited to a consideration of hydrophilic compositions in which photosensitivity is imparted by a metal salt and the monomers involved are derivatives of acrylamide. (AUTHOR)

Light sensitive salts of iron, cerium and managanese form useful initiators in the photopolymerization of acrylamide and its derivatives. Generally speaking, the ferric, ceric and manganic salts of alpha hydroxycarboxylic acids are sensitive to visible light. Figures 1 through 5 depict the spectrophotometric curves of aqueous solutions of these salts. Absorption peaks, it will be noted, range from 400 millimicrons (ferric benzilate) to 550 millimicrons (manganic citrate). The light-sensitivity of the ferric, ceric, or manganic salt of an alpha hydroxy acid seems to be associated with two characteristic features of these compounds - a five- or six-membered colored ring compound or chelate is formed, incorporating the anion of the acid and the metallic cation in its higher valence state and an alpha hydroxycarboxylic acid generally requires little energy for its oxidation. The photoenergy absorbed by the colored complex apparently is sufficient to accomplish this oxidation. On the other hand, there are other well-known colored complexes, for example, that of ferric acetylacetonate, which are not easily photooxidized and are, therefore, stable to visible light.

In Figures 6 through 9, there are portrayed the structures of several of the light-sensitive complexes we are discussing. Selected photodecomposition reactions of these complexes are illustrated in Figures 10 through 13, showing the appropriate photodecomposition products.

In the photopolymerization reaction the action of light eventually gives rise to a free radical. This radical by the combined action of chain propagation and the crosslinking of linear macromolecules produces a water-insoluble polymer in the areas which have been exposed to light. The initiating radical may be derived from the anion by the removal of an electron during the exposure step. This electron is, of course, transferred to the metallic cation associated with the anion, thereby lowering its valence state. As examples, we may cite the formation of a radical from ceric or manganic oxalates, as well as its formation from ferric benzilate (Figure 14). There is an alternative method by which a radical may be generated, a method which seems to be limited to the case of ferric salts. In this instance, the photoproduced ferrous ion is allowed to react with hydrogen peroxide. A hydroxyl radical is thereby released which has been shown to be very efficient at initiating the polymerization of vinyl monomers (Figure 15). Instead of hydrogen peroxide an organic hydroperoxide (e.g., cumene hydroperoxide) may be employed. In the latter instance, an alkoxy radical initiates the desired chain propagation (Figure 15). It should be noted that the alkoxy radical derived from an organic hydroperoxide bears a formal similarity to the organic radical derived from ferric benzilate (Figure 16).

Having reviewed briefly the light-sensitive metal salts available, let us turn our attention to the preparation of coated layers. In practice, a photopolymerizable composition consists of a light-sensitive metal salt, a monomer or monomers, and a film former such as gelatin or polyvinyl pyrrolidone. The solution is coated on a suitable support such as film, paper or glass and allowed to dry. Exposure is followed simply by washout in the case of coatings based on ceric or manganic salts. When ferric ammonium oxalate or ferric ammonium citrate is used as sensitizer, the exposure step is followed by a hydrogen peroxide afterbath before washout. If an organic hydroperoxide has been incorporated into the coated layer, washout suffices.

The photographic speed of a photopolymerizable composition may readily be determined by exposure through a step tablet. It varies considerably with at least two important components of the formulation. One of these is the nature of the metallic salt. A composition in which ceric oxalate comprises the photoinitiator shows greater speed than one incorporating ceric citrate. The difference may depend to a considerable extent upon the lifetime or reactivity of the photoformed radical. Little is known about the identity of these radical intermediates or their properties; consequently, it is difficult to control photographic speed in this manner with knowledge on hand.

A second and more readily controlled variable which affects the photographic speed of a photopolymerizable composition is based on the nature of the monomer employed. It is the structure of the monomer that determines its solubility and consequently how much of a given monomer may be dissolved in a formulation. Generally optimum photographic speed is attained at saturation concentration of a given monomer. Furthermore, certain structural features in the monomer are, of course, reproduced in the polymer derived therefrom, thus affecting the solubility of the polymer formed in the photopolymerization reaction. For example, the concentration of omega acrylamidocaproic acid (Figure 17) that can be incorporated in a coated layer is much lower than the concentration of acrylamide alone, whether on a weight- or mole-basis. Yet, the photographic speed attained with a coating containing omega acrylamidocaproic acid as the only monomer, has a speed four-thirds that of a coating saturated with acrylamide. The reason probably concerns the relative solubility of polyacrylamidocaproic acid and the polyacrylamide product.

The question may be raised: How can an insoluble polymeric image be formed from a linear monomer such as acrylamide, since linear polymers are generally water soluble when the original monomer unit is water soluble? It should be pointed out that there is the possibility of grafting of the polymer to the network of the binder or film-former used (gelatin, for example) which can give rise to a three-dimensional network. It is, however, generally true that the photographic speed attained with a mono-functional monomer alone is usually much lower than that attained when a bi-functional monomer or crosslinking agent is also incorporated in the coated layer. Addition of a crosslinking agent insures the formation of a three-dimensional network with consequent insolubilization of the polymer in the peroxide bath, or in the coated layer when peroxide is unnecessary.

Turning our attention more directly to the subject of bi-functional monomers, it has been found that a photopolymer image is readily obtained when a bi-functional monomer alone is present in the formulation. N,N'-methylene bisacrylamide has been widely used as a bi-functional hydrophilic monomer, mostly because of its availability. The solubility of MBA in water is limited to 4 per cent, however, and the maximum photographic speed attained with MBA is derived from a coating saturated with this monomer (Figure 17). One can, however, improve upon the speed attained with MBA alone, by adding to the formulation acrylamide or omega acrylamidocaproic acid at the respective saturation levels of each monomer.

It should be mentioned in passing that while a multitude of acrylamide derivatives can be prepared and, in fact, have been synthesized, we shall limit our discussion to those derivatives having a significant effect on photographic speed. The two linear monomers shown on slide 17 suffice to show what can be done with a monofunctional acrylamide. More significant is the effect on speed attained with a bifunctional monomer of higher solubility (Figure 18). Ethylene bisacrylamide dissolves to the extent of about 12 per cent in water. This improved solubility permits the preparation of a coated layer containing double the concentration of EBA as compared with MBA. When the photographic speeds of photopolymerizable compositions are compared, it is observed that when the weight of EBA is roughly equivalent to that of MBA the photographic speed is about the same as that of the MBA coating. However, when we increase the EBA concentration to its saturation level (Figure 18), the photographic speed is increased by a factor of 2 to the third power (in photography this is termed three "stops"), or eight times the speed achieved with a photopolymer composition saturated with MBA. Moreover, the speed is improved still further by the addition of omega acrylamidocaproic acid to a formulation saturated with EBA.

In recent formulations, a photographic speed at a level 64 times that of a composition at MBA alone has been reached. There are indications that further improvement in photographic speed is entirely possible.

Approximate thickness measurements of coated layers are listed in slide 18. In the process of coating each formulation, an effort was made to cover an equal area of film or glass. As expected, therefore, the thickness of a coated layer is observed to increase somewhat with higher solids contents. This does not imply, however, that the photographic speed of a given formulation is improved by increasing the thickness of the coated layer. As a matter of fact, thicker coatings of MBA were made in several different ways without significantly increasing photographic speed.

While the thickness of unprocessed coated layers ranged from 12 to 33 microns as shown in slide 18, it is interesting to note that the thickness of a photopolymer image from an MBA composition measured only 4 microns.

The Exposure Indexes (ASA Speeds) of several photopolymer compositions are listed in Figure 19. These values were determined using EK Spectroscopic Film, Type 649·GH, as a basis of comparison. (Exposure Index = .025, Tungsten light). In making these determinations, equivalent exposures with tungsten light were given the photosensitive materials. The EK film was processed with its appropriate developer and fixer. The photopolymer compositions when prepared with gelatin as a film former were bathed in hydrogen peroxide and subjected to washout with water at 40°C. Several of the compositions listed in slide 19 were repeated using polyvinyl pyrrolidone as film former. In these instances, it was found that immersion in aqueous hydrogen peroxide at room temperature (in safe light) was sufficient to dissolve away the unexposed areas within 30 to 60 seconds, leaving the polymeric image intact. Substitution of PVP for gelatin in a given monomer composition did not affect the photographic speed.

From the data presented, it appears that photographic speed is dependent to a considerable extent on monomer concentration. This suggests that greater amplification is realized in the photopolymerization process when more insoluble polymer can readily be produced in the immediate environment of the photoformed ferrous ion. Each composition in Figure 19 incorporated the same concentration of ferric ammonium oxalate. With a fixed exposure, the number of ferrous ions formed should be about the same, this figure being fixed by the quantum efficiency of ferric ammonium oxalate. Probably an equivalent number of hydroxyl radicals would be derived from each exposed composition when immersed in the peroxide bath. However, when more bifunctional monomer is available in the immediate vicinity of the initiating radical, one might reasonably expect that relatively more three-dimensional polymer would be formed. A higher photographic speed would then be shown after a step tablet exposure. The addition of selected mono-functional monomers might further improve photographic speed by adding to the insoluble character of the photopolymer. There is abundant evidence that the upper limit of photographic speed has not been reached in the photopolymerization process.

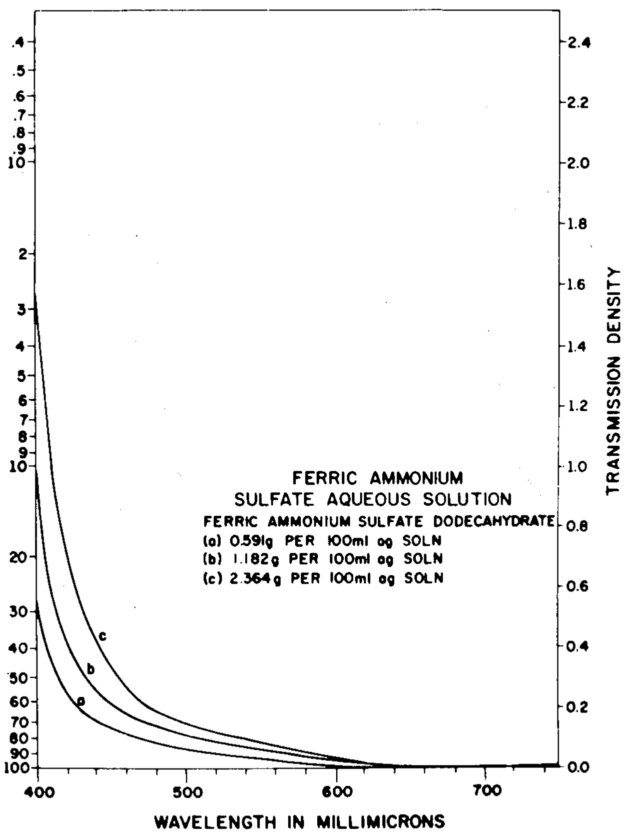


FIGURE 1

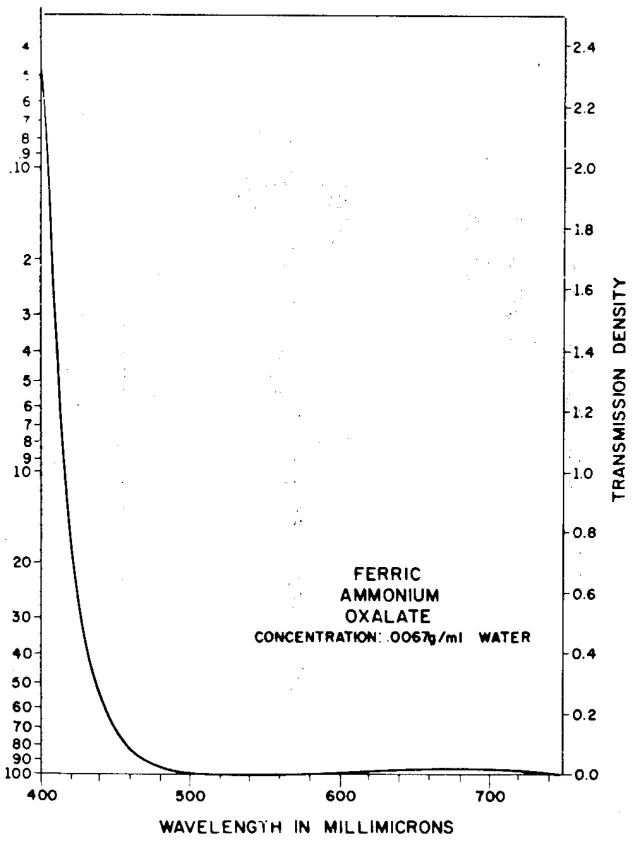


FIGURE 2

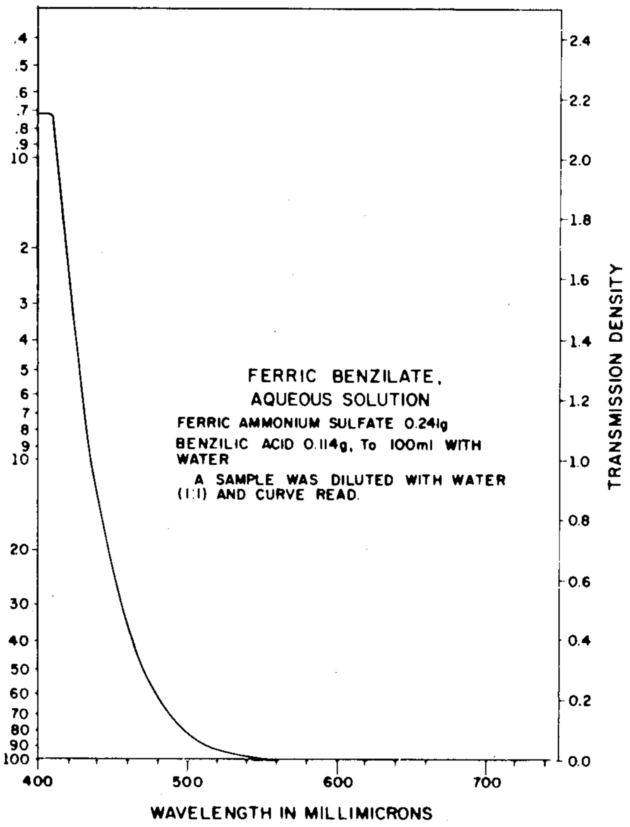


FIGURE 3

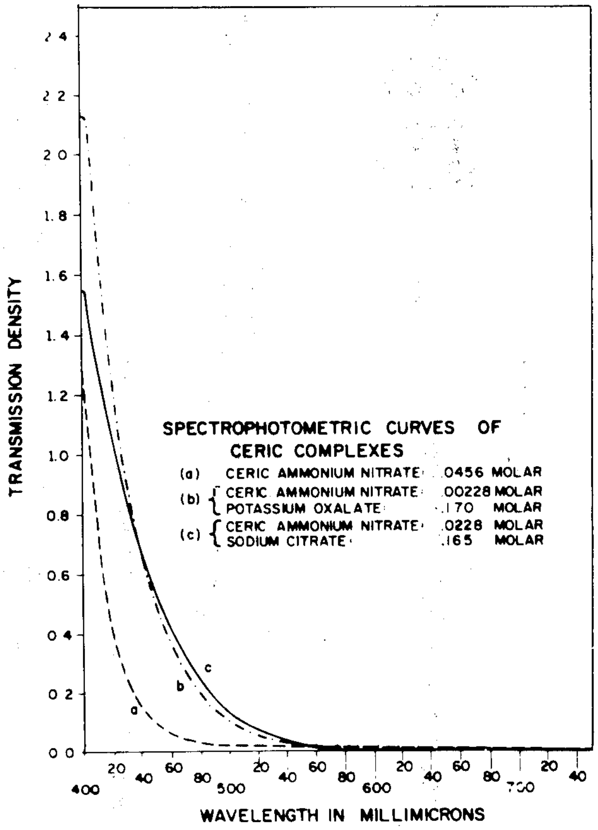


FIGURE 4

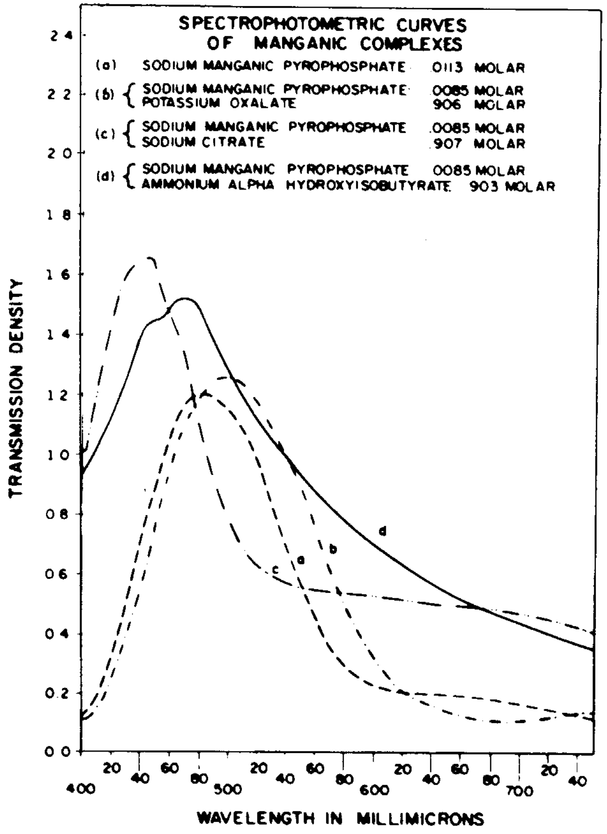
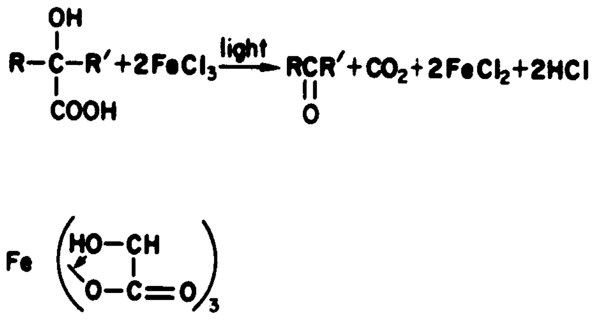


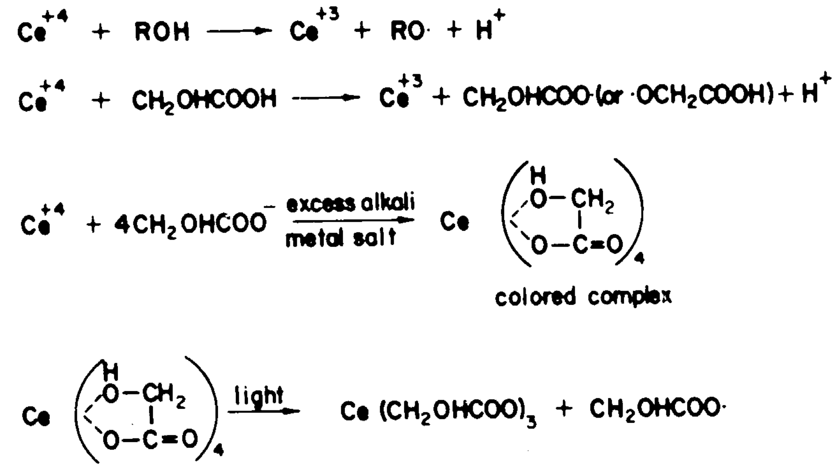
FIGURE 5



$$R-\overset{\displaystyle OH}{\underset{\displaystyle COOH}{C}}-R' + 2FeCl_3 \xrightarrow{light} \underset{\displaystyle O}{\overset{}{RCR'}} + CO_2 + 2FeCl_2 + 2HCl$$

Ferric Glycolate: 440mμ Peak Absorption

FIGURE 6



$$Ce^{+4} + ROH \longrightarrow Ce^{+3} + RO\cdot + H^+$$

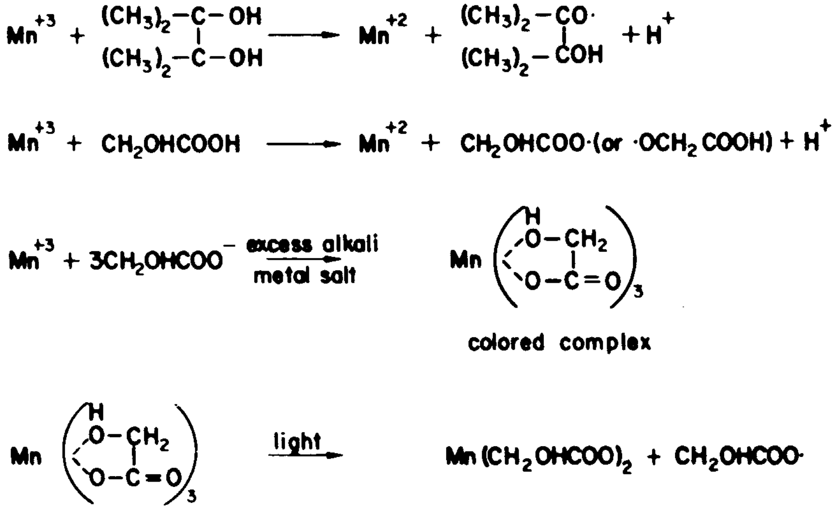
$$Ce^{+4} + CH_2OHCOOH \longrightarrow Ce^{+3} + CH_2OHCOO\cdot(\text{or } \cdot OCH_2COOH) + H^+$$

$$Ce^{+4} + 4CH_2OHCOO^- \xrightarrow[\text{metal salt}]{\text{excess alkali}} Ce$$

colored complex

$$Ce \xrightarrow{light} Ce(CH_2OHCOO)_3 + CH_2OHCOO\cdot$$

FIGURE 7



$$Mn^{+3} + \begin{matrix}(CH_3)_2-C-OH\\ (CH_3)_2-C-OH\end{matrix} \longrightarrow Mn^{+2} + \begin{matrix}(CH_3)_2-CO\cdot\\ (CH_3)_2-COH\end{matrix} + H^+$$

$$Mn^{+3} + CH_2OHCOOH \longrightarrow Mn^{+2} + CH_2OHCOO\cdot(\text{or } \cdot OCH_2COOH) + H^+$$

$$Mn^{+3} + 3CH_2OHCOO^- \xrightarrow[\text{metal salt}]{\text{excess alkali}} Mn$$

colored complex

$$Mn \xrightarrow{light} Mn(CH_2OHCOO)_2 + CH_2OHCOO\cdot$$

FIGURE 8

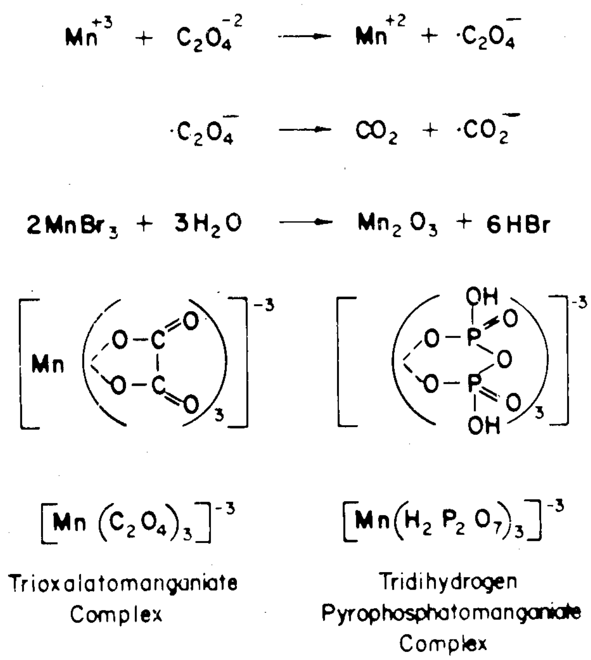


FIGURE 9

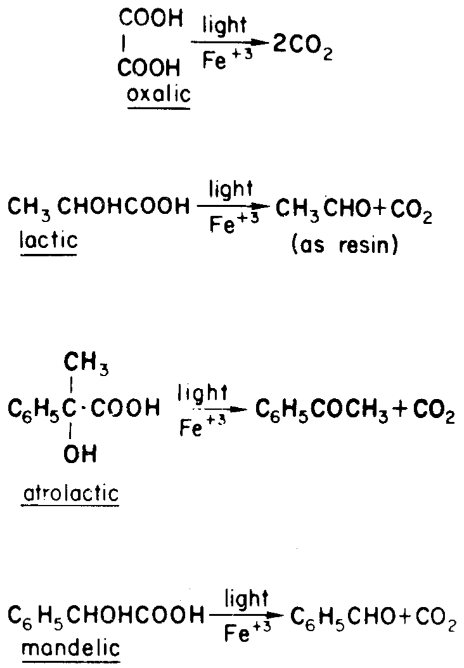


FIGURE 10

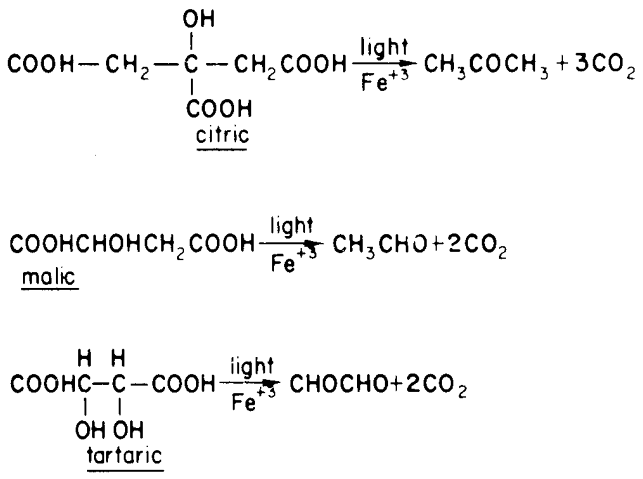


FIGURE 11

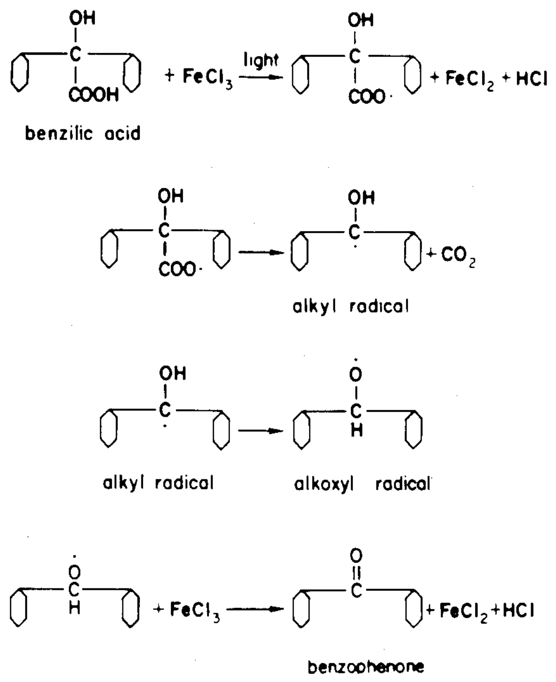
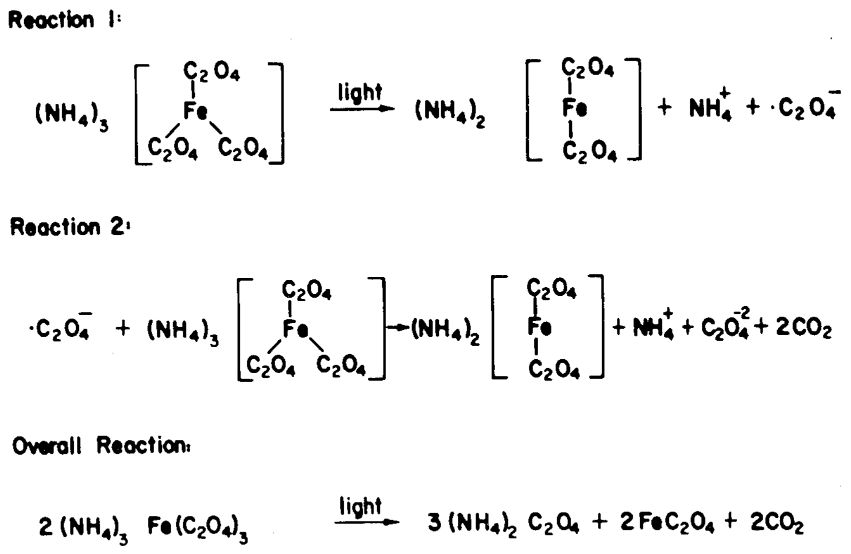
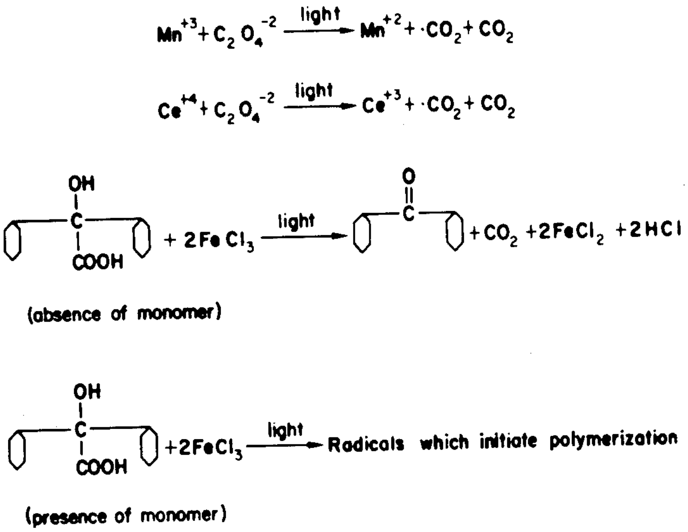


FIGURE 12



$$2\,(NH_4)_3\,Fe(C_2O_4)_3 \xrightarrow{light} 3\,(NH_4)_2\,C_2O_4 + 2\,FeC_2O_4 + 2\,CO_2$$

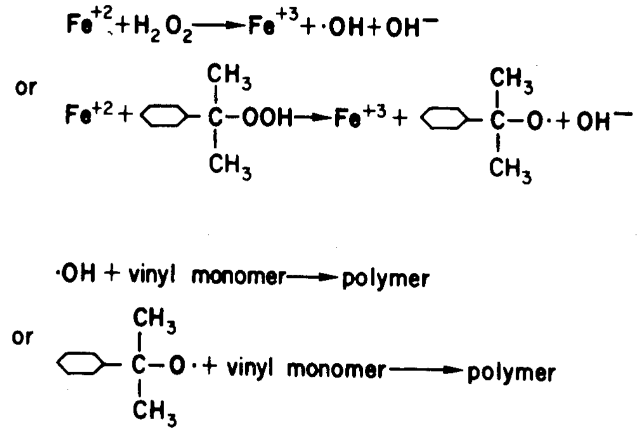
FIGURE 13



$$Mn^{+3} + C_2O_4^{-2} \xrightarrow{light} Mn^{+2} + \cdot CO_2 + CO_2$$

$$Ce^{+4} + C_2O_4^{-2} \xrightarrow{light} Ce^{+3} + \cdot CO_2 + CO_2$$

FIGURE 14



$$Fe^{+2} + H_2O_2 \longrightarrow Fe^{+3} + \cdot OH + OH^-$$

$$\cdot OH + \text{vinyl monomer} \longrightarrow \text{polymer}$$

FIGURE 15

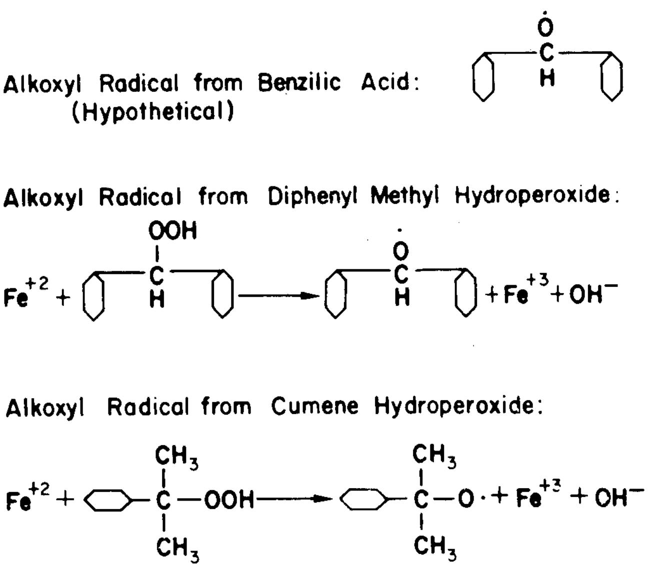


FIGURE 16

MONOMER (At saturation level)	RELATIVE PHOTOGRAPHIC SPEED (MBA = 1.0)
$CH_2 = CHCONH_2$ (acrylamide)	0.75
$CH_2 = CHCONH(CH_2)_5COOH$ (Omega acrylamidocaproic acid)	1.0
$(CH_2 = CHCONH)_2CH_2$ (MBA)	1.0
MBA + acrylamide	8.0
MBA + omega acrylamidocaproic acid	16.0

FIGURE 17

MONOMER (At saturation level)	RELATIVE PHOTOGRAPHIC SPEED (MBA = 1.0)	COATING THICKNESS (Microns)
None (Binder & Iron Salt only)	0	12
$CH_2 = CHCONHCH_2NHCOCH = CH_2$	1.0	15
$CH_2 = CHCONHCH_2CH_2NHCOCH = CH_2$	8.0	20
MBA + omega acrylamidocaproic	16.0	26
EBA + omega acrylamidocaproic	44.8	28
Recent formulations	64.0	33

FIGURE 18

MONOMER (At saturation level)	RELATIVE SPEED	EXPOSURE INDEX
MBA	1.0	.00014
EBA	8.0	.0011
EBA - omega acrylamidocaproic	44.8	.006
Recent formulations	64.0	.009
EK Spectroscopic Film, Type 649-GH	179.2	.025

FIGURE 19

SOME FUNDAMENTAL ASPECTS OF DYE-SENSITIZED PHOTOPOLYMERIZATION

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Celanese Research Co.

Summit, N. J.

ABSTRACT

The structural importance of photosensitizers has been demonstrated via investigation of dye-sensitized photopolymerization of acrylamide induced by visible ~~light.~~ Based on results ~~both~~ in spectroscopy and polymerization kinetics it ~~has been~~ is concluded that (1) the monomeric form of the dye is a photosensitizer, while the associated form a terminator; (2) electron-donating substituents activate, while electron-withdrawing substituents deactivate the dye molecule as a sensitizer; (3) enhanced rates and quantum yields can be achieved by suitable combinations of a cationic and an anionic dye as a result of an interaction to form more effective new species. (Author, modified)

Polymerization in air follows a nonsteady-state kinetic scheme and unimolecular termination in aqueous solution but a steady-state scheme and bimolecular termination in ethylene glycol. Significantly higher polymerization rates and quantum yields are obtained in ethylene glycol also. These differences can be attributed to the degree of association of the dye molecules. In aqueous solution the molecules are partially associated while in ethylene glycol primarily in the monomeric form.

Removal of oxygen favors the polymerization. Higher rates and quantum yields and different kinetics result. The induction period is either eliminated or considerably shortened.

INTRODUCTION

Dye-sensitized photopolymerization induced by visible light was first reported by Bamford and Dewar[1] for styrene, by Oster and coworkers[2-7] for acrylamide and more recently by other investigators.[8-11]

In Oster's system, a photoreducible dye and a weak reducing agent were used in the monomer solution. An appropriate amount of oxygen was suggested to be essential for the initiating of polymerization. The mechanism for the free radical formation proposed was as shown in eqs. (1)-(4).

$$D + RH_2 \xrightarrow{\text{Dark}} \text{no reaction} \qquad (1)$$

$$D \xrightarrow{\text{Light}} D^* \qquad (2)$$

$$D^* + RH_2 \longrightarrow LD + R^{\circ} \qquad (3)$$

$$LD + O_2 \longrightarrow SD^{\circ} + OH^{\circ} \qquad (4)$$

$$D \xrightarrow{\text{Light}} D^* \qquad (5)$$

$$D^* + OH^- \longrightarrow SD^\circ + OH^\circ \qquad (6)$$

Dye-sensitized photopolymerization usually proceeds rapidly. In addition, high quantum yields are obtained. Since visible light constitutes ~40% of sunlight received on earth surface and artificial incandescent sources are easily accessible, polymerization induced by invisible light should find many practical applications. Some of the applications already have been demonstrated, e.g., in photography by Oster.[3,6,7] For the purpose of evaluating the application possibilities more fully, investigations to reveal some fundamental aspects of visible light-induced polymerization has been undertaken at American Cyanamid Company. This is a review of the results which have been reported.[12,13]

EXPERIMENTAL

Polymerization of acrylamide sensitized by thiazine dyes in presence of triethanolamine as the reducing agent has been investigated under various conditions. A 250-watt General Electric infrared lamp with a reflector was used as the light source. The lamp was calibrated against a tungsten lamp with standard color temperature by means of a Beckman DK-2A spectrophotometer using an integrating sphere. Absorption spectra of the dye solutions were ascertained by using a Cary Model 14 spectrophotometer. They were replotted as extinction coefficient versus wave number for more convenient presentation and comparison. Polymerizations were carried out in a 50-ml cylindrical cell, 4 cm in diameter. For de-aerated systems the cell was evacuated by the thrice freezing-thawing technique and sealed under a vacuum of 1 x 10^{-5} mm Hg. A 10-ml portion of an acrylamidetriethanolamine solution was pipetted into the cell. The thickness of the solution was 0.8 cm. The cell was centered at a fixed distance underneath the lamp and immersed in a constant temperature bath. While in the dark, an appropriate amount of preprepared dye solution (0.1 ml) was pipetted into the cell. After mixing and allowing the solution to attain temperature equilibrium, the lamp was switched on for a predetermined interval of time. Immediately after switching off the light, the polymer formed was precipitated in excess methanol and collected on a sintered glass filter. The per cent polymerization was determined gravimetrically. The molecular weights of the polymers were determined by measuring the intrinsic viscosities of the polymers in 1N NaCl solution at 30°C. Weight-average molecular weights ($\overline{M}w$) were calculated according to the following relationship,[14]

$$\left[\eta\right]^{30}_{1N\ NaCl} = 3.73 \times 10^{-4}\ (\overline{M}w)^{0.66} \qquad (7)$$

The total energy absorbed by a dye solution was calculated by integrating the area under the absorption spectrum between wave number 24000 and 13000 cm^{-1}. The energy absorbed in each 500 cm^{-1} was ascertained by means of the absorption spectrum and the spectral energy distribution of the light source. The total energy absorbed (mw/cm^2) was taken as the sum of the energy between 24000 and 13000 cm^{-1} at the thickness of the cell used. It was then converted to the total energy absorbed (milliwatts) corresponding to the size of the polymerization cell (12.57 cm^2 x 0.8 cm). When the interference filter was used, spectra of the filter alone and the filter plus a solution, which was of the actual concentrations of the dye and acrylamide employed in polymerization, were obtained. Enerby absorbed in each case was calculated, the difference between the two values was taken as the energy absorbed by the solution. Quantum yields were calculated for the polymerization experiments where the interference filter was used. One quantum energy, $E = h\nu = hc/\lambda$ was calculated, based on $\lambda = 663$ mμ, to be 2.997×10^{-2} ergs. The quantum yields in monomer consumption (ϕm) were calculated as the number of monomer molecules consumed per one quantum of light absorbed. The values for quantum yields in polymer formation (ϕp) were obtained by dividing ϕm by $\overline{M}$n of the polymers.

RESULTS AND DISCUSSION

A. Polymerization of Acrylamide in Aqueous Solution Sensitized by Methylene Blue-Triethanolamine System in Presence of Air

1. Polymerization Kinetics

The conversion versus time curves for the polymerization of 1, 2, 4 and 7M acrylamide solutions (7.0×10^{-5} M methylene blue - 2.0×10^{-2} M triethanolamine) at 25°C are shown in Figure 1. The initial nonlinear portion of the curves represents the polymerization before the complete fading of methylene blue while the latter linear portion represents that after fading. It should be noted that before fading of the dye, the rate actually increases with time. In the rate expression,

$$-dM/dt = k_p \, [M] \, [R\cdot] \qquad (8)$$

where $[M]$ is the monomer concentration, k_p is the rate constant for propagation, and $[R\cdot]$ is the radical concentration, if it is assumed that k_p is a constant, the increase in rate with time can be attributed only by an increase in $[R\cdot]$. Thus, if $[R\cdot] \propto t$, the rate can be expressed as the following:

$$-dM/dt = Kt \, [M] \qquad (9)$$

or

$$\log ([Mo]/[M]) = (K/4.606)t^2 \qquad (10)$$

where $[Mo]$ is the initial monomer concentration, $[M]$ is the remaining monomer concentration, t is the polymerization time, and K is a proportionality constant including initiation, propagation, functions of dye concentration, and light intensity. When the initial part of the nonlinear portions of the curves in Figure 1 are replotted as $\log ([Mo]/[M])$ against t^2, straight lines are obtained as represented in Figure 2. The slopes are values for K/4.606 and represent the rates of polymerization.

The molecular weights of the polymers were observed to remain essentially unchanged with conversion or to increase somewhat with conversion in more concentrated acrylamide solutions (4M, 7M). These results indicate that chain transfer might be taking place. Alcohols are efficient chain transfer agents for the polymerization of acrylamide; triethanolamine, $N(CH_2CH_2OH)_3$, used here thus might serve both as a reducing agent for the dye and as a chain transfer agent for the polymerization of acrylamide. In more concentrated solutions, the medium becomes quite viscous as the polymerization proceeds. The increase in molecular weight with conversion could be explained by the increasing viscosity of the medium and a resultant decrease in the rate of diffusion of the chain transfer agent to the growing polymer chains.

2. Effects of the Concentration of Methylene Blue

a. On Light Absorption

The absorption spectra of methylene blue solution in water at four molar concentrations are depicted in Figure 3. There are two peaks in the absorption spectrum of methylene blue in the visible region: $\lambda_{max} \simeq 610$ and 665 mμ (or $\nu \simeq 16400$ and 15040 cm^{-1}). These represent two forms of the dye molecules. In unbuffered solutions, the relative intensities of the two peaks vary with the concentrations of the dye. The four spectra depicted in Figure 3 are so chosen that such variation is indicated clearly. It has been known for a long time that the absorption spectra of the majority of organic dyestuffs in aqueous solution do not obey Beer's law.[15-18] The deviation from Beer's law is accounted for by the hypothesis of a reversible dimerization and "polymerization" of the dye molecules. The peak at the higher wave lengths (α band) represents the unassociated dye molecules, while that at the lower wave lengths (β band) represents the associated dye molecules. In Figure 4 the following results are plotted: (1) the total energy absorption (circles), (2) the extinction coefficients of the peak at $\lambda \simeq 610$ mμ (ϵ_{610}, squares), and (3) the extinction coefficients of the peak at $\lambda = 665$ mμ (ϵ_{665}, triangles), as a function of the concentration of methylene blue. It is shown that ϵ_{610} increases with the concentration of methylene blue, but, on the other hand, ϵ_{665} first increases with the concentration of methylene blue, reaching a maximum, and then decreases with increasing concentration. The total energy absorption, obtained by means of area integration, increases with the concentration of methylene blue.

b. On Polymerization

The relationship between the rates of polymerization, taken as the slope of the straight lines of log ($[M_o]/[M]$) vs. t^2 plots, and the concentration of methylene blue is represented in Figure 5.

In the same figure also are shown the corresponding molecular weights. The polymerization rate varied in the similar way as the ϵ_{665} absorption: it first increased with the concentration of methylene blue, reaching a maximum, and then decreased with the dye concentration. The molecular weight of the polymers decreased with the concentration of methylene blue. This indicates that high concentrations of dye also terminate the polymer chain.

Based on the observations both in spectroscopy (Fig. 4) and in polymerization (Figure 5), it is suggested that the unassociated form of methylene blue (λ max = 665 mμ) is a photosensitizer, while the associated form (λ max = 610 mμ) is a chain terminator, probably by degradative chain transfer, and is eventually an inhibitor for polymerization.

B. Enhanced Sensitization by Combination of a Cationic and an Anionic Dye

Enhanced rates and quantum yields of polymerization were achieved by employing suitable combinations of a cationic and an anionic dye. Methylene blue (I), a mono-charged cationic blue dye, and eosin Y (II), a double-charged anionic red dye, were chosen for this investigation (Figure 5A).

1. Spectroscopy

A comparison of the absorption spectra of aqueous solutions of (1) 7.0 x 10^{-5}M methylene blue alone, (2) 3.0 x 10^{-5}M eosin Y alone, and (3) a mixture containing 7.0 x 10^{-5}M methylene blue and 3.0 x 10^{-5}M eosin Y is shown in Figure 6.

It is shown that the spectrum for the mixture differs significantly from the spectra for individual dyes. It is reasonable to ascribe these results to an interaction between the two dyes in the mixture forming new species of different electronic structure. The total energy absorbed (400-770 mμ) by the polymerization system was somewhat higher when the dye mixture was employed than the sum of energy absorbed when each individual dye of the corresponding concentration was present (16.7 vs 14.7 mw). This is a result of the shift of absorption to the longer wave lengths where the output of our light source is higher.

2. Polymerization

The results for the polymerization os 7M acrylamide at 25°C are represented in Figure 7 for (1) 3.0 10^{-5}M eosin Y, (2) 7.0 x 10^{-5}M methylene blue, and (3) 7.0 x 10^{-5}M methylene blue plus 3.0 x 10^{-5}M eosin Y.

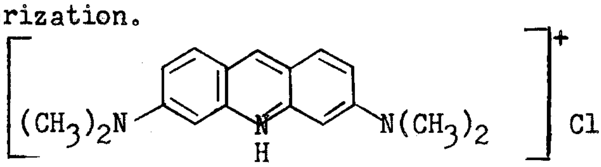
The rate of polymerization with the dye mixture as the sensitizer was considerably higher than the expected additive rates when the two individual dyes of corresponding concentrations was employed. The rate was 3.5-fold higher than that when methylene blue alone was employed. The enhanced rate cannot be accounted for by the small increase in energy absorption by the system. More reasonably it can be attributed to the interaction between the two dyes resulting in species of different electronic structure which are more efficient photosensitizers.

The enhanced rate which resulted when a mixture of 7.0 x 10^{-5}M methylene blue and 3.0 x 10^{-5}M eosin Y was employed as the sensitizer was further confirmed by carrying out the polymerization at 0°C. The results are represented in Figure 8. Here, a 6-7 fold increase in rate was obtained. The higher increase in rate at 0°C over that at 25°C could indicate that the interaction between the two dyes was temperature dependent also.

In order to assess the effects of the presence of excess eosin Y in a combination of the two dyes, a mixture of 7.0 x 10^{-5}M methylene blue and 6.0 x 10^{-5}M eosin Y was employed as the sensitizer for the polymerization. Here the ratio in charge equivalents, methylene blue: eosin Y = 7.0 x 10^{-5}: 12x10^{-5}, is considerably less than one. Figure 9 represents a comparison of the spectra of (1) 7.0 x 10^{-5}M methylene blue, (2) 6.0 x 10^{-5}M eosin Y, and (3) a mixture of 7.0 x 10^{-5}M methylene blue and 6.0 x 10^{-5}M eosin Y.

Again, an interaction between the two dyes was indicated. The absorption spectrum of the mixture deviated greatly from those of the individual dyes at the same concentrations. It also differs from the mixture, shown in Figure 8, where methylene blue is in excess. The polymerization data both at 25°C and 0°C indicated, in contrast to the above-described cases, there was no enhancement in the power of sensitization. These results are significant, for they point out that only suitable concentration ratios of a cationic and an anionic dye can result in the enhancement of sensitizing power for polymerization.

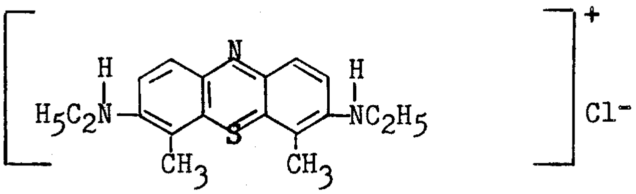
When methylene blue was used in combination with another cationic dye, acridine orange (III), no substantial change was observed in the spectrum of the mixture as compared to the spectra of the individual dyes. Also, there was no substantial change in the rate of polymerization.



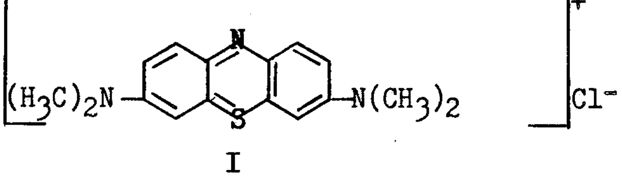
III

C. Structural Effects of Thiazine Dyes

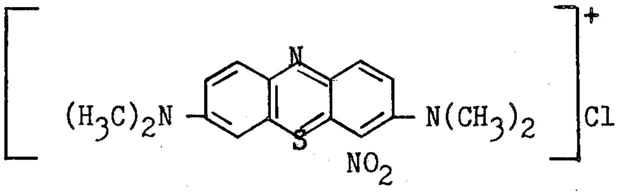
The effect of change of electronic structure of methylene blue produced by chemical substitution was ascertained. New methylene blue N(T(CH_3)$_2$), with two electron-donating methyl groups in the 2- and 10-position, and methylene green (I(NO_2)), with an electron-withdrawing nitro group in the 2 position of methylene blue (I, 3,9-bisdimethylaminophenazothionium chloride) were employed and compared with methylene blue itself.



I (CH_3)



I



I(NO_2)

1. Polymerization Kinetics

In contrast to the results obtained with the methylene blue-triethanolamine system and similar to those observed for riboflavin by Oster, Oster and Prati,[3] induction periods were observed for both the new methylene blue-triethanolamine and the methylene green-triethanolamine systems when they were used as photosensitizers. The induction period decreased with increasing dye concentration and with decreasing intensity of the incident light. Considerably longer induction periods existed for methylene green than for new methylene blue N(.°. Induction period: I(NO_2)>I>I($(CH_3)_2$). The conversion versus time curves after the induction period followed the same nonsteady-state pattern as described for methylene blue. Straight lines were obtained when log $([M_o]/[M])$ was plotted against t^2 for the initial stages of the polymerizations. The slopes were the values for K/4.606 which represented the rates of polymerization. The intercepts with the χ axis provided another means to ascertain the lengths of the induction period in addition to the experimental observations.

2. Effect of the Dye Concentration

a. Spectroscopy

The absorption spectra of new methylene blue N and methylene green were obtained at different concentrations. In each case the relative intensity of the α to the β peak changed with the total concentration of the dye. By comparing the spectra of the three dyes at the same concentration, the ease of association of the molecules was in the order of I($(CH_3)_2$)>I>I(NO_2). Plots of (1) the total energy absorption, (2)$\epsilon\alpha$ peak (628 mμ for new methylene blue N and 655 mμ for methylene green), and (3) $\epsilon\beta$ peak ($\sim$588 mμ for new methylene blue and $\sim$610 mμ for methylene green) vs. the dye concentration showed that the results are similar to those discussed for methylene blue.[1]

b. Polymerization

The relationship between the rates of polymerization (represented by K/4.606) and the concentration of the dye are presented in Figure 10 for new methylene blue N and methylene green. In the same figure the corresponding molecular weights are also shown.

As was observed for methylene blue, in both cases the polymerization rates passed through a maximum, and the molecular weights of the polymers decreased with the increase in concentration of the dye. These results again supported the conclusion that the unassociated molecules of the dye were the photosensitizer, while the associated ones the terminator.

3. Effect of the Structural Features of the Thiazine Dyes on the Polymerization

A comparison of the rates of polymerization and the molecular weights of the polymers is displayed in Figure 11. On the left side are the values of K/4.606 divided by the number of milliwatts of energy absorbe (representing a comparison of quantum yields), and on the right side the molecular weights are plotted against dye concentration. The quantum yield increases in the order: $I(CH_3)_2>I>I(NO_2)$. These results suggest that when thiazine dyes are used as photosensitizer of the redox type, nuclear substitution of electron-donating groups is activating, while that of electron-withdrawing groups is deactivating. The molecular weights of the polymers obtained when new methylene blue N was used as the sensitizer were the same as those obtained with methylene blue, while the molecular weights were invariably higher when methylene green at the same concentrations was used.

4. Combination with an Anionic Dye-Eosin Y

a. Spectroscopy

The absorption spectra of aqueous solutions of (1) 7.0 x 10^{-5}M new methylene blue N, and (2) a mixture of 7.0 x 10^{-5}M new methylene blue N and 3.0 x 10 M eosin Y are depicted in Figure 12 and those of (1) 7.0 x 10^{-5}M methylene green, and (2) a mixture of 7.0 x 10^{-5}M methylene green and 3.0 x 10^{-5}M eosin Y in Figure 13.

Among the three dyes, at the specified concentrations the extent of interaction with eosin Y is in the following order: $I(CH_3)_2>I>I(NO_2)$. In the case of new methylene blue N both the α and the β peaks combined into a depressed broad band in the mixture. In the case of methylene green, the changes in absorption in the mixture were similar to those described for methylene blue-eosin Y except to a lesser degree.

b. Polymerization

Enhancement in rate was observed with the methylene green-eosin Y mixture (1.9 fold), but not with the new methylene blue-eosin Y mixture. The latter results resembled what was described above for 7.0 x 10^{-5}M methylene blue - 6.0 x 10^{-5}M eosin Y system where drastic interaction between the two dyes was indicated by the fact that the α and the β peaks of methylene blue approached one broad band (Figure 9); however, essentially no change in the rate of polymerization was observed.

D. Enhanced Rates of Polymerization in Ethylene Glycol

1. Methylene Blue System

a. Absorption Spectra in Ethylene Glycol

Figure 14 depicts two representative spectra of the concentrations 6.88×10^{-5}M and 96×10^{-5}M, respectively. These spectra differed from those in aqueous solutions of comparable molar concentrations in the following manner (compare with Figure 3): (1) the α-peak was predominant, the β-peak appearing only as a shoulder; (2) the relative intensity of the α and the β peaks remained unchanged with the concentration, and (3) Beer's law was obeyed. It was thus indicated that in ethylene glycol, methylene blue existed primarily as unassociated molecules, even up to a relatively high concentration of 1×10^{-3}M.

b. Polymerization Kinetics

An induction period for polymerization was observed and thereafter the per cent polymerization was linear with time. Figure 15 shows plots of per cent polymerization versus time, up to the complete fading of methylene blue. The rate of polymerization was calculated as the slope of the straight lines. The molecular weights of the polymers were lower than those obtained for the corresponding aqueous systems since ethylene glycol was a more powerful chain transferring agent for the polymerization of acrylamide.

C. Effect of the Dye Concentration

The data for the polymerization of 2M acrylamide at different methylene blue concentrations are presented in Figure 16. The results derived from the data are shown in Figure 17. The rate of polymerization increased with the dye concentration instead of passing through a maximum. This could be attributed to the relatively unassociated state of the methylene blue molecules in ethylene glycol. The molecular weight of the polymers decreased with the increase in methylene blue concentration.

Similar results, both in spectroscopy and in polymerization were obtained for new methylene blue N and methylene green. In all three cases, aside from the difference in kinetics (steady state vs. non-steady state), the polymerization proceeded faster in ethylene glycol than in water. The differences in polymerization kinetics and rate could not be attributed to the difference in viscosity of the two solvents and were primarily due to the different electronic states of the dye molecules.

2. Sensitization in Combination with Eosin Y

In ethylene glycol, as indicated in Figure 18, virtually no interaction was present in a solution of 7.0×10^{-5}M methylene blue and 3.0×10^{-5}M eosin Y. As was the case for a single dye solution, the molecules of both dyes simply behave independently of others present. The results for polymerization are recorded in Figure 19. No enhanced sensitization resulted from the combination of the cationic and the anionic dye. Furthermore, eosin Y had a little hindering effect on methylene blue.

E. Effect of Light Intensity

1. In Aqueous System

The rates were calculated from the slopes of log $([M_0]/[M])$ versus t^2 plots. The relationship of the rates and light intensity was derived as rate $\propto$ $[\text{light intensity}]^{1.0}$ for all the three thiazine dyes investigated. The molecular weights were not affected greatly by the light intensity. Based on the first-order dependence of the light intensity it can be concluded that the termination of the kinetic chains is unimolecular. This is in agreement with the proposition that a terminator is present, since in its absence free radical polymerization is terminated by combination (bimolecular termination) and the rate would depend on the square root of the light intensity.

2. In Ethylene Glycol System

The rates of polymerization were calculated from the slopes of per cent polymerization vs. time plots. The rate of polymerization was found to be approximately proportional to the half power of the intensity, suggesting essentially a bimolecular termination. This result was in contrast to the unimolecular termination observed for the corresponding aqueous system and again supported the hypothesis that associated molecules of the dye was a terminator. Since in ethylene glycol system only a low concentration of the associated dye molecules was present, the termination of the kinetic chain was, therefore, essentially by the combination of two propagating polymer chains.

The molecular weight of the polymers was independent of the light intensity and was controlled by chain transfer processes.

F. Polymerization in Deaerated Systems

1. Aqueous Polymerization

a. Polymerization Kinetics

Typical per cent polymerization and molecular weight vs. time relationships under various experimental conditions are represented in Figure 20. In contrast to the corresponding polymerizations under ambient atmospheric conditions, the initial polymerization was linear with time, showed no induction period, and proceeded at considerably greater speed. Figure 20 shows the polymerization before complete fading of the dye. The polymerization slowed down after a certain period of time. The rates of polymerization were taken as the slopes of the initial straight-line portions of the plots. The molecular weights (top, Figure 20) seemed to remain essentially constant with time or with the per cent polymerization and were in the similar range to those obtained in the corresponding systems under ambient atmosphere conditions. These results again indicate that the molecular weights are controlled by a chain transfer process as discussed previously.

b. Effect of Dye Concentration

The effect of dye concentration on polymerization rate and molecular weight of polymers is shown in Figure 21 for 2M and 7M acrylamide solutions. As discussed previously for the corresponding systems in air, the rate passed through a maximum, and the molecular weight decreased with the increase of the dye concentration.

c. Combination of a Cationic and an Anionic Dye

In Figure 22 are shown a comparison of rates of polymerization and molecular weights of the polymers for polymerizations of 7M acrylamide sensitized by (1) 7.0 x 10^{-5}M methylene blue, (2) 3.0 x 10^{-5}M eosin Y, and (3) a mixture of 7.0 x 10^{-5}M and 3.0 x 10^{-5}M eosin Y, respectively. The results differed significantly from those obtained under ambient atmospheric conditions, where enhancement of polymerization was observed. This contrast in polymerization behavior between the two cases suggests that the initiation mechanisms are different under atmospheric conditions and in deaerated systems.

2. Polymerization in Ethylene Glycol

a. Polymerization Kinetics

Linear conversion vs. time relationships were obtained, typical results are shown in Figure 23. The molecular weight remained essentially constant with time or per cent polymerization.

G. Quantum Yields

A comparison of quantum yields (ϕm) for the polymerizations in ethylene glycol in air and in corresponding deaerated systems with the use of 7.0 x 10^{-5}M methylene blue and new methylene blue N, respectively, is shown in Figure 24. Significantly higher quantum yields were obtained in deaerated systems. This is attributed primarily to the elimination of the induction periods in the deaerated systems.

CONCLUSIONS

In dye-sensitized photopolymerization of the redox type, the electronic structure of the dye molecules is of great importance. It has been shown that a change of their electronic structure either by physical or by chemical means alters their power of sensitization. As a result, the polymerizations are quite sensitive to the experimental conditions. It has been shown that different kinetics and rates of polymerization can result simply by changing the solvent or by eliminating oxygen. This versatility offers advantages in practical applications. It can be visualized that different polymerization kinetics and rates can be advantageously adapted for specific applications. For instance, while extremely fast reactions and high quantum yields are essential in photography, an induction period may be desirable in some other application. A fundamental understanding of the mechanism of formation of the reactive species will give us more insight into photo-initiated polymerizations or reactions and their practical applications. It will also lead us to understand more about photo-induced degradation and become more equipped to overcome practical problems such as "photo-tendering" of fibers, plastics or surface coatings.

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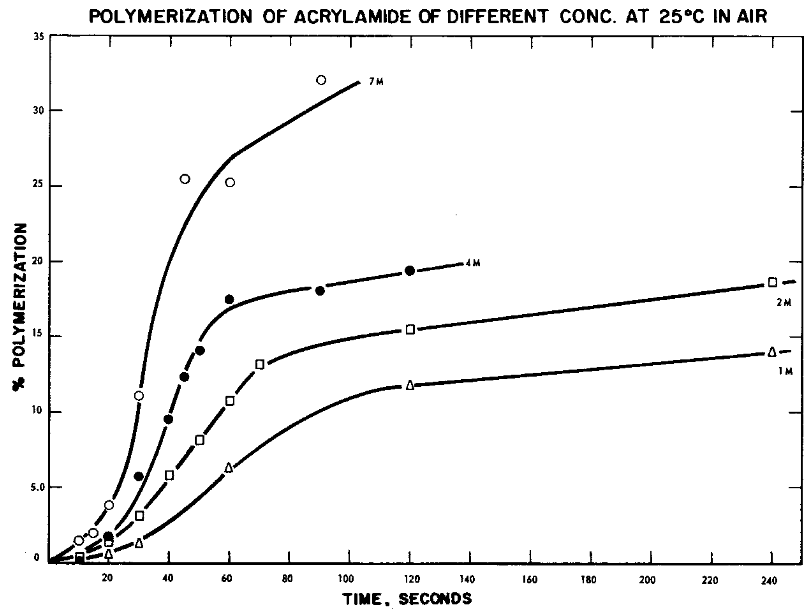
POLYMERIZATION OF ACRYLAMIDE OF DIFFERENT CONC. AT 25°C IN AIR

FIGURE 1

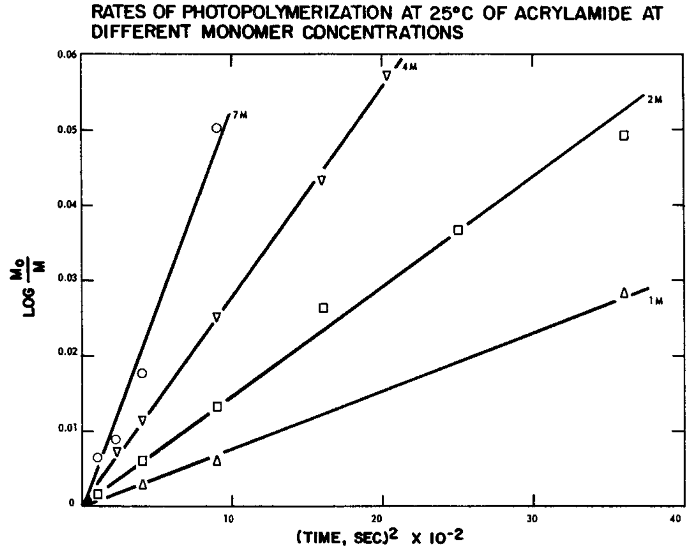
RATES OF PHOTOPOLYMERIZATION AT 25°C OF ACRYLAMIDE AT DIFFERENT MONOMER CONCENTRATIONS

FIGURE 2

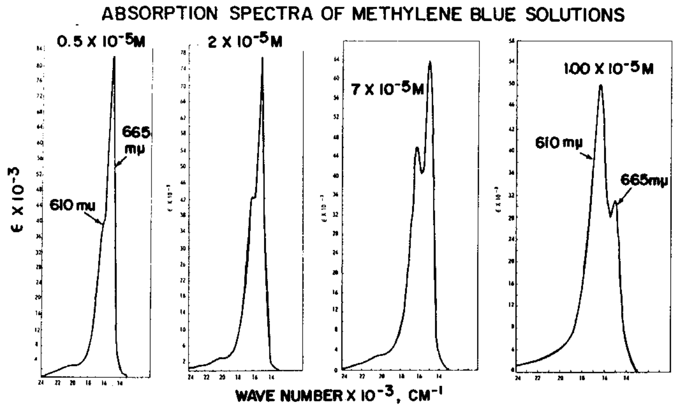
ABSORPTION SPECTRA OF METHYLENE BLUE SOLUTIONS

FIGURE 3

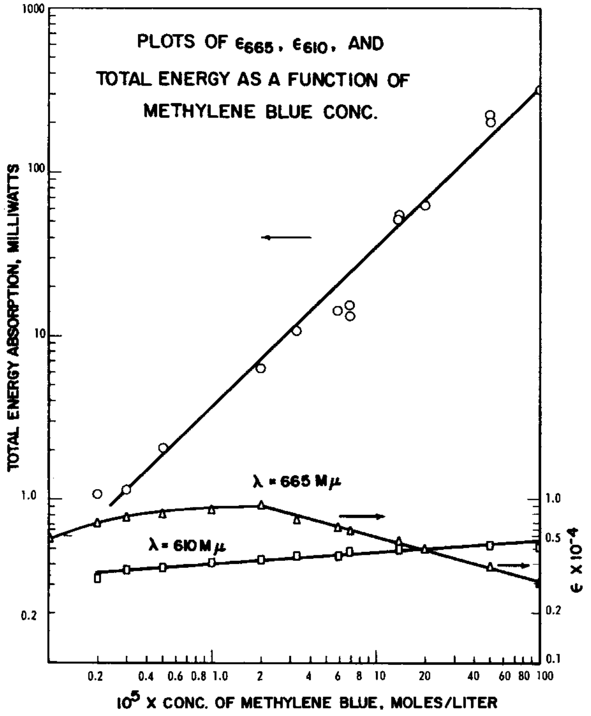

FIGURE 4

EFFECT OF METHYLENE BLUE CONC. ON POLYMERIZATION

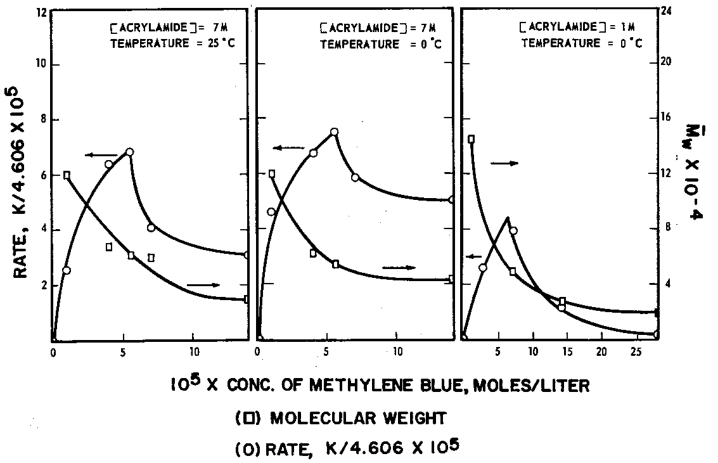

FIGURE 5

ABSORPTION SPECTRA

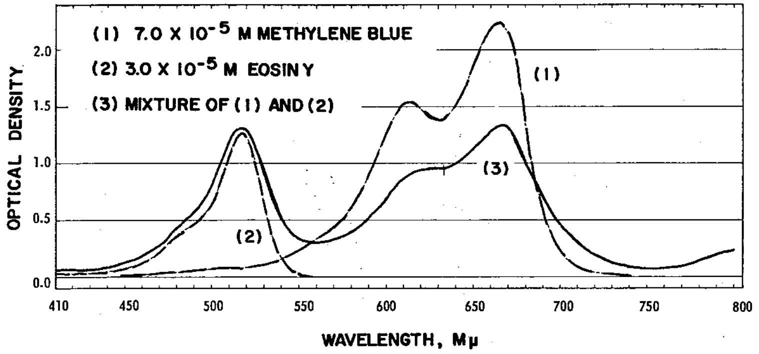

FIGURE 6

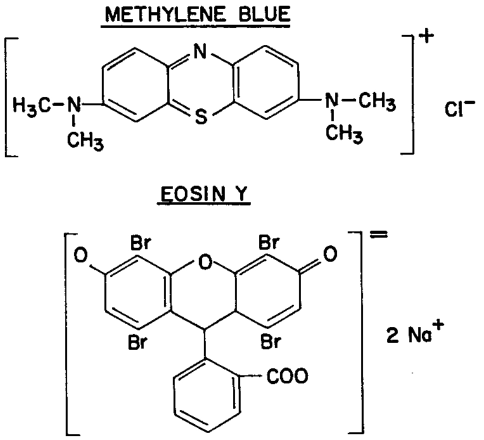

FIGURE 5A

POLYMERIZATION OF 7M AQUEOUS ACRYLAMIDE AT 25°C

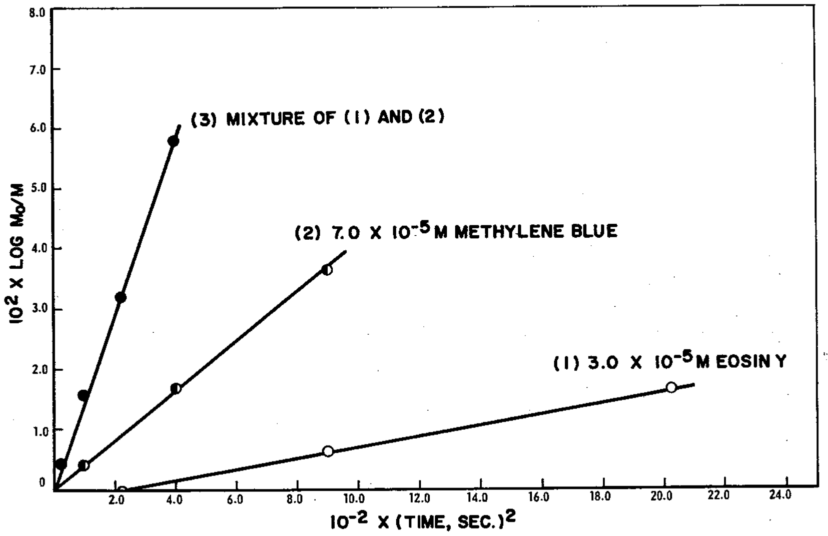

FIGURE 7

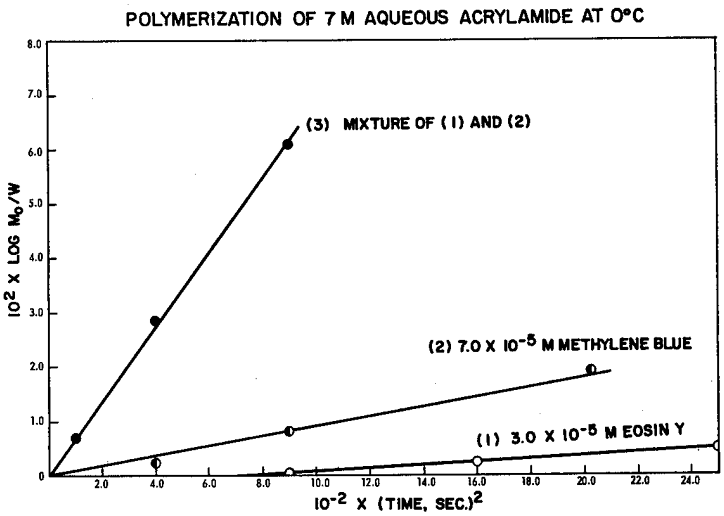

FIGURE 8

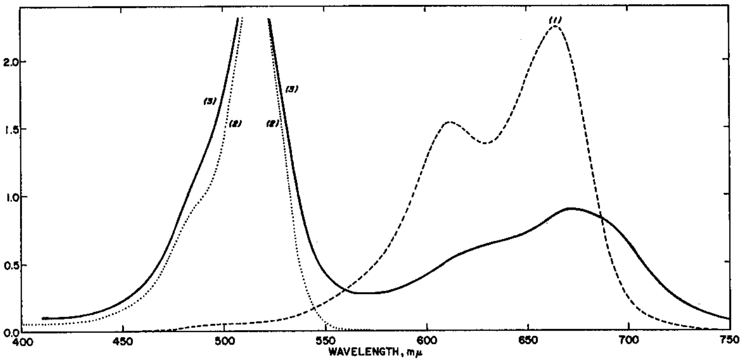

FIGURE 9

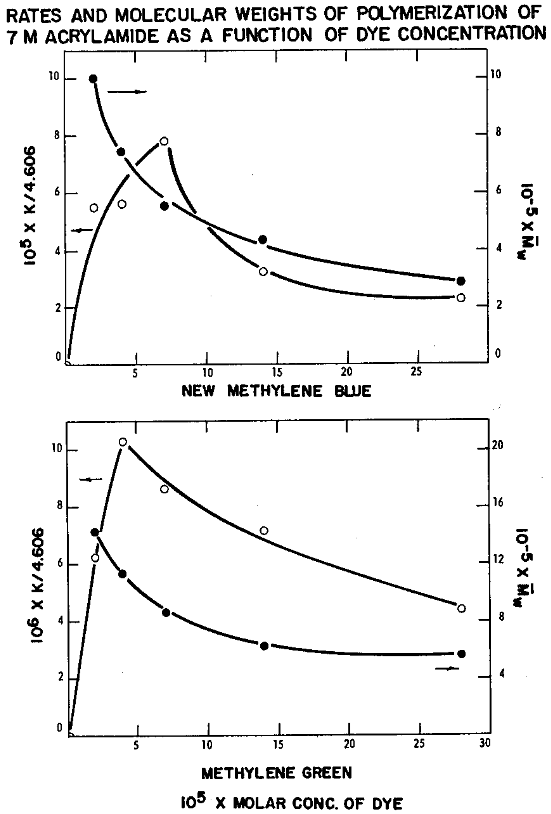

FIGURE 10

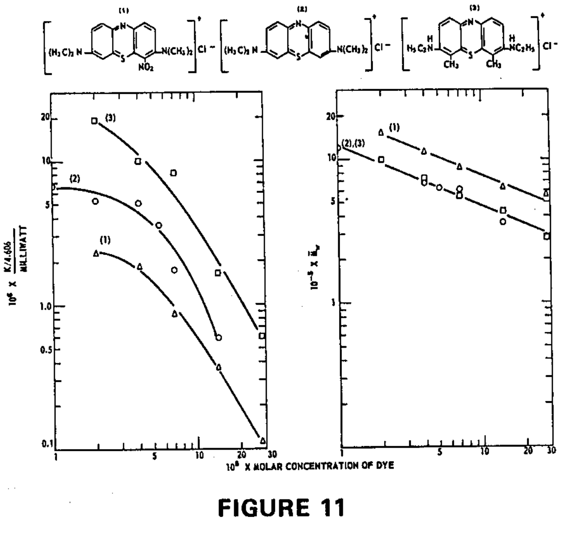

FIGURE 11

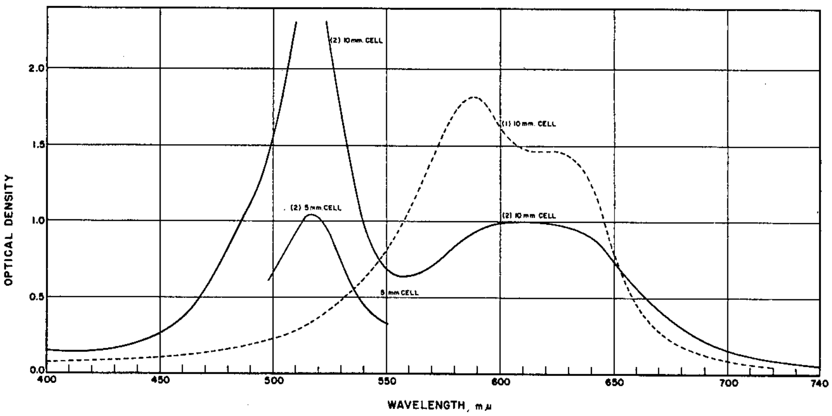

FIGURE 12

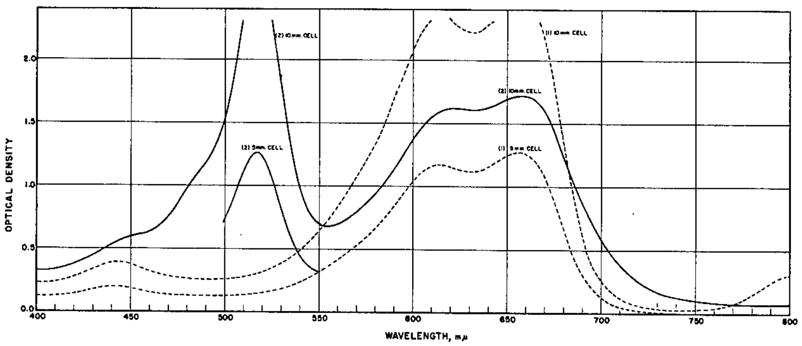

FIGURE 13

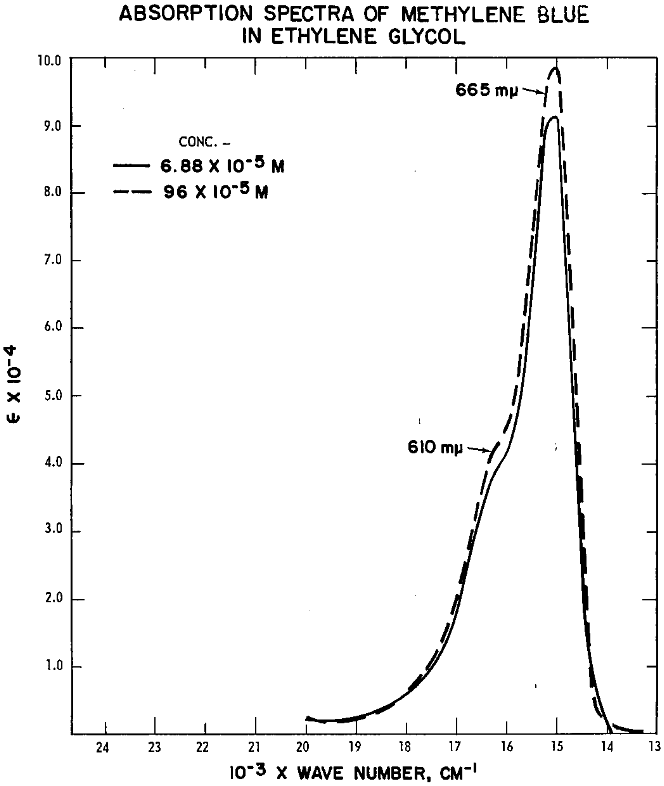

FIGURE 14

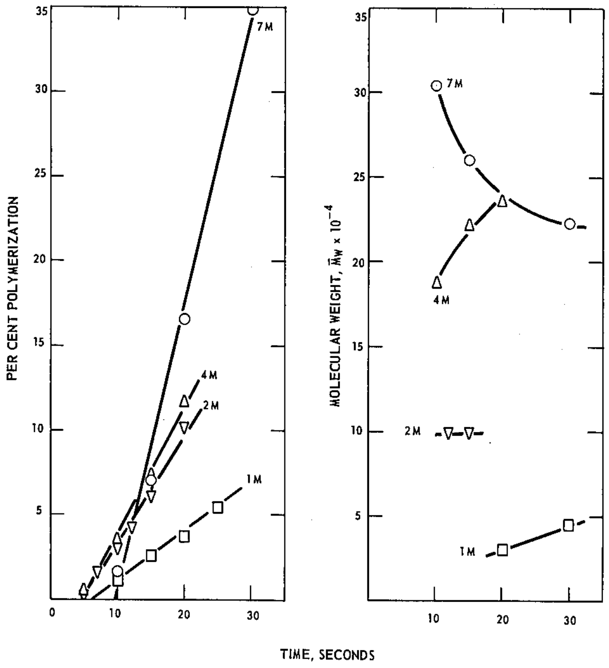

FIGURE 15

POLYMERIZATION OF 2M ACRYLAMIDE AS A FUNCTION OF METHYLENE BLUE CONCENTRATION AT 25°C IN AIR

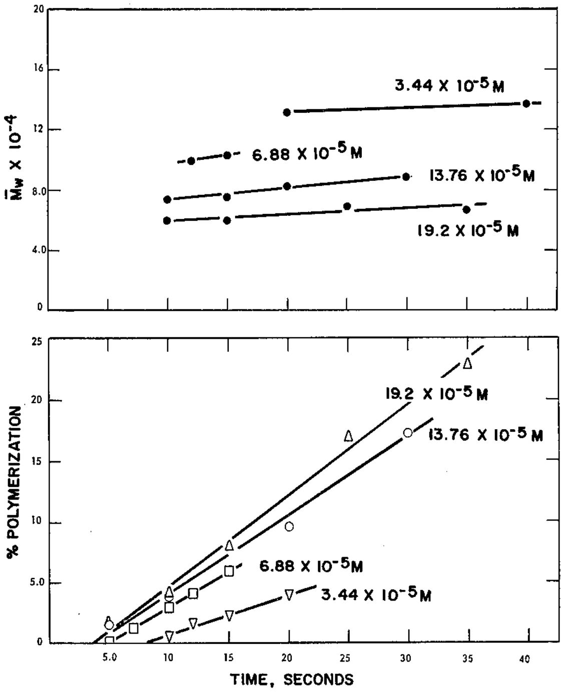

FIGURE 16

PLOTS OF RATE, $\bar{M}_w$ AND INDUCTION PERIOD AS A FUNCTION OF THE CONCENTRATION OF METHYLENE BLUE

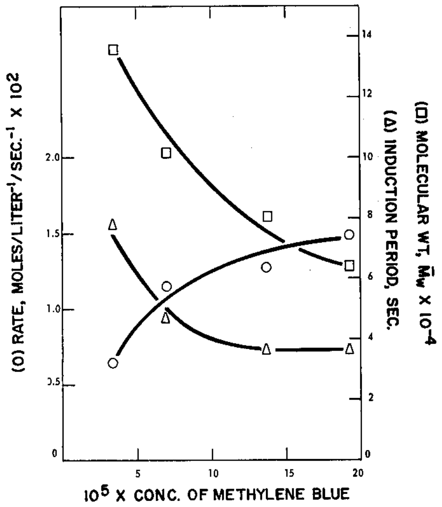

FIGURE 17

COMPARISON OF THE ABSORPTION SPECTRA OF ETHYLENE GLYCOL SOLUTIONS

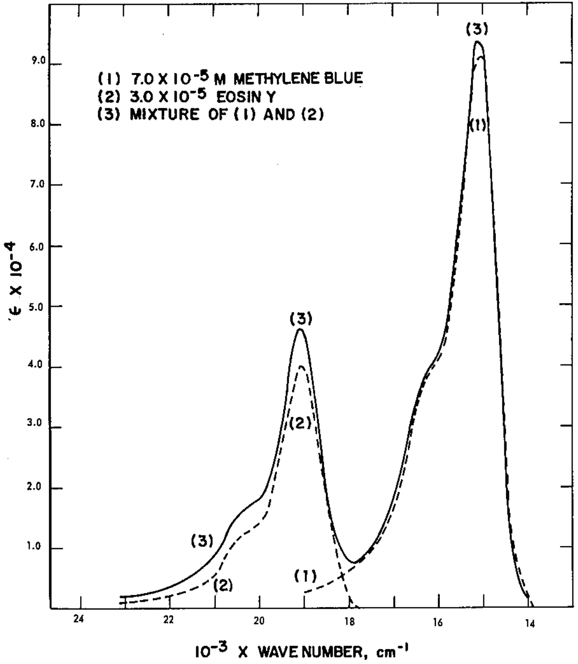

FIGURE 18

COMPARISON OF POLYMERIZATION OF 7M ACRYLAMIDE IN ETHYLENE GLYCOL AT 25°C

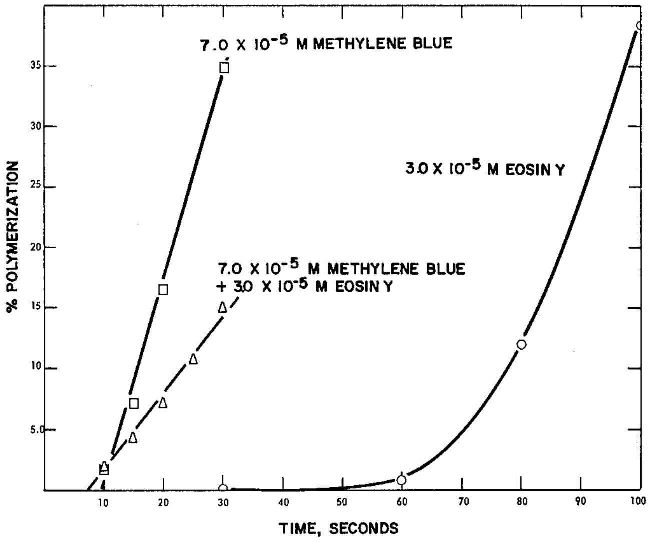

FIGURE 19

POLYMERIZATION OF DEAREATED AQUEOUS ACRYLAMIDE AT DIFFERENT CONCENTRATIONS

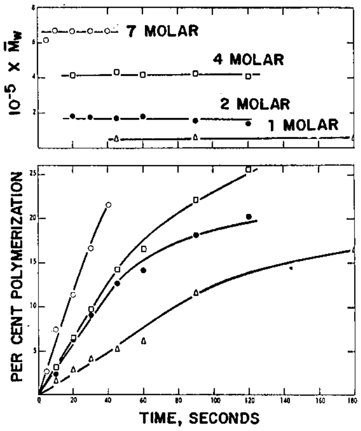

FIGURE 20

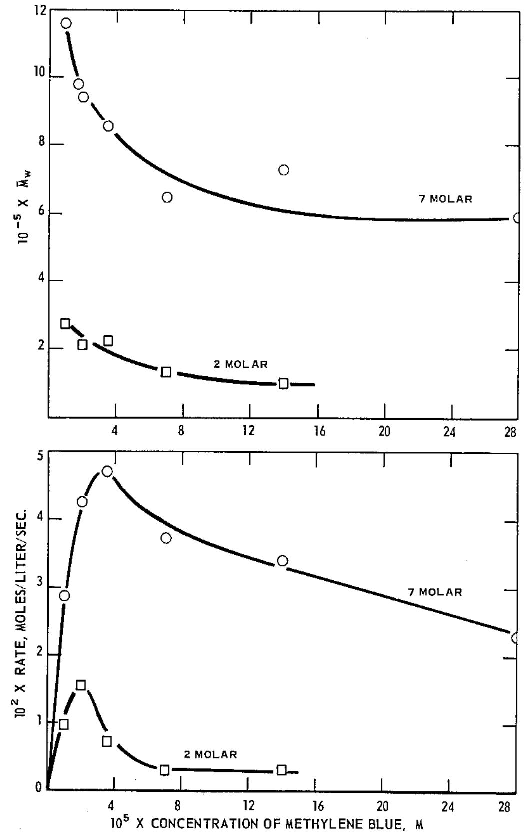

FIGURE 21

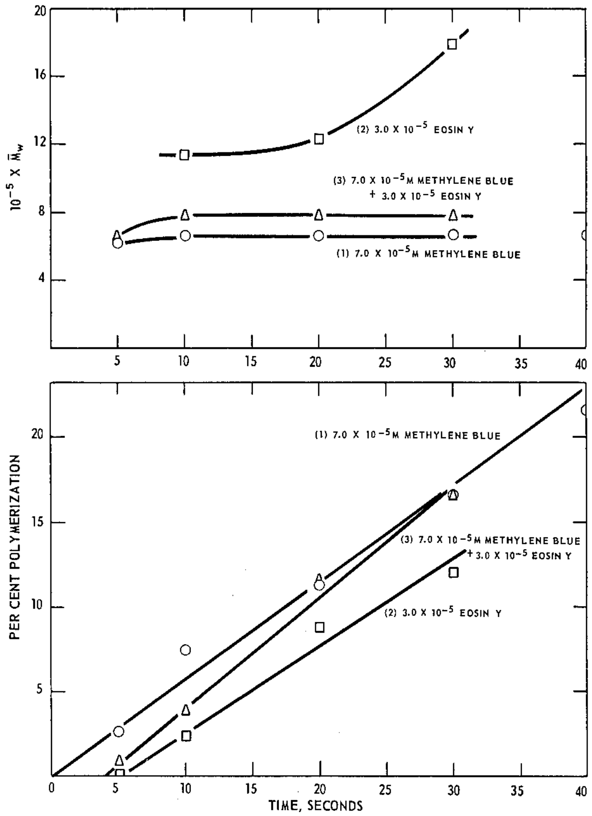

FIGURE 22

POLYMERIZATION OF DEAREATED ACRYLAMIDE IN ETHYLENE GLYCOL AT DIFFERENT CONCENTRATIONS

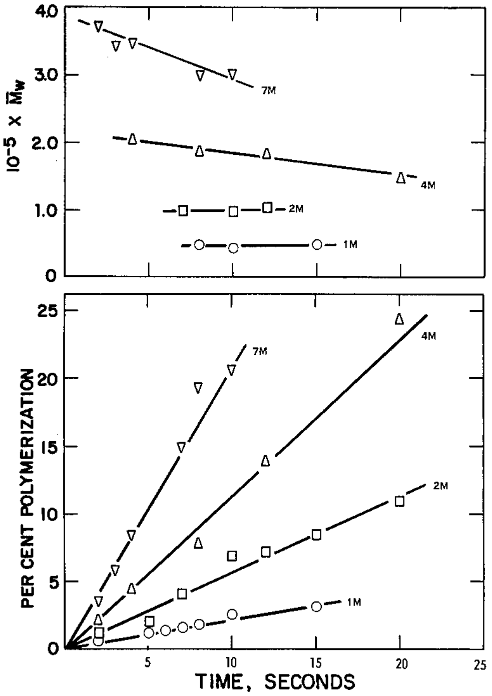

FIGURE 23

COMPARISON OF QUANTUM YIELDS FOR THE POLYMERIZATIONS IN ETHYLENE GLYCOL

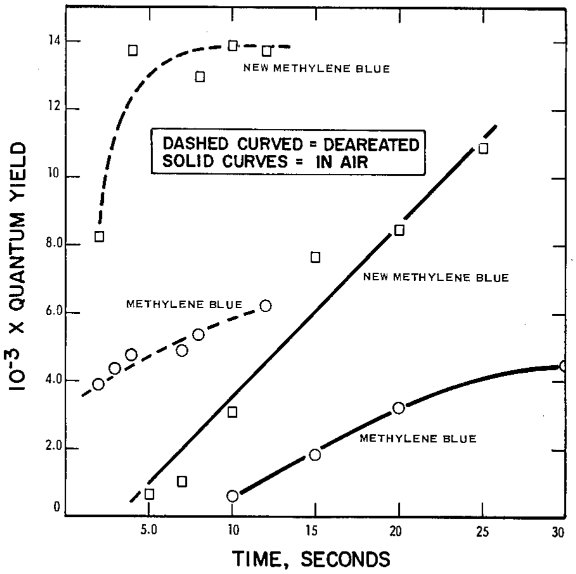

FIGURE 24

A BASIC STUDY ON NOVEL PHOTOPOLYMERIZATION SYSTEMS INITIATED BY CHARGE TRANSFER REACTIONS

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INTRODUCTION

It has long been believed that photochemical process could bring about only radical polymerization of vinyl compounds. Since the energy of photon is not sufficiently high to ionize organic molecules directly unless vacuum ultraviolet light is used, ionic initiating species are not presumably formed. Although this is true for conventional photosensitized systems, there seem to be good possibilities of producing ionic catalytic species other than by direct photoionization.

~~The subject of~~ The present article ~~is to~~ explores new types of photosensitized polymerization.[1] The principle is based either on charge transfer reaction or on photochemical production of ionic catalysts. The ~~first case, namely, the application~~ of charge transfer reaction for initiating polymerization, has been demonstrated thermally in polymerization of N-vinylcarbazole[2] and its analogs.[3] Photochemical systems have been, however, left largely unexplored. Under suitable conditions, photoexcitation of a charge transfer complex would bring about formation of ion-radical which initiate either ionic or radical polymerization, or probably both. The second case, namely, photochemical production of ionic catalyst, has not been practiced, but there seems to be a good possibility.

The best advantage of non-radical photopolymerization in practical application would be the inertness of reaction system to the presence of oxygen.

RESULTS AND DISCUSSION

Polymerization of N-vinylcarbazole (VCZ) by Na $AuCl_4.2H_2O$ in nitrobenzene.[4] Particular feature of the polymerization is the strong photosensitization as shown in Figure 1, although the polymerization proceeds by thermal process as well as after an induction period. Effects of additives on polymerization are shown in Table I. Inhibition by ammonia and decreases in molecular weight in the presence of water indicate the cationic nature of propagation process. An interesting finding is the acceleration of polymerization and the disappearance of induction period in the presence of reducing agent such as mercury, ascorbic acid or ferrocene as shown in Figure 2 and Table I. A likely explanation is to consider that the polymerization is initiated by lower valency state of gold, possibly by Au^{II}

produced either by reaction of Au^{III} with monomer on reducing agents, or by photochemical process. Photochemistry of gold salts is still unknown, although the metal salts have been widely used in photographic industry. Photochemical process in the present system seems to proceed independent of the presence of VCZ. The enhanced rate of polymerization was also observed when nitrobenzene solution of the gold salt alone was irradiated for a few minutes followed by addition of monomer.

Radical mechanism for this polymerization is difficult to consider. The polymerization is neither retarded nor inhibited in the presence of DPPH, oxygen or nitrobenzene. In addition, the results of copolymerization with iso-butyl vinylether initiated by the gold salt are similar as those initiated by conventional cationic catalysts such as trichloroacetic acid, as shown in Figure 3.

An attempt to confirm the production of Au^{II} by ESR spectroscopy was failed. Although the presence of Au^{II} state was confirmed in different systems[5] by isolation as crystals and their ESR measurement, the concentration of Au^{II} in the present system would be far too small to be detected by ESR measurement. However, a clear singlet ESR signal is observed for both thermal and photopolymerization systems as shown in Figure 4. This is a good indication for electron transfer reaction between VCZ and Au^{III} and/or Au^{II} species.

The sequence of redox potentials of various materials used in the present system does not contradict to the present concept. Since the values of redox potential shown in Table II were not determined under the same conditions, the sequence of redox potential may have only qualitative importance. As judged by the redox potentials, nevertheless, the reducing agents are all capable of reducing Au^{III} quickly, whereas VCZ would proceed rather slow redox reaction with Au^{III}, which reflects in the presence of induction period. If Au^{II} is once formed, VCZ would react with Au^{II} quickly.

On the basis of following elementary reactions, kinetic study was made.

1) Initial process

i) in dark:

$$Au^{III} + M \rightleftharpoons \underset{I}{(Au^{III} - M)}$$

$$I \longrightarrow Au^{II} + X$$

ii) in light:

$$Au^{III} \xrightarrow{h\nu} Au^{II}$$

iii) in the presence of reducing agents:

$$Au^{III} + \text{Red.} \longrightarrow Au^{II} + \text{Oxd.}$$

2) Initiation, propagation and termination

initiation: $Au^{II} + M \longrightarrow Au^{I} + M^*$

propagation: $M^* + M \longrightarrow P_1^*$

$P_n^* + M \longrightarrow P_{n+1}^*$

termination: $P^* + M \longrightarrow P$
(quarternization of carbazyl nitrogen)

Rates of dark polymerization in the presence and absence of reducing agents, and of photopolymerization, induction period and molecular weight, are satisfactorily explained. Full details of the kinetic interpretation will be published elsewhere.[11]

In conclusion, this is a clear example of accelerating ionic polymerization by photochemical formation of catalytic species. At present, it is not possible to discuss photochemical effect on direct reaction of VCZ with Au^{III} and/or Au^{II}.

PHOTOPOLYMERIZATION BY ORGANIC DONOR-ACCEPTOR INTERACTION

A. Acrylonitrile (AN)-VCZ System

Thermal polymerization of this system was first studied by Ellinger[12] who reported the production of VCZ homopolymer alone. However, AN can be polymerized as well depending upon reaction conditions as shown in Table III. Time-conversion curves are shown in Figures 5 and 6. This system is a heterogeneous polymerization system and the rate of photopolymerization slows down with conversion due to decreased transmission of light. Thermal rate under conditions of photopolymerization is practically zero. Peculiar features of this polymerization are the facts that VCZ content in the product is affected by additives and also by reaction conditions and that the product consists of two polymers, namely, benzene soluble and benzene insoluble fractions. The benzene extract was precipitated in methanol and was confirmed to be homopolymer of VCZ by infrared spectroscopy. Since there is no fraction extractable by saturated zinc chloride aqueous solution which can dissolve polyacrylonitrile, the product seems to be a mixture of poly-VCZ and copolymer of AN with VCZ.

These results can only be understood if one assumes simultaneous occurrence of two polymerization mechanisms. Additive effects on product composition (Figure 7) indicate that poly-VCZ and the copolymer are formed by cationic and radical mechanisms, respectively. Although water and air influence scarcely the total polymer yield, change in product composition is drastic. Presence of ammonia even enhances the total yield (Figure 8), whereas the formation of poly-VCZ is completely suppressed. If cationic and radical species exist independent of each other, such sequence of additive effect could not be expected. These results suggest convertibility of initiating species between radical and cation. The most likely explanation would be given on the basis of the formation of ion-radicals at the initial stage.

The difference in product compositions for photo and thermal polymerization is far too big to be attributed to the difference in reaction temperature (30° for photopolymerization and 60° for thermal polymerization). Photochemically produced ion-radicals are in excited state according to the Franck-Condon principle and would be expected to have different reactivity for cationic and radical initiation from thermally produced one.

Composition curves for photopolymerization of VCZ-AN system are shown in Figure 9 together with composition curve of radical copolymerization. Influence of air on copolymer composition seems to be due to formation of homopolymer of VCZ. Analysis of polymer after 3 days' extraction by benzene at 60°, indicates that compositions of benzene insoluble copolymers prepared in air and in vacuo are nearly the same and their compositions approach to those prepared by conventional radical polymerization as shown in Figure 10.

B. AN-N-ethylcarbazole System

In the preceding section, both donor and acceptor are polymerizable monomers. This is, however, not a necessary condition for photosensitized charge transfer polymerization. When donor molecule is not polymerizable, prominent photosensitization is also observed as shown in Table IV. Differences from the results are the facts that thermal polymerization does not occur at all and the polymerization proceeds entirely by radical mechanism as judged by copolymerization with styrene and retarding effect of oxygen and DPPH. Retardation by hydrogen chloride, however, might indicate participation of anionic species at the initiation process.

C. VCZ-acetonitrile System

Contrary to ii), acceptor molecule does not bear vinyl group. Prominent acceleration by photo-irradiation is shown in Table V. The photopolymerization is retarded by both DPPH and ammonia. Addition of small amount of ammonia decrease the polymer yield to about one-third, but further addition of ammonia does not influence the polymer yield. The photopolymerization is, therefore, thought to be radical-cationic. Thermal rate is extremely slow.

D. Polymerization Systems Which do Not Contain One or Both of Donor and Acceptor

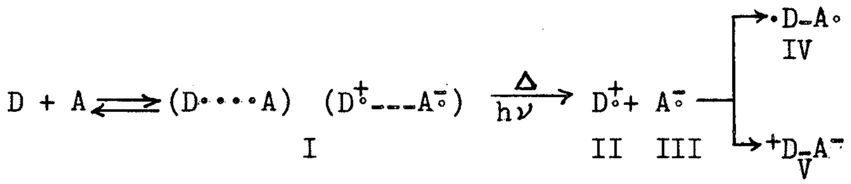
When donor or acceptor is added to neutral monomer such as styrene, photo and thermal polymerization are all very slow as shown in Table VI. The combination of acetonitrile with N-ethylcarbazole is also ineffective for photosensitized polymerization of styrene as shown in Figure 11. Presence of acceptor for donor monomer or donor for acceptor monomer is absolutely necessary for photosensitization of polymerization.

E. General Discussions

Weak donor-acceptor pairs which contain at least one polymerizable monomer as a component may be thermally stable but show prominent photosensitivity. In fact, the charge transfer pairs between nitriles and carbazoles seem to have very weak interaction, since charge transfer band is not detected for any of these pairs. This is not surprising since carbazoles show their own absorptions up to very near ultraviolet region which would conceal the absorption due to weak charge transfer interaction.

Other weak donor-acceptor systems such as VCZ - nitrobenzene and VCZ- p-nitrostyrene were also proved to be photosensitive.

On the basis of charge transfer initiation of polymerization, the general scheme may be expressed as follows:



$$D + A \rightleftarrows (D\cdots A)\quad \underset{\text{I}}{(D^{+\cdot}\text{---}A^{-\cdot})} \xrightarrow[h\nu]{\Delta} \underset{\text{II}}{D^{+\cdot}} + \underset{\text{III}}{A^{-\cdot}} \begin{cases} \rightarrow \underset{\text{IV}}{\cdot D\text{–}A\cdot} \\ \rightarrow \underset{\text{V}}{{}^{+}D\text{–}A^{-}} \end{cases}$$

I: polymerization by mesomeric polarization
II: cation radical → cationic and/or radical
III: anion radical → anionic and/or radical
IV: diradical → radical
V: cation anion → cationic and/or anionic

At least five active species, namely, charge transfer complex itself, cation-radical, anion-radical, diradical and cation-anion can be considered. For the interpretation of experimental results, more than two of these active species have to be considered to take part simultaneously in initiation of polymerization. Ellinger assumed that charge transfer complex itself was the initiating species, but his explanation is apparently not sufficient to interpret all results indicating duality of initiation mechanism. Formation of diradical and cation-anion from charge transfer interaction of donor- and acceptor ethylenic compounds was considered as intermediates of 1,2-cycloaddition reaction promoted either thermally or photochemically.[13] Consequently, contribution of diradical and/or cation-anion is likely in the polymerization of VCZ - AN system system. So far, evidence which confirms the type of initiating species has not been obtained.

EXPERIMENTAL

A. Materials

VCZ (Koch-Light Lab.) was recrystallized from n-hexane. m.p. 65.2°. N-Ethylcarbazole (Chemical Pure Grade) was decolorized by active charcoal and recrystallized twice from methanol.

Styrene, acrylonitrile, benzene, acetonitrile and nitrobenzene were purified by accepted procedures. Particular care was taken for purification of nitrobenzene to avoid light during distillation. Sodium chloroaurate dihydrate (purity 99.3%), ferrocene, ascorbic acid, DPPH and mercury were the best commercial materials and used without further purification. Liquid ammonia prepared by warming concentrated aqueous ammonia was dried by passing through the barium oxide tube and purified by trap-to-trap distillations.

B. Light Source

A 300W high pressure mercury lamp was the light source. The lamp having a 15 cm long of illuminating part was installed vertically in a thermostated water bath. Since cylindrical reaction vessels were used, absolute photointensity could not be measured. The rate of reduction of potassium ferrioxalate actinometer ($[Fe^{III}] = 6 \times 10^{-3}M$)[14] as a measure of relative light intensity using same reaction vessels as polymerization was 7.15 7.60 x $10^{-5} m.l^{-1}.s^{-1}$. for the polymerization by organic donor-acceptor interaction and 3.4 x $10^{-6} m.l.^{-1} s.^{-1}$ for the polymerization by sodium chloroaurate.

C. Polymerization

1. Polymerization of VCZ by $NaAuCl_4 \cdot 2H_2O$ in Nitrobenzene

All polymerization was carried out at 30°. The rate of polymerization was measured by a dilatometer and also weighing the polymer after precipitated in methanol. All operations were carried out under dry nitrogen atmosphere but no special care was taken to eliminate dissolved air in reaction mixture. The effect of trace amount of water was found to be negligible and later, polymerization was carried out in open system. Identical results were obtained for polymerization in dry atmosphere and in air. For the polymerization in light, the ultraviolet region (below $\lambda = 320$ mμ) of light was cut off by the glass wall (~1 mm thickness) of reaction vessel but the light was panthromatic in the visible region.

Molecular weight of polymer was determined by viscosity measurement according to the following equation.[15]

$$[\eta] = 3.35 \times 10^{-4} M^{0.58} \quad \text{at } 25^{\circ} \text{ in benzene}$$

Copolymer composition of VCZ - isobutyl vinylether system was analyzed by electronic spectroscopy. The absorption band due to π-π^* transition of carbazole group at 345 mμ was used as key band. The intensity was exactly proportional to the concentration of poly-VCZ as calibrated for the mixture of poly-VCZ and poly-isobutyl vinylether.

2. Photopolymerization by organic donor-acceptor interaction

Polymerization vessel was a bard glass ampoule (ϕ - 12 mm). Most of polymerization are heterogeneous and the polymer yield was determined by weighing the polymer after precipitation, washing with methanol and drying. For the polymerization in vacuo, the polymerization mixture was degassed by several freeze-thaw cycles at a pressure of 10^{-4} mmHg.

Analysis of polymer containing VCZ and AN was made by both elemental analysis and infrared spectroscopy. Absorptions at 2240 cm^{-1} and at 930 cm^{-1} are used as key bands for AN and VCZ, respectively. Since agreement between two analytical methods were satisfactory as shown in Figure 9, infrared spectroscopy alone was used in the later experiments.

Copolymer composition of styrene-AN system was determined by elemental analysis.

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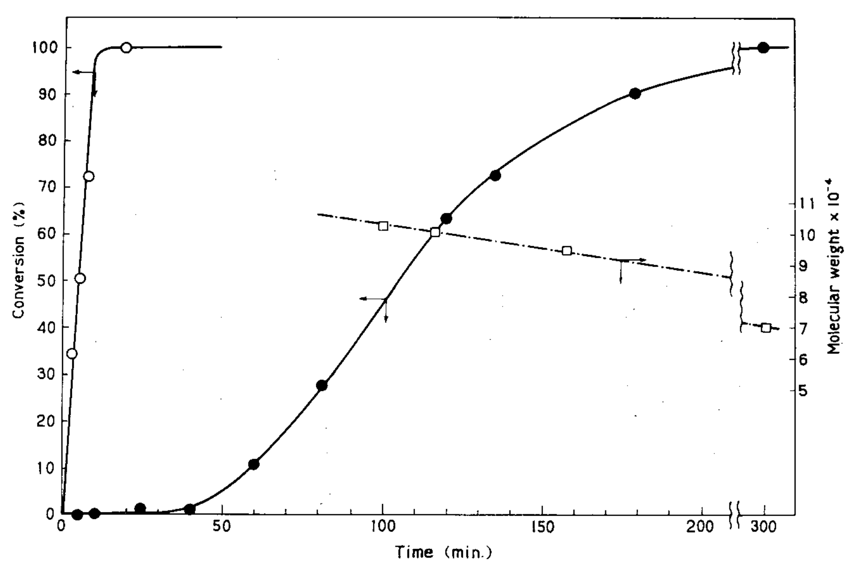
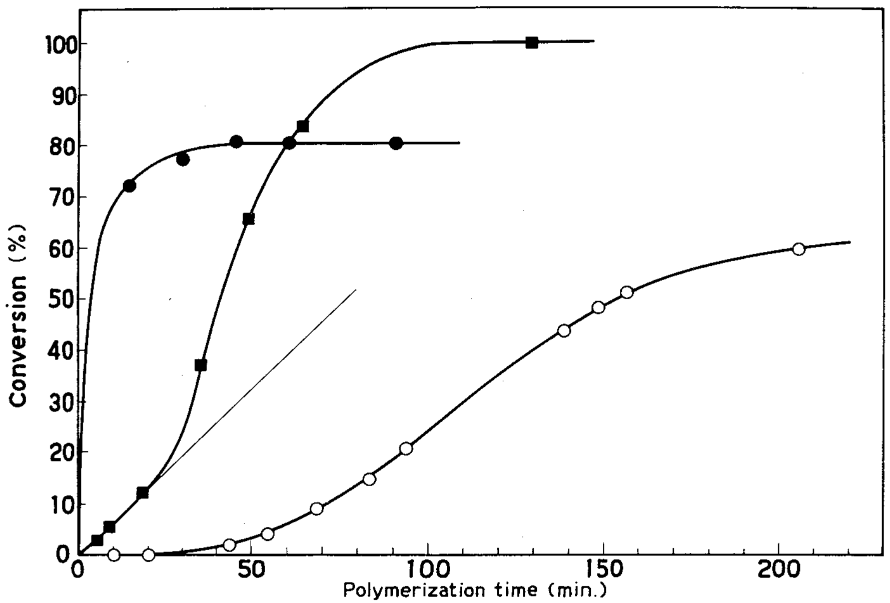


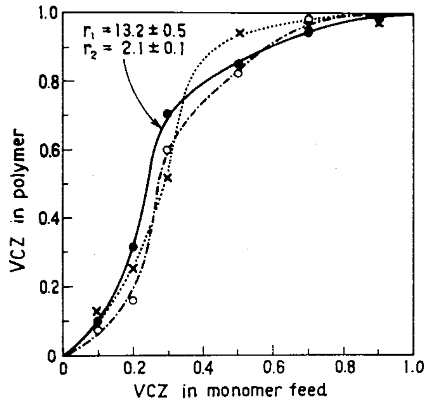
Polymerization of VCZ in Nitrobenzene at 30°C.
[NaAuCl$_4$·2H$_2$O] = 1.0 x 10^{-4}M. [VCZ] = 0.25M
—●— : in dark
—○— : irradiated
—□— : molecular weight of PVCZ obtained in dark

FIGURE 1



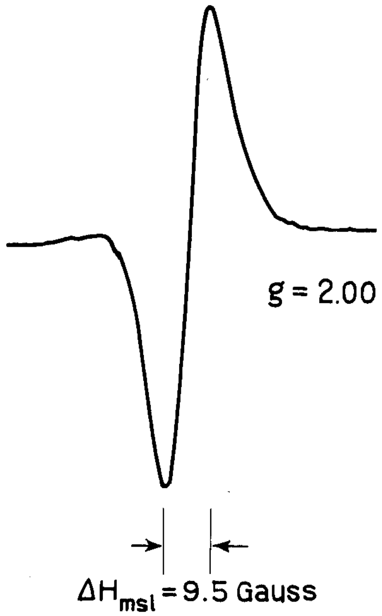
Effect of Ferrocene on the Polymerization of VCZ in Dark.
—○— : [VCZ] = 0.25M. [NaAuCl$_4$·2H$_2$O] = 5.0x10^{-5}M [Ferrocene] = 0
—■— : 〃 5.0x10^{-5}M 〃 = 2.5x10^{-5}M.
—●— : 〃 1.0x10^{-4}M 〃 = 1.0x10^{-3}M.

FIGURE 2



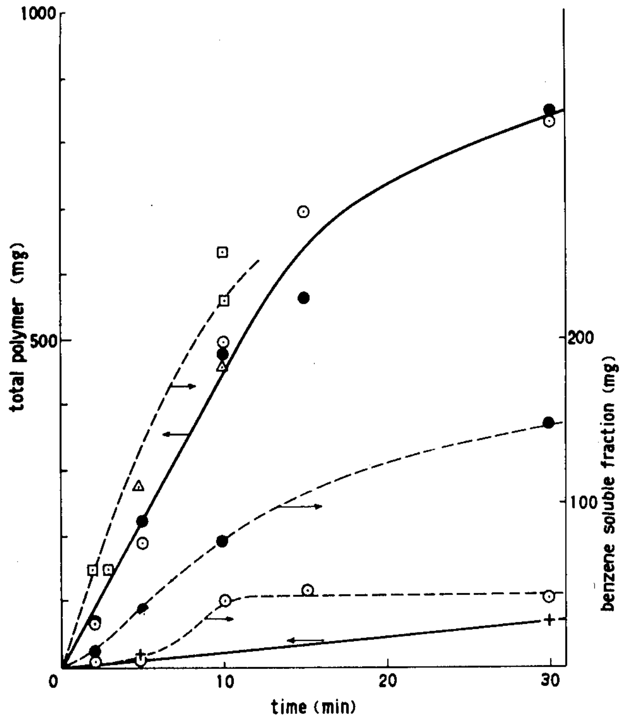
Copolymerization of VCZ - isobutyl vinylether
VCZ = M$_1$, total monomer : 0.5M. in nitrobenzene. 30°C.
—●— : Catalyst = NaAuCl$_4$·2H$_2$O in dark.
-·-○-·- : 〃 = 〃 in light.
·····×····· : 〃 = trichloracetic acid.

FIGURE 3



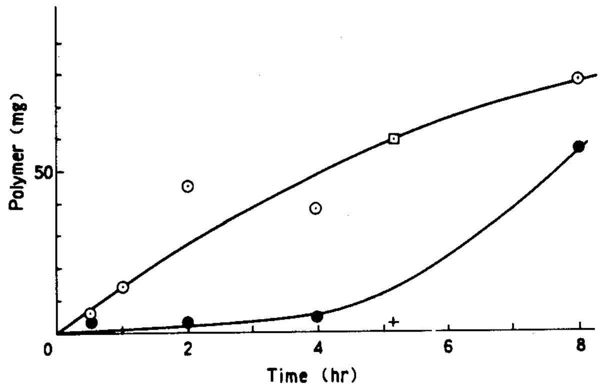
The ESR Signal of Photoirradiated VCZ-Nitrobenzene-$NaAuCl_4 \cdot 2H_2O$ System. [VCZ] = 0.5 M. [Au^{III}] = 7.5×10^{-3} M.

FIGURE 4



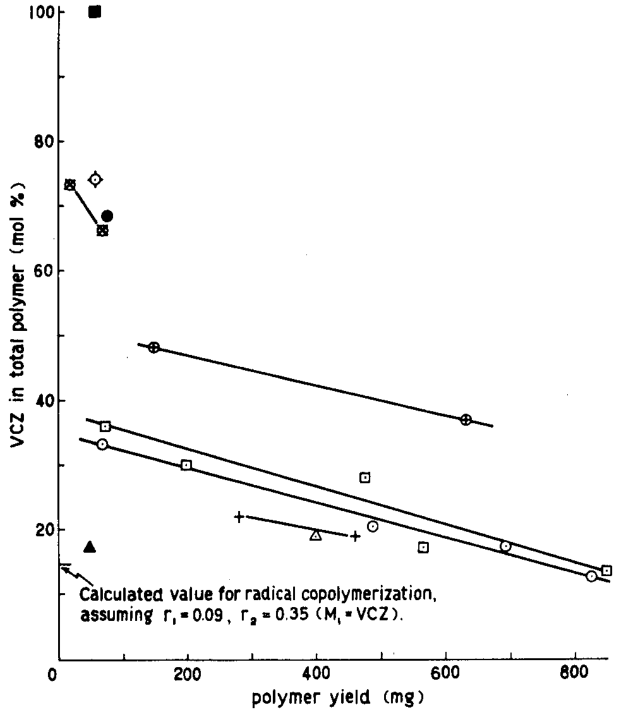
Photopolymerization of VCZ-AN systems
[VCZ] = 1 M in AN. 3 ml. (VCZ = 582 mg. AN = 2070 mg) 30°C.
⊙ in vacuo. ⊡ in vacuo, H_2O 0.1 M added.
● in air. + in vacuo, DPPH 10^{-3} M added.
△ in CO_2 gas.

FIGURE 5



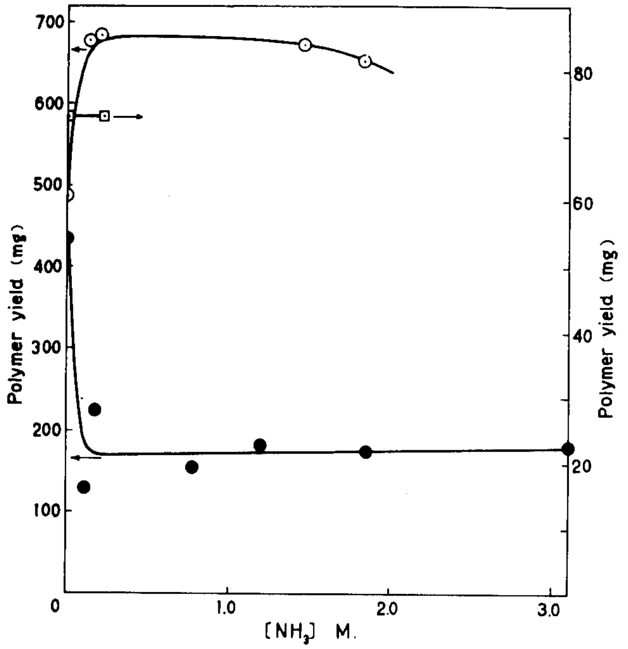
VCZ-AN dark polymerization.
VCZ = 582 mg, AN = 2070 mg, 60°C.
⊙ : in vacuo, ● : in air, ⊡ : in vacuo, H_2O 0.1 M added, + : in vacuo, DPPH 10^{-3} M added.

FIGURE 6



Plots of mol % of VCZ in Polymer vs. Polymer Yield.
VCZ 582 mg. AN 2.07 g. 30°C. for hν, 60°C. for thermal reaction.
□ : hν in air, ⊙ : hν in vacuo, ⊕ : hν in vacuo, [H_2O] = 0.1 M,
⊠ : hν in vacuo, [DPPH] = 10^{-3} M, △ : hν in vacuo, [NH_3] = 0.4~0.75 M,
+ : hν in CO_2, ◇ : thermal in vacuo, [H_2O] = 0.1 M, ▲ : thermal in vacuo, [NH_3] = 0.176 M, ■ : thermal in air, ● : thermal in vacuo.

FIGURE 7



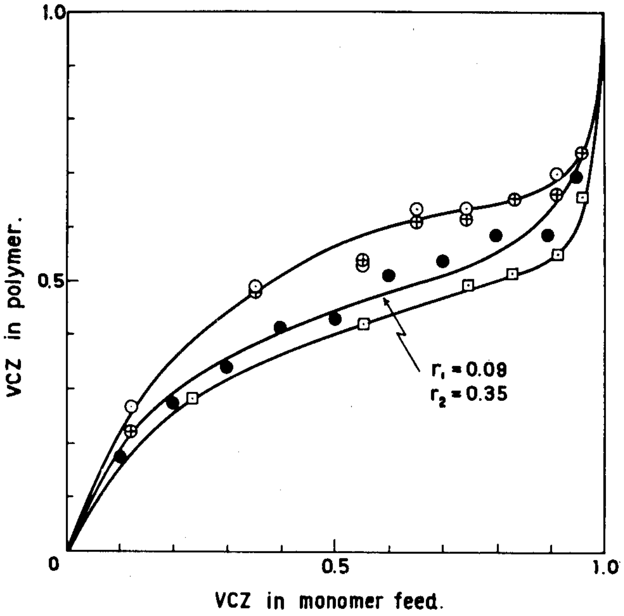
Effect of Ammonia on Polymer Yield.

⊙ : VCZ-AN (VCZ : 582 mg, AN : 2.07 g) photopolymerization in vacuo at 30°C. for 10 min. volume of reaction mixture : 3 ml.

● : VCZ-CH_3CN (VCZ : 582 mg, CH_3CN : 2.58 ml.) photopolymerization in vacuo at 30°C. for 60 min. volume of reaction mixture: 3 ml.

⊡ : VCZ-AN (same as ⊙ but containing 10^{-3} M of AIBN) dark polymerization at 60°C for 20 min.

FIGURE 8



Photopolymerization of VCZ-AN without sensitizer

[VCZ] + [AN] = 5 m mol. benzene 2 ml.

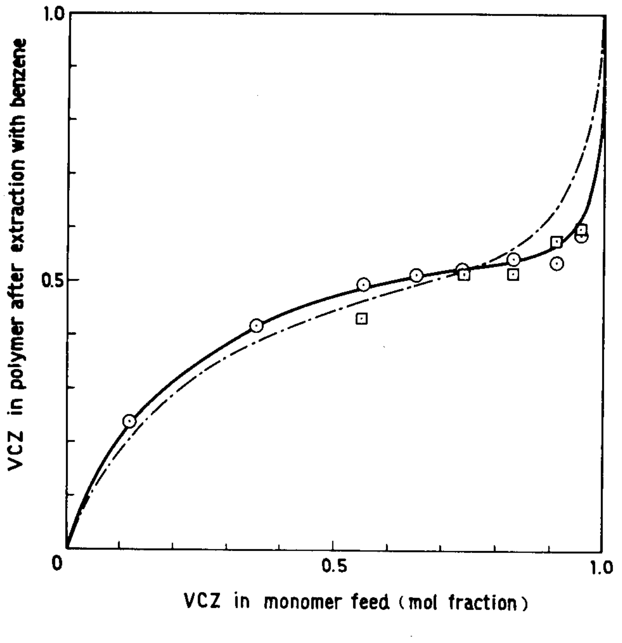
⊕,⊙ : photopolymerization in air ⊙ : from N content

⊕ : from IR spectrum.

⊡ : 〃 in vacuo, from IR spectrum

● : polymerization in dark, 60°C. from IR spectrum [VCZ] + [AN] = 2.5 mol/l. [AIBN] = 10^{-2} M.

FIGURE 9



Composition curve for Benzene insoluble fraction produced by photopolymerization of VCZ-AN system.

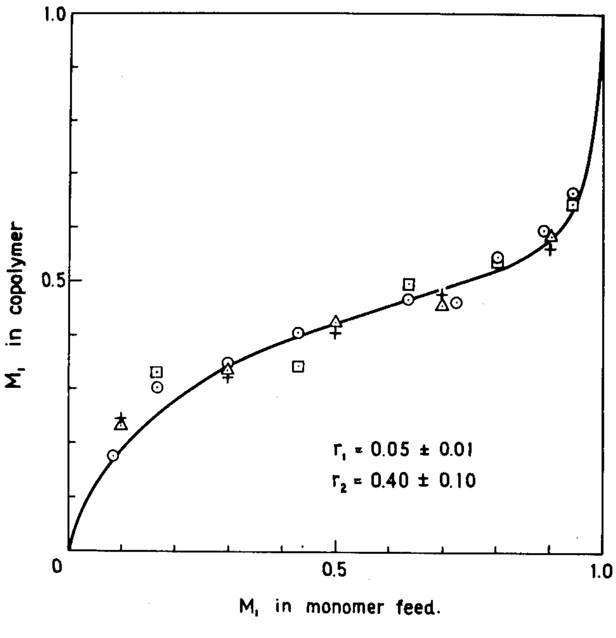
[VCZ] + [AN] = 5 mmol, benzene 2 ml.

⊙ : photopolymerization in air at 30°C.

⊡ : 〃 in vacuo at 30°C.

-·-·- : for radical polymerization at 60°C.

FIGURE 10



Photopolymerization of AN-Styrene systems at 30°C.

⊙ : AN-St-AIBN (10^{-2} M)

⊡ : AN-St-Ferrocene (10^{-3} M)

+ : AN-St-ECZ in air

△ : AN-St-ECZ in vacuo

FIGURE 11

Polymerization of VCZ in the Presence of Various Additives

[VCZ]=0.25M, $[Au^{III}]=1.0\times10^{-4}$M, solvent : nitrobenzene

Additive	Polymerization time (min.)	Conversion (%)	Remarks
none (standard)	120	67.5±5	$\overline{MW}$ = 98,000 see Fig.1 ~~and 8~~.
none, preirradiated*	80	86	
none, irradiated	20	100	$\overline{MW}$ < 40,000
ammonia 10^{-2}~10^{-3}M	120	0	
water 10^{-2} M	160	~90	$\overline{MW}$ = 66,000
〃 10^{-1} M	180	~90	〃 = 35,000
N-ethylcarbazole 0.125M	80	50	〃 = 94,000
〃 0.25M	90	50	〃 = 90,000
ascorbic acid**	120	100	
mercury metal**	120	100	
ferrocene 5×10^{-5}M	30	100	
DPPH 10^{-4}M	90	96	

* Catalyst solution was irradiated before mixing with monomer.

** Additive is insoluble

TABLE I

Standard Redox Potentials of Relevant Compounds.

redox pair	E° volt	method of determination
$AuCl_4^-/Au^{II}_{Cl}$	-0.5~-0.96	estimation from redox reaction (6) polarography in DMF (5a)
$Au^{II}_{Cl}/AuCl_2^-$	> -1.4	estimated from redox reaction (6)
VCZ^+/VCZ	-1.3	polarography in DMF (7)
$Ferrocene^+/Ferrocene$	+0.56	e.m.f. in alcohol (8)
$Hg_2^{2+}/Hg(\ell)$	-0.792	e.m.f. (9)
ascorbic acid	+0.1~+0.3	e.m.f. (10)

TABLE II

Polymerization of VCZ-AN system

[VCZ] = 1.0 M in AN, volume of solution: 3 ml.

(VCZ 582 mg + AN 2.07 g).

Reaction at 30° for photopolymerization and at 60° for thermal polymerization.

photo or thermal	atmosphere	additive	time (min)	yield (mg)	D_{2240}/D_{930}	VCZ in total polymer (mol%)	benzene soluble fraction 2) (wt%)
photo	vacuo	none	10	490	4.05	20.8	8.3
"	air	"	10	477	2.72	28.1	16.3
"	vacuo	$[H_2O]$ = 0.1 M	3	149	1.16	48.2	
"	"	"	10	630	1.96	36.8	35.6
"	"	[DPPH] = 10^{-3}M	5	18	0.453	73.0	
"	"	"	30	68	0.601	66.2	41.0
"	"	NH_3 0.047 ml	5	400	4.39	19.4	0
thermal	vacuo	none	480	77	0.573	67.8	
"	air	"	480	56	0.0	100	
"	vacuo	$[H_2O]$ = 0.1 M	311	59	0.437	74.1	
"	"	[DPPH] = 10^{-3}M	311	1	—	—	
"	"	$[NH_3]$ = 0.025 ml	2880	47	5.12	17.1	

1) Intensity ratio of infrared spectra at 2240 cm^{-1} and 930 cm^{-1}.

2) Extracted fraction after treating the total polymer with benzene at 60° for 3 days.

TABLE III

Polymerization of AN-N-ethylcarbazole (ECZ) system.

AN: 1.5 ml, ECZ: 0.35 g,

30° for photopolymerization, 60° for thermal polymerization.

photo or thermal	atmosphere	additive	time (min)	yield (mg)
photo	vacuo	none	60	245, 234
"	air	"	60	112, 105
"	vacuo	[DPPH] = 10^{-3}M	60	20, 31
"	air	"	60	15, 12
"	vacuo	[HCl] = 0.1 M	60	71, 75
"	air	"	60	11, 14
thermal	vacuo	none	360	0
"	air	"	2900	0

TABLE IV

Polymerization of VCZ-acetonitrile system.

[VCZ] = 1.0 M in acetonitrile, volume of solution: 3 ml.

(VCZ = 582 mg, acetonitrile = 2,58 ml)

30° for photopolymerization, 60° for thermal polymerization.

photo or thermal	atmosphere	additive	time (min)	yield (mg)
photo	vacuo	none	60	432
"	air	"	60	445
"	vacuo	[H_2O] = 0.1 M	60	441
"	"	[DPPH] = 10^{-3}M	60	4.7
thermal	vacuo	none	200	4.5
"	"	"	1440	15.5
"	air	"	200	6.0
"	"	"	1440	16.4
"	vacuo	[H_2O] = 0.1 M	1440	1.6
"	"	[DPPH] = 10^{-3}M	180	3.7
"	"	"	1440	13.1
"	"	NH_3 0.045 ml	1440	5.7
"	"	NH_3 0.015 ml	1440	4.8

TABLE V

Slow polymerization systems without charge transfer interaction.

30° for photopolymerization, 60° for thermal polymerization.

polymerization system	photo or thermal	atmosphere	time (min)	yield (mg)
VCZ 0.3 g benzene 1.0 ml	thermal	air	1140	2.7
" "	photo	"	150	10.0
VCZ 0.3 g styrene 1.0 ml	thermal	"	270	0.4
" "	photo	"	300	69.3
ECZ 0.35 g styrene 1.5 ml	photo	vacuo	61	10.7
" "	photo	"	61	3.6
Styrene 0.34 ml CH_3CN 2.58 ml	photo	"	460	0
" " "	thermal	"	460	0
AN 1.5 ml	photo	"	60	0
Styrene 2.0 ml, ECZ 600 mg. CH_3CN 0.16ml	thermal	"	1920	39.0
" "	"	air	1920	34.2
styrene 2.0 ml	"	vacuo	1920	52.7

TABLE VI

SURFACE-PHOTOPOLYMERIZATION OF VINYL AND DIENE MONOMERS

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In 1961, White reported that gaseous 1,3-butadiene in contact with metallic substrates polymerized under the influence of ultraviolet light.[1] The growth rate varied inversely as the temperature of the substrate. Although there has been some subsequent mention of the process and of the properties of the polymeric films,[2] little has yet been published about this technique. I wish to report some of the results of our work on ultraviolet surface-photopolymerization, especially that part that leads to the formation of novel materials in thin-film form.[3]

The process is schematically described in Figure 1. The medium pressure mercury arc is usually positioned about two inches above the substrate surface. A quartz window permits transmission of light over the ultraviolet region to the substrate surface. After pre-evacuation to about 10^{-6} torr, the gaseous monomer is maintained at a pressure ≤ 4 torr in the reaction zone during the deposition. The temperature on the surface of the substrate is controlled by cooling the substrate holder.

The polymeric films may be dielectrically characterized by construction of crossed film capacitors such as illustrated in Figure 2. This technique also provides a convenient method for thickness (hence growth rate) measurements once the dielectric constants of the films have been determined. The chemical structure of the thin films may be conveniently studied by multiple-reflection infrared absorption. However, a particularly facile area of study of the thin films deposited by the ultraviolet surface-photopolymerization process is that of electron microscopy. The inert nature of the films permits them to be picked up on microscope grids, without carbon support, after removal from metallic or other substrates by dissolving the latter in concentrated acids. There is no need for platinum replication and the films may be examined directly, in transmission.

For deposition from 1,3-butadiene, Figure 3 demonstrates the linear dependence of film thickness on irradiation time, and the inverse dependence of growth rate on substrate temperature. A negative activation energy of about 7 kcal/mole is indicated by the Arrhenius plot in Figure 4. Infrared absorption, Figure 5, shows evidence (~ 966 cm^{-1}) for the thermodynamically favored trans-1,4 form of addition, while the presence of CH_3 groups (~ 1375 cm^{-1}) indicates that the films are not simply polybutadiene. Small amounts of hydrogen associated with carbon-carbon triple bonds are indicated by absorptions at 3300, 2110 and 697 cm^{-1}. The complex nature of the photopolymerization process is indicated by the identification of at least thirteen gas phase products. These closely resemble those identified during the gas phase photolysis of butadiene.[4] A slight increase in the C/H atomic ratio in the films by elemental analysis to 0.73, from the value of 0.66 for polybutadiene, parallels a lowered C/H ratio averaged over the major gas phase products. Differential scanning calorimetry shows no transitions between -80° and 325°C, but endothermic behavior above 130°C. Although this behavior has not been detected from other monomers, thicker films from C_4H_6 exhibit instability in the presence of air or moisture at elevated temperatures and often peel from metallic substrates.

Extension of the surface-photopolymerization technique to other diene and to vinyl monomers is illustrated by Figure 6. The selected values for growth rate and dielectric properties demonstrate the unique nature of the films deposited from each monomer. The controlled energy of the ultraviolet irradiation process permits retention of the individual properties such that the films bear a close resemblance to polymers formed from each monomer by more conventional techniques.

The extension of the surface-photopolymerization process to vapors not subject to conventional forms of polymerization has proved to be of particular interest. Hexachlorobutadiene, for example, is a quite inert molecule that behaves as though fully saturated.[5] It is not subject to polymerization or copolymerization by conventional techniques.[5,6] However, the vapor in equilibrium with the liquid at about 18°C, i.e., at a pressure of about 100 torr, is readily polymerized by the ultraviolet irradiation technique. The growth rate shows a negative activation energy of about 8 kcal/mole, as illustrated in Figure 7. The solid circle represents growth on the surface at a temperature of about 177°C, i.e., on an uncooled substrate. The deposited film is not simply "polyhexachlorobutadiene" and the polymerization does not proceed by a simple addition mechanism. Elemental analysis indicates a C/Cl atomic ratio of about 2/1, while the eliminated chlorine has been identified as the major (and almost sole) gas phase product. The process leads, however, to the deposition of a perchlorinated films are essentially transparent. However, contrary to the behavior of the films deposited from hydrocarbon monomers, these films show no significant CO absorption ($\sim$1725 cm^{-1}) on exposure to steam at 100°C. Although differential scanning calorimetry indicates no detectable first order transition over the range 40° to 400°C, an exothermic reaction does occur in nitrogen at temperatures above 300°C and the films lose weight. Figure 8 illustrates the kind of structure that may be located by transmission electron microscopy on a few isolated areas of the thinner, nonsupported films from C_4Cl_6. This structure is not representative of the surface of the as-polymerized films as a whole. Selected-area electron diffraction studies on such structures indicate a single-crystal pattern with repeat distances of 18 and 11 Å. The close agreement in repeat distances for these minute areas of extreme crystallinity as produced in the films from a wide variety of monomers suggests that they may result from localized crystallization of carbon-containing by-products formed by a minor photodegradation process.

Deposition of thin, continuous films from tetrafluoroethylene represents extension of the surface-photopolymerization process to the formation of a polymer in a useful form that is not obtainable by conventional polymerization processes. Infrared studies, Figure 9, on the transparent films deposited from TFE, at a growth rate of about 30 Å/min. at a substrate temperature of about 30°C, do indicate some structural differences from PTFE, e.g., the presence of some CF_3 groups as shown by absorption at 980 cm^{-1}. Differential scanning calorimetry shows no evidence for the first order, crystal-crystal transition characteristic of PTFE at about 20°C. The presence of a considerable amount of low molecular weight material in the as-polymerized films is further indicated by a loss in weight in air beginning at about 220°C.

Of the many people who contributed to this work, I particularly wish to thank R. A. Mazzarella and W. R. Burgess for assistance with the depositions and R. M. Chrenko and W. J. Barnes for the infrared and electron microscope measurements.

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PHOTODEPOSITION PROCESS

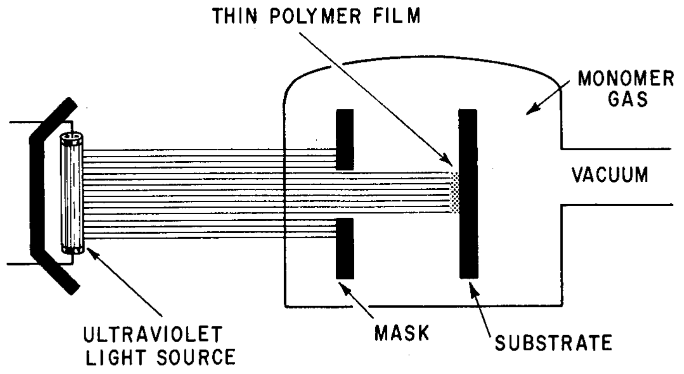

FIGURE 1: Schematic of ultraviolet surface-photopolymerization process.

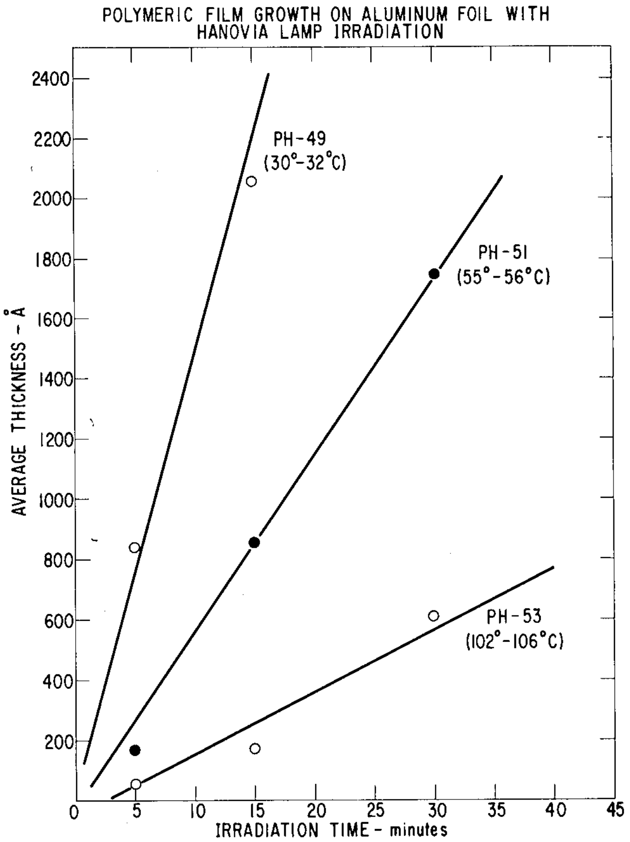

FIGURE 3: Growth of polymeric films from 1,3-butadiene.

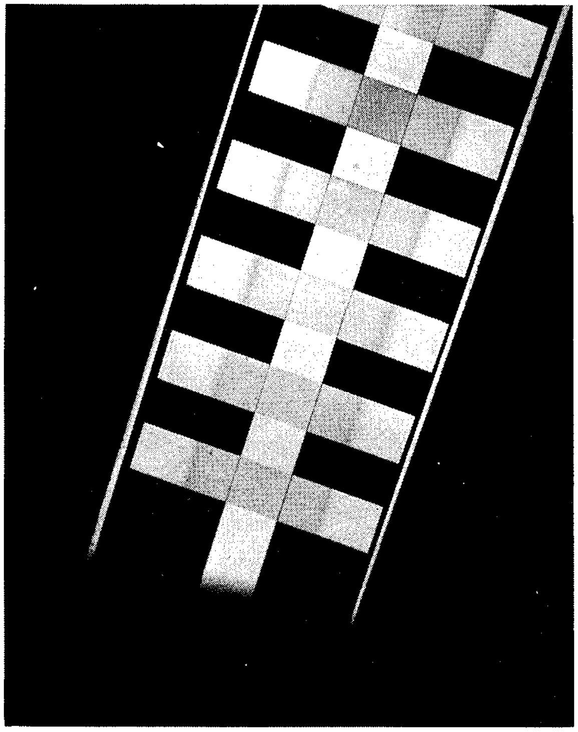

FIGURE 2: Films from C_4H_6 on evaporated aluminum with evaporated aluminum counterelectrode.

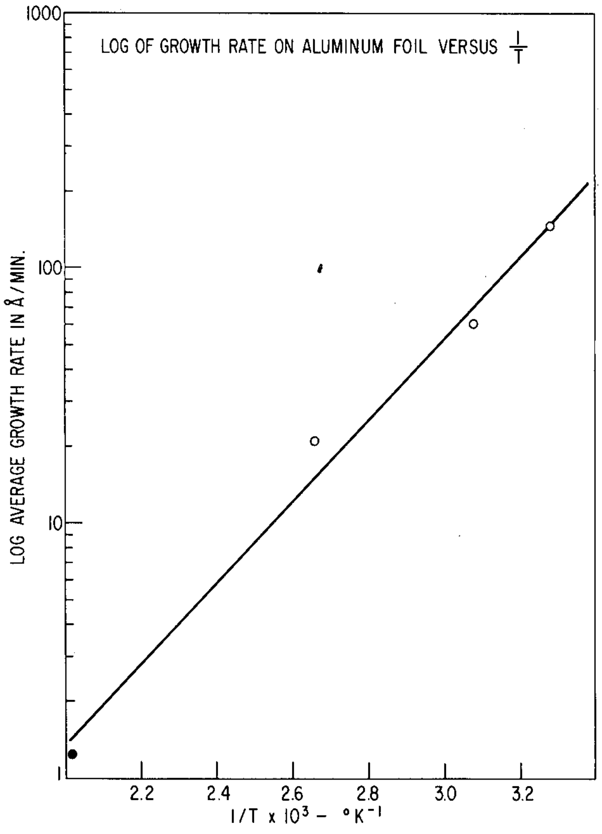

FIGURE 4: Log of growth from C_4H_6 on aluminum foil vs. 1/T.

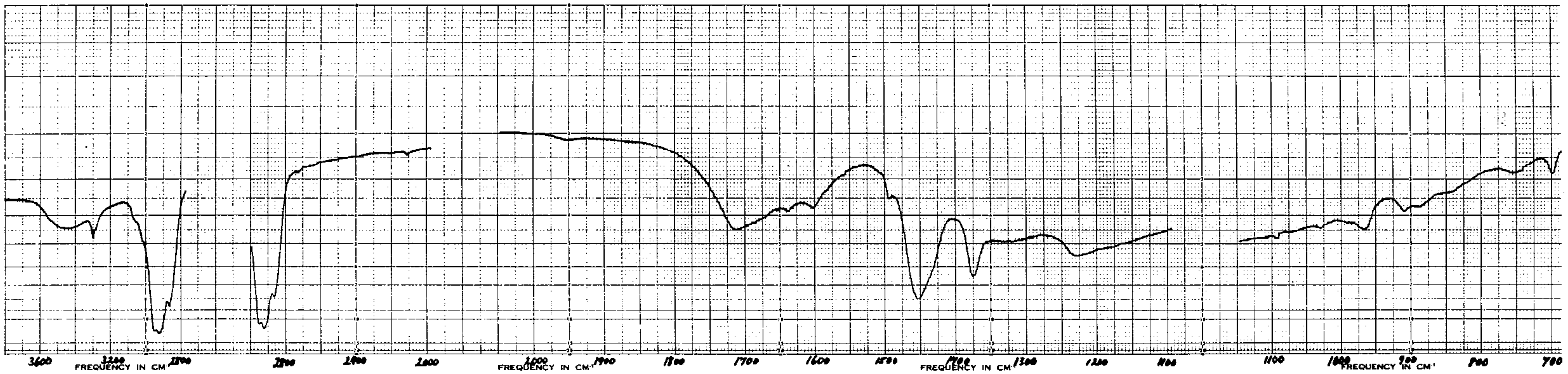

FIGURE 5: IR absorption spectrum of films (~ 20,000 Å) from C_4H_6 on evaporated aluminum.

POLYMERIC FILMS FROM VINYL MONOMERS

MONOMER	MEASURED GROWTH RATES Å/min.	SURFACE POLYMERIZATION TEMP. °C	BREAKDOWN STRENGTH volts/cm X 10^{-6}	DIELECTRIC CONSTANT
1,3-BUTADIENE	120	33	1.9	2.6
1,5-HEXADIENE	34	84	2.0	≥1.7
2,4-HEXADIENE	610	112	0.6	≥3.7
ACRYLONITRILE	661	58	0.4	≥5.8
STYRENE	247	108	1.0	2.8
METHYL-METHACRYLATE	2	217 (UNCOOLED)	1.7	≥1.6

FIGURE 6: Polymeric films from vinyl and diene monomers.

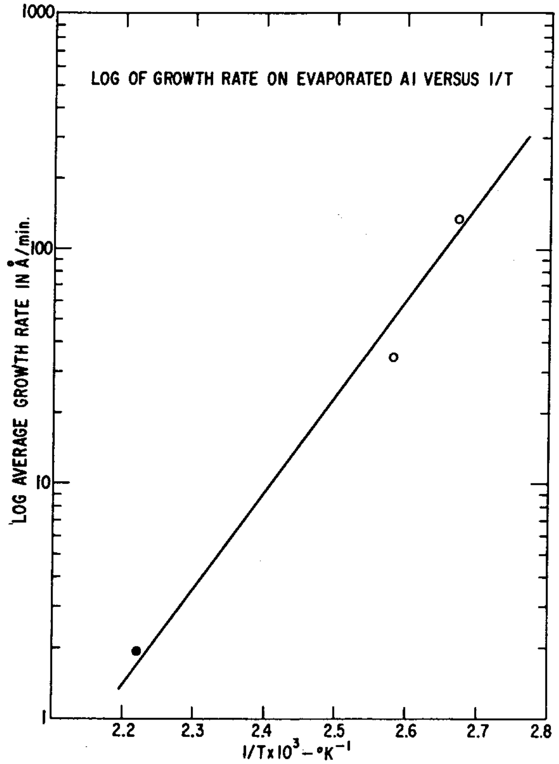

FIGURE 7: Log of growth rates vs. 1/T for C_4C1_6.

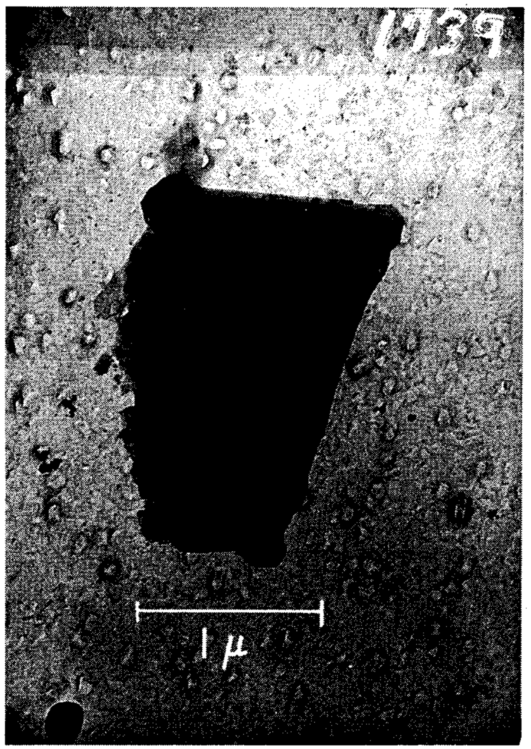

FIGURE 8: Electron microscope examination of films from C_4C1_6.

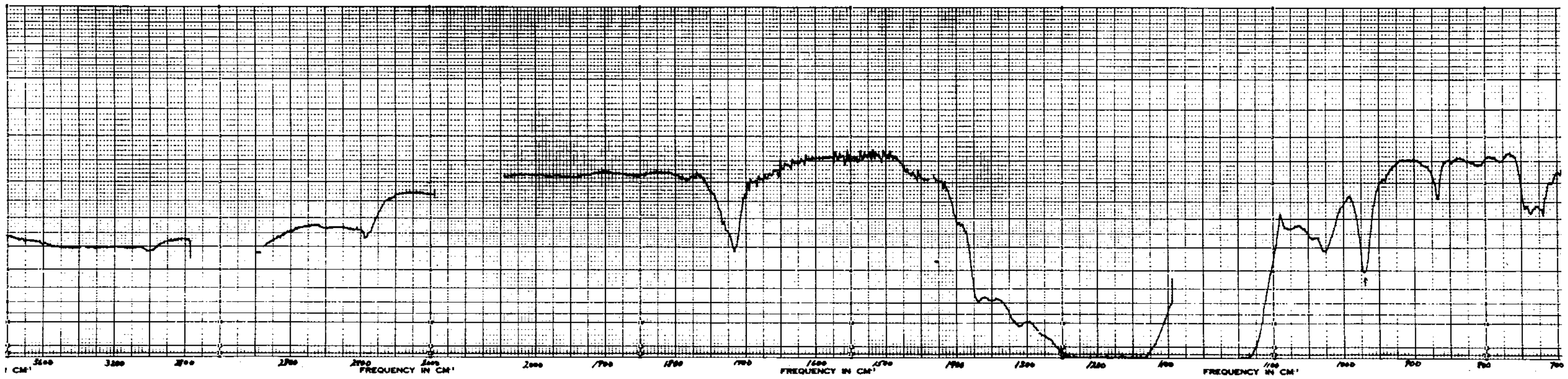

FIGURE 9: IR absorption spectra of films from TFE.

PHOTOPOLYMERIZATION INITIATORS CONTAINING STRONG OXIDIZING AGENTS*

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INTRODUCTION

Attempts have been made to use the visible-light-triggered photopolymerization reactions described by Oster[1,2] as a basis for the fabrication of a photographic receptor. Preliminary studies in dilute solution indicated that initiator systems containing a dye and an electron donor were limited in their reactivity. With the exception of acrylamide, acrylic acid and its salts, and acrylonitrile, very few monomers could be polymerized with any degree of efficiency. The use of β-diketones as the electron donors produced improvements in initiation efficiency[3,4] but did not appreciably increase the number of monomers that could be photopolymerized. The photoreduction of the dye appeared to have a detrimental effect on the course of the polymerization. On the other hand, this reaction removed light absorber from the system; on the other hand, the reduced form of the dye often functioned as a polymerization inhibitor. Oxidizing agents were added to the dye-electron donor system to counteract these effects.

The initiator systems for this work utilized thionine or methylene blue as the dyes and either tertiary amines such as triethanolamine and ethylenediaminetetracetic acid or β-diketones such as acetylacetone or 5,5-dimethyl-1,3-cyclohexanedione as the electron donors. The reduced forms of both dyes, leucothionine and leucomethylene blue, are strong reducing agents. In combination with an oxidizing agent, they may be expected to form a redox initiator. Secondary radical generation from this initiator should enhance the polymerization step and the regeneration of dye should enhance the photoinitiation step. The addition of cumene hydroperoxide, cupric ions, diazonium compounds and related materials to the dye-electron donor system improved polymerization. Typical results are shown in Figure 1. The greatest improvement occurred in the later stages of the reaction where the absence of dye and presence of leuco dye normally prevent further polymerization. The dye fading reaction was suppressed but not completely eliminated.

During attempts to photopolymerize monomers not usually responding to the dye-electron donor initiator systems, a slight turbidity was often observed immediately after exposing the system to strong light. Nothing further happened and no detectable polymer formation occurred. The amount of turbidity appeared to increase when oxidizing agents were added, but it was still difficult to detect

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**Now with Prototech, Inc., Cambridge, Mass.

polymer formation in most cases. On the assumption that the polymerization of some monomers might be extremely susceptible to inhibition by leuco dyes, stronger oxidizing agents were added in an attempt to control the dye fading reaction. The addition of sodium periodate or sodium vanadate to the dye-electron donor initiator systems strongly suppressed dye fading and allowed the isolation of polymer from aqueous solutions of monomers such as methyl vinyl ketone, methyl methacrylate, α-chloroacrylamide and 2-methyl-5-vinylpyridine.

A qualitative measure of the improved efficiency of these more complex photoinitiator systems was obtained by measuring the time required for gel formation on irradiating a solution containing initiator, 5% of dimethylaminoethyl methacrylate, and 2% of sodium polystyrene sulfonate. Experiments carried out at pH 7.0, where the tertiary amine group of the monomer can serve as the electron donor, and at pH 4.3, where an outside electron donor must be added, are summarized in Table I.

EXPERIMENTAL

Studies of the kinetics of polymer formation in 5% solutions of acrylamide had been performed with standard dye-electron donor photoinitiator systems. The experimental procedure was as follows: Individual solutions of dye, electron donor and monomer were prepared at concentrations approximating 10^{-3}M, 10^{-2}M and 1.4M, respectively. Aliquots of these solutions were mixed in an optical cell (5.5 cm cube), the pH was adjusted with phosphate buffer and sufficient distilled water was added to bring the total volume to 100 cc. Final concentrations were approximately 10^{-5}M for dye, 10^{-4}M for electron donor and 0.7M for monomer. The solution was purged with helium for a two hour period to reduce the oxygen level below 0.1 ppm, then irradiated with a beam of light from a Schoolmaster projector (500 W lamp) for a 5 minute period. The light beam was filtered with an appropriate Wratten filter to restrict the light output to the spectral region of the dye absorption band. A monochromator-recorder setup was used to monitor a wave length in the region of the absorption maximum of the dye during the run. Polymer was isolated at timed intervals during the reaction by removing 2 cc samples of solution, drowning them in excess methanol and centrifuging out the separated polymer. Polymer molecular weights were determined viscometrically. Systems with added sodium periodate or sodium vanadate were compounded and analyzed in the same manner.

RESULTS

In dilute solution, the addition of sodium vanadate to the initiator system did little to improve the photopolymerization. When the concentrations of dye, electron donor and oxidizing agent were increased well beyond the range normally studied, the polymerizations followed the course shown in Figure 2. The initiator systems containing added sodium periodate, however, produced a much enhanced photopolymerization and were subjected to more intensive study.

In solutions 1 x 10^{-5}M in methylene blue, 8 x 10^{-5}M in acetylacetone and 0.7M in acrylamide, the addition of sodium periodate at concentrations greater than 8 x 10^{-5}M produced a three-fold increase in the initial rate of polymerization (see Table II). The optimum pH range for the polymerization was found to be between 8 and 10 and all subsequent polymerization runs were carried out at pH 9.0. When the concentration of sodium periodate was held constant at 1.6 x 10^{-4}M and the concentration of acetylacetone was varied, the erratic results shown in Table III were obtained. Periodate ion in solution, if contaminated or exposed to light, decomposes readily to iodate ion. The latter ion was eliminated from consideration as a source of trouble when it was found to have no influence on the polymerization at

1.6×10^{-4}M concentration. The oxygen level of the solution proved to be the critical parameter. A radical-producing dark reaction occurs between sodium periodate and acetylacetone when the oxygen concentration of the solution has been reduced to a certain level. This level is dependent on the amounts of periodate and acetylacetone present, as shown in Table IV. The dark reaction produces polymer at an almost steady rate of 0.5% per minute. Illumination of the solution at the first sign of dark polymerization greatly accelerates the rate of polymer formation (Figure 3). The initial rate of photopolymerization is 60 times higher than the initial rate of dark polymerization. The molecular weight of polymer formed in both cases is approximately 2×10^6. If the oxygen purge is stopped at a level 0.2 ppm above the critical level and the solution is kept in a sealed container in the dark no polymer can be detected over a period of at least a month.

Both acrylonitrile and methyl methacrylate have been photopolymerized with visible light in the presence of periodate[5] and solutions of methyl methacrylate have been polymerized in the dark (in the absence of oxygen) by radicals generated from the reaction of equivalent quantities of aniline and periodate.[6] In all cases, the presence of hydroxyl radicals was detected. Illumination of purged solutions of periodate and monomer in our experimental cell did not produce polymer within the time span of a normal run. The direct dye-sensitized decomposition of periodate, however, produced polymer at a rate comparable to the rate of polymer production for a methylene blue-acetylacetone initiator system (Figure 4).

Other dye-electron donor initiator systems containing sodium periodate were studied. Polymerization was enhanced when periodate was added to the methylene blue-triethanolamine initiator but, as the concentration of the amine was increased, the polymerization rate fell off. The thionine-ethylenediaminetetracetic acid combination provided more information. Normally, the photopolymerization or a 5% acrylamide solution is negligible when an initiator system 1×10^{-5}M in thionine and 8×10^{-4} in ethylenediaminetetracetic acid is used at either pH 5.0 or 8.5. The rate of the dye fading reaction, 26.6×10^{-8} moles l^{-1} sec.$^{-1}$, is so rapid that over 10% of the dye is converted to leucothionine within four seconds and the polymerization is effectively inhibited. The addition of periodate does not suppress the dye fading reaction completely but slows it enough that high yields of polymer are obtained. Data on fading rates and polymer production are included in Figure 5. Thionine was not as efficient as methylene flue for the dye sensitized decomposition of periodate. Polymer formation was observed in the thionine-periodate-acrylamide system but only after an induction period of at least one minute.

APPLICATIONS

The potential utilization of the new initiator systems in coatings was tested in a preliminary way in thick (1/16 inch) slabs. The standard slab was prepared by gelling a solution containing 5% acrylamide, 3×10^{-3} moles/l. of acetylacetone and 8×10^{-5} moles/l. of thionine or methylene blue. Agarose was the preferred gelling agent since it was effective at a 2% concentration. The efficiency for photopolymer formation in the standard slab was 0.3 polymer molecules/photon. The addition of sodium periodate (concentration in original solution, 1.7×10^{-4} moles/l) raised the efficiency to 1.6 polymer molecules/photon while the addition of ammonium vanadate (concentration in original solution, 3.4×10^{-3} moles/l) gave the slightly higher efficiency of 2.2 polymer molecules/photon. The response of the systems was dependent on the age of the slab, since both oxidizing agents appeared to react slowly with other ingredients in the slab.

To prepare a thin film coating for testing as a photographic receptor, it was necessary to find a coating vehicle compatible with strong oxidizing agents. Limited success was obtained using a copolymer of dimethylaminoethyl methacrylate and methyl methacrylate. Coatings containing acrylamide, thionine and sodium periodate were exposed sensitometrically and found to have a photographic speed (measured as the reciprocal of the exposure in meter-candle-seconds required to produce a detectable step) of 10^{-4}. This was not appreciably different from the speed of a standard system containing no added oxidizing agent.

SUMMARY

The addition of sodium periodate to aqueous solutions of a dye-electron donor photopolymerization initiator system produces a marked increase in polymerization efficiency, ~~This increase in efficiency is~~ due partly to the additional radical generating possibilities of the system and partly to the suppression of leuco dye formation. Complete suppression of leuco dye formation ~~appears~~ is ~~to be a~~ necessary condition for the efficient visible light photopolymerization of many monomers. The increased efficiency could not be extended to coated systems because of the reactivity of sodium periodate toward most coating vehicles. (Author, modified)

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TABLE I

PHOTOPOLYMERIZATION OF DIMETHYLAMINOETHYL METHACRYLATE

Dye	Added Electron Donor	pH	Oxidizing Agent	Time Required for Gel Formation, sec*
Thionine	None	7.0	None	45
	None		IO_4^-	5
	Benzenesulfinic acid or N-phenylglycine	4.3	None	30
	Benzenesulfinic acid		Cu^{+2}	< 5
	Benzenesulfinic acid		IO_4^-	5-10
	N-phenylglycine		IO_4^-	10
	N-Phenylglycine		Cu^{+2}	20
Methylene blue	None	7.0	None	> 60
	Acetylacetone		VO_3^-	< 5
	None		IO_4^-	15
Eosin	None	7.0	None	> 60
	None		IO_4^-	< 5
	Benzenesulfinic acid	4.3	None	30
	Benzenesulfinic acid		IO_4^-	5

*2% sodium polystyrenesulfonate present in solution

TABLE II

EFFECT OF PERIODATE CONCENTRATION ON R_p IN METHYLENE BLUE-AA-ACRYLAMIDE SYSTEM

$NaIO_4$ Concentration (moles/ℓ x 10^5)	R_p x 10^4
0	9.40
1	9.40
4	7.45
8	25.40
16	31.00
32	33.50
64	25.00

TABLE III

EFFECT OF AA CONCENTRATION ON R_p IN THE METHYLENE BLUE-AA-$NaIO_4$-ACRYLAMIDE SYSTEM

AA Concentration (moles/ℓ x 10^5)	R_p x 10^4	
	No $NaIO_4$	1.6 x 10^{-4}M $NaIO_4$
8	9.4	30.3
16	9.4	42.6
32	13.9	57.8,15.1
48	-	11.9
64	18.1	19.2
128	15.7	-
256	18.7	-

TABLE IV

INFLUENCE OF OXYGEN ON DARK POLYMERIZATION OF PERIODATE-CONTAINING SYSTEMS*

AA Concentration (moles/ℓ x 10^4)	Oxygen Level at Which Polymer was First Detected (ppm)
0.8	No polymer after 2 hr. purge (<0.1 ppm O_2)
1.6	No polymer after 2 hr. purge (<0.1 ppm O_2)
2.4	0.8
3.2	0.7 ± 0.1
6.4	1.4

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*Acrylamide, 5%; methylene blue, 10^{-5}M; $NaIO_4$, 1.6 x 10^{-4}M

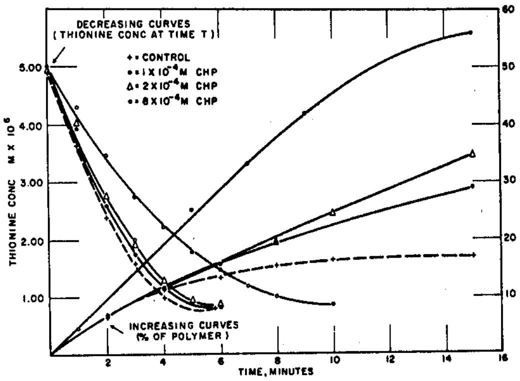

FIGURE 1

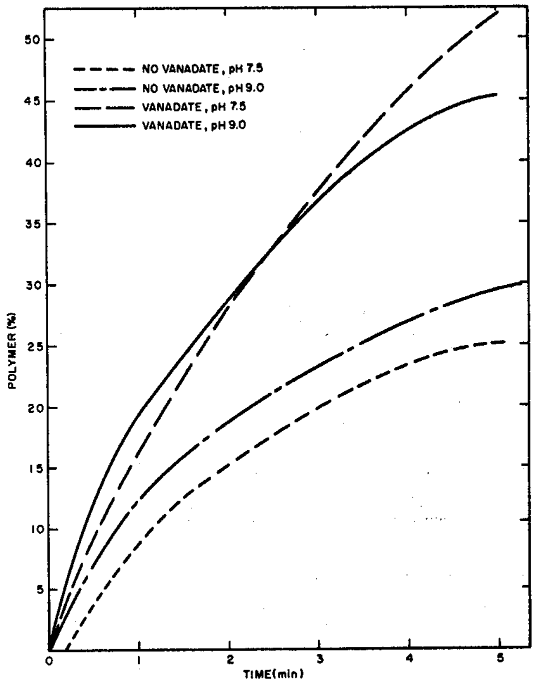

FIGURE 2

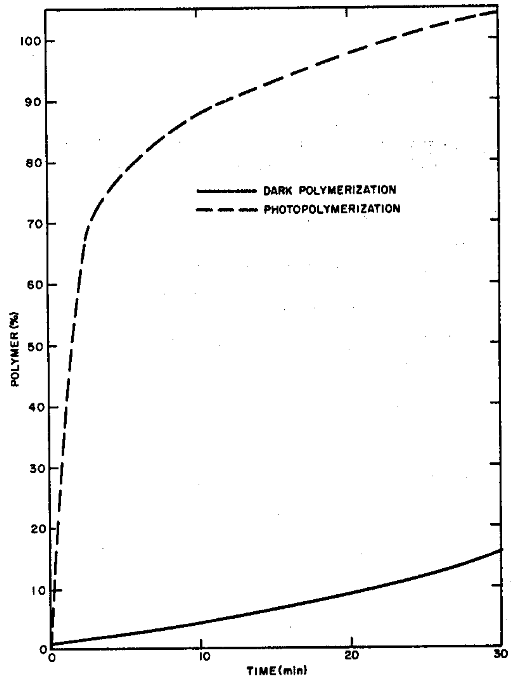

FIGURE 3

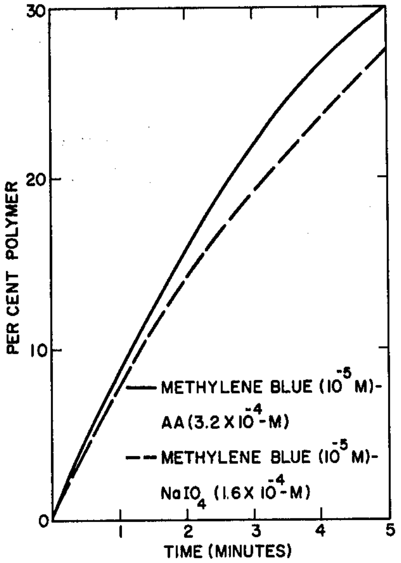
PHOTOPOLYMERIZATION BY DIRECT DYE-SENSITIZED DECOMPOSITION OF PERIODATE

FIGURE 4

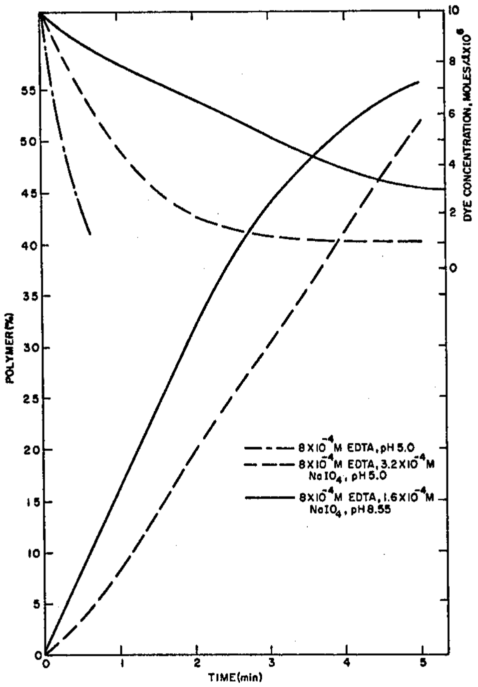

FIGURE 5

PHOTOCROSSLINKABLE POLYMERS

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HISTORICAL

The historical beginnings of applications of photocrosslinkable polymers date back to ancient times. The Babylonians used a form of pitch to prepare decorations. This was accomplished by exposure of a coating of pitch through a stencil and subsequent development in some kind of solvent. In 1815 Niepce[1] discovered that the natural sensitivity of Syrian asphalt could be used to prepare a bleach-out photograph. Some time later, he reported[1] that the exposed asphalt images could be developed in turpentine. Niepce went so far as to copy existing engravings by this process. For this it was necessary to print through the document. He was then able to develop the resist and subsequently engrave the surface in an imagewise manner. Even more than this, Niepce was able to copy a landscape "from life" by means of the first practical camera. This was accomplished before Daguerrotype and silver processes functioned. Thus, Niepce has been dubbed the "world's first photographer". He accomplished this step with a polymer. Shortly after this, in 1852, Lemercier[1] employed asphaltum in order to sensitize litho stones. In all these cases, the level of sensitivity of the resists or asphalt, as you may prefer to call them, was very low and stemmed from their natural or inherent sensitivity to light. Exposure times of hours were necessary.

Historically at least, it appears that there is a large time gap between this early work and later developments with asphalts or polymers. However, other organic natural polymers such as albumin, gelatin, fish glue, shellac, and gum arabic received attention and filled in the gap up to the early 1900s. In the early 1900s, people began to add other materials to resins in order to hasten or accomplish their crosslinking, examples of which are bichromate, diazo compounds, iron salts, and silver halides.

A. Murray,[2] in the 1920s, sensitized products of aldehydes, ketones and amines with iodine compounds such as iodoform. Upon exposure, the polymeric or resin carrier was made to solubilize. Such a photoresist, called "Neokel", was sold in 1926. It consisted of "furfurane-pyrrol-thiophene" resin which could be developed in naphtha. It is worthwhile to mention these resins only in passing because this discussion will be limited to polymers which contain within themselves the light-sensitive units which cause the photocrosslinking reaction. Systems in which the polymer is attacked by a photosensitive low-molecular-weight compound in order to produce sites which can subsequently crosslink will be neglected. However, to separate historically, photocrosslinkable polymers from photopolymerization is somewhat difficult. For example, in the 1920s coumarones were employed as photosensitive resists but they had very little sensitivity to light. In the 1930s, Murray showed that alketones could be used to form resists on exposure to light. He showed that a noncrystallizing layer of shellac containing cicinnamoylacetone would form photoinsolubilized images.

MODERN PHOTOCROSSLINKABLE POLYMERS

The major breakthrough in the photocrosslinkable polymer field was accomplished by Minsk[3] during the late 1940s who prepared poly(vinyl cinnamate) (Figure 1), and who, together with his co-workers, found that incorporation of dyes into the coatings of poly(vinyl cinnamate) provided a means of optical sensitization of these polymers. A very practical result of optical sensitization was a decrease in the required exposure time to give imagewise insoluble crosslinking of poly(vinyl cinnamate). Minsk and co-workers[4] discovered a whole range of optical sensitizers which could be used with poly(vinyl cinnamate). Since that basic work was accomplished, a large number of modifications of the structures of polymers containing units which resemble the cinnamate group have been carried out by several groups in several countries.

From the early work of Minsk[3] and the followup work of others in this field, it is obvious that the basic unit necessary to produce crosslinking in polymers based on poly(vinyl cinnamate) is the C=C-carbonyl unit. Minsk recognized this fact at the outset. This unit can be attached to many polymers in many manners and, depending on its configuration in the polymer chain, or when appended to the polymer chain, the light-sensitivity and the physical properties of the polymer can be modified. When this unit is incorporated with supplemental units; for example, if a nitro group is placed in the benzene ring of the cinnamoyl residue, the optical response of the polymer can be extended more toward the visible.

The light-sensitivity and the physical properties of the polymer can be controlled or modified by the manner in which the units are attached to the polymer chain. Another quite different group of light-sensitive polymers was synthesized by Merrill and Unruh[6] (in the Kodak Laboratories) when they began their work on the preparation of azido polymers. In this case, an azide group usually attached to an aromatic nucleus is appended to, or incorporated within, a polymer chain (Figure 3).

These units, that is to say, the azido units on the polymer, have been found to respond quite effectively to sensitization[6] much in the manner of that found earlier for poly(vinyl cinnamate).

SENSITOMETRY

A sensitometric method for the evaluation and comparison of light-sensitive polymers was developed by Minsk and co-workers.[4]

Coatings of polymers of various compositions or containing different sensitizers were exposed through a step tablet to controlled quantities of light. The unexposed or partially exposed soluble polymer areas were dissolved away by solvents in a developing step. The resulting image was made visible by inking of the residual polymer. Others have used interference microscopic[7] and gravimetric methods[8] to compare the density of the residual polymer on the various steps. From the number of residual steps a speed factor or glass factor is calculated.[4]

By comparison of the minimum amount of light required to produce the weakest appearing step, the comparative speed value of the polymer in question is assessed. Poly(vinyl cinnamate) is taken as a value of 1.0.

SENSITIZATION OF LIGHT-SENSITIVE POLYMERS

Early in their work, Minsk and co-workers[3,4] found that the effective speed and spectral response of poly(vinyl cinnamate) could be increased by added sensitizers as follows: Spectral response can be determined by use of action spectrograms (Figures 4, 5, 6 and 7).

It is worthwhile to represent the wide variety of structures of light-sensitive units that have been appended to or incorporated into the chains of polymers. To this end, it is of interest to summarize the various photosensitive functional groups which have been attached to or incorporated within polymer chains. They are shown in Figure 8.

Units used for attaching or condensing photosensitive groups to polymer chains can be drawn from esters, carbonates, phosphates, urethanes, ethers, amides and sulfonamides.

Combinations of these types of photosensitive units and various polymer chains are illustrated by the polymers in Figures 9 through 18.

The work on light-sensitive polymer being done at the present time has literally mushroomed out of the first work done on poly(vinyl cinnamate) by Minsk. Originally, poly(vinyl cinnamate) was developed for lithographic purposes. In the intervening years the electronic industry has made use of photoresists to an unprecedented degree. Thus, although the original polymer, poly(vinyl cinnamate), was designed for lithography and chemical engraving, it was adopted into the electronics industry. It has contributed inestimably to the progress made in printed circuits, micro circuitry, and solid state devices.

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POLY(VINYL CINNAMATE) - AN ESTER

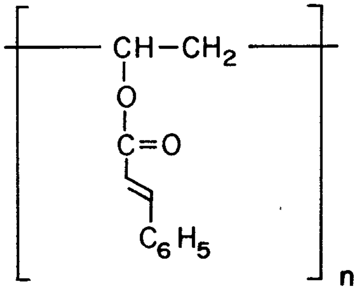
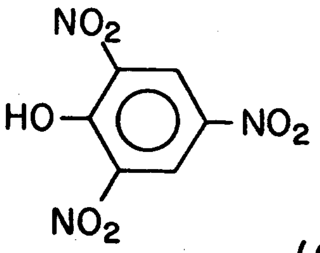


FIGURE 1



(GF 300)

FIGURE 4

Chalcones

ADDITION POLYMERS

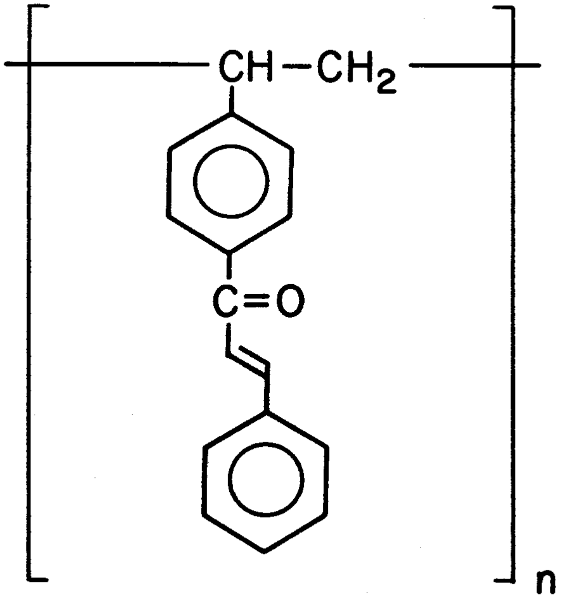


FIGURE 2

AZIDE POLYMERS

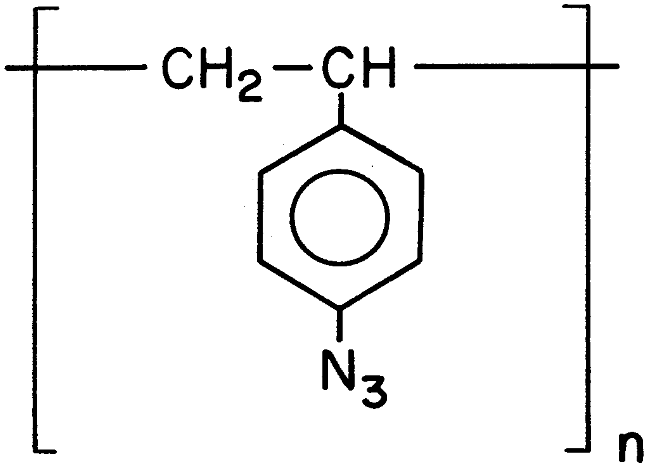
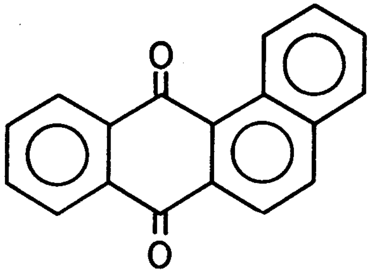
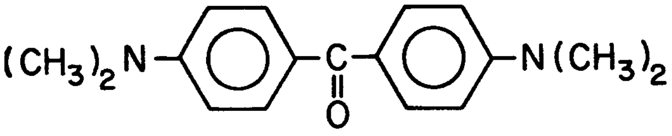


FIGURE 3



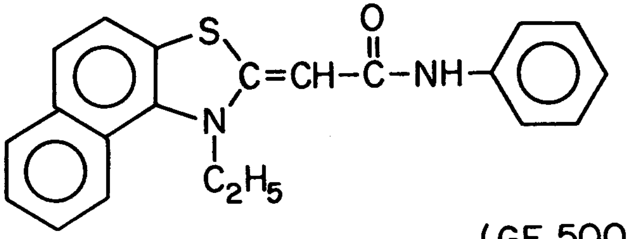
(GF 500)

FIGURE 5



(GF 650)

FIGURE 6



(GF 500)

FIGURE 7

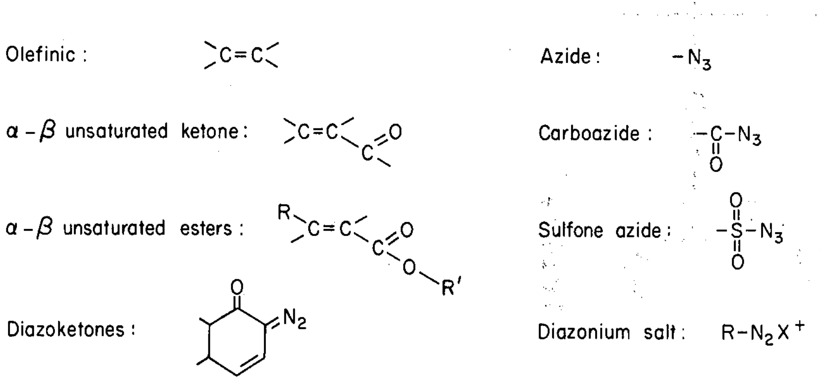


FIGURE 8

POLY(VINYL CINNAMATE) - AN ESTER

CINNAMATE - URETHANES

AMIDE

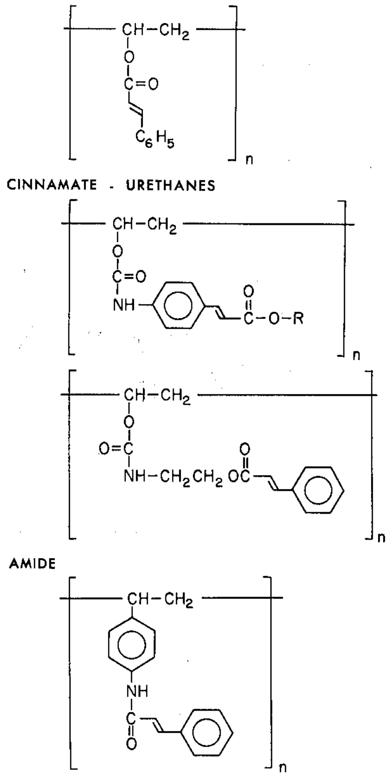
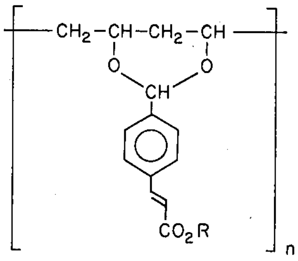


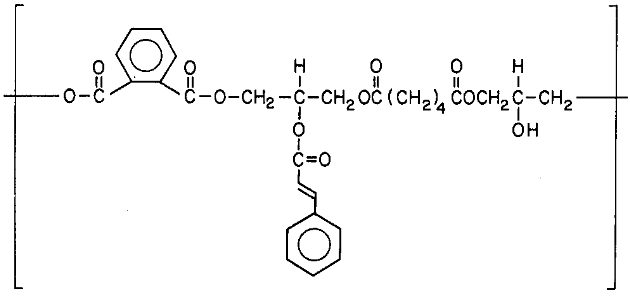
FIGURE 9

Acetal



Condensation Polymers

Esters



Ester - Urethane

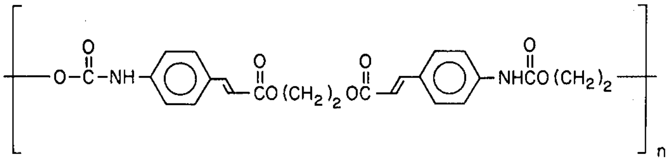
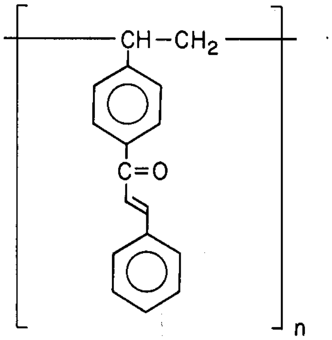


FIGURE 10

Chalcones

ADDITION POLYMERS



PHOSPHONATES

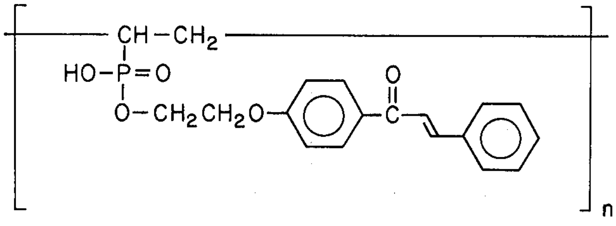
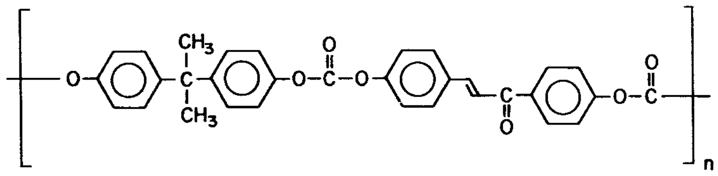


FIGURE 11

Condensation Polymers

Polyester (carbonate)



Epoxy Polymer

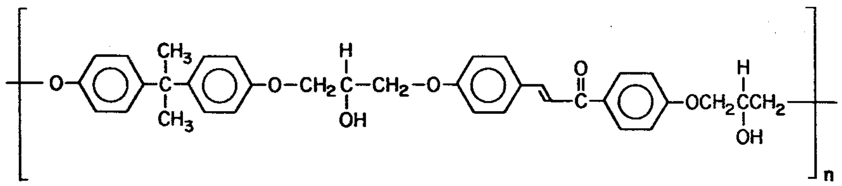


FIGURE 12

ACETAL

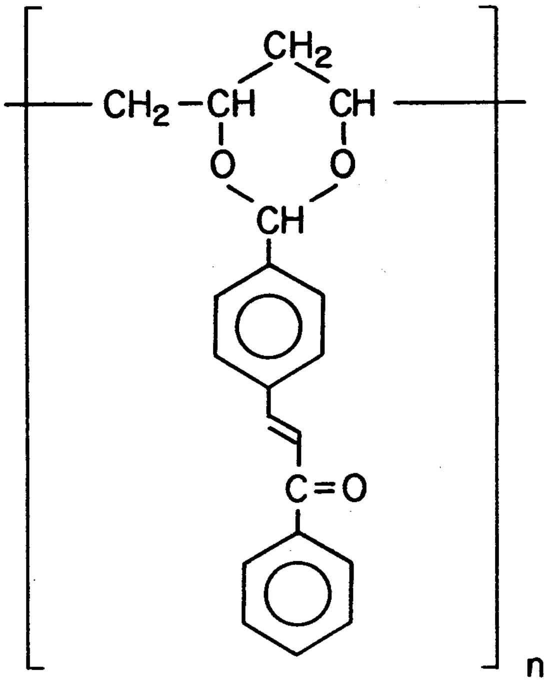
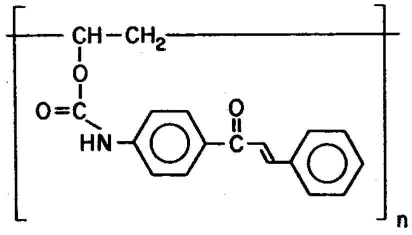


FIGURE 13

URETHANE



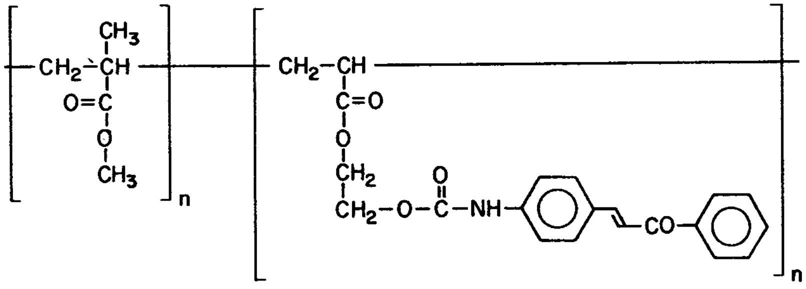
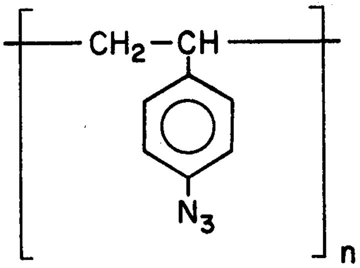


FIGURE 14

AZIDE POLYMERS



ESTER

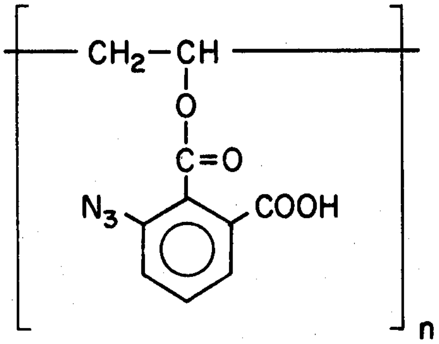


FIGURE 15

Diazonium Salts

AMIDE

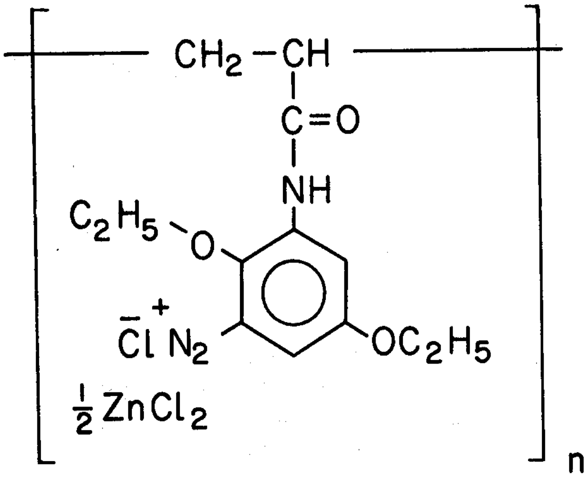
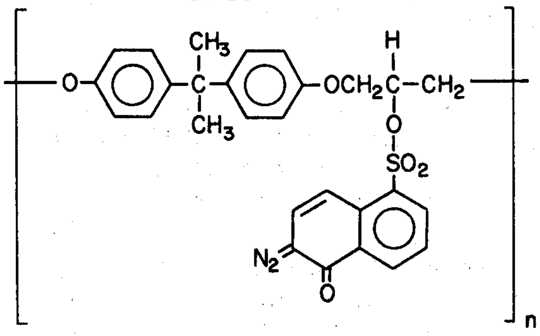


FIGURE 17

DIAZOKETONE



URETHANE

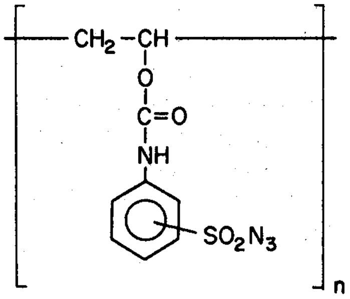


FIGURE 16

CONDENSATION TYPE DIAZO RESIN

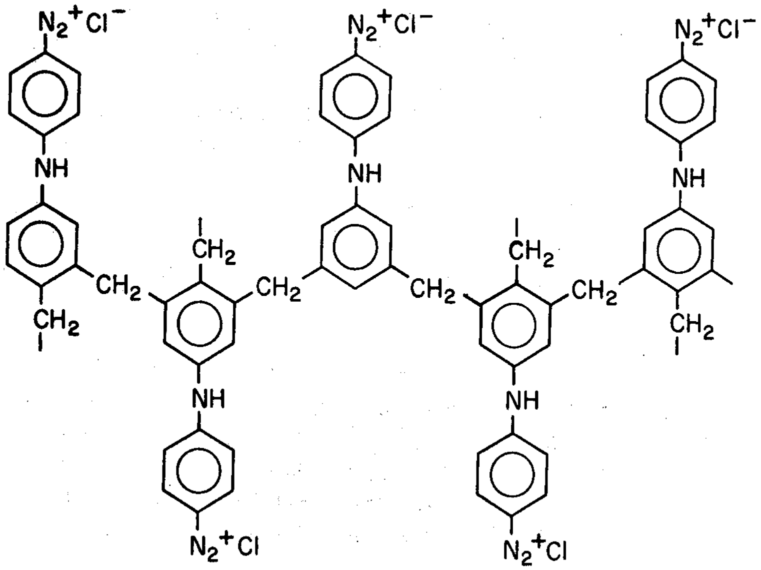


FIGURE 18

PHOTOINITIATED CROSSLINKING OF POLYETHYLENE IN THE PRESENCE OF ANTHRONE

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Crosslinking of polymers is a well known industrial art. The crosslinking process may be effected during polymerization by utilizing bifunctional groups which ultimately serve as links joining the long polymeric molecules together in a three-dimensional network. Alternately, the crosslinking step may take place after polymerization. In such instances, the polymer is sometimes molded or shaped into the desired final form prior to crosslinking. This is particularly the case with polyethylene, since crosslinking during the fabrication process makes the raw material difficult to work with. Polyethylene is generally crosslinked by the addition of radiant energy to the system. This energy may take the form of high energy electrons and X-rays[1] or ultraviolet radiation.[2] In the latter case, a sensitizer mix which accelerates the crosslinking process is incorporated in the monomer prior to fabrication. Polyethylene, crosslinked by either method, has an increased thermal dimensional stability, tensile strength, melting point and resistance to solvent action than its uncrosslinked counterpart.

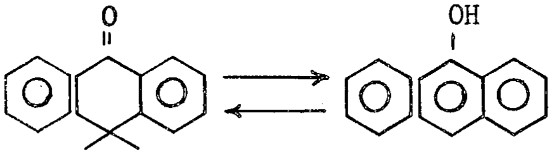
Absorption of ionizing radiation probably results in the ultimate loss of a hydrogen atom from the polymer chain as well as direct fragmentation or dislinking.[3] When two radical sites on different chains are proximate, coupling produces a crosslink. Alternatively, unsaturation may occur if the radicals combine on the same chain.[4] With ultraviolet induced crosslinking, direct dislinking is unlikely since the sensitizer absorbs relatively low energy photons. Crosslinking and unsaturation are produced in much the same manner as with ionizing radiation with the initial radical being produced from an abstraction reaction by the excited carbonyl oxygen. This process should produce pinacols as a by-product.

Benzophenone[5] is perhaps the best known photosensitizer for these type reactions. We have recently found that anthrone is also suitable. As Table I indicates, anthrone is nearly twice as effective as benzophenone in producing crosslinking in polyolefins.[6]

Figure 1 shows the variation in crosslinking with time of irradiation. In this instance, the anthrone was incorporated in the 4 mil thick polyethylene film prior to irradiation by a bank of 16 watt low pressure mercury lamps. Note that the gel fraction quickly attains a maximum value. This probably corresponds to complete destruction of the sensitizer although it is possible that the gel fraction attains a constant value but the crosslinking density is increased with continued irradiation. The ratio of the volume of the solvent-swollen crosslinked polymer to the volume of the same dried polymer (the swell ratio), is a relative measure of crosslinking density. As Figure 2 indicates, it seems that the crosslinking density reaches a corresponding plateau with continued irradiation.

In order to gain some insight into the processes going on in the polymer system during the crosslinking steps, spectrophotometric techniques were employed. Figure 3 illustrates a typical sequence of absorption spectra with photolysis time. There seems to be several gross effects worth noting: There is an increase in absorption shortly after the sample is irradiated. A whole new band appears toward the longer wave lengths. After continued irradiation the transmission finally approaches a limiting value and a broad, structureless absorption band remains. Assuming the final moiety is continually being produced, its contribution to the overall spectrum may be subtracted out. Figure 4 shows the result of such an operation. Here the absorbance of the 2600 Å peak is plotted against photolysis time. Note the correspondence to Figure 2.

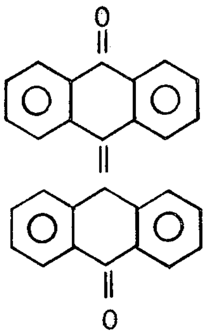
In order to determine whether or not the initial new absorption band is characteristic of the anthrone itself or is some phenomenon associated with the immobile environment of the plastics film, a hexane-anthrone system was investigated. Figure 5 depicts these results. It is clear that the same absorbing species is produced in both instances. For convenience, a spectrum of a thicker sample of film is shown in the same figure. Anthrone is known to exist in equilibrium with its enol tautomer, but under normal experimental conditions the equilibrium exists far to the keto side. Note that the enol form is highly conjugated and anthracenic in character whereas the keto form should be a typical carbonyl with a weak n- * transition in the region 3400 - 4000 Å. In light of this, the enol tautomer, anthranol, was prepared[8] at low temperature and under a nitrogen atmosphere. Its absorption spectrum in methylene chloride at -30 C is shown along with that of anthrone at room temperature in hexane in Figure 6.



A characteristic of the anthranol is that it is readily oxidized in the presence of oxygen. When the film or the hexane solution was exposed to oxygen in the dark, the band attributed to the enol disappeared.

There is little effect of oxygen on crosslinking in the film. In fact, upon continued irradiation, the crosslinking was found in several instances to increase in an oxygen atmosphere. In general, lack of an oxygen quenching effect in films has been attributed to the slow permeability rate of the gas relative to the photolysis rate. As with high energy irradiation of polyethylene, however, aliphatic carbonyls (along with trans-ethylenic groups) were detected with infrared spectroscopy in the anthrone impregnated film after photolysis. Anthroquinone is readily formed when a hexane solution of anthrone is photolyzed in an oxygen atmosphere.

It is known that anthrone does not form a pinacol when irradiated in solution. Rather, a "dimer" is formed. We have irradiated anthrone in chloroform and isolated this dimer. Mass spectral studies indicate that the dimerization process results in loss of four hydrogen atoms. Infrared spectroscopy finds oxygen groups conjugated to the ring. The structure of the dimer is thus

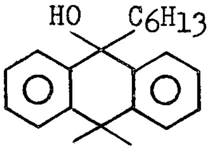


This compounds, bis anthrone, is a known thermochromic substance. Its absorption is shown in Figure 7. Note the characteristic band at 3000Å. The spectrum of the residual species formed in the film does not have this absorption band and we can thus state that if the dimer is produced in the film it is either a minor product, or its absorption band at 3000Å is suppressed by another product having a minimum or an inflection at that wave length.

Since it has been postulated that, at least in the polyethylene-benzophenone system, ultraviolet and high energy irradiation produce the same number of crosslinks and dislinks, the absorption spectrum of polyethylene irradiated with 2 mev electrons with a 20 megarad dose was obtained. The resultant spectrum is also shown on Figure 7. It is very similar to that of the residual absorbing species produced in the anthrone photolysis case. In the absence of any evidence to the contrary, we can tentatively presume that photo-crosslinking produces species that are also produced when the same film is irradiated with high energy electrons.

An attempt was made to leach out any compounds formed in the crosslinking process with negative results. Decomposition of the crosslinked material at 200°C under vacuum using a Bendix mass spectrometer with a direct probe showed only the presence of some anthrone. It has been speculated[9] that the inability to leach out material from the crosslinked network of the polyethylene-benzophenone system may be due to free radicals attached to the chain. If this is true, an esr signal should be seen at room temperature. Figure 8 shows the esr spectrum of the polyethylene-anthrone system after photolysis. Note that at 77°K not only is a spectrum attributable to anthrone present, but alkyl free radicals are also present. Warmup causes the radicals produced from the polyethylene to disappear but radicals produced from the anthrone are apparently stable for periods in excess of 24 hours. Figure 9 shows a similar spectrum of anthrone in chloroform at low temperature. There is evidence for radical sites originating from the chloroform as well as the anthrone. This signal completely disappears upon warmup.

The inability to detect any free products from the photosensitized crosslinking process may also be attributed to sensitizer molecules acting as bridges for crosslinking or incorporation of the sensitizer photolysis product in the polymer chain. If this were true, analogous products should be found when anthrone is photolyzed in hexane. Quite unexpectedly, irradiation of this system not only produced no pinacol, but also no dimer was found. Instead, mass spectral evidence shows that the main product is hexane attached to an anthrone molecule with minor amounts of higher molecular weight hydrocarbons similarly appended. Infrared indicated that the hydrogens in the 10 position are still intact and there is evidence for hydroxyl group absorption. The adduct thus appears to be



If now, instead of hexane, a polymer molecule was attached to the anthrone, the product could not be leached out of the film and mass spectral analysis of decomposition products would not be able to distinguish the adduct as a separate product. Note, however, that this process produces no crosslinks.

The fact that no pinacols are produced is probably a reflection of the planarity of the anthrone molecule. It appears that stearic hindrance is appreciable for coupling between the two radicals produced by the hydrogen abstraction reaction. Benzophenone, being nonplanar, apparently does not experience this effect.

If the anthrone-polymer adduct were oxidized to the corresponding anthroquinone (it has already been noted that anthrone is readily oxidized in this manner), another hydrogen atom abstraction reaction could ensue. In this instance, an analogous polymer addition step would result in a crosslink. In this case, the anthrone moiety would act as the bridge between two polymer chains. As such, products could also not be isolated. This process explains the increased crosslinking when the doped films were irradiated in an oxygen atmosphere.

It is not yet clear what effect the photoenolization step has on the crosslinking process. Investigations with 10,10 dimethyl anthrone should contribute to an understanding of this aspect. One could speculate that, if the hydrogen atom in the 10 position does not migrate intramolecularly, a hydrogen atom could be abstracted from the polymer on the 0 atom with concommitant expulsion of a 10 position hydrogen. This sequence could result in a crosslink if the leaving hydrogen atom contained enough energy to abstract another hydrogen.

Charlesby has developed a technique for measuring the relative contributions of dislinking (po) to crosslinking (qo) density in a polymeric system bombarded by high energy radiation.[3] The intercept of a $s+\sqrt{s}$ versus reciprocal dose plot is related to the ratio of po/qo. Charlesby extended this approach to photosensitized crosslinked systems using reciprocal sensitizer concentration as the proper measure of dose. Such plots are shown in Figure 10 for the systems being studied here. The intercepts are very nearly equal. Similar results were obtained with the benzophenone-polyethylene system.[9] In the latter instance, the results were interpreted as an indication that high energy and photosensitized induced crosslinking produce the same ratio of dislinks and crosslinks and, therefore, polymer samples with equal values of $s+\sqrt{s}$ contain the same number of crosslinks. This appears to be the case with the present system. This conclusion, however, should be tempered by the fact that a linear $s+\sqrt{s}$ vs. reciprocal dose relationship is strictly valid for the determination of qo/po when the molecular weight distribution of the polymer is random. For high energy irradiation at large doses (over 10 mrads) this is probably true, but whether a similar tendency toward a random distribution occurs with ultraviolet radiation is a tenuous assumption.

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TABLE I

ULTRAVIOLET IRRADIATION OF HIGH DENSITY POLYETHYLENE

Sensitizer	Per Cent of Insolubles			
	Run No. 1	Run No. 2	Run No. 3	Run No. 4
Anthrone	45.0	40.9	50	43
Benzophenone	28.6	16.7	20	27
None	0.75	1.3	-	-

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[1] The amount of sensitizer was 0.5 per cent of the weight of the polyethylene used.

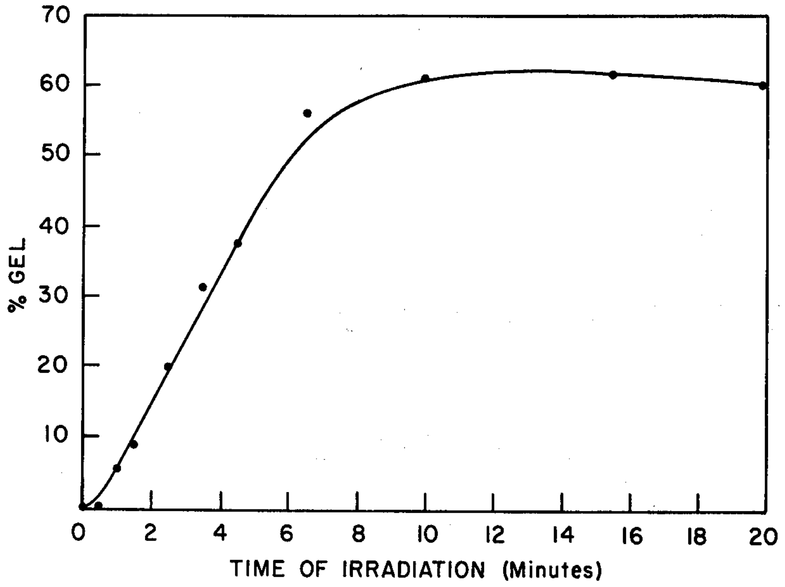

FIGURE 1: % Gel as a function of irradiation time.

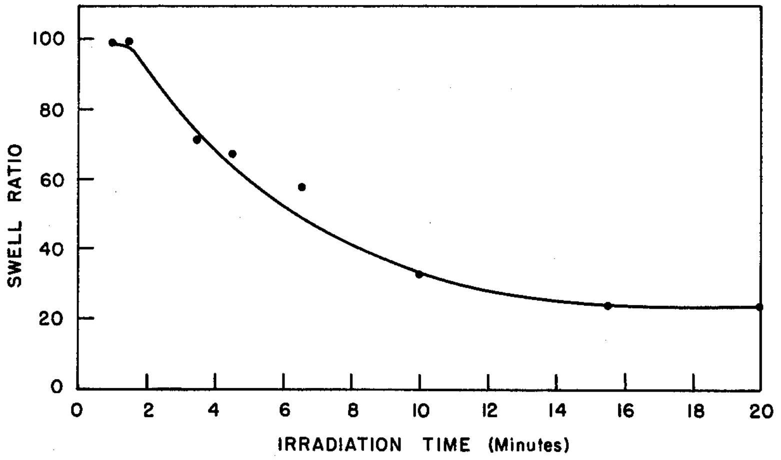

FIGURE 2: Swell ratio as a function of irradiation time.

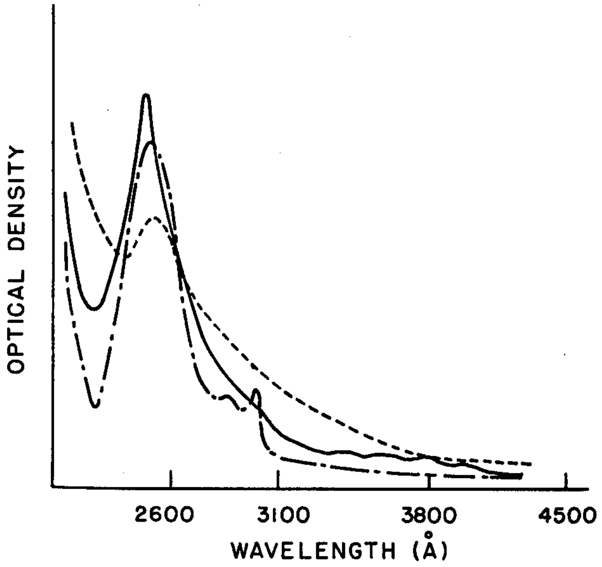

FIGURE 3: Absorption spectrum of a 1 ml thick sample of polyethylene with anthrone.

— — — 0 time

——— 15 sec

- - - - - - 16 min

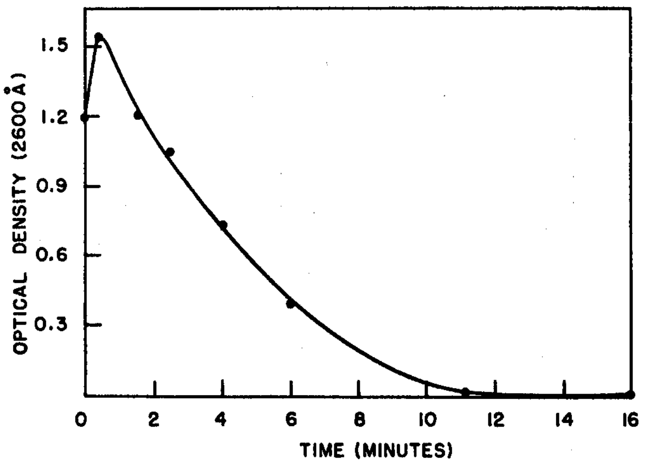

FIGURE 4: Optical density at 2600 Å with the contribution from the residue spectrum subtracted out as a function of irradiation time.

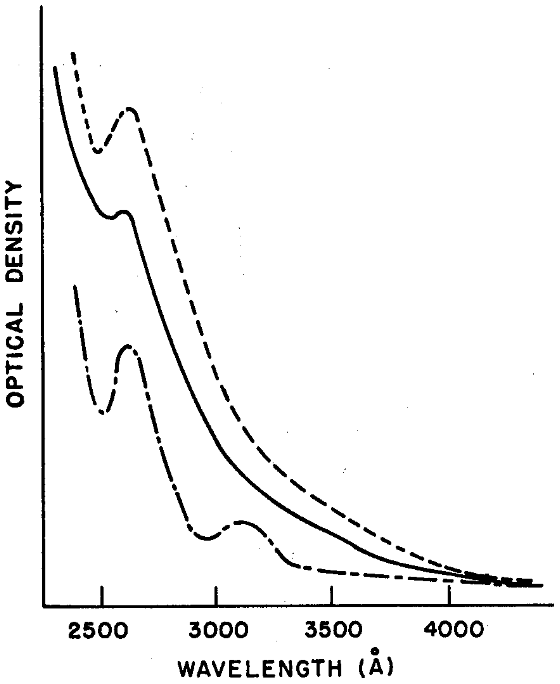

FIGURE 5: Absorption spectra of anthrone.

———————— in hexane (0 time)
– – – – – – in hexane (15 sec irradiation)
—— – —— in 4 ml polyethylene film (15 sec)

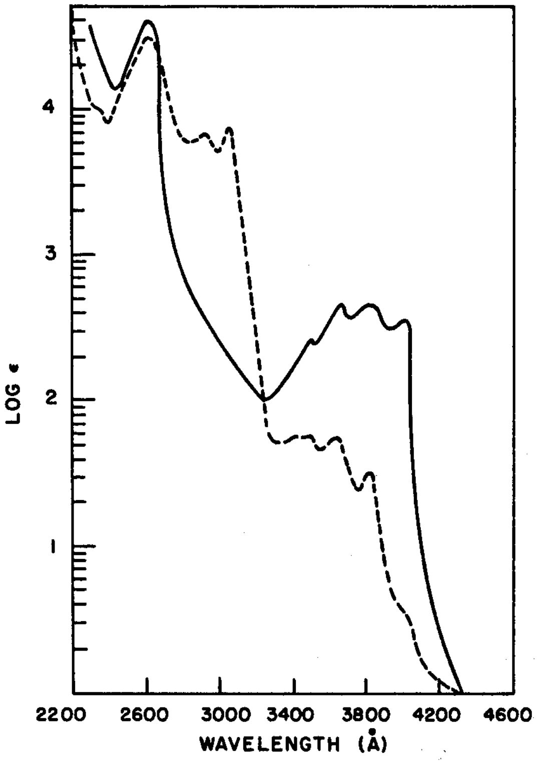

FIGURE 6: Absorption spectrum of

———————— 9 anthranol
– – – – – – anthrone

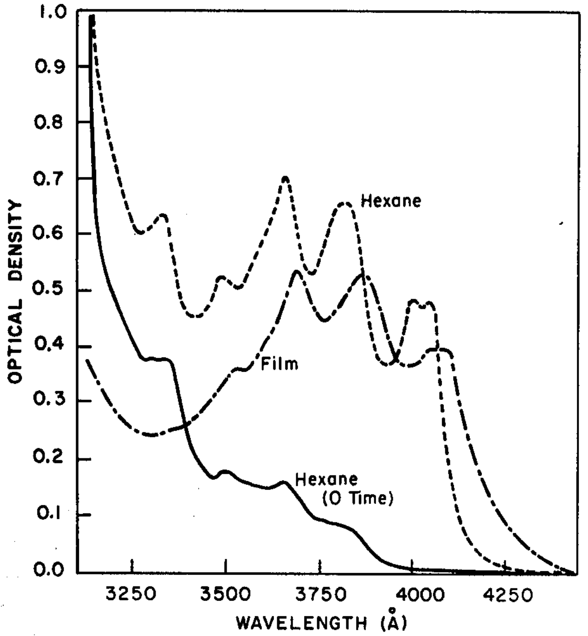

FIGURE 7: Absorption spectra of

– – – – – – anthrone in polyethylene film (16 min uv irradiation)
———————— polyethylene film (10 megarads, 2 mev electrons)
—— – —— bis anthrone

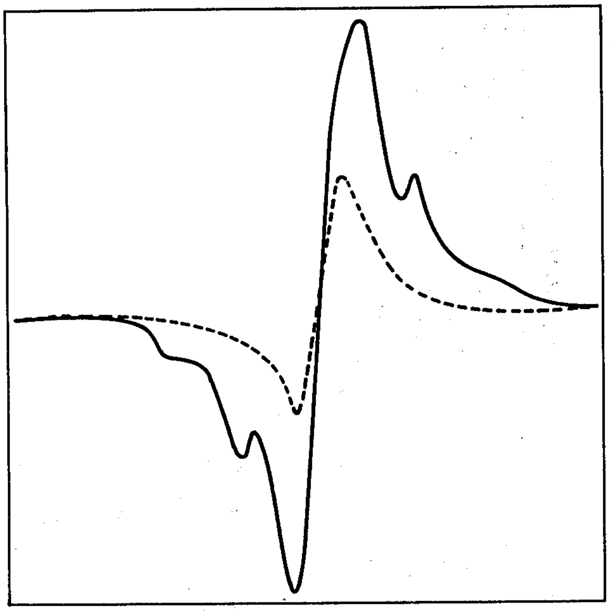

FIGURE 8: Esr spectrum of anthrone in polyethylene

——————— at 77° K

– – – – – – at room temperature

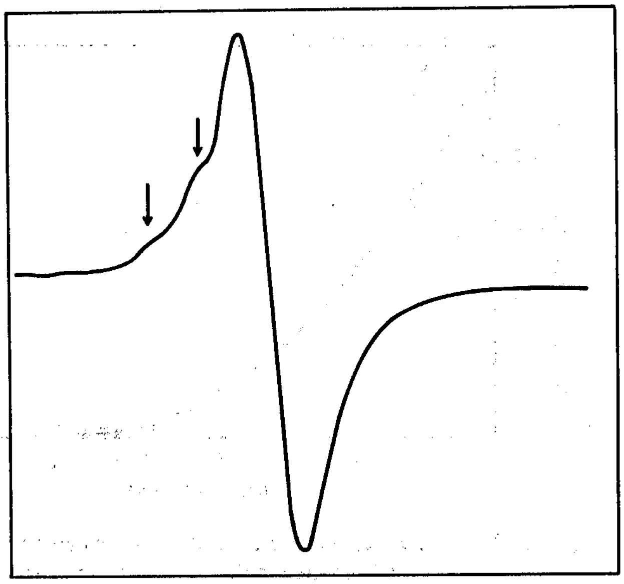

FIGURE 9: Esr spectrum of anthrone in chloroform at 77° K. There is no signal at room temperature

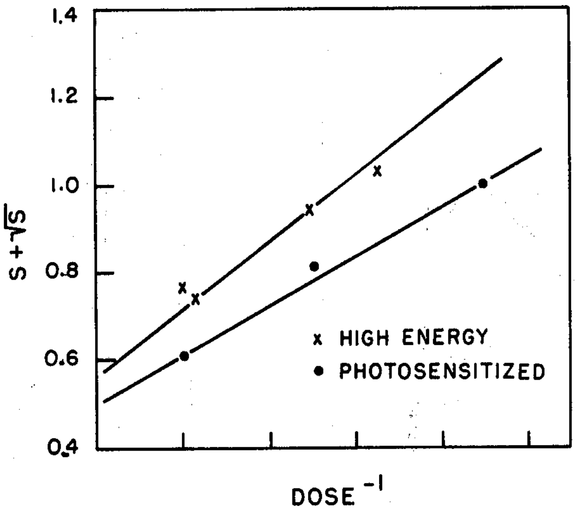

FIGURE 10: S+ √S as a function of reciprocal dose (in arbitrary units).

X high energy electron irradiation of polyethylene film with dose in megarads

• ultraviolet irradiation of anthrone in polyethylene film with dose in anthrone concentration

Irradiation time was 20 minutes

PHOTOCROSSLINKING OF POLYMERS BY REACTIVE INTERMEDIATES WITH AN ELECTRON SEXTET. 3-SYNTHESIS AND PROPERTIES OF 1,2,3-THIADIAZOLE POLYMERS*

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INTRODUCTION

The ever increasing demand for photosensitive polymers in connection with a great number of technical applications whereby use is made of etching, promoted the synthesis and the study of new light-sensitive systems. Besides the possibility of polymer insolubilisation by dimerisation of photo-excited carbon-carbon unsaturation such as in cinnamate containing substituents, the photolytic decomposition of several light-sensitive functions offers another way to crosslink the macromolecules.

A general feature of the photolysis of light-sensitive functions containing two or three interconnected nitrogen atoms is the loss of a nitrogen molecule and the formation of a highly reactive intermediate with an electron sextet.

Several examples of such functions are known and their applications in the photoinsolubilisation of polymers have been described;[1,2] they are mainly based on the photolysis of azide groups.

→The ~~present~~ report is devoted to a new class of photosensitive polymers containing 1,2,3-thiadiazole functions as the light-sensitive elements. The synthesis of the light-sensitive polymers and the results obtained from the study of the light-sensitivity are described. (Author, modified)

EXPERIMENTAL - 1,2,3-THIADIAZOLE COMPOUNDS

A. 1,2,3-Thiadiazole-4-Carboxylic Acid (II)

This compounds was obtained according to the procedure described by Hurd and Mori[3] starting from pyruvic acid ethoxycarbonylhydrazone (I).

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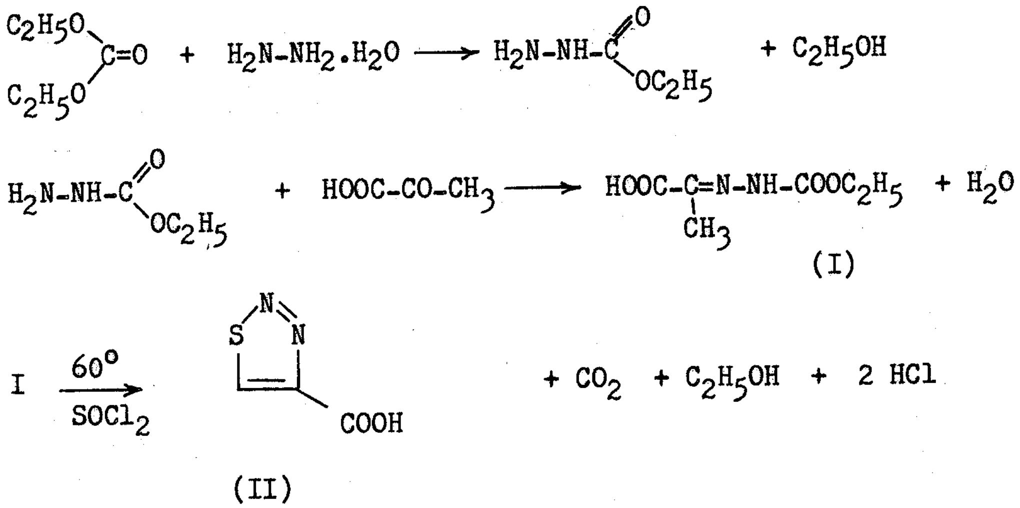
The general synthesis is given on Chart I.

CHART I



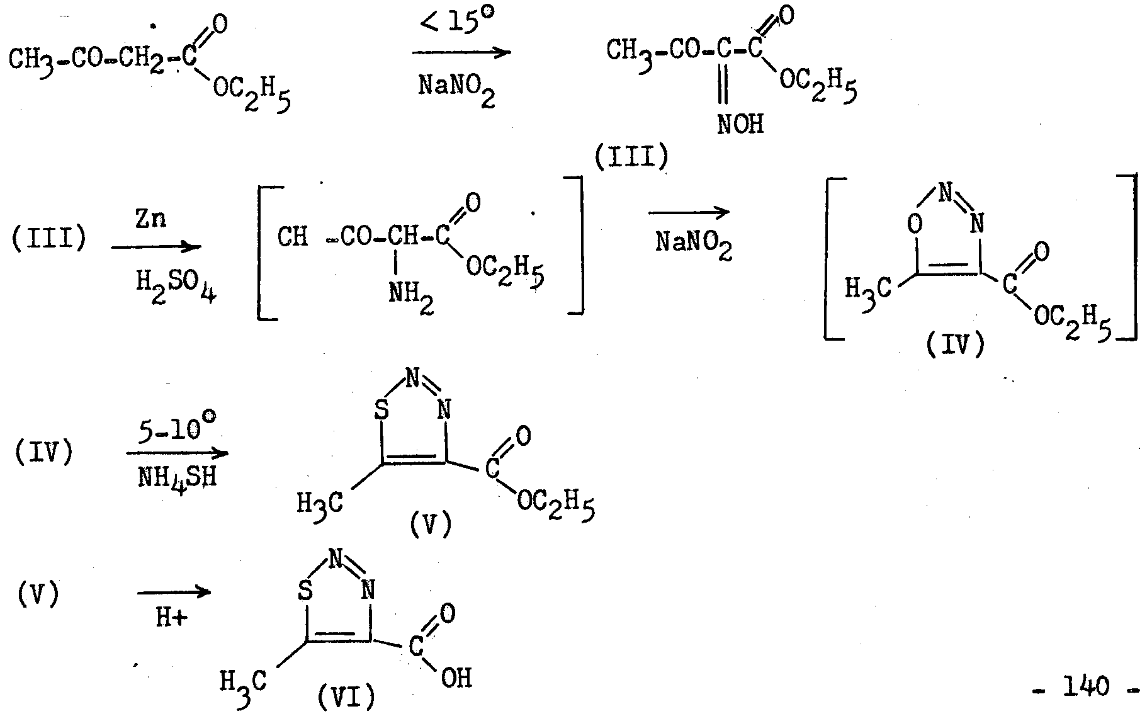
(II) Anal: Calcd : S, 24.60
found : S, 24.56
m.p. 227-228°C

The carboxylic acid was further transformed into the corresponding acid chloride by treating with thionyl chloride.

B. 5-Methyl-1,2,3-Thiadiazole-4-Carboxylic Acid (VI)

The methyl substituted derivative of 1,2,3-thiadiazole-4-carboxylic acid was synthesised from the corresponding diazoanhydride according to the procedure described by Wolff, Bock, Lorentz and Trappe[4] and represented schematically on Chart II.

CHART II



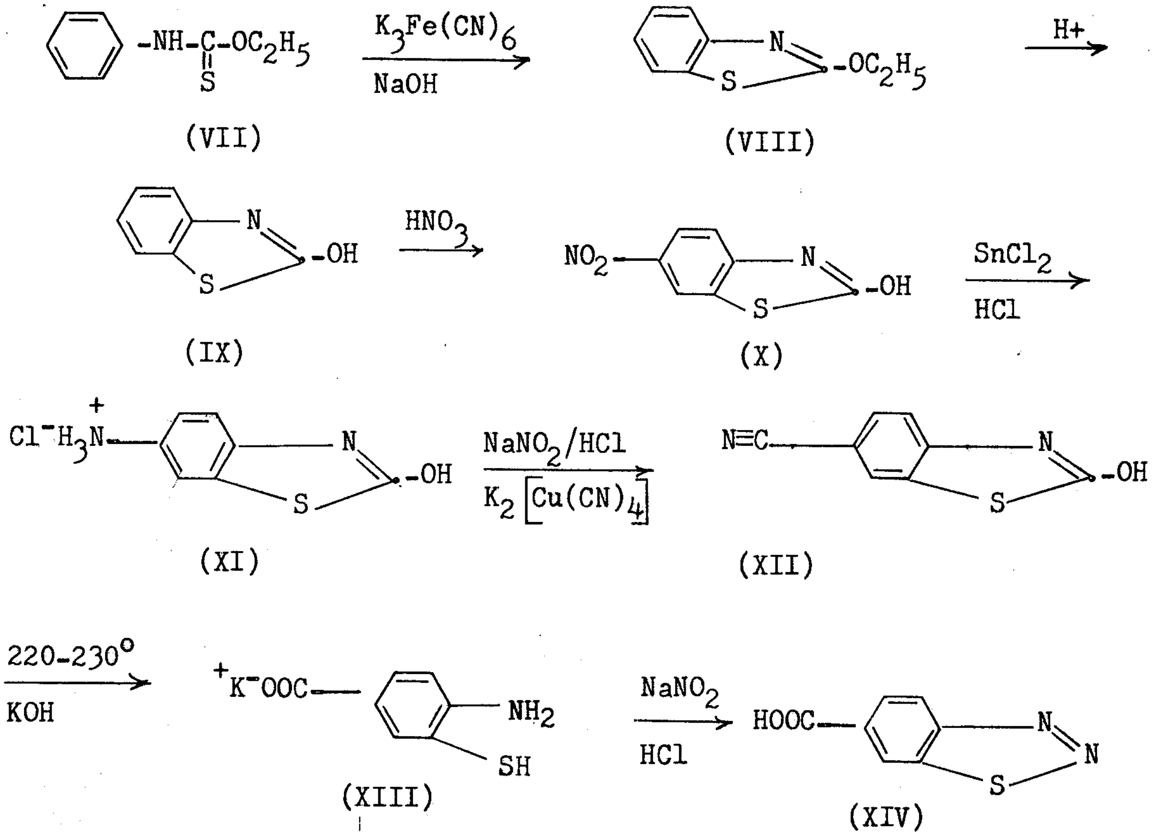
(VI) Anal. Calcd : S, 19.75
Found : S, 19.97
m.p. 74-75°C (monohydrate)

This compound was similarly transformed into the corresponding acid chloride by reaction with thionyl chloride.

C. Benzo-1,2,3-thiadiazole-6-carboxylic acid (XIV)

This derivative was obtained according to the procedure described by Jacobson,[5] starting with o-ethylphenylthiocarbamate (VII) which was transformed as shown on Chart III.

CHART III

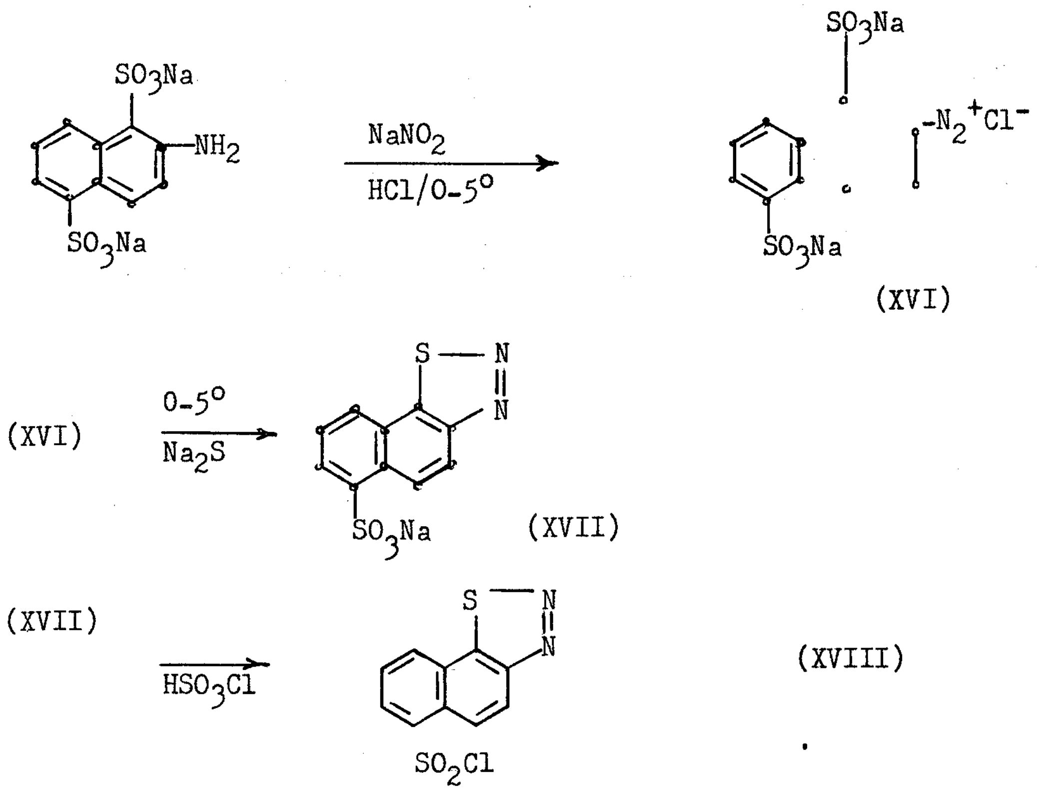


Compound XV was purified by esterification followed by hydrolysis and transformed into the corresponding acid chloride by subsequent reaction with thiony chloride.

D. Naphtho- 2,1-d -1,2,3-Thiadiazole-6-Sulfonyl Chloride (XVIII)

Compound XVIII was obtained from disodium-2-amino-1,5-naphthalene disulfonate (XV) according to the procedure described by Schmidt and Voss.[6] The synthesis of this derivative is schematically represented on Chart IV.

CHART IV



(XVIII) Anal. Calcd : Cl, 12.47
Found : Cl, 12.74

E. 5-[(6-Naphtho-]2,1-d[-1,2,3-thiadiazole)sulfonyloxy]isophthalic acid (XX)

A solution of 1.2 g sodium hydroxide and 1.82 g 5-hydroxyisophthalic acid (XIX) in 50 ccs. of water is placed in a 250 ccs. flask equipped with stirrer and funnel. A solution of 2.85 g of naphtho-[2,1-d]-1,2,3-thiadiazole-6-sulfonyl chloride (XVIII) in 30 ccs. acetone is added dropwise to this mixture while stirring and cooling in ice water. After an additional stirring for 30 minutes at room temperature the solution is filtrated and the filtrate is acidified with HCl, 6N. The acidified solution is poured into 200 ccs. of water. The precipitate is isolated by suction, washed with water and dried at 150°C. Yield 2 g; melting point :> 250°C.

This synthesis is represented on Chart V.

CHART V

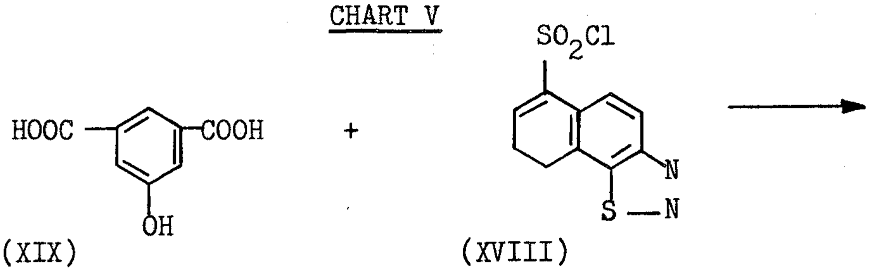
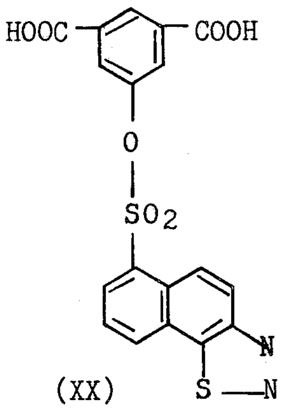


CHART V (Cont'd.)



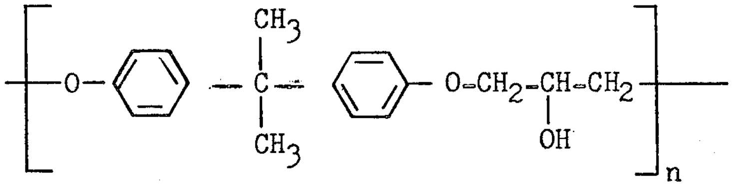
(XX)

The compound (XX) was further transformed into the corresponding acid chloride by treating with thionyl chloride

POLYMER SYNTHESIS

A. 1,2,3-Thiadiazole Substituted Polyhydroxyethers

The preparation of a naphtho-[2,1-d]-1,2,3-thiadiazole substituted polyhydroxyether (Polymer III, Table I) is given as a typical example of the general synthesis of those photosensitive polymers. The structure and composition of the synthesised polymers are given on Table I. Bakelite Brand Phenoxy resin PKDA-8500 (UCC) is used as basic polymer because of its outstanding metal coating properties. The Phenoxy resin is a copolymer of bisphenol A and epichlorhydrin having the following molecular structure:



$$\left[-O-C_6H_4-C(CH_3)_2-C_6H_4-O-CH_2-CH(OH)-CH_2-\right]_n$$

(n = 100)

1 g phenoxy resin and 1 g compound XVIII are dissolved in a mixture of 10 ccs. methylene chloride and 1 cc. pyridine. After standing in the dark for 48 hours, the solution is diluted with 20 ccs. methylene chloride and filtrated. The polymer is precipitated by addition of methyl alcohol while stirring, separated and dried in vacuo. The polymer can be purified by dissolution in methylene chloride and reprecipitation with methyl alcohol.

Polymers II and IV are obtained by similar procedures while polymer I requires a higher reaction temperature (50-60°C/2 hours).

B. 1,2,3-Thiadiazole Substituted Copolyester

Interfacial polycondensation has been shown to be very convenient technique for obtaining photosensitive arylazidopolymers.[2] The

same procedure could also be used for the synthesis of a 1,2,3-thiadiazole substituted polyester described in Table I as Polymer V. 0.912 g Bisphenol A is dissolved in 8 ccs sodium hydroxide 1N.
The solution is placed in a 100 ccs. flask equipped with stirrer and funnel. 0.02 g triethylbenzylammonium chloride dissolved in 2ccs. methylene chloride are added to this solution as catalyst. A solution of 0.406 g isophthaloyl chloride and 0.934 g acid chloride of compound (XX) in 8 ccs. methylene chloride is added dropwise to the alkaline bisphenol solution while stirring and cooling in ice water. After an additional stirring for 30 min. the supernatant aqueous layer is separated and discarded. The polymer containing organic phase is washed with water and diluted with methylene chloride. The polymer precipitates on addition of methyl alcohol, is separated and dried in vacuo.
Yield: 2 g.

SPECTRAL ANALYSIS

The ultraviolet spectra of the 1,2,3-thiadiazole substituted polymers are characterized by absorption bands between 300 and 360mμ. The band structure is more pronounced when going from polymers I and II to polymers III, IV and V. The spectra are represented on Figure 1 and the absorption characteristics are given in Table I.

The ultraviolet spectra were registrated with a Unicam SP700 Recording Spectrophotometer.

SENSITIVITY EVALUATION

The qualitative determination of a relative sensitivity scale was based on the procedure described by Minsk and coll.[7] The experimental technique was based on the irradiation of coated layers on an aluminium support under a neutral density step wedge with a 0.15 constant by means of a stabilized high-pressure percury vapour lamp, type Philips 57.235 E/25, of 80 watt at a distance of 15 cm for 15 min. The same procedure was used for both unsensitized and sensitized coatings. Wet films of uniform thickness are cast with a Garner Film Casting Knife with the knife blade at the desired opening, usually 1 mil, and laying the applicator at the upper end of a clean aluminium foil held down by a Bird Vacuum Plate. The coating material consisting of a solution of 50 mg of a photo-sensitive polymer dissolved in an appropriate solvent (methylene chloride, 2 ccs/sym.tetrachlorethane, 1cc) is then poured directly in front of the knife blade and the knife is drawn towards the lower end at a uniform speed. The layer is then allowed to dry in the dark before irradiation. The sensitivity values, defined as the reciprocal of the exposure required to insolubilize the polymeric coating, under a standard set of conditions, were calculated from the equation:

$$S_x = S_o \frac{\text{antilog } D_x}{\text{antilog } D_o}$$

where D_x and D_o refer respectively to the highest optical density of the neutral step-wedge for which the sample and the reference polymer are sensitive.

RESULTS AND DISCUSSION

A. Sensitivity of the 1,2,3-Thiadiazole Substituted Polymers

Unsensitized polymer coatings obtained from polymers I, II and V appeared to be unsensitive in these experimental conditions and, therefore, required longer periods of irradiation in order to become insolubilized. This lack of sensitivity can be explained on spectral grounds for polymers I and II but not for polymer V whose spectrum is analogous to that of the sensitive polymer III. This sensitivity difference between polymers V and III can tenatively be attributed to solubility and adhesion characteristics.

The sensitivity of the five 1,2,3-thiadiazole substituted polymers can be markedly increased by addition of sensitizers, particularly carbonyl containing derivatives. Table II gives the results of the sensitization of the 1,2,3-thiadiazole substituted polymers expressed as relative sensitivity (S_x) versus the unit sensitivity ($S_o = 1$) of an unsensitized sample.

The sensitization by those carbonyl compounds can probably be attributed to the possibility of triplet energy transfer from the sensitizer to the 1,2,3-thiadiazole units. Similar energy transfer processes are effectively known for other diazo derivatives.[9] Moreover, due to the presence of the sensitizer, a more efficient use is made of the mercury emission lines. The influence of the sensitizer concentration p,p'-bisdimethylaminobenzophenone- on the sensitivity of polymer III was also studied. The results represented on Figure 2 show a linear dependence for low concentrations and a saturation value at a concentration of about 10% by weight vs. the polymer. This saturation can be attributed to a complete absorption of the incident light at higher concentrations of the sensitizer and establishment of a front-effect.

B. Influence of the Degree of 1,2,3-Thiadiazole Substitution on the Photosensitivity

In order to determine the effect of the degree of 1,2,3-thiadiazole substitution upon the sensitivity of the polymers, a series of sensitive polyhydroxyethers was prepared by reacting the base phenoxy resin with various amounts of 1,2,3-thiadiazole-4-carbonyl chloride. The sensitivity of the polymers depends on the degree of 1,2,3-thiadiazole substitution along the polymer chains as indicated in Table III and shown on Figure 3.

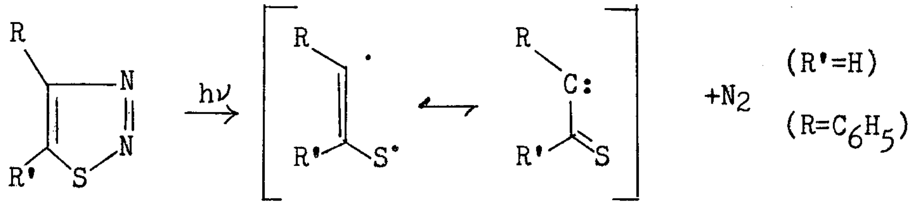
The sensitivity is expressed in a relative scale with respect to arylazidopolyesters described by Delzenne and Laridon.[2] A unit sensitivity value was attributed to the reference polymers with an equal molar degree of substitution of the light-sensitive functions and irradiated in the same experimental conditions.

At degrees of substitution below 15 mole % (i.e., at a low sensitivity level) the 1,2,3-thiadiazole substituted polyhydroxylethers are more sensitive; for higher degrees of substitution, however, the sensitivity of the arylazido polyesters prevails.

Excepting the necessary two per cent substitution claimed for statistical reasons, the 1,2,3-thiadiazole substituted polymers do not require any further substitution before becoming active and do not exhibit a threshold degree of substitution as arylazido polyesters do. The photolytically active fragments formed act as crosslinking sites from the very beginning and do not seem to undergo any wastage reactions.

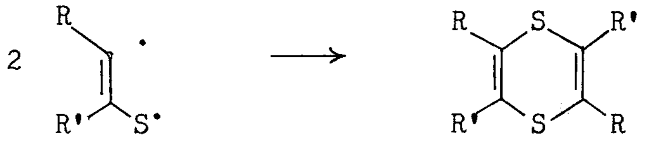
The photolysis of 1,2,3-thiadiazole derivatives was studied by Kirmse and Horner.[8] These compounds may be considered as resulting from the replacement by sulphur of the oxygen in the diazoketone structure, followed by cyclisation to a characteristic heterocyclic unit. Although the acid resistance and the thermostability are increased, it is, therefore, not surprising that the photosensitivity is maintained. Irradiation of 4-phenyl-1,2,3-thiadiazole for example, gives rise to several decomposition products which can be assigned to a primarily formed thioketocarbene intermediate (reaction a).

(a)



Starting from the thioketone intermediate several recombination reactions are possible: (1) Dimerization to form 2,5-disubstituted-1,4-dithiacyclohexadiene (reaction b) (XXI):

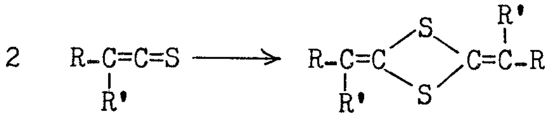
(b)



(XXI)

(2) Dimerization of thioketone resulting from a Wolff rearrangement of the thioketocarbene (reaction c):

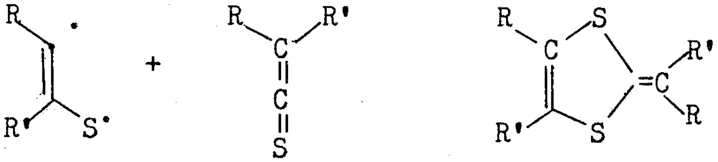
(c)



(XXII)

(3) Combination of thioketone with a non-rearranged fragment, giving rise to 1,4-dithiafulvene structures (XXIII) (reaction d):

(d)



(XXIII)

These recombination possibilities are able to form crosslinks between two polymeric chains.

Other reaction possibilities of the thioketocarbene intermediate or of the thioketone, including reaction with residual hydroxyl groups, are also to be taken into account as crosslinking potentialities. The identification of the structure of the reticulating points is very difficult and could not yet be made.

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TABLE I

STRUCTURE AND COMPOSITION OF 1,2,3-THIADIAZOLE SUBSTITUTED POLYMERS

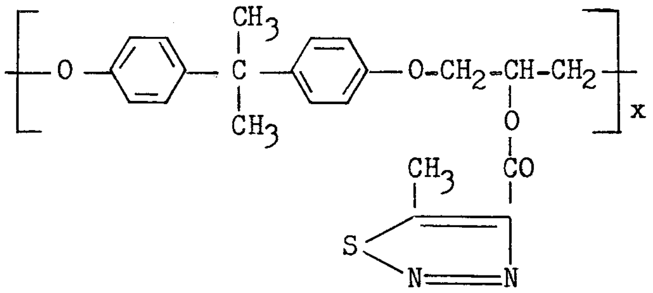
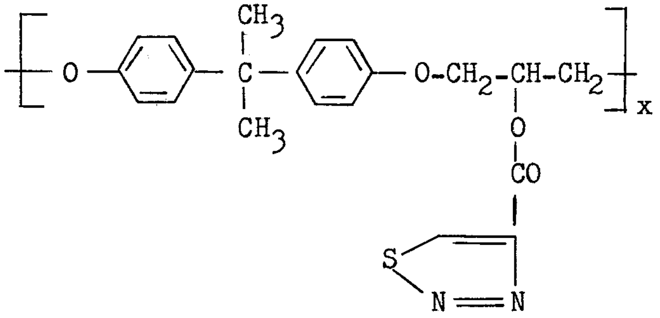
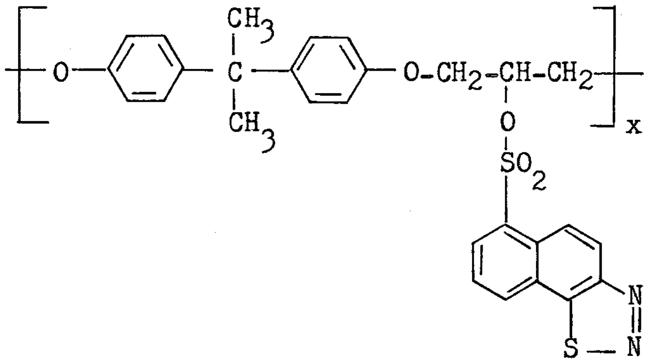
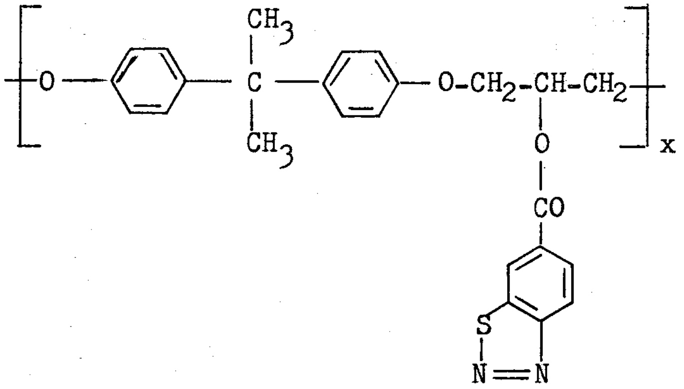
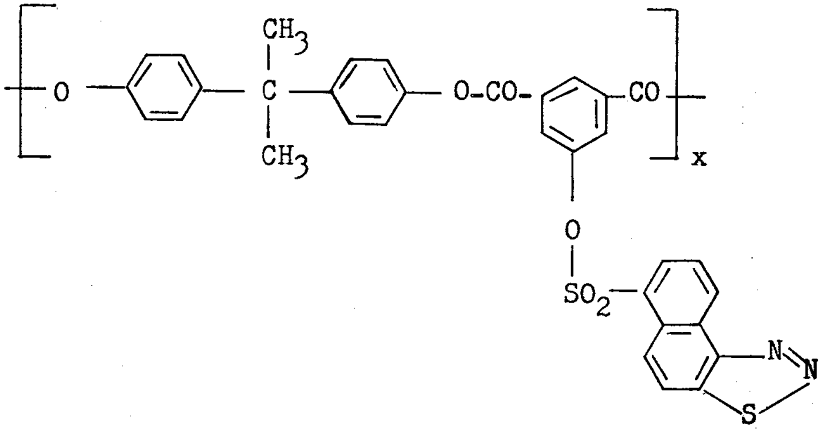
Sample	Structure of light-sensitive units	Composition		Spectra	
		Analysis	Mole % 1,2,3-TD units	λ max	Ɛ(1/mole, cm)
I		A-N:3% B-N:3.11% C-N:5.02%	35 37.5 65	309(sh) mμ	3210(a)
II		A-N:0.5% B to F see Table III	5	-	-
III		A-N:2.17% S:5%	28	339mμ 353mμ	143(b) 130(b)

TABLE I (Cont'd.)

IV		B-S:1385%	12.5	325 $m\mu$	2540(b)
V		A-N:2.49% S:4.78%	37.5	336 $m\mu$ 350 $m\mu$	215(b)

(a) Solvent: Sym. Tetrachlorethane
(b) Solvent: Methylene chloride

TABLE II

INFLUENCE OF THE SENSITIZER ON THE PHOTOSENSITIVITY OF 1,2,3-THIADIAZOLE POLYMERS

(Sensitizer concentration: 10% bw. vs. polymer)

Sensitizer / Polymer		p-dimethyl aminobenzaldehyde	p-dimethyl aminoacetophenone	p-dimethyl aminobenzophenone	p,p'-bis(dimethylamino) benzophenone
Polymer I	C	-	-	-	15.85
	B	18.85	15.85	2.82	11.2
Polymer II	B	-	-	-	44.6
Polymer III	A	-	-	-	3.95
Polymer IV	B	-	-	-	5.62
Polymer V	A	-	-	-	2.82

TABLE III

INFLUENCE OF THE DEGREE OF 1,2,3-THIADIAZOLE SUBSTITUTION ON THE PHOTOSENSITIVITY

Polymer	% S	Mole % 1,2,3-TD*	D_x	D_o**	S_x
II C	1	10	0.15 0.30	-	1.4*** 2
II D	1.66	15.5	0.6	0.75	0.71
IIE	2	20	0.6 0.75	1.35	0.178 0.25
IIF	2.39	25	0.9	1.2	0.46
IIG	4.8	50	1.5	1.95	0.356
IIB	6.29	96	1.65	2.1(100%)	0.355

* TD = Thiadiazole units

** Sensitivity of arylazidopolyesters with equal degree of substitution.

*** Minimum values.

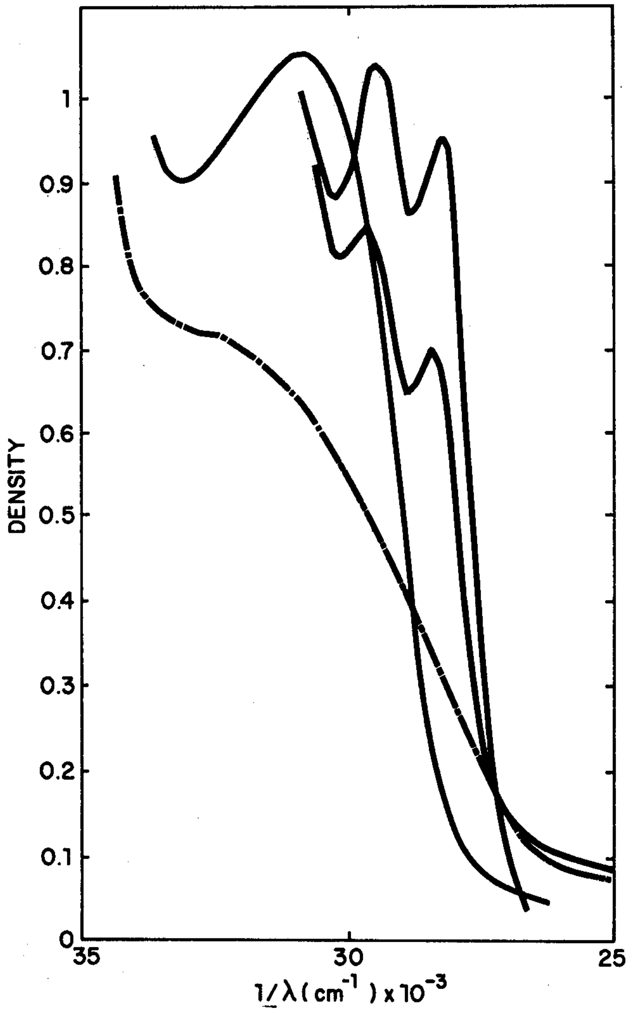


FIGURE 1: Ultraviolet absorption spectra of the 1,2,3-thiadiazole substituted polymers.

——+——+——	Polymer I : Concentration : 0.2 g/litre Solvent : sym. Tetrachloroethane.
————————	Polymer IV : Concentration : 1 g/litre Solvent : Methylene chloride.
——.——.——	Polymer III : Concentration : 0.5 g/litre Solvent : Methylene chloride.
—— —— —— ——	Polymer V : Concentration : 0.5 g/litre Solvent : Methylene chloride.

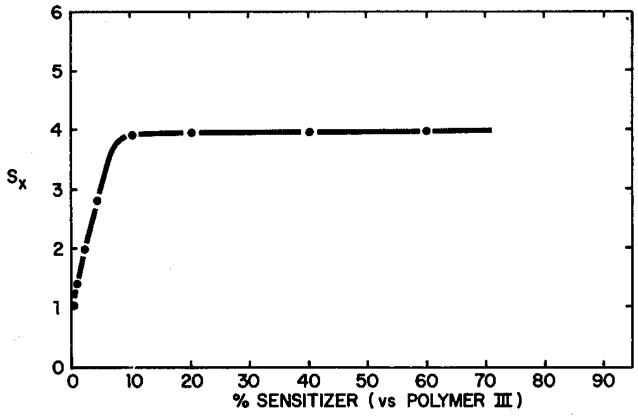


FIGURE 2: Influence of the pp'bisdimethylaminobenzophenone concentration on the photosensitivity of a 1,2,3-thiadiazole substituted polymer (III).

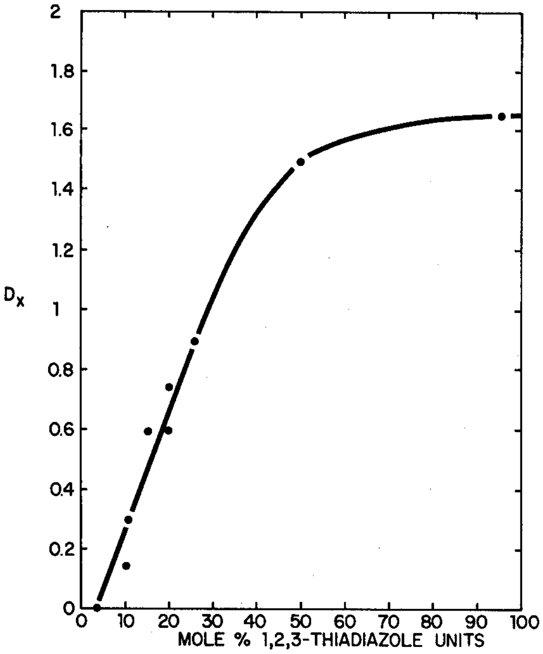


FIGURE 3: Influence of the degree of substitution on the photosensitivity of a 1,2,3-thiadiazole substituted polymer (Polymer II).

PHOTOCHEMICAL MECHANISM OF INTRAMOLECULAR HYDROGEN ATOM ABSTRACTION IN POLYESTERS

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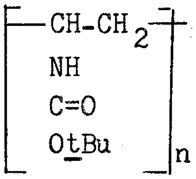
The quantum yield (ϕ_{II}) for cycloelimination of isobutene and CO_2 from thin films of poly-t-butyl-N-vinylcarbamate  $\left[\begin{array}{l} -CH-CH_2- \\ NH \\ C=O \\ OtBu \end{array}\right]_n$ was found to be 0.01. In contrast, quantum yields in alcoholic solvents were 0.04 and hydrocarbon media gave values of 0.16.

From the solvent shifts of the electronic spectra and approximate phosphorescence lifetimes, the lowest reactive excited state in hydrocarbon solvents was deduced to be of (n,π^*) character, while in alcoholic solvents and film form, a carbonyl excited state of (π,π^*) in nature, abstracted the β-ester proton.

It was found that intermolecular hydrogen bonding (N-H----O=C) of the gauche rotamer of the ester moiety played a significant role in reducing the quantum yield in thin films. Evidence for this was gained from solution and thin film infrared spectral data analyzed relative to the temperature dependence of the cycloelimination quantum yield.

INTRODUCTION

Previous studies[1] on the solid state photochemistry of poly-t-butylacrylate have shown that the primary process is a Norrish type-II elimination yielding isobutene and polyacrylic acid. In addition, the photoreaction was found to take place from an (n,π^*) state of the carbonyl group.[1b] Another aspect of the previous work was that a photoinduced rotational isomerization occurred between the cis and gauche forms of the ester with subsequent cycloelimination from the cis rotamer. → This ~~present~~ study EXPLORES ~~pertains to a relationship between~~ the photochemical and spectroscopic properties of poly-t-butyl-N-vinylcarbamate. Comparative experiments were made with poly-t-butylacrylate to [illegible] ~~better understand~~ the effect of (NH) substitution between the polymer backbone and ester group. ~~Particular~~ Emphasis was given to details of the nature of the excited states involved and intermolecular bonding of the carbamate (CO-NH) group to rationalize differences between the polycarbamate and polyacrylate solid phase quantum yields (ϕ_{II}). Varions in ϕ_{II} for the carbamate in film form and in alcoholic and hydrocarbon solvents was examined in relation to inversion of excited states and intermolecular hydrogen bonding. (Author modified)

Recent work on similar photoprocesses in substituted aromatic ketones and esters have established that the electron density distribution about the carbonyl group has a profound effect on its inter[2a] or intramolecular[2b] hydrogen atom abstracting ability. Such results have been explained in terms of the relative transition energies and reactivities of (n,π^*) and (π,π^*) states. The (n,π^*) type of excitation results in a reduction in charge on the oxygen atom, whereas the (π,π^*) state yields an increased negative charge on the carbonyl. The relative position of states in a molecule could be altered by changing the electron donating character of the substituent or solvent polarity.[3] The gradations in triplet lifetimes of 4-aminobenzophenone with variation in solvent polarity[3] indicated that an inversion in levels did not necessarily yield states with completely separate identities but rather a mixing of levels can occur.

The lack of any detailed photochemical studies on carbamates gives significance to the present study. The work of Booth and Norrish[4] on monomeric amides gave further impetus to our work because type-II eliminations were found in a variety of amide compounds containing γ alkyl-hydrogens.

Finally, since carbamates are monourethanes, the photochemical study of this system may gain insights into efficient ways of stabilizing polyurethanes.

EXPERIMENTAL

A. Materials

The sample of poly-*t*-butyl-N-vinylcarbamate (I) was supplied by Dr. H. James Harwood of the University of Akron and has been previously characterized.[5] The model compound, *t*-butyl-N-methylcarbamate (II) was prepared according to the method of Hart[6] and was found to have a boiling point of 70-72°C at 20mm. The ultraviolet absorption coefficients of compounds I and II agreed to within five per cent.

B. Solid Phase Photolysis

Product characterization and the temperature dependence of Φ_{II} was achieved in a system which has been previously reported.[1,7]

Uniform polymer films of from 0.4μ to 0.8μ were obtained on quartz microscope slides by dip-coating from dilute toluene solutions. Average films weighed from 1 to 2 mg. The solvent was removed from the slides by vacuum drying at 50 C for *ca*. 24 hr. Polymer thickness measurements were made with a Watson 16mm interference objective.

The light source for 2537Å excitation was a Hanovia 83A-1 low pressure mercury lamp fitted with both a Corning 7-54 filter and Baird-Atomic 254mμ Interference Filter. Above 3000Å, polymer excitation was accomplished with a GE S-4 100 watt mercury arc and a water filter. Spectral purity of the light transmitted in each system was evaluated with a No. 1700-11 Czerny-Turner spectrometer. Lamp intensities were measured with an Eppley Thermopile in conjunction with a Hewlett Packard 3420B DC Differential-Voltmeter.

Photolytic gaseous reaction products were separated and quantitatively analyzed by gas chromatography. Product identification was by infrared spectroscopy following classical microisolation techniques.

C. Liquid-Phase Photolysis

All polymer solutions were vacuum degassed five times in quartz cells by the freeze-pump-thaw technique (ca. 2×10^{-6}mm) prior to photolysis. Quantum yields at 25°C in methanol and 3-methylpentane were determined by the method of Beckett and Porter.[8] The carbonyl absorption band at ca. 200mμ was used to monitor initial rates of disappearance of the carbamate.

Methanol (Baker Analyzed Spectrophotometric), cyclohexane (Eastman Spectro Grade), and 3-methylpentane (American Instrument Co.) were used without further purification.

D. Spectroscopy

Ultraviolet and infrared, thin film and solution spectra were recorded on a Beckman DK-2A Ratio Recording Spectrophotometer and Beckman IR-10 Infrared Spectrophotometer. The temperature dependence of the infrared absorption spectrum of I in film form and $CDCl_3$ (Merck Sharp and Dohme Ltd.) solution was taken using a Limit Research J-1 Electrically Heated Cell.

Under 2537Å excitation, phosphorescence spectra and the lifetimes of I and poly-t-butylacrylate were obtained at 77°K. A Czerny-Turner spectrometer, equipped with an RCA IP-28 photomultiplier tube and Esterline Angus Model S-601-S Speed Servo Recorder was used to measure the emitted light. Approximate phosphorescence lifetimes were obtained by the use of a simple shutter and fast chart speed (3-6 in/sec). Satisfactory first-order decay curves were obtained in both cases.

RESULTS

A. Ultraviolet Spectra

A strong similarity in electronic spectral properties of the polymer in film form and in methanol is shown in Figure 1a and b, respectively. On the other hand, the ultraviolet spectra of I differs with the nature of the solvent. In cyclohexane, a new band emerged at 225mμ. This transition is partially resolved in Figure 1b. Assuming additivity of optical densities, the absorption had an extinction coefficient of 40ℓ mole^{-1}cm^{-1}. An intense band ($\epsilon = 1 \times 10^3 \ell$ mole^{-1}cm^{-1}) observable at 202mμ in methanol was blue shifted to 198mμ in cyclohexane. The third transition in the ultraviolet was a long wave length band at 260mμ. It had an absorption coefficient of 29ℓ mole^{-1}cm^{-1}. This band showed a slight red shift from methanol to cyclohexane.

B. Volatile Products and Thin Film Decomposition

The major volatile products of the 2537Å photolysis of poly-t-butyl-N-vinylcarbamate were found to be isobutene and carbon dioxide. Table I gives the quantum yields for formation of isobutene as a function of temperature. Carbon dioxide was found to have identical quantum yields. First order kinetics were observed by monitoring the formation of these compounds chromatographically in ten minute intervals. Above the glass transition temperature (T_g), a two-fold increase in quantum yield was found after correcting for a slight contribution from thermal cycloelimination. The film thicknesses were small enough ($\sim 0.5\mu$) so that diffusion controlled rates were not observed at any temperature. Above ~140°C the thermal decomposition competed severely with the photochemical processes, consequently, the photolysis temperature range was not extended. The order of magnitude lower yields of isobutane assured that the evolution of isobutene was not from a radical process, i.e., disproportionation of isobutyl radicals.

The formation of a primary amine as a solid product after elimination of isobutene and CO_2 was confirmed by absorption at 1630 cm^{-1}. This was assigned to the NH_2 internal deformation mode.[9] It was observed, using infrared spectroscopy, that the gauche ester spatial conformation did not decrease in concentration. This is in marked contrast to the acrylate polymer photochemistry[1] (vide infra) where a photo-induced rotational isomerization was found to be operative.

A single room temperature photolysis experiment was carried out using a broad spectral distribution of wave lengths >3000Å. No product formation was observed for an exposure equivalent to the 254mμ photolyses.

C. Liquid Phase Photochemistry

Quantum yields at 254m excitation for the formation of isobutene and CO_2 from 7.00×10^{-3}M I in metha nol and 1.50×10^{-2}M I in 3-methylpentane were found to be 0.04 and 0.16, respectively. Photochemical conversions were maintained at ~5% and the yields for the disappearance of poly-t-butyl-N-vinylcarbamate were determined spectrophotometrically (vide supra) and from gpc analyses of the gaseous products. Solutions had to be degassed as oxygen was found to quench the reaction by ca. 50%.

D. Infrared Spectrum and Hydrogen Bonding in the Carbamates

The aforementioned quantum yield results suggested a possible hydrogen-bonding investigation of the pertinent functional groups involved in the photochemistry of I, using infrared spectroscopic techniques. The same types of media were used, i.e., thin films and alcoholic vs. hydrocarbon solvents. Portions of the infrared spectra of the model compound (II) in an alcoholic and nonpolar media are shown in Figure 2. Also shown is the polymer (I) in film form. Since the monomeric equivalent (II) and polymer were found to show the same spectroscopic band positions and intensities, II was used in the majority of infrared absorption experiments because of the low polymer (I) solubility in hydrocarbon solvents. The use of CCl_4 as a substitute for hydrocarbon solvents in infrared studies was advanced by Brealey and Kasha[10] in their work on relating hydrogen bonding effects to (n,π^*) blue shifts.

The infrared spectrum of 0.3M II in CCl_4 (Figure 2a) was characterized by an intense free N-H band at 3440cm^{-1} and a lower intensity bonded N-H absorption at 3360cm^{-1}.[11] The order of intensity was reversed when 0.1M ethanol was added. The free (1730cm^{-1}) and bonded (1710cm^{-1}) carbonyl frequencies were similarly affected. In addition reduction of the concentration of II from 0.3M to 0.1M resulted in an increase in free N-H at the expense of bonded N-H (Figure 2a). Also, from Figure 2b, compound II in neat form appeared to exist exclusively in a bonded state as noted by the absence of the 3440cm^{-1} transition.

Bands arising from the different spatial isomers of the ester group were observable in the 1200-1300cm^{-1} region. The 1240cm^{-1} and 1278cm^{-1} transitions were previously assigned,[12,1b] in other ester systems, to the C-O vibration of the planar cis form and three-dimensional trans (gauche) isomer, respectively. The relative proportions of the two isomers in solution were consistent with conclusions arrived at from dipole moment measurements on carbamates.[13] Interestingly, thin films of II exhibit a greater concentration of the gauche rotamer.

Previous work on acrylates[1b,12] have demonstrated that the cis and gauche rotamers are interconvertible with heat[1b,12] or light.[1b] The temperature dependence of the absorbance ratio of low energy to high energy isomer of I shown in Figure 3 was essentially the same as for the acrylate film. The notable difference between the two systems was that I displayed a temperature dependence of the absorbance ratios in $CDCl_3$ solution, whereas the acrylate isomer ratio was temperature independent.[1b] In Figure 4, the ratios of bonded to free N-H are shown as a function of film and solution temperatures. Similar to the ester conformational bands, little change in bonding was observed up to the Tg of 120°C. Above this temperature, the concentration of free N-H (3440cm^{-1}) increased quite dramatically. This is pertinent in view of the dramatic increase in Φ_{II} in this region.

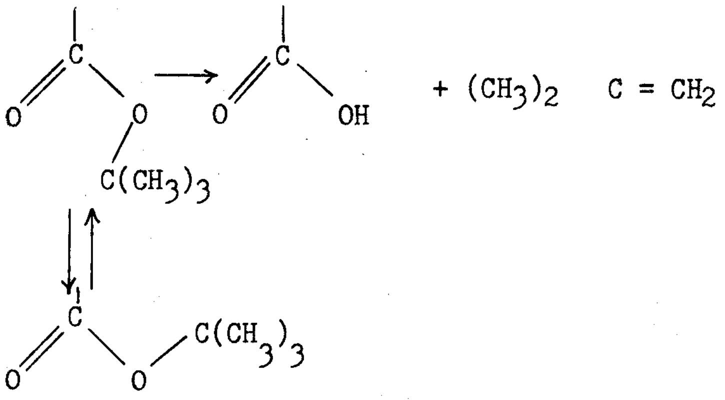
E. Phosphorescence of Carbamates and Acrylates

Previous photochemical studies of ester systems,[1b,2b] as well as this work, show that cycloelimination occurs at least in part from the lowest triplet state of the carbonyl. Hence, any properties of the respective triplet states involved in the work was of value in analyzing the wide variation in Φ_{II} with structure and solvent properties.

Phosphorescence spectra of the carbamate (I) in 10^{-2}M solutions of 3:7 isopropanol-isopentane and 3-methylpentane were run at 77°K in order to obtain the triplet decay times. Phosphorescence experiments with thin films of poly-t-butylacrylate and I provided similar information. The film thicknesses were controlled in order to assure that equivalent concentrations of each polymer was excited. The results of these experiments are in Table II. The phosphorescence intensities were very weak and no detectable fluorescence was observed from either polymer. While the techniques used were admittedly crude, the order of magnitude trends are significant. The emission spectrum and approximate lifetime[2b] of butyrophenone was used as a calibration standard.

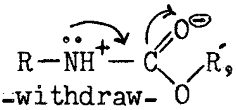
DISCUSSION

The first long wave length electronic transition in poly-t-butylacrylate corresponds to an (n,π^*) transition.[1a] The absorption band is characterized by an extinction coefficient of 67ℓ mole^{-1}cm^{-1} and a bathochromic shift from 212mμ in methanol to 217mμ in cyclohexane. The 254mμ quantum yield for isobutene formation at 25°C in thin films was found to be 0.08. An analysis of infrared spectroscopic and kinetic data was consistent with the following mechanism:



The corresponding details of the poly-t-butyl-N-vinylcarbamate photochemistry were analyzed relative to the acrylate photolysis. Features of the carbamate system worthy of detailed discussion were the wide variations of Φ_{II} in film form, alcoholic and nonpolar solvents.

The two long wave length electronic transitions of I at 225mμ and 260mμ are assigned to (n,π^*) excitations of the lone pair electrons on the carbonyl oxygen and nitrogen atom, respectively. The extinction coefficients of 40ℓ mole^{-1}cm^{-1} and 29ℓ mole^{-1}cm^{-1}, respectively, and the absorption band red shifts in cyclohexane relative to methanol were good evidence that this assignment was correct. It was apparent that the lower energy transition belonged to excitation of the lone pair electrons about nitrogen because nitrogen has a lower electron affinity than oxygen.[14] Also, excitation into the long wave length tail of 260mμ band yielded no photochemistry. For similar reasons, i.e., magnitude of the extinction coefficient and "solvent shift", the 200mμ band was related to a (π,π^*) level.

Excitation of I at 254mμ in film form gave a Φ_{II} of 0.01. This is to be compared with a quantum yield of 0.08 for poly-t-butylacrylate. That the carbamate (n,π^*) carbonyl absorbed at a lower energy than the acrylate (n,π^*) (225mμ vs. 215mμ) was surprising because of the lower cycloelimination quantum yield. This is because the substituents that decrease the electron density about a carbonyl oxygen generally lower the energy of the (n,π^*) transition and increase the quantum yield for intra or intermolecular hydrogen atom abstraction. Such interpretations are common through the extensive work by Porter and Suppan[2a,3] and Pitts, et al.[2b] Compared with acetates, formates, amides, etc., the carbamates have a lower energy (n,π^*) state because resonance donating effects, i.e.,  $R-\overset{..}{N}H^{+}-C(=O^{\ominus})-O-R'$, are nonnonexistent.[15] Thus, the nitrogen acts as an electron-withdrawing group through an inductive effect.

The (n,π^*) band was hidden beneath the (π,π^*) band in thin films and alcoholic solution as shown in Figure 1. Φ_{II} under 254mμ excitation changed from 0.16 in hydrocarbons to 0.01 and 0.04 in thin films and alcohols, respectively, indicating that the quantum yield decreases were due, at least in part, to a change in the lowest reactive state from (n,π^*) to a (π,π^*) character. It is well known that (π,π^*) states have a larger electron density on the oxygen and subsequently yield a significantly smaller quantum yield for hydrogen atom abstraction.[2b,3] For ease of discussion, only two types of states have been advanced. However, it is well known that mixing of states can occur.[3]

It is well established[2a] that the relative order of states in most carbonyl systems is the same in both singlet and triplet manifolds. Therefore, a comparison of the spectroscopically observed states (Figure 1) and any properties of the states derived from low temperature emission experiments (Table II) was meaningful. The relatively long phosphorescence lifetimes in film form and alcoholic media support a (π,π^*) type triplet state whereas the shorter lifetimes for the acrylate in film form and carbamate in hydrocarbon solvent are indicative of an (n,π^*) level. Lifetimes are useful for characterizing such states since a delocalized excited electron and a localized ground state electron, ^{3}(n,π^*), have a much greater probability to interact and spin flip than a delocalized excited and ground state electron, ^{3}(π,π^*). Therefore, it is reasonable that $\tau^3(\pi,\pi^*) > \tau^3(n,\pi^*)$.

The change in the nature of the lowest reactive excited state would account for quantum yield variations between the polyacrylate and I in film form and I in hydrocarbon and alcoholic media. However, the strong similarity in absorption and emission properties of I in film form and methanol suggest the lowest reactive state to be of a (π,π^*) nature in both environments. There is compelling evidence to support a relationship between Φ_{II} and degree of hydrogen bonding to explain this variation, i.e., as the concentration of $N-H \cdots O=C$ decreases, Φ_{II} increases. This was shown in Table I and Figure 4 for data on the temperature dependence of the thin film quantum yields and (N—H) absorbance ratios, respectively. More specifically, hydrogen bonding of the gauche rotamer and Φ_{II} are related in that there is no photorotational isomerization observed. Supporting evidence demonstrating that the gauche isomer is preferentially hydrogen-bonded was that in the most highly bonded media, i.e., neat film, the gauche isomer predominates. It should be emphasized that in the poly-t-butylacrylate system the trans form was found to photoisomerize to the cis isomer. The spatial conformation of the three-dimensional trans isomer (gauche) of the ester is such that the t-butyl-methyl groups are rotated out of the plane of the carbonyl group[16] leaving the oxygen atom more susceptible to hydrogen bonding. The cis isomer cannot hydrogen bond so easily since the methyl groups stagger the carbonyl oxygen. It is apparent that bonding of an intermolecular nature is operative in these carbamate systems. The essential evidence lies in the fact that the ($N-H \cdots O=C$) bonds are broken upon dilution and the N—H absorbance ratio was temperature dependent in solution.[12a] This is in marked contrast to the polyacrylate system. It is concluded that a dominant factor reducing the type II quantum yield in thin films is due to a releasing of the energy absorbed by the gauche isomer via some non-radiative process or processes.

Qualitative evidence supporting a relationship between energy dissipation via a non-radiative process and hydrogen bonding was advanced by Cowgill[17] in work on fluorescence quenching of tryptophanyl and tyrosyl peptides.

CONCLUSIONS

The conclusions may be arrived at by inspection of the data in Table III. The influence of hydrogen bonding on the type-II quantum yields from I was found to be dependent upon whether the reaction took place in thin films or solution.

In the solution phase experiments, Φ_{II} decreased from 0.16 in 3-methylpentane to 0.04 in methylalcohol. A solvent shift causing an inversion of the (n,π^*) and (π,π^*) levels was also found to occur. Thus, the variation in Φ_{II} was explained on the basis of a change in electron density distribution in the excited states. Comparisons of the electronic absorption spectra with the phosphorescence lifetimes gave evidence for this interpretation.

Secondly, the significant lower quantum yield of I in film form compared to the polyacrylate film or its yield in alcohol was rationalized on the basis of degradation of the excitation energy via some radiationless process occurring from a resonance-stabilized hydrogen bonded gauche isomer. Evidence for this was found from infrared studies which showed a photochemically inactive, intermolecularly bonded gauche isomer. In addition, Φ_{II} in thin films was found to increase by a factor of two in the temperature region (>Tg) where the concentration of $N{-}H \cdots O{=}C$ bonds decreased by $\sim$10%.

Therefore, the photochemistry of poly-t-butyl-N-vinylcarbamate appears to be controlled by the subtle interplay of at least two factors: (1) a solvent effect which changes the character of the lowest reactive state; (2) energy degradation via hydrogen bonding. Further experiments that will hopefully clarify the mechanism will be the subjects of further investigations.

ACKNOWLEDGMENTS

Dr. H. James Harwood of the University of Akron, and Miss Anita VanLaeken of this laboratory, are sincerely thanked for the synthesis of I and II, respectively. Informative discussions with Drs. J. B. Flannery, D. L. Stockman and M. S. Walker are acknowledged with pleasure.

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TABLE I

QUANTUM YIELDS FOR 2537A PHOTOELIMINATION OF ISOBUTENE FROM POLY-t-BUTYL-N-VINYLCARBAMATE THIN FILMS

Film Temp., °C	Φ_{II}
25	0.01
66	0.01
120 - Tg	-
136	0.02

TABLE II

EMISSION FROM THE POLYCARBAMATE AND POLYACRYLATE AT 77°K AND 254m EXCITATION

Compound	Phase	0 —— 0 Phosphorescence Band, mμ	Measured Lifetime, (τ) sec
I	10^{-2} alcohol	380	4
I	10^{-2} hydrocarbon	380	<0.1
I	thin film	380	4
Poly-t-butylacrylate	thin film	370	<0.1

TABLE III

COMPARISON OF TYPE-II QUANTUM YIELDS FOR THE POLYCARBAMATE AND POLYACRYLATE AT 254mμ EXCITATION

Compound	Phase	Φ_{II}	Reactive State
Polyacrylate	thin film	0.08	n,π^*
Polycarbamate	thin film	0.01	π,π^*
Polycarbamate	alcohol	0.04	π,π^*
Polycarbamate	hydrocarbon	0.16	n,π^*

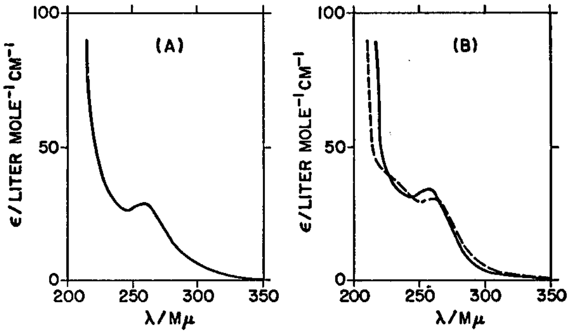

FIGURE 1: Ultraviolet Spectrum of Poly-t-butyl-N-vinylcarbamate at 25°C:
(A) 6.4μ film.
(B) ——— 6.90 x 10^{-3}M in methanol;
– – – 6.90 x 10^{-3}M in cyclohexane.

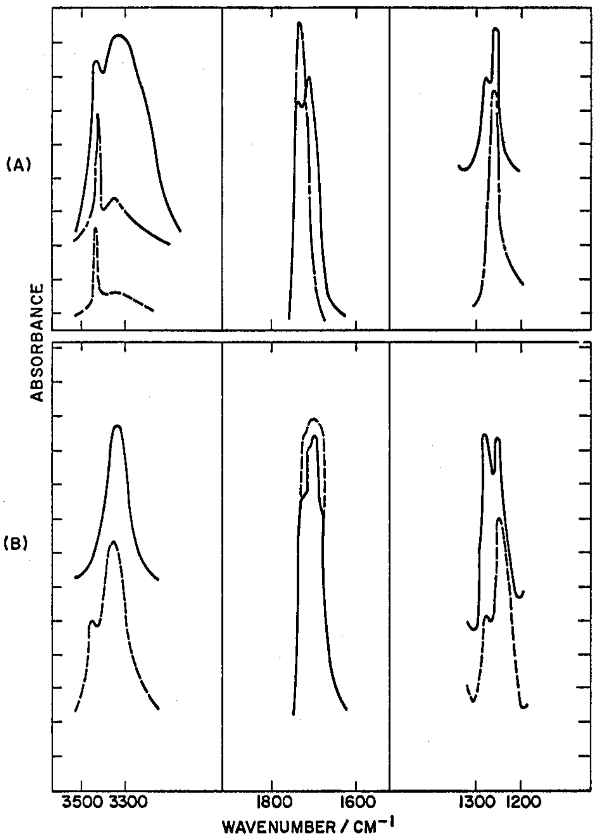

FIGURE 2: Infrared Spectra in N-H, C=0 and C–0 Regions at 25°C:
(A) —— – —— 0.3M II in CC1_4;
——— 0.3M II in 0.1M Ethanol/CC1_4;
– – – – 0.1M II in CC1_4.
(B) ——— II, neat; – – – – I, ~ 1μ film.

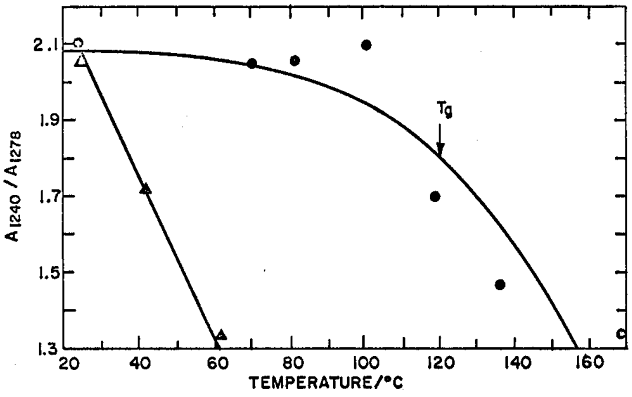

FIGURE 3: Temperature Dependence of the Absorbance Ratio A_{1240}/A_{1278} for I:
● 1μ film; ▲ CDC1_3 solution.

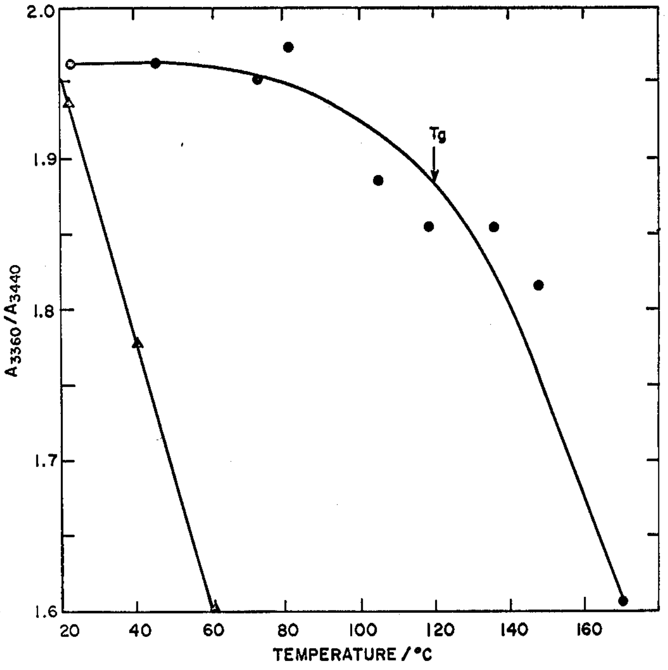

FIGURE 4: Temperature Dependence of the Absorbance Ratio A_{3360}/A_{3440} for I:
● 1μ film; ▲ CDC1_3 solution.

PHOTOCHEMICAL BEHAVIOR OF POLYVINYL CINNAMATE-BASED PHOTO-RESISTS

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IBM Corp.

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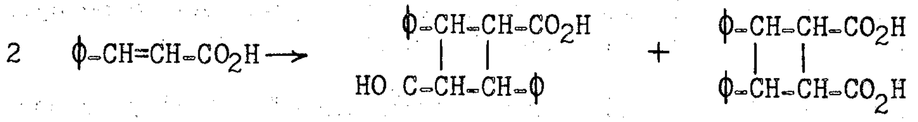
The photochemical reactivity of compounds containing an α,β-unsaturated carbonyl system, has been recognized as early as 1895, when Bertram and Kürsten[1] made the observation that solid cinnamic acid undergoes a chemical change when exposed to daylight. About seven years later, Riiber[2] established that the reaction which had taken place was a dimerization of two cinnamic acid molecules to form a cyclobutane derivative. Cinnamic acid can cyclodimerize in two ways giving truxillic and truxinic acids:



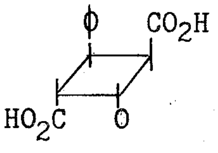
$$2\quad \phi\text{-CH=CH-CO}_2\text{H} \longrightarrow \begin{array}{l}\phi\text{-CH-CH-CO}_2\text{H}\\ \qquad |\quad\ |\\ \text{HO C-CH-CH-}\phi\end{array} \quad + \quad \begin{array}{l}\phi\text{-CH-CH-CO}_2\text{H}\\ \quad\ |\quad\ |\\ \phi\text{-CH-CH-CO}_2\text{H}\end{array}$$

$\phi = C_6H_5$

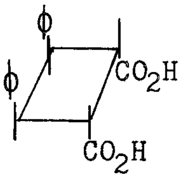
truxillic acid

truxinic acid

Each of these dimer molecules can exist in a number of stereoisomeric configurations depending upon the positions of the four substituents in relation to the cyclobutane ring. The two isomers obtained from the reaction of cinnamic acid are α-truxillic and β-truxinic acid.



α-truxillic acid

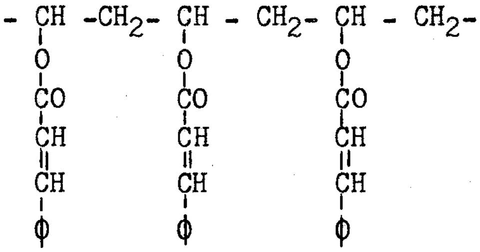


β-truxinic acid

The photodimerization of cinnamic acids formed the subject of extensive studies during the first quarter of this century. It was taken up again in 1958 by Schmidt and coworkers[3-5] who were able to provide answers to some previously unsettled questions regarding reaction mechanism, due to the combined use of chemical and X-ray crystallographic methods. Some of their most interesting conclusions were: a) in the cinnamic acid series, photodimerization is entirely controlled by the crystal lattice, b) dimerization was found to occur whenever the olefinic double bonds of nearest neighbor molecules in the crystal were at a distance of 4.1A or less, and c) dimerization did not take place when this distance was 4.7A or greater.

With this knowledge about the photochemical behavior of cinnamic acid the incorporation of a cinnamic acid moiety into a polymeric structure appears to be a logical step in the development of a photosensitive polymer. This subject has been widely investigated and received special attention in the laboratories of Eastman Kodak (see e.g., Minsk and coworkers).[6]

The cinnamoyl groups when attached to an aliphatic chain as in polyvinyl cinnamate:



$$-\underset{\text{OCOCH=CH}\phi}{\text{CH}}-\text{CH}_2-\underset{\text{OCOCH=CH}\phi}{\text{CH}}-\text{CH}_2-\underset{\text{OCOCH=CH}\phi}{\text{CH}}-\text{CH}_2-$$

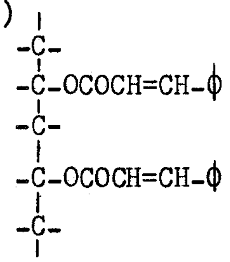
are forced into maintaining some degree of order in relation to each other, a degree obviously much lower than that of a crystal lattic, but also considerably higher than the one prevailing in a true solution of cinnamic acid, in which dimerization has not been observed.

It was reasonable to assume that the irradiation of polyvinyl cinnamate would result in changes similar to those observed in cinnamic acid. In fact, a theoretical study of the problem was based on this assumption.[7] In a recent paper, Curme and coworkers[8] describe the formation of dimers (presumed to be cyclobutane derivatives) in the sensitizedirradiation of liquid ethyl cinnamate.

Let us now consider the possibilities of reaction of polyvinyl cinnamate:

I. <u>Truxinic dimerization</u>

a)

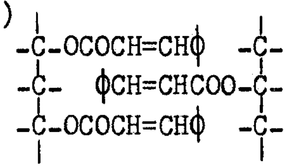


b) folded chain

c) parallel chains

II. <u>Truxillic dimerization</u>

a)



b) folded chain

A truxinic dimer will result from the reaction between nearest neighboring cinnamoyl groups of the same chain (Ia). A similar reaction can also occur between cinnamoyl groups belonging to the same chain but farther apart from each other when the chain is folded (Ib). A truxinic dimerization can also take place between cinnamoyl groups belonging to two different chains if these find themselves lying parallel and at the appropriate distance, a situation simulating the arrangement of a crystal lattice. A truxillic dimer will be the result of a reaction between cinnamoyl groups belonging to different chains arranged as shown in IIa. An intra-chain reaction from a suitably folded configuration can also give rise to a truxillic dimer (IIb). Of all the possibilities mentioned, it seems probable that reaction will occur most frequently according to Ia and IIa. Finally, the possibility of polymerization of the olefinic double bonds must also be considered.

That such process is possible is shown by the behavior of some cinnamic esters,[9] as well as one cinnamic acid, namely, 5-bromo-2-methoxy-cis-cinnamic acid, whose molecular packing in the crystal promotes polymerization alongside dimerization.

The goal of ~~our~~ the work was to identify the chemical change which is responsible for the insolubilization of films based on polyvinyl cinnamate, under the influence of light. ~~Both polyvinyl~~ cinnamate and Kodak Photo Resist 2, a commercial material based on polyvinyl cinnamate, were used in our experiments. (The polyvinyl cinnamate was synthesized from a high molecular weight polyvinyl alcohol, Gelvatol 1-90, Shawinigan Resins Corp.). The most important difference between the two materials was the presence of a sensitizer in KPR 2. The light source used for irradiation was a Hannovia high pressure quartz mercury lamp, type SH.

The time of irradiation of the polymer film was chosen on the basis of the following experiment, using parallel samples on a quartz disc and on a metallic substrate. The metallic substrate was coated with KPR 2, irradiated through a photographic pattern and processed in order to obtain an adequate etched pattern. The corresponding quartz disc, which was coated and exposed under identical conditions, was used for UV measurements. The results are shown in Table I, giving the decrease in optical density (OD) at the absorption maximum of 273 millimicrons, as a function of time of irradiation.

These results show that only a small decrease in unsaturation is necessary in order to produce a sufficient decrease in the solubility of the polymer film for use in a practical application.

A comparison of the reaction rates of polyvinyl cinnamate and KPR 2 was made by measuring the decrease of their absorption maximum at 273$m\mu$. Thin films of the two materials were coated on quartz discs which were then used for absorption measurements as shown in the Figure 1.

The six delineated areas were used for the measurements and their average taken in order to compensate for differences in film thickness. The results are shown in Tables II and II, and Figure 2. It can be seen that the decrease in unsaturation in KPR 2 after an irradiation of 8 minutes is more than twice as great as that of a film of polyvinyl cinnamate after 30 minutes. The presence of the sensitizer thus greatly affects the reaction rate.

The most direct approach to the problem was the attempt to identify the reaction products. This approach was based on the rather simple lines of first splitting the ester into the alcoholic and acidic parts as shown in Table IV, with subsequent analysis of the acidic fraction.

Paper chromatography was tried as a method for the identification of the acidic fraction and was found adequate. Sheets, 52 by 20 cm, of Whatman No. 1 filter paper were used and the most suitable solvent system, with the corresponding separation as expressed in R_f values is shown in Table V. A detailed description of this method can be found under the given reference.

Saponification of the unirradiated polymer was easily performed in alkaline medium. It turned out, however, that transesterification of the polymer with methanol and subsequent hydrolysis of the methyl ester lent itself better for use in conjunction with the paper chromatographic method mentioned. The transesterification proceeded at room temperature in THF in the presence of catalytic amounts of sodium hydroxide. The hydrolysis of the methyl esters was accomplished at 60° in aqueous ethanol, in the presence of sodium hydroxide.

The workup of the irradiated material was somewhat more complicated due to its very low solubility. THF was used as solvent in this case also, but sodium hydroxide was replaced by potassium hydroxide. Transesterification could be obtained in samples which were irradiated for a maximum of 10 seconds. No appreciable transesterification could be obtained after longer exposures due to insufficient solubility. In a typical experiment, the quantities were: 380 mg polymer, 4.5 ml THF, 4 mg KOH and 2.5 ml MeOH. The mixture was finely ground (using a Wiggle Bug) and then stirred at room temperature. After the subsequent hydrolysis the reaction mixture was used as such for paper chromatography. The R_f values of the acids were somewhat lower when compared to those obtained from the pure materials due to the presence of the metallic ions. Standards of the corresponding alkali salts of the three acids were, therefore, run on the same chromatographic sheets with the reaction products.

The result from the chromatographic test showed a spot for α-truxillic acid at $R_f=0.30$ and a much larger spot at $R_f=0.52$ corresponding to the large excess of cinnamic acid. No β-truxinic acid was found and there were no other spots, except for those of the metallic ion, indicating the absence of other possible stereoisomeric forms of the dimers.

The large effect of the relatively minimal loss in unsaturation on the solubility of the polymer can easily be understood in terms of formation of an α-truxillic structure. This reaction, probably proceeding via path IIa, represents a most efficient crosslinking mechanism. Our results do not rule out the formation of a polymer from the olefinic double bonds of the cinnamoyl groups. If formed, such a polymer would either remain as undissolved starting material or be filtered off with the polyvinyl alcohol formed during the transesterification. However, qualitatively speaking, a polymerization seems rather unlikely as the effect per disappearing double bond on the solubility would be considerably reduced. This is in contradiction to our findings of the large effect a small decrease in unsaturation has on the solubility of the polymer. Our results suggest, therefore, that α-truxillic formation is the important reaction at least during the early stages of irradiation.

The large effect the sensitizer has on the reaction rate is rather remarkable. It suggests that a triplet intermediate is involved in the reaction. Support for such an assumption is also given by Curme[8] who found that the phosphorescence of certain sensitizers is quenched by polyvinyl cinnamate. The slow reaction of the unsensitized material can, therefore, be interpreted as being due to inefficient crossover of the excited singlet state, obtained in the direct irradiation, to the reacting triplet. A dimerization from the singlet excited state itself cannot be excluded. However, if such reaction occurs at all, it must also be very inefficient.

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TABLE I

CHANGE OF ULTRAVIOLET ABSORPTION SPECTRA OF IRRADIATED KPR2 FILMS

Sample Number	Time of Irradiation	OD at 273mμ Initial	 Final	 Decrease	 %
1	40 sec.	1.21	1.20	0.01	0.8
2	2 min.	1.11	1.08	0.03	2.7
3	4 min.	1.26	1.21	0.05	4.0

TABLE II

CHANGE OF ULTRAVIOLET ABSORPTION SPECTRUM OF IRRADIATED POLYVINYL CINNAMATE FILM

Area No.	OD_0	OD_4	OD_8	OD_{30}	OD_0-OD_4	OD_0-OD_8	OD_0-OD_{30}
1	1.200	1.185	1.160	1.115	0.015	0.040	0.085
2	1.210	1.190	1.175	1.135	0.020	0.035	0.075
3	1.200	1.175	1.165	1.115	0.025	0.035	0.085
4	1.175	1.155	1.155	1.105	0.020	0.020	0.070
5	1.190	1.190	1.160	1.110	0.000	0.030	0.080
6	1.185	1.180	1.160	1.105	0.005	0.025	0.080

Average values:

$OD_{0,\,av} = 1.193$ $\quad 100 \times \dfrac{OD_{0,\,av} - OD_{4,\,av}}{OD_0} = 1.2\%$

$OD_{4,\,av} = 1.179$

$OD_{8,\,av} = 1.163$ $\quad 100 \times \dfrac{OD_{0,\,av} - OD_{8,\,av}}{OD_0} = 2.5\%$

$OD_{30,\,av} = 1.114$ $\quad 100 \times \dfrac{OD_{0,\,av} - OD_{30,\,av}}{OD_{0,\,av}} = 6.6\%$

TABLE III

CHANGE OF ULTRAVIOLET ABSORPTION SPECTRUM OF IRRADIATED KPR2 FILM

Area No.	OD_0	OD_4	OD_8	OD_8-OD_4	OD_0-OD_8
1	1.065	0.960	0.905	0.105	0.160
2	1.070	0.955	0.925	0.115	0.145
3	1.000	0.890	0.885	0.110	0.115
4	1.085	0.945	0.930	0.140	0.155
5	1.080	0.945	0.865	0.125	0.215
6	1.030	0.925	0.875	0.105	0.155

Average values:

$OD_{0,\ av} = 1.055$

$OD_{4,\ av} = 0.937$

$OD_{8,\ av} = 0.898$

$$100 \times \frac{OD_{0,\ av} - OD_{4,\ av}}{OD_{0,\ av}} = 11.2\%$$

$$100 \times \frac{OD_{0,\ av} - OD_{8,\ av}}{OD_{0,\ av}} = 14.9\%$$

TABLE IV

HYDROLYSIS OF POLYVINYL CINNAMATE

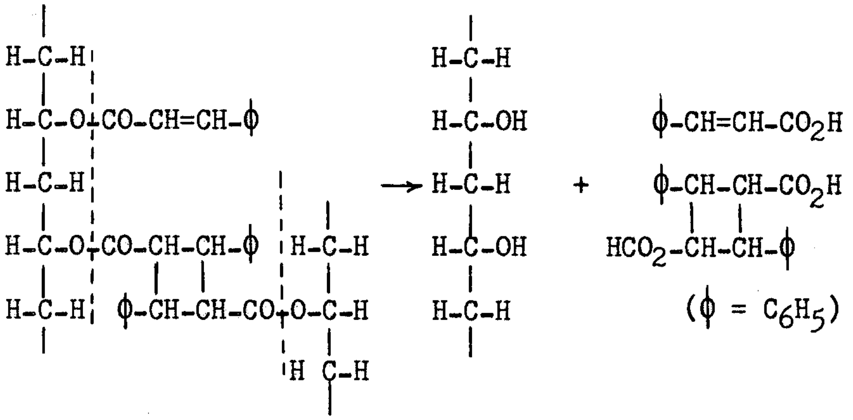
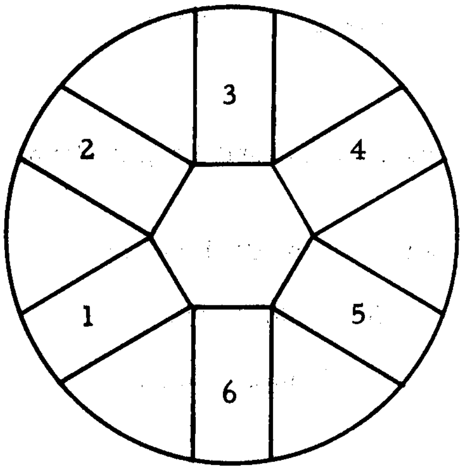


TABLE V

80 (vol) parts EtOH
10 (vol) parts Water
5 (vol) parts Ammonia

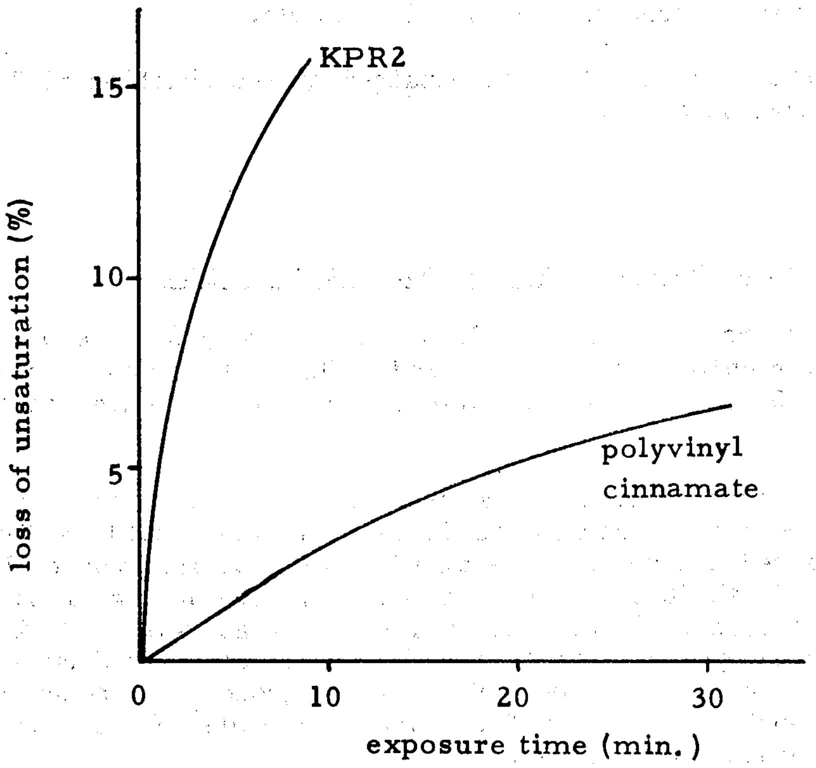
R_f		
	cinnamic acid	0.56
	α-truxillic acid	0.36
	β-truxinic acid	0.27

J. Chromatog., 26, 544 (1967)



Quartz disc showing delineated areas used for ultraviolet absorption measurement.

FIGURE 1



Reaction rates of films of polyvinyl cinnamate and KPR2 as shown by the decrease of unsaturation on exposure to ultraviolet light.

FIGURE 2

NEW AZIDE POLYMER

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When the aromatic azides decompose photochemically or thermally, active free radicals are formed.[1]

If the polymer has the azide groups as the side group, it crosslinks on exposure to light and can be used as a photosensitive polymer.[2]

The Authors synthesized the new polymers having the aromatic azides as the photo sensitive group. One is the novolak type polymer which was obtained by condensation of phenol with m-nitrobenzaldehyde and then converting the nitrogroup to azide. Another is the condensation product from formyl-1-naphthyl azide (II) and polyvinyl alcohol. 1-naphthyl azide (I) was prepared by diazotization of α-naphthyl amine, followed by treatment with sodium azide. (Author)

Formyl-1-naphthyl azide (II) was obtained by the reaction of N-methyl formanilide and 1-naphthylazide (I).[3]

EXPERIMENTAL

A. Preparation of Novolak Type Photosensitive Polymer

25g of m-nitrobenzaldehyde, 13g of phenol and 5-6 drops of concentrated hydrochloric acid were mixed. The mixture was stirred for 2 hrs. at 120°C. After the reaction, the mixture became reddish and viscous.

If a small portion of the condensation product is cooled to the room temperature and it becomes rigid, the reaction should be finished. The condensed polymer was dissolved in ethanol and reduced by reflux for 2 hrs. with 30 cc of 80% hydradine hydrate and 3g of palladium-carbon catalyzer. After reducing, the filtrate was acidified with concentrated hydrochloric acid. Then, two mols of sodium nitrite (aqueous solution) to 1 mol of the amino group, were added drop by drop at 0-5°C, and stirred for 1 hr. The azide polymer was precipitated by adding water (Figure 1).

B. Preparation of PVA-azide Naphthalene Polymer

To the mixture of 43g of α-naphthylamine, 50 cc of water and 135 cc of concentrated hydrochloric acid was added gradually at 20-30°C. To the mixture which was cooled down to 0-5°C, 43.5g of sodium nitrite in 150 cc of water was added and then it was stirred for 2 hrs. After filtration, 25g of sodium azide in 100 cc of water was added to the filtrate, and the solution was stirred for 2 hrs. 1-naphthylazide (I) was extracted by ether and obtained by vacuum distillation after removing ether. The yield of I was 35g (b.p. 75-80°C/10^{-3} Torr, m.p. 120°C).

To the mixture of 81g N-methyl formanilide and 60 cc of o-dichlorobenzene, 81g of phosphorous oxychloride was added gradually at 0-5°C, and then 50.7g of I was added. After reaction for 4 hrs. at 70°C, the reaction product was diluted by the aqueous solution of sodium carbonate and o-dichloro benzene was removed by steam distillation. 15g of formyl-1-naphthyl azide (II) was obtained by vacuum distillation of the residue, b.p. 100-120°C/10^{-2} Torr. (Anal. Found: N 20.42%; Calcd. for $C_{11}H_7ON_3$: N 21.31%).

1g of polyvinyl alcohol (degree of polymerization, 2000) was dissolved in the mixed solution of water 6cc and acetic acid 40g on a water bath. Acetal of polyvinyl alcohol was obtained by reacting with II in the presence of a trace of sulfuric acid for approximately 1 hr. at 80°C.[4]

After dilution with acetone, the mixture was poured slowly with vigorous stirring into water. The condensation product of polyvinylalcohol and II was isolated and it was soluble in acetone and dioxane. (Anal. Found: N 5.83%, C 60.42%, H 6.86%), Figure 2.

RESULTS

Novolak type photopolymer is soluble in methanol, ethanol and acetone. This polymer coated on the zinc plate, is insolubilized in the above solvent by 4 minutes' irradiation with 450W Hg lamp, through a negative pattern. Development by methanol gives the positive image. The photo-insolubilized image can be used as the resist for etching after heat treatment at 180-200°C for 3 min. In this polymer, the photo-sensitive group is azide benzene and its absorption band is in the ultraviolet region (Figure 3). So the intense ultraviolet light is necessary to irradiate it.

By exposure through negative to a thin layer on zinc plate which is coated with acetone solution of PVA-azide naphthalene polymer, the polymer is selectively crosslinked and insolubilized in the image areas. The unexposed polymer was removed with aqueous methanol to give a clear image.

The photolytic rate of the azide group by the irradiation of the ultraviolet ray was examined by the measurement of the optical density at 245$m\mu$ (Figure 4).

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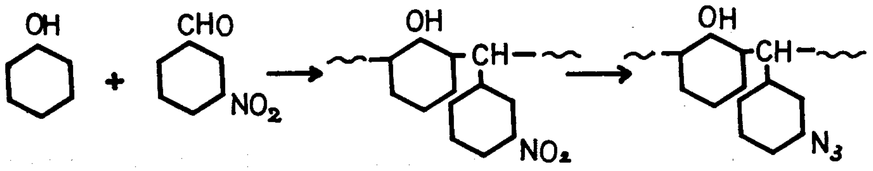

FIGURE 1

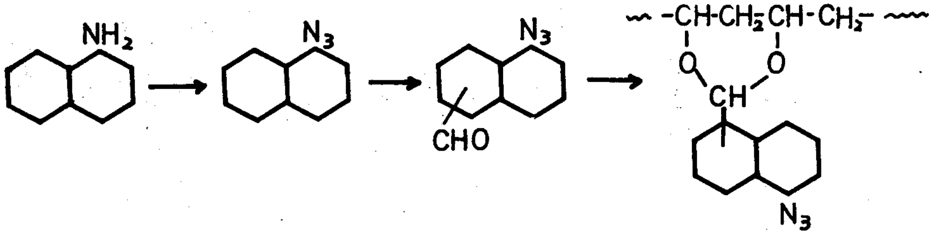

FIGURE 2

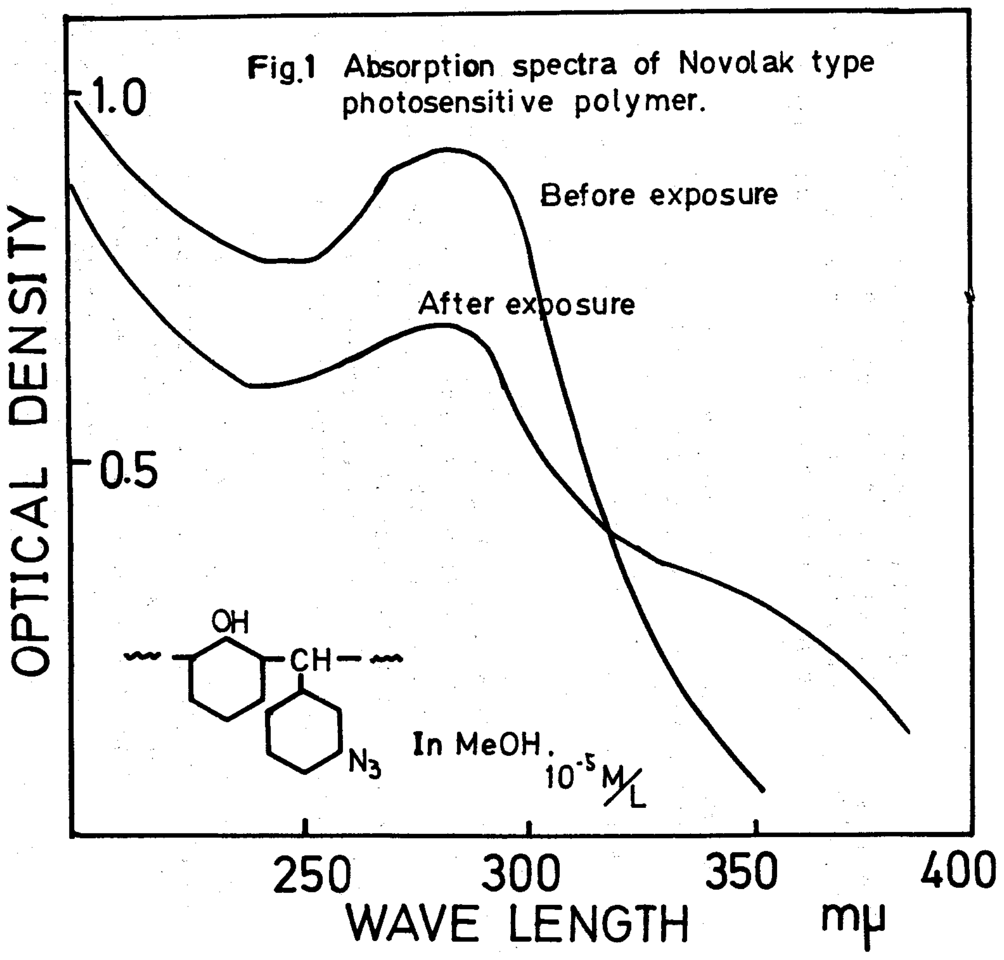
Fig.1 Absorption spectra of Novolak type photosensitive polymer.

FIGURE 3

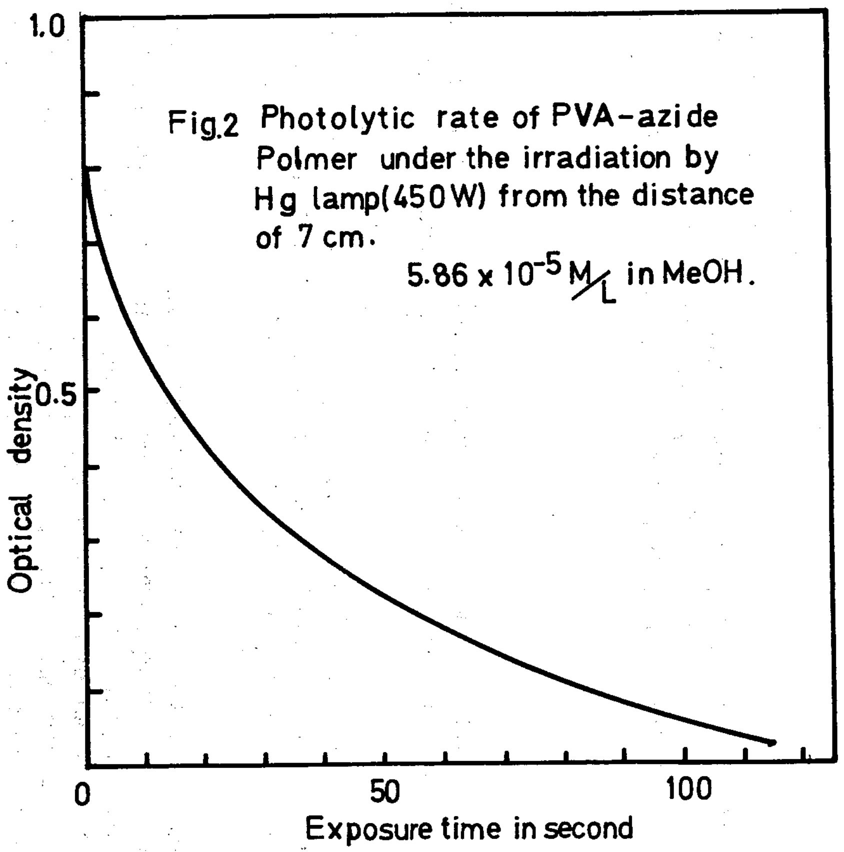
Fig.2 Photolytic rate of PVA-azide Polmer under the irradiation by Hg lamp(450W) from the distance of 7 cm.
5.86×10^{-5} M/L in MeOH.

FIGURE 4

THE PHOTO-CROSSLINKING OF POLYVINYL CINNAMATE

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~~The~~ Photo-crosslinking and sensitization mechanisms of polyvinyl cinnamate were studied by measuring ESR spectrum of the irradiated resin and phosphorescences of cinnamic acid and sensitizers; which ~~ESR spectrum of the irradiated polyvinyl cinnamate~~ showed that ~~two~~ 2 types of free radicals, main chain radical and cinnamoyl radical, were produced by ultraviolet light. The sensitization was made clear by the triplet energy transfer mechanism. Cinnamic acid ~~was found to~~ emits a phosphorescence at about 20,000 cm^{-1}, and phosphorescences of sensitizers is ~~to be~~ quenched by cinnamic acid in epa solution. The critical separation between donor, sensitizer and acceptor, cinnamic acid, was estimated at about 10Å. (Author, modified)

INTRODUCTION

Polyvinyl cinnamate is one of the most common photosensitive resins which becomes insoluble by ultraviolet light. It is a resin of the crosslinking type. In industry, resins, crosslinking type, are mainly in use, and many resins of this type have been reported and synthesized. However, the photocrosslinking methanism of these resins seem to be similar to each other. Therefore, the authors studied the photocrosslinking mechanism of polyvinyl cinnamate.

Since the first report on the synthesis, the sensitometry and sensitization of polyvinyl cinnamate was presented by Minsk, et al,[1] many studies on sensitometry, sensitization and synthesis have been made of.

Inami, et al,[2] studied on the structure of the light-irradiated polyvinyl cinnamate by IR technique, and clarified that the α, β double bond of cinnamoyl group was destroyed to single bond by the irradiation. But the photo-crosslinking mechanism of this resin has not been made clear.

On the other hand, sensitized polyvinyl cinnamate is widely sensitive, including in the visible region, while non-sensitive one only in the ultraviolet region. This fact is very interesting. Then the authors have studied the photocrosslinking and sensitization mechanisms of polyvinyl cinnamate, by measuring ESR spectra of the irradiated polyvinyl cinnamate at low temperature, and phosphorescence spectra of cinnamic acid and sensitizers, and calculating the electronic structure of cinnamic acid.

THE ELECTRON SPIN RESONANCE SPECTRA OF LIGHT-IRRADIATED POLYVINYL CINNAMATE

In the previous paper,[3] the photo-isomerization and photo-dimerization of cinnamic acid were discussed from the standpoint of the electronic structures, and it was shown that the radical reactivities at α- and β- carbons of cinnamic acid were increased by the electronic excitation. It seems reasonable to assume on the basis of these results, that the radical is produced by the irradiation of polyvinyl cinnamate with ultraviolet light, since the electronic structure of cinnamoyl group in polyvinyl cinnamate and that of cinnamic acid are essentially identical.

The samples sealed in quartz tubes were exposed to ultraviolet light at 77°K with a 500W high pressure mercury lamp. A filter of Toshiba UV-D25, transparent from 240 mμ to 350 mμ, was used. The irradiated polyvinyl cinnamate gives ESR signals shown in Figure 1, while the unexposed resin does no signal. The spectroscopic splitting factor of the spectrum was found to be 2.003.

It appears that the spectrum consists of two components, a broad singlet and a quartet. The component of the broad singlet is stable at 77°K. When the resin was kept in the dark at 77°K for several hours after exposure, the quartet signal was found to disappear, while the intensity of the singlet not to decrease. The spectrum of the resin kept in dark at 77°K for an hour after exposure is shown in Figure 2. The quartet signal decayed to a great extent, but the intensity of the singlet signal is as large as that in Figure 1. These facts suggest that two species of radicals are produced by the irradiation of the resin.

The value of the ΔH_{msl} of the broad singlet was found to be 15.8 gauss. Tamura[4] reported that when molecular chain is in the rigid state at low temperature, the spectrum which has a fine structure at higher temperature changes to the dull broad spectrum. Therefore, the observed singlet spectrum may be the smeared-out spectrum of hyper-fine structure. Using the data of molecular orbital coefficient calculated by LCAO-SCF-MO method,[3] the ESR signal of cinnamoyl radical may be expected to be as is shown in Figure 3. The hyperfine splitting, a_i, is evaluated by:

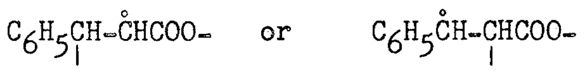
$$A_i = Q\rho_i$$

where Q is 23 gauss and ρ_i is the electron density of i atom that is calculated by the MO coefficient of the upper occupied molecular orbital for the cinnamoyl cation radical. The broken curves in Figure 3 represent the calculated absorption curve by assuming that the resolving power of spectrum is 5 gauss. The value of ΔH_{msl} was estimated to be 13 gauss. This is in reasonable agreement with that of the observed value for the broad singlet.

When polyvinyl cinnamate is irradiated to ultraviolet light, the crosslinked reaction arises and the polymer becomes insoluble to any solvent:

$$-CH_2\overset{|}{C}HOCOCH{=}CHC_6H_5 \xrightarrow{h\nu} -CH_2\overset{|}{C}HOCOCH{-}\overset{|}{C}HC_6H_5 \qquad C_6H_5\overset{|}{C}H{-}\underset{|}{C}HCOO\underset{|}{C}HCH_2-$$

Then the species of the broad singlet may be the crosslinked cinnamoyl radical produced by the light-irradiation:



$$C_6H_5\underset{|}{C}H{-}\overset{\circ}{C}HCOO- \quad \text{or} \quad C_6H_5\overset{\circ}{C}H{-}\underset{|}{C}HCOO-$$

The hyperfine splitting of the quartet was found to be 23.0 gauss. It is reasonable to assume that the splitting is caused by the α- and β-hydrogen atoms. Then the quartet signal seems to be due to the main chain radical of polyvinyl cinnamate, $-\underset{|}{C}H-\dot{C}H-\underset{|}{C}H-$. It seems that this radical is produced by the hydrogen-abstraction of the cinnamoyl radical.

THE PHOSPHORESCENCE SPECTRA OF CINNAMIC ACID AND SENSITIZERS

In order to study the sensitization mechanism of polyvinyl cinnamate, the authors measured the phosphorescence spectrum of cinnamic acid, for the electronic structures of both cinnamic acid and cinnamoyl group in polyvinyl cinnamate are essentially identical.

The phosphorescence spectrum of cinnamic acid was measured in epa solution at $77^{o}K$. The observed spectrum is shown in Figure 4. The 0-0 band for the phosphorescence of cinnamic acid was found to be 20,000 cm^{-1}. All effective sensitizers for polyvinyl cinnamate emit phosphorescences in this region as shown in Table I.

The probability for energy transfer increases as the phosphoresence spectrum of acceptor approaches to that of donor. Tsuda[5] has shown that the compound of which the lowest triplet energy is larger than that of cinnamoyl group, is effective to the sensitization of polyvinyl cinnamate.

Then we measured the quenching effects for phosphorescences of sensitizers by cinnamic acid in order to make the energy transfer clear. The typical phosphorescence spectrum quenched by 2-nitrofluorene is shown in Figure 5. The phosphorescence was quenched by cinnamic acid, and the concentration $[A]_{1/2}$ of cinnamic acid, which quenches half of phosphorescence of 2-nitroflorene, was about 0.7M.

Forster[6] has shown that the critical separation between a donor and an acceptor, for which energy transfer from donor D* to acceptor **A** and emission from d* are equally probable, may be calculated from the experimental equation:

$$R_o = \frac{7.35}{\sqrt[3]{[A]_{1/2}}} \quad \text{in } \mathring{A}$$

The authors found that R_o was 8.2 Å for the system, 2-nitrofluorene and cinnamic acid. Critical separations for other sensitizers were found to be a similar value to that for 2-nitrofluorene.

The most effective concentration for the sensitization of polyvinyl cinnamate has been reported to be very high. It seems that this concentration effect is owing to the fact that the transfer rate of energy of sensitizer is very low in the region, $R < 10\mathring{A}$.

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TABLE I

TRIPLET STATE ENERGIES AND PHOTOSENSITIVITIES OF SENSITIZERS[1,5]

Sensitizer	Phosphorescence energy	Photosensitivity
2-nitrofluorene	20810 cm^{-1}	113*
5-nitroacenaphthene	19940	84*
p-nitroaniline	19750	110
phenanthrene	21640	14
anthracene	19000	7.7
naphthalene	22000	2.6
phenol	28570	1.8

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*The determined method for these two values is different from that for other values. 5-nitroacenaphthene is about 10 times more sensitive than p-nitroaniline.

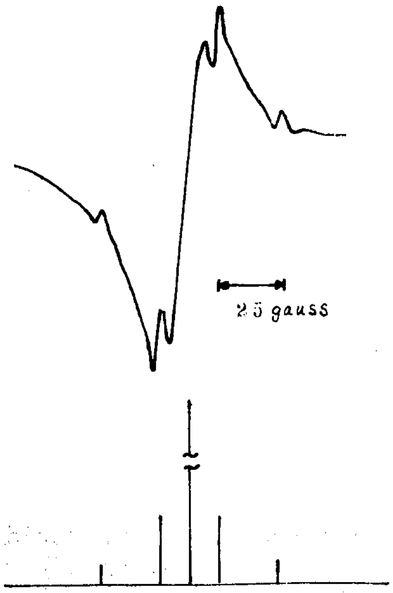

FIGURE 1: ESR spectrum of the light-irradiated polyvinyl cinnamate at 77° K: irradiated for an hour.

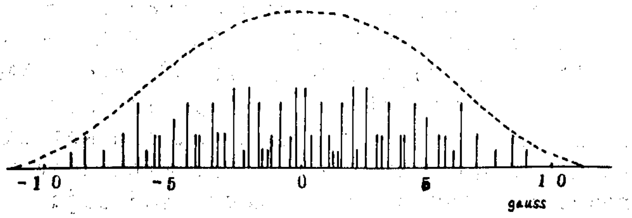

FIGURE 3: The calculated signals of cinnamoyl radical.

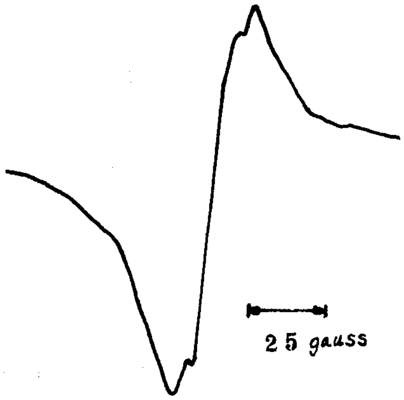

FIGURE 2: ESR spectrum of the light-irradiated polyvinyl cinnamate at 77° K: kept in the dark for an hour after the irradiation.

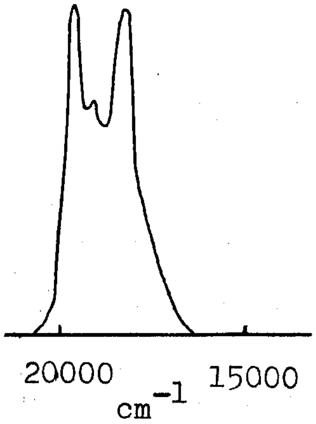

FIGURE 4: Phosphorescence spectrum of cinnamic acid.

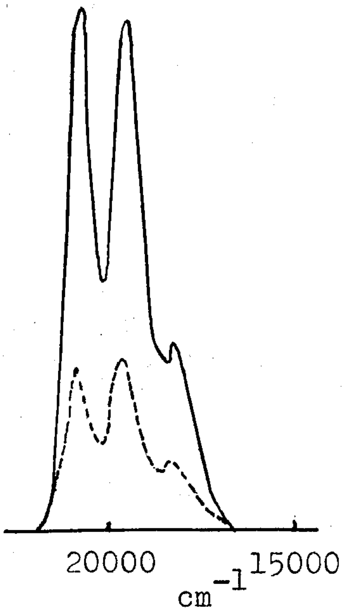

FIGURE 5: Phosphorescence spectra of 2-nitrofluorene:
solid curve: added no accepter
broken curve: added 1M-cinnamic acid.

EVOLUTION OF A PHOTOPOLYMER PRINTING PLATE

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At the conclusion of World War II it was obvious that the old, staid business of printing and publishing had to change. The technological fallout from research that produced the nuclear age should also be applied to the business of writing, printing and distributing news publications. Time, Inc., as one of the leaders of the publishing field, established a technical Research & Development center in Springdale, Connecticut, which became known as the Springdale Laboratories, to introduce these newly available technologies into the magazine industry. There were many areas that requireddrastic improvements in both efficiency and operating speed if the magazine business was to continue to be profitable. One of these was the matter of the printing plates that put the ink image onto a web of paper. The conventional printing plate at that time was made entirely of metal. In fact, about 95% of its structure was composed of lead - a printing plate with a weight of 8 to 12 pounds was the rule. To obtain an acceptable printed result with a system utilizing this type of printing element required many hours to mount and adjust the plates on the press cylinder, and by the nature of the plate's mass and poor integral strength the printing press web speeds were kept down in the range of 700 to 800 feet a minute.

In addition, the manufacture of this lead-backed electrotype required a time span from 6 to 10 hours and the expenditure of many man-hours of direct labor. However, keep in mind that the electro-type was and still is a vital element in an information processing system that employed metal type casters and etching of metal engravings. The combining of these elements and many other metal parts was necessary as a page of copy was changed from the editor's instructions in the form of pencil notes and glossy pictures onto a metal surface that would print the page image with ink on paper.

In the late 1940s a new concept was born that could revolutionize the process of converting editorial text into the slick finished printed magazine page. This new system involved the use of electronics and photography which at first included the photographic typesetter where type images appear on film and later half-tone dot pictures that could be made without the need for the engraving of metals.

At that time also, the use of wirephoto facsimile became widespread and later supported the concept that an editorial office in New York could quickly compose and transmit finished magazine page images to any remote printing point for the rapid manufacture of printing plates and the early start-up of the printing presses. Rather than taking a day to change the editor's instructions into a finished page of print, it could now be seen that this would be possible in hours.

The development of the high speed color scanner suddenly reduced the man-hours, and, therefore, the time span, between the editor's decision to run a certain color picture and the time that the full color image could be turned out of the printing press.

New hard metal offset plates that are made directly from film copy had been developed. So, in essence, the publisher of news periodicals could see the opportunity of a new way of life where his publications were delivered to the subscriber before they became stale. This was a process that offered the opportunity to combat somewhat the ever-rising costs of an industry that was tied to the manual performance of its many elements.

Time, Inc. decided to explore this new copy handling system but one critical element of the system was missing and this was a high quality, long wearing letterpress plate that could be made directly from the same photographic image as was employed to make the planographic litho plates. There were some substantial reasons supporting the continued use of the high speed letterpress equipment that was being used to print Time, Inc.'s publications. First, there was a large capital investment in these printing machines which meant scrapping and replacing them with lithographic presses would be economically unsound. Second, they had a marked superiority in performance in printing the long run editions of national news magazines.

Besides encouraging and needling the large chemical and metals producing companies, Time, Inc. decided the missing element was important enough to embark on its own research program. The requirement was very simple - a printing plate must be made from a film image in less than an hour; it must reproduce exactly the image elements in the film master; it must have the potential of a press life of at least one and a half million prints; and, of course, it must be made of commercially available, reasonably inexpensive materials, and the platemaking process must be relatively simple and foolproof.

With this in mind, the first investigations in the late 1940s were with metals but it soon became evident that the chemical etching of metals using a resist image on top was too unpredictable due to side etching which did not allow 1:1 reproduction. However, the directional etching of metal by liquid suspended abrasive particles known as vapor blasting showed more promise in tone scale reproduction but presented some formidable problems in abrasive resistance of the protective film layer. Many photosensitive resists were explored, including rubber. One of the materials that best withstood the ravages of the grit blast was a nylon interpolymer. It was applied in a thin film from solution, sensitized with potassium dichromate and then exposed through a negative. The unexposed or non-printing areas were developed out with alcohol, leaving uncoated bare metal ready for grit erosion. The remaining nylon stencil which protected the printing elements was not thick enough to allow deep etching of the metal. Etch depths in the neighborhood of .003" were obtained in metal surfaces such as aluminum and magnesium but these were a long way from the .020" or more necessary for a practical printing plate. Research was undertaken to develop new light sensitizing systems which would produce thicker nylon stencils. It became evident that, as the nylon thickness increased, it lost its role as a resist and, in essence, became a printing plate. We then decided to dispense with vapor blasting and make the entire printing plate out of light sensitive nylon. This approach produced a "one-bite" relief printing image for both type and half-tone that was truly 1:1 in reproduction characteristics. This was unique in the letterpress printing plate field at that time. By 1957, the techniques of compounding, molding, laminating, exposing and developing had progressed to the point where field testing was in order. In addition to a pilot plant in Springdale for blank manufacture, a small plant was set up in Chicago to image the plates for use by one of our printers. Over 1000 of these prototype plates were run on production presses successfully in 1957.

Producing the film matrix or negative was a problem in those days because we had to convert metal relief images to film images through a camera lens where resolution left a great deal to be desired. To use this plate at that time as a substitute for the electrotype with the film converting methods of the day was felt economically unsound. There were photocomposing machines available then but they were not much faster than metal line casting machines. The methods of handling copy by attritional multiple keyboarding of stories also left a lot to be desired. In simple terms, the nylon plate was ahead of its time, and so it was shelved until 1963 when the rest of the system appeared to be catching up. By 1964 the application of the digital computer into the process of preparing copy for the printing press added a greater stimulus to the development of the new copy preparation system.

The reactivation of a project after 6 years of dormancy took some time and by 1965 a new pilot plant was set up in Chicago, but this time with improved equipment which had been developed with the benefit of the experience gained in 1957 on the old machines. Blank manufacture also had been improved along with conversion methods. We are currently running 200 plates a week on our publications and expect to be running 2000 a week by mid-1969 at which time the most essential elements of the new pre-press system will be ready.

This will include a copy processor computer connected to a high speed electronic phototypesetter that will process text for any magazine from a memory stored one line story to a full multicolumn page on film in less than a minute. The equivalent of this as it is done today using teletypesetters and metal casting techniques requires about two hours per page. High quality half-tone pictures will be produced and combined with the text by computer controlled cameras hooked up with automatic film processing equipment in minutes instead of hours as required by today's engraving methods. Such a system coupled with the nylon plate will afford our editors tremendous flexibility. They will be able to close stories on late happening events without causing delivery delays to the readers. Also, finished pages will be immediately available to them at any time during the editorial process instead of the unjustified hard copy that they now must struggle with.

I would like to give you a brief description of the plate composition and how we manufacture and image it. The basic ingredients are a nylon polymer, a monomer, a photo-initiator and a thermal inhibitor, all of which are dissolved in alcohol. This rather heavy solution is poured onto a slowly moving Teflon coated glass cloth belt where it is partially dried. This photosensitive mixture is then granulated and further dried in a vacuum oven. It is then compression molded into a plaque about .080" thick containing one very smooth side which will be the printing surface. In a set of very accurate male and female dies this plaque is then laminated to a precurved aluminum saddle to give it rigidity and accurate caliper. It is then trimmed and/or bevelled on all four sides to match the press lockup. Here you see a picture of the molding powder, the molded plaque and the aluminum saddle. A strippable coating is applied to the blank face for protection and it is then ready for shipment to the printer.

The imaging begins by applying a hard dot negative which is held in intimate contact with the blank face by vacuum. On this exposing machine the nylon blank and negative are mounted on a drum which revolves in front of some high intensity mercury vapor lamps. This ultraviolet exposure takes one minute. The exposed blank is then placed on a spool which in turn is mounted in a developer or washout machine where the unexposed portion of the image is dissolved away by spraying alcohol on the plate. This process requires 9 minutes to get .018" of type depth which is an etch rate of 2 mils per minute. The surface absorbed alcohol is then driven off in a drier after which the plate is ready for press.

The Time nylon plate which will be manufactured and marketed under the trade name of Tilon by Printing Developments, Inc. (PDI), a totally owned subsidiary, will play an important role in the future of high speed magazine publishing. Right now a plant has been designed and will be built by mid-1968 to manufacture this plate in large enough quantities to supply Time, Inc. and its printers. After Time, Inc.'s requirements are met, it will be available to the rest of the graphic arts industry where the need for a photosensitive letterpress printing plate of high quality and long life is growing steadily.

ASSOCIATION POLYMERS FOR PHOTOLITHOGRAPHY

J. L. Silver

Union Carbide Corp.

Bound Brook, N. J.

INTRODUCTION

Association polymers are mixtures of resins which interact primarily by hydrogen bond formation. The association products often have properties which are peculiar to themselves rather than simple averages of the properties of the constituent materials. From groups of these polymers we have developed one which is uniquely suitable for photolithography and related applications. The system is based on poly(ethylene oxide)[1] and phenol-formaldehyde resin. When properly blended, these materials associate through extensive hydrogen bonding.

Poly(ethylene oxide) is available in a variety of grades varying in average molecular weights from less than 50,000 to more than 5,000,000. The very high MW materials are best for this application. The resin is thermoplastic, water soluble, well over 90% crystalline with high viscosity melts and is readily degraded in air at high temperatures.

Phenolic resins are readily manufactured to have extreme ranges of properties depending on the type of phenol, type of catalyst and reaction conditions. The resins are thermosetting, brittle and usually water insoluble, although some special water soluble resins can be prepared.

These particular association products are specially formulated to produce materials which are very hydrophilic as well as very tough and abrasion resistant. The products are non-crystalline and are thermoset despite the fact that poly (ethylene oxide) is present. Additionally, the products are not sensitive to oxidative degradation. The phenolic resins do not cause the products to be brittle or oleophilic. The association products can be prepared as coating solutions or as solids suitable for forming into film.

THE UNION CARBIDE LITHO-PLATE

Various materials which are photo-initiators may be incorporated into the coatings. This results in the areas exposed to light becoming permanently oleophilic. The properties of initial hydrophilicity, development of oleophilicity on exposure to light and toughness provide a surface eminently suitable for photolithography.

Preparation of the plates involves coating substrates with a solution of the association product followed by baking to produce crosslinking. The photo-initiator is applied from solution and the solvent allowed to evaporate.

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[1] Polyox is the Union Carbide Corporation trademark for poly(ethylene oxide).

There is a fundamental difference between our plates and conventional long-running diazo resin-aluminum lithoplates. The latter consist of a light-sensitive coating on a hydrophilic substrate. After exposure, the "unhardened" coating is removed to uncover the hydrophilic substrate. These plates consist of two surfaces whereas our plates provide for both image and nonimage areas to be on a single plastics surface. The substrate is a support only and need not be hydrophilic.

The Union Carbide plate requires no processing, lacquering or gumming. The plate is ready for printing use after exposure. Desensitization to light is readily accomplished either by removal of the photo-iniator by the press dampeners or by the customary wipe down of the plate after mounting on the press.

Conventional plates are subject to dot sharpening and blinding from wear of the oleophilic areas as well as to adhesive failure of the exposed coating. The Union Carbide plate has only one surface and thus there is no tendency for dot sharpening or blinding. The absence of processing provides for better dot reproduction and resolution of fine lines. Press runs in excess of 100,000 impressions have been made.

PHOTO-INITIATORS

The choice of photo-initiator is very broad and, in general, includes materials which produce free radicals or which undergo photoreduction on irradiation. Among these materials are diazonium salts and organic azides, aliphatics containing a multiplicity of halogens on a single carbon atom such as iodoform, acetone-bromoform or carbon tetrabromide, inorganics such as ferric chloride, ferric ammonium citrate, complex salts of vanadium, tungsten or molybdenum, miscellaneous materials such as N-bromo succinimide, photo-reducible dyes or dichromates.

The mechanism through which the coating is converted to an oleophilic surface changes with the type of photo-initiator. Evidence for different mechanisms with various photo-iniators has been collected but in no case has the exact mode of operation been proven. The presence of a number of resins and their interaction with light induced products of the photo-initiator creates a complex situation.

SCREENLESS PRINTING

The properties of the coatings can be varied to great extremes because of the wide choice of phenolic resins, catalysts and additives. This flexibility has enabled us to produce positive-working plates, electrostatic printing plates, lithoplates which require only exposure to strobe or flash gun light or a few seconds to incandescent light and plates suitable for screenless printing.

Screenless printing is of great interest because of the innate ability to obtain great resolution of detail, superior color reproduction and more economy in copy preparation compared to printing in half-tone.

We have developed a plate which prints in continuous-tone. At present, the plate can be run to about 20,000 impressions before a detectable grey scale shift occurs. Negatives of a density range of 1.0 can be printed but the correlation between the printed scale and the negative scale is linear for about 0.7 density units. Linearity over the entire scale can be approached either with masks or by preparing the negative with an electronic scanner. Exposure is not critical in that underexposure can be corrected by simple processing. Overexposure is not correctable. A precise exposure time is not necessary; variation of ±20% will produce plates which still require no processing.

The Union Carbide screenless plate is more akin to collotype plates than to the diazo resin wipe-on positive plates which have recently been employed for screenless printing. Collotype plates have little abrasion resistance, require special handling and are unsuitable for use on offset presses, whereas the Union Carbide plate is tough and all printing is done with conventional handling on ordinary offset equipment. Both are similar in being single-phase plates but are not related in their chemical compositions. Diazo resin-aluminum plates are two-phase plates involving the variables inherent in processing as well as the problems of wear which are responsible for change in grey scale values during press runs and difficulties in printing of highlights.

ACKNOWLEDGMENTS

The foregoing discussion includes the valued contributions of various members of the R&D staff of Union Carbide Corporation at Bound Brook, New Jersey. These include Drs. Quarles, Carrick, Shaw, Pollart, Mr. J. Wheeler, and others.

PHOTOPOLYMERS FOR PHOTOENGRAVING AND PHOTOLITHOGRAPHIC PRINTING PLATES, PHOTOGRAVURE TISSUES, AND PHOTOSCREEN STENCILS

Jack J. Bulloff

Columbus Laboratories

Battelle Memorial Institute

Columbis, Ohio

Despite widened interest (1-10) for use of photopolymers in making printing plates (11-15) for letterpress (16-17), lithography (18-21), gravure (22-24), screen (25), and other printing processes that employ photomechanical platemaking (26-37), the polymer chemist rather than the polymer engineer has been asked to lead the way to improved printing. There has thus been a tendency to fit photolithography (42-45), photogravure (46-47), photoscreen (48), collotype (59-50), and other photoreproduction (51) without considering that the special solid-state properties of polymeric systems, like cohesion and adhesion (52), might permit more revolutionary innovations in platemaking and printing press operation. This chemical concentration and physical unawareness is amply reflected in the literature of photoresist (53-255, P1-P134) and other photosensitive (256-257, P135-P270) coatings. Once the literature has been surveyed, this condition and its remedy can be more definitively discussed.

PHOTOENGRAVING

The literature of photoengraving best reflects the present status of photopolymer chemistry and engineering in the graphic arts. Two kinds of engraved plates may be made, raised-image plates where nonimage areas are cut away leaving image above the base metal to be inked on rolls and squeezed onto paper for printing, and sunken-image or intaglio plates, where image areas are cut into the plate so they can hold ink after inking from rolls and doctoring excess ink off the raised areas. Then the ink in the depressed areas is queezed out onto paper to give the so-called gravure image.

In photoengraving, the engraving metals are used to make the plate-copper, zinc, magnesium, aluminum or special alloys. The metal is coated either with a photosensitive resist or with a resist that is then made photosensitive by imbibition of a photosensitizer. The dried plate is exposed to a photographic negative transparency under actinic light. The resist in the image areas is thus photohardened or photoinsolubilized against removal by developer which more readily dissolves nonphotoexposed resist on the nonimage areas. After development, the plate is ready for etching away of the nonimage areas.

Some resists are not hard enough to withstand etching without further hardening by oven baking. There are also resists whose development requires heating before development. But whether a hot or a cold processing is used, the etch-ready plate ultimately consists of an image protected against etchant by a resist and of nonimage area that is bare metal. The etching process is then analogous mechanically to the development process for photopolymer letterpress plates like the DuPont Dycril Photoplate described in this journal's report of the First Technical Conference on Photopolymers of the Society of Plastics Engineers, Inc., which was held in Ellenville, New York, on November 6 and 7, 1967. The same problems of etch factor and image undercutting have to be considered, but here they are the concern of the metal chemist and metallurgist rather than of the polymer chemist and the polymer engineer.

The concerns of the latter have to do with the resistance of photohardened polymer coatings to photoengraving etchants like nitric or hydrochloric acids, ferric chloride or peroxydisulfate solutions, and to the chemical milling of coatings that directed splashing in mechanical etching tends to enhance. Before photopolymers came upon the scene, various colloids sensitized by ammonium dichromate solution were the mainstay of a variety of photoengraving coatings.

Albumen, process glue or gelatose, shellac or cold enamel, and casein were used as the colloids, and always with ammonium dichromate as the preferred dichromate salt photosensitizer (53). The dichromate ion set photosensitivity at 300 and 380 millimicrons (54-57), and provided unwanted dark reaction.

Polymers entered photoengraving successfully with the study of dichromate-poly(vinyl alcohol) photoresists as substitutes for process glue (58). Dichromate-PVA systems had become of interest earlier (P1-P3) in attempting to control natural variations in gum arabic used in deep-etch photolithography by isolating gum components and making photosystems out of them, e.g., dichromate-arabogalactan (P4). Such systems have continued to be of lithographic interest (P5-P9). Another early attempt involved the photosensitization of phenol-formaldehyde resins (P10); the low photosensitivity was ultimately corrected by using iodoform as a photoabsorbing photoradical sensitizer, a ketone as an added photoradical generator, and resorcinol as a hardening or crosslinking agent for the phenol-formaldehyde system (59). The improved photoresist could only be developed with ketone-alkanol mixtures.

Once nonaqueous development, with all of its disadvantages, was accepted for photoengraving, aqueously sensitive photolytes could be avoided and durable photoresists could be sought more easily. One line of investigation, Eastman Kodak Company's, led to the well-known poly(vinyl cinnamate) photoresists.

POLY(VINYL CINNAMATE) PHOTORESISTS

Kodak's studies had started with a consideration of the shortcomings of dichromate-colloid photosystems. During the period 1936 to 1952, patents were taken out on systems like that of piperine, which was photopolymerized to piperite using benzoyl peroxide photoinitiator. The piperite resist still required thermal hardening to serve as a photoengraving resist, but it resisted swabbing with soapy water, solution by ink vehicles, and dissolution by acids and alkalies (P11). The rationale developed during this period of research led to the discovery of cellulose-poly(vinyl cinnamate) photoresists (P12-P20), initially photosensitized by nitroaryl compounds (P12). Typical nitroaryl sensitizers are p-dinitrobenzene, 1-nitronaphthalene, and beta-nitrostyrene (P16).

Poly(vinyl cinnamate), usually 95 to 97 per cent cinnamoylated poly(vinyl alcohol) (PVA), was probably the material first marketed as Kodak Photo Resist (KPR). After photohardening (by at least a dimeric crosslinking), often with post-development thermohardening, and development with 75:25 toluene:chlorobenzene mixture, KPR can withstand etches for copper. The unsensitized material has a photosensitivity of 2.2 x 10^{-8} metercandle-sec^{-1} (60,P13).

Spectral sensitization increases the photosensitivity greatly. At practical, 5 to 10 weight per cent levels, Crystal Violet carbinol makes poly(vinyl cinnamate) 100 times as sensitive. The carbinol's decomposition product, Michler's ketone, is even more efficacious, giving 250-fold photosensitization. With 3-methyl-1,3-diaza-1,9-benzanthrone, 500-fold sensitivity is attained; peak absorption is shifted from 320 to 470 millimicrons and the absorption limit from 470 to 490 millimicrons. The way poly(vinyl cinnamate) and its analogues (60-61) are photosensitized, and the electron-sensitivity of KPR and its homologues--KMER, KOR and KTFR (62)--is superficially like that of silver halide emulsions (63-69). The spectral sensitization of poly(vinyl cinnamate) and related photoresist materials can also be brought about ty dyes like those used in silver-halide spectral sensitization (65, 69-76).

SPECTRAL SENSITIZATION

Photoresponsive materials must be photoabsorbing (77-83). In general, photoabsorption is electronic in nature. Data on IR (84-88), visible or optical (89), and UV (89-91) spectral absorption indicate the relation of electronic band (92-97) and bond (98-104) structure to the photoabsorption. Absorptimetric data relevant to photographic imaging have been gathered for conventional or silver-halide (63-68, 105-109) and unconventional or nonsilver halide (1-11, 110-119) photographic materials. These data include absorptimetry of dyes and pigments (120-124), but the absorptions of greatest relevance are those involved in the specific study of spectral sensitizers (63, 65, 69-76, 125-132).

Absorption deepens and tends to shift toward longer wave lengths as more electrons are involved per unit area and unit volume of absorber. Resonance favors photoabsorption, so multiple-bond absorption is greater than single-bond absorption, and conjugated-multiple bond absorption is greater than unconjugated-multiple bond absorption, and planar molecules absorb better than nonplanar ones of equivalent bond order. If resonance is sufficient to cause delocalization of electrons from the valence into the conduction band, causing semiconduction, as in the phthalocyanines (133) or the highly-conjugated polymethine or polycarbocyanine dye sensitizers, properties develop that make the photoabsorbers poor film formers and poor polymerizers, as well as insoluble and incapable of change of solubility by photoreaction.

Thus, there are limits to what can be done for autosensitization of polymeric systems. In ethylenic monomers that polymerize by addition, and are small molecules, multiple bonding, especially if conjugate, gives rise to extreme susceptibility to thermal polymerization. Even in large molecules increasing the double-bond frequency on a straight chain leads to chemical instability (72). Avoiding chemical instability by use of aromatic resonance in condensed rings works, but at the cost of good filming and coating properties. Side-chain photoabsorption might be better to introduce than main-chain photoabsorption in monomers or prepolymers since photoabsorption would then not dwindle as polymerization reaction chains were initiated, propagated or transferred, and terminated. This approach is as valid for crosslinking as it is for intramolecular growth from a monomer or live polymer in producing photoinsolubilization or photohardening; it has to be modified where scission or degradation is required for imaging by, e.g., photosolubilization or photosoftening.

Where monomers or prepolymers are insensitive to wave lengths of photomechanical interest, currently near 3650A, and the desired spectral response and speed of photoresponse cannot be provided integrally, external sensitizers mus be employed (133-152). The different mechanisms for polymerization and photopolymerization (153-197) often require different sensitization than do silver-halide photomaterials (198-215). With present knowledge of the mechanisms, it is not easy to distinguish between spectral and chemical sensitizers, i.e., between the photoinitiation of polymerization and the improved activation of photopolymerization. Much study is required to uncover radicals and photoradicals that initiate and transfer polymerization chains and crosslinks without unduly promoting premature dark or thermal polymerization or providing undesirably increased chain termination. Certainly, more active radicals than those the monomers might provide would often be wanted for sensitization, and the most photoactive monomers possible would also be sought. A second part of the search would be for polymers with the desired film-forming, coatable, developable (soluble), etch-resistant (photoinsolubilized and photohardened), and sometimes mechanical (hardness, tenacity, adherence) properties need for photoengraving or other photomechanical application. None of these can be divorced safely from spectral sensitization.

Thus, special cognizance must be taken of the fact that in the literature there can often appear confusion between photoinitiators or photopromoters of polymerzation and photopolymerization, between the trade term sensitizing and the scientific terms chemical and spectral sensitizing, and between increasing the speed of photoresponse with and without a shift of the wave length or the change in the extinction coefficient or physical thickness of a photomechanical coating. In this paper, every attempt has been made to use references where confusions of these kinds are absent or minimal.

In addition, the reader can refer to detailed and unambiguous basic studies of known photoreactions in mobile (216-227) and rigid (228-236) systems. Such simpler systems, rather than the complex one of complicated application are actually the basis of what theories yet exist for the discovery and spectral sensitization of solid-state photopolymerization in photomechanics.

OTHER CINNAMOYLATED PHOTOENGRAVING RESISTS

The success of KPR-type photoresists (60-62, P12-P20) was preceded and followed by studies of other like materials, e.g., cinnamates and cinnamals. In early work (P21-P22), anisal cinnamal acetone, isocis-cinnamal acetic acid, and dicinnamal acetone were studied as photohardeners of shellac (i.e., as bichromate substitutes for cold top photoengraving, e.g., P23), particularly in the special application of etching glass (in 48 per cent HF, P24). Where a graphic arts application was in prospect, such resists were dyed for readout of the image (P25) formed after solvent development (P26-P27). Often it is advantageous to have photoresists that change color intrinsically during photoexposure, so imaging can be followed without development, and to have aqueous rather than nonaqueous development. The latter often requires flammable or nonious solvents, and may create a sewage disposal problem in plant operation. Thus, one aspect of uncovering new photoengraving resists is the provision of chromophore (or colorant, 120-121) and hydrophile (these are discussed for photolithographic coatings) functional groups in the monomer-polymer system.

Cinnamoylated materials were first used for their ketonic, >C=O, rather than for their ethylenic, -C=C-, functionalities. They were selected to function like such sensitizers as isonitrosoacetophenone (P21-P22), piperonalacetophenone, benzalacetophenone, alketones [RCH:C.C(:O)C(:CHR).X, R = furfuryl, styryl, or aryl, X = 5 or 6 carbon cyclic structure, P27], ketones [O.CH:.CH:C.C.(O) or $(C:C)_x$-(C(:O)CC:C$)_y$, $x + y > 1$, x or y = 0, 1, 2 or 3, P28], furylideneacetone (P29), aldehydes [R$(CR':CR'')_x$CHO, x = 1 or 2, R = aryl or heterocycle, R' and/or R" = H, aryl, or alkyl, P30], piperonylideneacetaldehyde, β-(2-furyl)acrolein, α-furfurylidenepropionaldehyde, 1-phenyl-1,3-pentadienal (and the corresponding dione), 2,5-difurfurylidenecyclopentanone, and RCH:CHC(:O)$(.CH:CH)_n$R', RCH:C.C(:O).C(:CHR).Z, and RCH:C.C(:O)Z, n = 0 or 1, R and/or R' = alkyl, aryl, aralkyl, or furyl, and Z = the completing atoms of a carbocyclic ring. Ketone sensitizers were both spectrally sensitized and marked for readout by use of cyanine dyes. Aldehydes were acid-developable, and thus served as resists for alkaline etching only, e.g., dissolving of zinc as zincate and of aluminum as aluminate.

Thermal inhibitors like hydroquinone, chloranil, thiazine dyes, 2-(cinnamylideneacetyl)thiophene (P29) and quinone (P31) had to be employed for ketones like 1-cinnamylidene-3-furfurylideneacetone, 1-cinnamylidene-3-(ar-methoxybenzylidene) acetone, cinnamylideneacetophenone, α-cinnamylidene-γ-citrylideneacetone, and α,γ-dicinnamylideneacetone. Otherwise cellulose ethers or acrylate resins (P24, P27) or other resist materials such sensitizers can photoharden are dark-hardened prematurely. Ketones like these suggested the use of the polymeric ketones discussed below, while the systematic study of acrylate resist materials and cinnamoyl sensitizers suggested the study of poly(vinyl cinnamate), which is essentially the phenylacrylate-acetate polyester of poly(vinyl alcohol) and of other polyesters, and from the study made, the KPR solvent-developable photoresists have emerged. Since, search has continued for analogous aqueously-developable resists.

Azido, nitro, amido, nitrilo and alkali-metal derivatives of cinnalylidenemalonic acids are developable in weak acids (P32-P33). The polyesters of such acids seem to yield good resists for copper (ferric chloride etch) photoengraving (P34). However, these have to be developed in cellosolves. Sensitizers like 2-(benzoylmethylene)-1-methyl-β-naphthothiazole were used for moieties like R':CH.CH:C(CO-)-(COORO-), where R' = alkylidene, aralalkylidene, or heterocyclic, and R = alkyl, and like R':CH.CH:$(COOH)_2$ in the early work (P35). In general, photoresists of (C:C.CO) esters developable in acetone differ in having both vinyl side chains on aryls as well as ester bonds to acids (like cinnamic, P36), and they crosslink after prepolymerization (P37).

Polyamides of the cinnamylidenemalonic acids, R:CH.CH:C$(COOH)_2$, photocondense with styrene-maleic anhydride copolymers, e.g., N-(m-hydroxymethyl)phenyl cinnamides, with sensitizers such as methyl-2-(N-methylbenzothiazolylidene)dithioacetate (P38) or 2-(benzomethylene)-1-β-naphthothiazoline (P39). Compounds that are related, like poly(vinyl-N-[p-cinnamoylphenyl] urethane) are 280 times as photosensitive as KPR (P40-P43). With the sensitizer just mentioned, maleic-anhydride copolymers terpolymerize with hydantoins, arylamines, hydroxyalkylrhodanines, acetophenones, and chalcones (P39, P44-P49), and the copolymers give nitric-acid etch resists with monocinnamic acid esters of glycols such as 2-hydroxyethyl, 4-hydroxybutyl, or diethyleneglycol, and with the mono-o-chlorocinnamate of the latter (P47). However, more versatile photoresists are obtained from poly(vinyl ketones) that are more simply compounded.

POLY(VINYL KETONE) PHOTORESISTS

The type poly(vinyl ketone) resists are derivatives of poly(4-vinyl acetophenone), e.g., benzaldehyde-ar-vinylacetophenone polymers, which resemble bis-(4-dimethylaminophenyl) ketone-sensitized poly(vinyl cinnamates) that may be used with them (P51-P54). In general, the monomers CH_2:$CHYCOCH_3$, Y = either substituted or unsubstituted cinnamaldehydes or else aromatic nuclei, form polymers, e.g., poly (cinnamylidene-ar-vinylacetophenone) or poly(benzylidene-ar-vinylacetophenone) that photoinsolubilize by crosslinking that is essentially dimeric (P53), in the manner of the closely-related poly(vinyl acetals), e.g., poly(vinyl monoterephthal-p-methoxyacetophenone) polymers (P55), and the styryl Ketone polymers (P56).

Poly(vinyl acetophenone-co-trans-benzalacetophenone) is about 640 times as photosensitive as poly(vinyl cinnamate) by standard sensitometry (237). Poly(4-vinylaralacetophenones) like poly(4-vinyl acetophenone-co-anisalacetophenone) can be 4600 times as sensitive (238) as poly(vinyl cinnamate), in contrast to the best of the cinnamoylated photoresists, which can be sensitized to a sensitivity 6000 times that of standard (95 per cent cinnamoylated; 5 per cent unhydrolyzed acetate) KPR (3, 239, cf. P57-P64, especially P61, involving 3-substituted cinnamoyl phthalic anhydride adducts of partially-hydrolyzed polyvinyl or cellulose acetates). Related salt-forming polymerizates have poorer photosensitivity and resist properties, and require oven-baking for ferric-chloride etch photoengraving, e.g., quaternary ammonium alkylsulfates like poly(4'-dimethylamino-1-methyl-5-vinyl-2-stilbazolium methosulfate) resist (P65-P68). However, these latter can be developed with alcohol, which is an advantage compared to the solvent development required by KPR, especially where etches against which KPR has to be heat-hardened anyway are to be used, as in printed-circuit and precious metal etching.

In these and similar photoresist materials (P57, P61, P69-P72), sensitization which may be both chemical and spectral, is given by cyanine and triphenylmethane dyes, quinones, anthraquinones, benzophenones, ketones like bis(cinnamylidenevinyl) ketone, benzanthrones, phenoxazines, and especially by thio-derivatives like thioxanthones and phenothiazines. Heavier chalcogenides ought to be even more effective because of heavy-atom slowed resonance favoring longer-wave length absorption and less stabilized bond configurations, e.g., selenium and tellurium compounds. So far, the polyketone resists have not been as useful as the poly(vinyl cinnamate) or certain azidovinyl type photoresists.

AZIDOPOLYMER RESISTS

Azidopolymers emerged from studies of photosensitive-azide (5) sensitization of nonphotosensitive colloids. These studies were made to discover dark-stable substitutes for bichromate sensitizers that might resemble dark-stable diazo photosensitizers (240-242). Polyazides like poly(vinyl acetate-co-4-azidophthalate) are 100 times as photosensitive as poly(vinyl acetate-co-cinnamate) and early sensitizing additives increased this photosensitivity by 400 times (243). The basic photosensitivity of poly(vinyl acetate-co-azidobenzoate) is only 50 times that of poly(vinyl acetate-co-cinnamate), and it can be sensitized to 1810 times the sensitivity of KPR. Sensitizers like disodium-1,9-disulfo-2,8-dimethoxy-3,7-bis(o-methoxybenzamido)-dibenzothiophene-5,5-dioxide (P73), like dioxides, and various stilbene and styryl compounds give 0.5-per cent ammonia-developable photoresists 800 times as fast as KPR.

Combinations of 3-azidophthalic anhydride, poly(azidostyrene), poly(vinylazidoacetate), and poly(*m*-azidobenzaldehyde vinyl acetal) give a variety of resists (P74). The azidopolymers have good film-forming properties if the azido groups are on the side rather than on the main chains (P75). The 4*a*-azanaphthalenes, 4-oxo-1,4*a*-diazanaphthalenes, 4-oxo-1-thio-3a,7-diazaindones, acridones and thioacridones sensitize such polymers (P76). Thus, poly(vinyl acetate azidobenzoate) 55 times as fast as KPR can be made 2000 times as fast with 4-oxo-4*a*-azanaphthalene, and 2500 times as fast with 4-thio-4*a*-azanaphthalene; it is intriguing to speculate what heavier seleno and telluro, and perhaps phosphorus and arsenic, substitutions and use of a larger nucleus than naphthalene might do. For without such enhancing substitutions, either 4-oxo-4*a*-azanaphthalene increase the speed of poly(vinyl acetate-3-[4]-azidophthalates) from 45 to 1400 times that of KPR.

Many azido photomaterials are copper-etch resistant, e.g., azido-ketones (P77), diazido-gum arabic compositions (P78), diazido-(polyacrylic acid and poly (vinyl pyrrolidone) polymer or copolymer) compositions (P79), and poly(*p*-azidocarbonylstyrenes) which are methylenechloride developable (P80), but often only after the use of heat-hardening before or after development, e.g., poly(vinyl pyrrolidone) photohardened by disodium 4,4'-diazido-2,2'-stilbenedisulfonate or sodium 4-azidobenzylideneacetone-2-sulfonate requires 5 to 10 minutes at 330°F to 350°F to withstand acid etching (P81). Other azide-colloid or azidopolymer systems abound (e.g., P82-P87), but in general, lack of etch resistance (rather than lack of photosensitivity) has made them less successful in photoengraving.

The photosensitivity of autosensitization can obviously be variously increased by side-chain substitutions of one or more kinds of spectrally and chemically (free-radical producing) sensitizing groups. This may be accompanied by various external sensitizations in addition. It remains to be seen how compatible all of these means are with maintaining desired coating, adhesive, cohesive, developable, and etch-resistant properties. So far, much remains to be said for use of materials that crosslink to give resists with the desired physico-chemical and mechanical properties on simple external sensitization with a dark-stable sensitizer that equals or exceeds bichromate sensitizers in performance.

DARK-STABLE SENSITIZERS

Dark-stable diazo compounds useful in diazotypy(5,240-242) are not necessarily useful for photoresists. Only those that do not impair the physical properties of a coating on photoexposure and washout development, and which generate photoradicals or other photolytes that promote polymerization and/or crosslinking adequately can be used. The so-called diazoresins (5) harden ethylenic, particularly vinylic or acrylic, polymers or copolymers best. Such resins were once viewed as low polymers of diazotized tetrachlorozincates of *p*-phenylenediamine. It is now apparent that they may be only monomer-dimer mixtures (244), and there may be uncertainty in the chemical composition and structure of other diazotated resinous materials (P88). The term "diazoresin" should perhaps not be applied to coprecipitates of diazotated *p*-phenylene with condensates of cresolsulfonic (P89), benzylnaphthalenesulfonic, naphthalenesulfonic, phenolcresolfulsonic, or like acids or 4,4-dihydroxysulfones (P90), which require reinforcement with a novolak like Alncval K429 to form a photoengraving resist (P88). Such resists have to be coated from ethyleneglycol monmethyl ether or like solvents but may be developed with 5 per cent sodium metasilicate solutions for etching with 35per cent ferric chloride.

Resists that may be developed in dilute sodium hydroxide solutions are formed from polymers formulated as $(2,3\text{-}XO_3S(\text{-}CH_2)6_6H_3)_n$, X = *o*-quinonediazide (really a diazoanhydride) of the benzene or naphthalene series, again with fortification by novolak (or polyester) resins for ferric-chloride or nitric-acid etch resistance (P91). Novolaks are distinguished from resoles (245-252) in that the former are nonthermosetting or thermoplastic, and formed by acid-catalyzed condensation of phenol with less than an equivalent (usually 0.8 to 1.0) of formaldehyde; the latter are thermosettable, and formed by base-catalyzed condensation with excess formaldehyde (usually 1.0 to 1.5 equivalents). One or the other dissolves in oil if the condensation is essentially linear, but for either, above a heptacondensate or with any branching, alkaline resin solubility becomes negligible (253).

Novolaks (and resoles) and condensed sulfonate resins, as well as poly(vinyl butyral), poly(vinyl acetate), poly(vinyl crotonate), or urea (or diazine or triazine)-formaldehyde resins, alone, or mixed, are photosensitized by *p*-morpholinobenzenediazonium chlorozincates (P92). The poly(vinyl butyral) photohardening permits it to withstand 40 per cent ferric chloride etch (P93). All the diazo sensitizers - there is no literature implying exception - seem convertible to diazido sensitizers by simple reaction with sodium azide (P94-P96).

Diazido compounds can be hardened without additives to resist copper etches (P77), e.g., 4,4'-diazidobenzeneacetone, 1,3-bis(*p*-azidophenyl)-2-propene-1-one, and 1,2-bis(*p*-azidocinnamoyloxy)ethane. Compounds like $4,2\text{-}N_3(NaO_3S)C_6H_3CH{:}CHCOMe$ (P78) photoharden gum arabic for 40 to 60 per cent ferric chloride etching in the presence of 0.13 per cent of free acid. The photohardening of gelating and its substitutes is accomplished by azides that are simple analogues of diazo compounds in structure (P94-P98), e.g., the hardening of poly(N-methylacrylamide) and poly(N,N-dimethylacrylamide) (P99), poly(vinyl pyrrolidone) (P81, P100), novolaks (P101), polyamides (P102-P111), poly(vinyl butyrals) (P107), elastomers (P82-P83, P109-P116), acrylonitrile and acrylic acid polymers and copolymers (P117), and methyl acrylate, vinyl alcohol and acetate, styrene, alkylamine and acrylamide polymers and copolymers.

Many dark-stable sensitizations are possible, as can be seen from the preceding and succeeding examples. Photoinitiations are possible for ionic as well as for free-radical polymerizations and crosslinkings, e.g., formation of polyoxymethylenes by cationic polymerization of monomers like vinyl-2-methoxyethyl ether, initiated by photolysis of $Ag_2B_{12}Cl_{12}$ or of $Ce_2(B_{12}C_{12})_3$ or other polyboron compounds (P118-P119). Photoinitiation of anionic polymerization also seems possible. Polymerization based on heterolytic photoscission is after all only a natural extension of that based on homolytic photoscissions which can yield electropositive and electronegative as well as relatively homopolar radicals; heterionic mechanisms should not differ too greatly kinetically from heteropolar biradical mechanisms.

Dark-stable sensitization makes factory-presensitized photoengraving plates possible (254). Presensitized plates, much better known in lithography than in letterpress or gravure printing, are more uniform than shop-sensitized plates and their use involves labor-saving processing and rationalized production. Presensitized plates have revolutionized short-run printing and in-house duplicating and have given small offset presses unprecedented popularity. So far, this growth has been for photomaterials exposed under negative photographic transparencies. Recently photomaterials exposable under positive phototransparencies have been prepared in dark-stable form, which will extend the presensitized-plate revolution further, not only from negative-working to positive-working platemaking, but also into the middle-length and long-run printing of newspapers, books, magazines, packages, and commercial format items in general.

POSITIVE-WORKING SENSITIZERS

Positive-working photomaterials can be derived by use of photosolubilizing or photosoftening materials, or by various post-photoexposure reversals of traditional negative-working (photoinsolubilizable or photohardenable) materials, or by photoinhibition of polymerization (255). The first approach is exemplified by the diazo oxides (P120-P122), e.g., N-dehydroabietyl-N-2-hydroxyethyl-2-diazo-5-oxo-1-naphthalene sulfonamide, N,N'-didehydroabietyl-N,N'-ethylenebis [6(5H)-diazo-6(H)-oxo-1-maphthalenesulfonamide]. Diazo oxides like these produce positive-working counterparts of negative-working diazido-sensitized coatings like, e.g., poly(vinyl ethers), poly(vinyl methyl ether-co-maleic anhydride), phenol-modified coumarone-indene resins (which resemble novolaks), and hydroxyethyl celluloses and cellulose ethers and esters, sensitized by disodium 2,2'-diazidostilbene-4,4'-disulfonate.

The use of solvents with different solvation parameters can give a choice as to whether the unexposed or photoexposed portion of a coating will be dissolved. Thus, alternate developments are available which can make a coating either positive-working or negative-working as is desired. Sensitizers so treatable include the stilbenes, e.g., 2,2'-disulfanilidostilbene and 4,4'-diacetylamino-2,2'-disulfanilidostilbene (5), sulfonic acids of the anhydrides of 1-diazo-2-naphthols and 2-diazo-1-naphthols(diazoanhydrides), and halo, nitro and other derivatives of bisdiazo-*p*-phenols or indazoletriazolenes (P123). The p-iminoquinone diazides (P124) give positive-working coatings either alone, or with poly(acrylic or methacrylic acids), or when used with other sensitizers, e.g., N-(4'-methylbenzene-1'-sulfonyl or 1'-anthracenesulfonyl)imino(1)-2,5-diethoxy (or methoxy or benzyloxy) benzoquinone-1,4-diazide(4) (P125), hydrazine derivatives of o-quinine diazides (P126), or variously substituted S-alkylthioarylamine perchlorates (P127).

Photodegelation softening (P128) yields positive-working resists, e.g., poly (acrylamide) coatings (P129). So does photosolubilization of formaldehyde condensate resins of $4\text{-}C_6H_5NHC_6H_7\text{-}NH_3^+PF_6^-$ internal salts; solubility in alkanols such as isopropanol is promoted for these alone or in admixture with poly(vinyl phthalates) or like resins (P130). Methylbenzothiazolylidene-sensitized tetramethylenecinnamylidene malonate-poly(tetramethyleneglycolcinnamylidene malonate) resins (P131) and cinnamylidene malonate coatings (P132) also photosoften. Direct positive images are also obtained from poly(vinyl alcohol) sensitized by benzoin (P133), and from anthrylenes (P134). But these and most of the preceding positive-working photosystems are not acid-resistant enough for the prolonged etching required in photoengraving, and are far more easily applied in making photolithographic plates where development and etching are done much more superficially and speedily.

PHOTOLITHOGRAPHIC PRINTING PLATES

Photolithographic plates (11-15, 18-21, 26-37, 42-45, 51, 64) can be divided into surface plates and deep etch plates. In surface plates, residual coating that is hard and insoluble is left on the developed plate to define and print out an image on the press. Traditionally, inks have been oily, and the residual coating has been oleophilic and hydrophobic so that it defines the image area in lithography; the nonimage area is made up of metal that is either hydrophilic or treated to be hydrophilic that is maintained oleophobic (or desensitized) by the presence of an aqueous fountain solution on the press. The fountain is usually acidic, and generally contains a hydrocolloid so it can renew the desensitization of nonimage areas.

Thus, the conventional surface plate is covered with a positive-printing coating that must be negative-working, i.e., delineated by photoexposure under a negative photographic transparency. Were aqueous inks used, then an oily fountain would have to be employed, and the coating would have to be hydrophilic and oleophobic, and the fountain would have to maintain a nonimage surface in oleophilic and hydrophobic desensitization. Alternatively, such a coating could be oleophilic, but exposed under a positive, and used with aqueous ink so the image could be printed out from the areas developed free of resist. Still another reversal is by direct use of a positive-working oleophilic resist. Innumerable changes can be rung so that a given photomaterial can be given either a negative-working or a positive-working or a negative-imaging or a positive-imaging character as is desired.

The conventional deep etch plate process involves the conversion of a conventionally negative-working coating into a positive-working plate. The coating is selected to be hydrophilic so that it photohardens to give an oleophobic residual on the plate, called a stencil. On development, the bared area is made ink-receptive (oleophilic) by coating with a lacquer which remains in the metal areas but not on the stencil areas that are then stripped to expose desensitizable metal (the lacquer is nondesensitizable). Deep-etch lacquers are applied after so-called deep etching has followed initial development, so they are intaglio relative to the stencil, which is thus in slight relief (actually, because ink film thicknesses are greater than the ultimate relief in a deep etch plate, such plates remain essentially planographic, as is characteristic of lithography). The relative lowness of lacquers compared to lithographic coating residuals tends to make deep etch plates able to print more copies without wear of the imaging layer than surface plates, even where the lacquer has no hardness advantage. But quite hard vinyl and epoxy lacquers can be made, and the photochemist's art has not yet secured like photohardening for thinnest photomaterials.

The length of run can be increased still further by replacing the lacquer with a relatively oleophilic metal by chemical (e.g., copperizing of aluminum, or Kanigen-plating of iron) or electrochemical plating. A still better way, and one which fixes deep etch depths precisely, is in the use of bimetallic or polymetallic plates in which a surface coating of a hydrophilic metal like aluminum is etched away to expose an image layer of copper. Obviously the opposite working or imaging is produced if it is copper that is etched away to expose aluminum. Thus, still another kind of reversal procedure is introducible into platemaking with photomaterials. Thus, both the negative-working (53-62, 238-242, 254, P1-P119) and positive-working (255, P120-P134) photomaterials already discussed can be applied to photolithography variously, as well as to photoengraving, and often may serve better as lithographic sensitizers than as engraving photoresists. But the best photolithographic coatings have been made from materials that evolved within lithography rather than from those that have been developed for other applications.

PHOTOLITHOGRAPHIC COATINGS

The photolithographic coatings used until recently were, as in the case of photoengraving coatings, bichromate-sensitized colloids (18-21, 31-36, 42-45). Egg albumin, usually written albumen, was the standard for surface plates, and gum arabic was the standard for deep etch plates. But other colloids, especially those applicable to photoengraving, were also used: gelatin, animal and fish glue, casein, soya bean protein, and shellac. More recently synthetic polymeric resins have been used: urea-formaldehyde, polyacrylic, polyvinyl alcohol (by itself, with the chloride, or with gum arabic); cellulose acetate has also been employed. Some of these macromolecular materials have been sensitized with silver halides or halogens (iodine is used specifically for the furfuraldehyde-amine resins), but the bichromates have always been preferred as photosensitizers.

More recently, other macromolecular materials have been used with bichromate sensitization: urea-aldehydes (P11), polyvinyls (P1-P3, P5-P9), arabogalactans (P4), alginates (P135), proteins (P136), methyl vinyl ethers and maleic anhydrides and maleamic acids (P137), dextran polysaccharaides (P138), polyvinylpyrrolidones and styrene-maleic anhydrides (P139), polyamides (P140), zein (P141), and poly (vinyl methyl ether-co-maleic anhydrides) (P142). Auxiliary hardening has been provided by the incorporation of bifunctional or polyfunctional hardeners such as mesoxydialdehyde for gelatin (P143), glyoxals (P144) for albumen (P145) or urea-formaldehydes (P146-P149), polyhydroxyaryl dyes for polyvinyls (P150-P151) or rubbers (P152), and various dialdehydes for poly(vinyl butyral), diazonovolak, polyamide, and hydroxymethylpolyamide photolithographic coatings.

Other photosensitizers have been studied for colloid photohardening, e.g., magnesium 1-nitronaphthalene-8-sulfonate for gelating (P153), bis(3-formyl-4-nitrophenyl)phthalate (P154), nitronaphthalenesulfonic acid amides and esters (P155), nitrocinnamaldehydes (P156), o-nitroaldehydes for novolaks (P157), 4,4'-dinitrostilbenes (P158) and other stilbenes (5, P158), nitrones (P159), sulfones (P160) and sulfone-cinnamaldehydes (P161), acenaphthenes (P162-P163), benzamidazoles (P164-P166), arylamides and fluorenes (P167-P168), phenothiazines (P169), hydrazines (P170), and phosphorylated vinylics (P171). Michler's ketone and hydrol were applied to sensitizing epoxy resins (P172) and methylvinylnitrosamine (P173) and allylpropenylnitrosamine (P174) to epoxides, e.g., poly(glycidyl methacrylate). The epoxies had to be drastically heated to make them etch resistant for photoengraving.

The most fruitful general sensitizing approach was to use diazo compounds (5) for sensitizing, first successful for presensitized paper plates for short-run lithography (P175-P176). Quinone diazides like sodium N,N-2,2'-disulfo-4,4'-bisphenylenebis(2-sulfamoyl-1,4-naphthoquinone-4-diazide) colored with erythrosin were used to photoharden poly(vinyl pyrrolidone) both for surface and deep etch plates (P177). The use of quinone diazides (5, P91, P123-P126), especially to photoharden novolaks (P178) for weak sodium phosphate solution development (P179-P180) is notable. Quinone diazides can also be condensed with novolaks (256, P181) to give polymeric surface plate coatings. The use of Alnoval 429 and similar novolaks (245-253, P88-P92, P157) has been often mentioned in diazo and other sensitization literature (257, P182-P188).

The quinone diazides used in such photohardenings (P91, P178-P180, P184, P189) were originally developed to do away with colloids altogether in photolithographic coatings. Instead, they have become better known for photohardeners of a range of macromolecular materials, ranging from polymeric polyelectrolytes (P190-P192) to covalent interpolymers, and a large literature has developed (P175-P180, P193-P208). Other diazo compounds seem equally adapted for noncolloid photolithographic coatings, especially those that are of high molecular weight per se (P209).

But the most successful diazo compounds, intended to be of high molecular weight, the diazoresins (5, 240-242), have turned out to be small molecules (244). They are described as macromolecular or polymeric, or assumed to be resinous in many publications (P210-P236). Neither these nor a large practical literature (5, P88-P90, P190-P191) on the resins and on the way they photoharden colloids or polymers (P237-P248) explain the photohardening mechanisms actually involved.

Despite this, diazoresins have led in the revolution of dark-sensitized coatings, presensitized plates, and wipe-on or thin-film plates that has changed the character of duplication and short-run offset printing in the United States most markedly. Current advances in platemaking without halftone screening, the so-called continuous-tone printing in full color, also emerge from the surface characteristics of diazoresin photolithographic coatings. Most important, the successes of diazoresin sensitizations have inspired searches for other sensitizers.

OTHER SENSITIZERS

While KPR-type (60-62, P11-P49), poly(vinyl ketone)-type (P51-P72), azidopolymer-type (P73-P87), and other dark-type sensitizers (5, 240-242, P88-P209) have not equalled diazoresins in popularity for sensitization of short-run presensitized plates, the hope of finding superior photolithographic coatings has inspired much research both for sensitizers and macromolecular materials they might photoharden. Even the photomaterials used for letterpress plates, like Dycril, have been studied, particularly the sensitizers such as benzoins (P249), peroxy compounds (P250), vicinal polycarbonyls (P251), polyketaldonyls (5), vicinal ketaldonyls (P252), and the other photoinitiators of ethylenic, vinylic, acrylic or related double-bond polymerization or photopolymerization (P253).

Anthracene, acridine, benzopyrene, phenazine, anthraldehyde, and similar photoabsorbers (P254) have been studied for hardening of cellulosic and poly (vinyl alcohol) coatings. Dycril-type photoinitiators have been tried for many kinds of vinylic polymers (P255). Even the ferrocitrates of blueprinting have been examined for photohardening potential (P256). Nitrothiophenes have been used to harden poly(vinyl pyrrolidones) and other hydrophilic colloids but development or hardening have required some heating after photoexposure (P257-P258). Perhalogen sensitization has been tried variously (P259-P263).

A second sector of this effort has been concerned with the use of bifunctional or polyfunctional cross-linking agents to assure greater photohardening, e.g., diacrylates or polyacrylates for acrylics (P253) and bisacrylamides or other agents for polyamide, particularly poly(acrylamide), systems (P264-P270). Many attempts either failed to attain photohardening adequate for photolithographic surface coatings or stencils, or else attained overhardening that hampered image development, stencil removal, or proper ink-water differentiation of image and nonimage areas.

PHOTOGRAVURE TISSUES

Photogravure resists are called tissues or carbon tissues (11, 22-24, 46-47) because originally the coating used, gelatin, was both pigmented with carbon black and spread thinly on a thin paper support. The pigment provided a visible image and limited light diffusion so that photohardening occurred from the exposed side down to a depth proportional to the photoexposure. Today reddish-brown iron oxide is used instead of carbon black as the pigment in gravure tissues. Tissues may be unsensitized, in which case potassium dichromate sensitization is effected by soaking before use, or else they are presensitized with silver halide. After photoexposure, the tissue is removed from the backing and deposited on gravure metal - either the cylinder or a wrap-around plate for a rotogravure-base cylinder - with the soft, unexposed resist outward. Then the soft gelatin is washed out leaving an image of variant thickness on the gravure metal. Etching is conducted through the image, with the depth of etching of ink cups greatest where there is no residual gelating and least where it is thickest and most photohardened against diffusivity.

Since the ink cups will print positively once the gelatin is removed and the metal is inked and the lands between cups are squeegeed free of ink, the image must perforce be a positive image, and the gravure resists that photoharden must be positive-working. The invention of a suitable positive-working photopolymer resist would be a boon to rotogravure printing. So would an easier method of etching. As yet, few suggestions have been made that would cheapen preparation of gravure printing plates to the point where small plates and short runs would be profitable. The polymer engineer versed in hydrocolloids and polyelectrolytes and their aqueous or solvent swelling can combine talents with the photochemist and the photopolymer chemist to secure the needed advances. Another area in which more talent has to be pooled for improvement is silk-screen printing.

SILK-SCREEN PRINTING STENCILS

The silk-screen printing process uses indirect tissue laydown on silk, metal, or other fabric screens in the manner of gravure tissue transfer and also employs direct resist application on the screen; again these may be freshly sensitized (bichromate, diazo, or diazido) or presensitized (silver halide, diazo, or diazido), and instead of gelating, poly(vinyl alcohol) or some other hydrocolloid or polyelectrolyte polymer material might be used. The literature on this fast-growing process is yet scanty and is procedural rather than analytical (25, 48).

The silk screen process is a typical stencil process like that involved in hand stencilling or in mimeography. Ink is squeezed only through areas where the screen is open; nonimage areas are filled with photohardened resist. There is little doubt that much of the progress that can be applied to screen printing has already been attained in the photosystems already reviewed here for photoengraving, photolithographic, and photogravure applications and elsewhere for photoletterpress platemaking and for general photopolymerization photography (5, 7, 146-147).

DISCUSSION

In most of the papers and patents reviewed the level of polymerization theory is no more advanced than it was at the time of Flory's paper on free radical vinyl polymerization published 30 years ago (258). Some papers present no polymer concepts unknown more than a century ago (259-260). Only a few reflect the vast amount of progress in polymerization that has been made since Staudinger's time (261-262). Despite the solid-state nature of resist coatings, the cage effect, recognized for over thirty years (263) is never discussed in graphic arts papers on photopolymerization. Practically none of the materials or systems properties vital to the plastics engineer are quantitatively discussed in any of the papers reviewed.

Thus, the published literature on photomechanical photopolymers seems dated to polymer chemists and engineers accustomed to modern ideas of the thermodynamics and kinetics of polymer formation and of the electronic, chemical, and solid-state structures and properties of polymeric and macromolecular materials. What goes on in the graphic arts laboratory is even more remote from the forefronts of today's polymer science and technology. The same functional groups are relied on for polymerization that provide adhesion to the plate base; photoreaction results in orange peel. Or the coefficients of elasticity are disregarded; the photoexposed coating is badly checked. An endless recitative of this kind can be given by most laboratories doing photomechanical research; what is published reflects the small percentage of research that has not been a failure despite lack of insight and provision for success.

What is required quite urgently in photopolymerization for improved photomechanics is the adequate and proper use of polymer engineering knowledge and polymer engineers, as well as less wasteful use of polymer chemistry and polymer chemists. Mere developability and etch resistance determination should be augmented by actual measurements of the hardness, solubility and adhesion and cohesion of candidate photomaterials. The functional groups responsible for various desired properties should be characterized and then incorporated in the measure needed by making use of block and graft copolymerization techniques as is necessary. Only when precautions such as these begin being routine will the tale of photopolymers in the graphic arts be one that can be told in other than an encyclopedic fashion.

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P117. French 1,153,617, Mar. 19, 1958 (Kodak-Pathe s.a.).

P118. Belgian 644,590, Sept. 2, 1964 (E.I. duPont de Nemours & Co., Inc.).

P119. British 1,007,345, Oct. 13, 1965 (E.I. duPont de Nemours & Co., Inc.).

P120. U.S. 2,797,213, June 25, 1957 (GAF Corp.).

P121. U.S. 2,772,972, Dec. 4, 1956 (GAF Corp.).

P122. U.S. 3,173,788, Mar. 16, 1965 (GAF Corp.).

P123. British 210,862, Nov. 7, 1922 (Kalle, A.G.).

P124. U.S. 3,050,388, Aug. 21, 1962 (Azoplate Corp.).

P125. U.S. 2,759,817, Aug. 21, 1956 (Azoplate Corp.).

P126. German 931,388, Aug. 8, 1955 (Kalle, A.G.).

P127. German 947,852, Aug. 23, 1956 (Kalle, A.G.).

P128. U.S. 2,548,537, April 10, 1951 and 2,568,503, Sept. 18, 1951 (Eastman Kodak Co.).

P129. U.S. 3,097,097, July 9, 1963 (by G. Oster).

P130. Belgian 609,759, April 30, 1962 (3M Co.).

P131. French Addn. 82,965 to 1,316,465, May 22, 1964 (Kodak-Pathe S.A.).

P132. French 1,316,465, Feb. 1, 1963 (Kodak-Pathe s.a.).

P133. U.S. , June 30, 1959 (E. I. duPont de Nemours & Co., Inc.).

P134. French 1,229,883, September 12, 1960 (Kodak-Pathe s.a.).

P135. U.S. 2,806,424 and 2,835,576, May 30, 1958 (by A.L. Ensink).

P136. U.S. 2,822,280, Feb. 4, 1958 (Harris-Seybold Co.).

P137. German 1,016,931, May 6, 1959 (Harris-Intertype Co.); cf. British 864,033.

P138. German 1,071,481, June 2, 1960 and U.S. 2,942,974, June 28, 1960 (Powers Chemco, Inc.).

P139. U.S. 3,023,099, Feb. 22, 1962 (Bjorksten Research Labs., Inc.).

P140. U.S. 3,102,030, Aug. 27, 1963 (by H. Hoerner).

P141. Belgian 633,808, Nov. 4, 1963 (Soc. Tech. d'Appl. Phys. et Chem. S.A.).

P142. British 979,552, Jan. 6, 1965 (PATRA).

P143. U.S. 1,870,354, Aug. 9, 1932 (Agfa Ansco Corp.).

P144. U.S. 1,941,852, Jan. 2, 1934 and 2,169,513, Aug. 15, 1939 (Agfa Ansco Corp.); cf. U.S. 2,180,335, Nov. 21, 1939 and Canadaian 383,373.

P145. U.S. 2,663,639, Dec. 22, 1953 (Harris-Seybold Co.).

P146. U.S. 2,237,240, April 1, 1941 (Kalle, A.G.).

P147. U.S. 2,153,264, June 20, 1939 (Bakelite, G.m.b.H.).

P148. U.S. 2,320,724, June 8, 1943 (Libby-Owens-Ford Glass Co.).

P149. U.S. 2,335,656, Aug. 22, 1944 (Eastman Kodak Co.).

P150. U.S. 2,830,899, April 15, 1958 (Jones Graphic Products Co.).

P151. German 807,440-1, June 28, 1951 and British 691,025 and 691,036-8, May 6, 1953 (British Resin Products, Ltd.).

P152. U.S. 2,415,796, Feb. 11, 1947 (Wingfoot Corp.).

P153. U.S. 2,099,404, Nov. 16, 1937 (Kalle, A.G.).

P154. German 936,371, Dec. 7, 1955 (Kalle, A.G.).

P155. U.S. 2,773,765, Dec. 11, 1956 (Azoplate Corp.); cf. German 943,209, May 17, 1951 (Kalle, A.G.).

P156. U.S. 2,757,090, July 31, 1956 (Azoplate Corp.).

P157. U.S. 2,773,766, Dec. 11,1956 (Azoplate Corp.).

P158. U.S.3,070,443, Dec. 25, 1962 (Azoplate Corp.).

P159. Netherlands Appl. 6,407,189, Jan. 5, 1965 (Kalle A.G.).

P160. U.S. 2,696,435, Dec. 7, 1954 (Azoplate Corp.).

P161. German 903,415, (Kalle, A.G.).

P162. German 885,198, Aug. 3, 1953 (Kalle, A.G.).

P163. U.S. 2,773,767, Dec. 11, 1956 (Azoplate Corp.).

P164. German 950,618, Oct. 11, 1956 (Kalle, A.G.).

P165. U.S. 2,958,599, Mar. 1, 1960 (Azoplate Corp.); cf. German 1,058,845 (Kalle, A.G.).

P166. British 837,368, June 15, 1960 (Kalle, A.G.); cf. German 1,047,622.

P167. U.S. 3,028,339, April 3, 1962 (Azoplate Corp.).

P168. German 945,673, July 12, 1956 (Kalle, A.G.).

P169. U.S. 2,859,111, Nov. 4, 1958 (Azoplate Corp.).

P170. U.S. 2,766,118, Oct. 9, 1956 (Azoplate Corp.).

P171. U.S. 3,197,308, Appl. Oct. 11, 1962 (Azoplate Corp.).

P172. German 1,106,181 and 1,108,078, Appl. Sept. 1, 1959 (R.C. Adams and Algraphy, Ltd.).

P173. British 912, 022, Dec. 5, 1962 (3M Co.).

P174. U.S. 3,074,869, Jan. 22, 1963 (3M Co.).

P175. U.S. 2,649,373, Aug. 18, 1953 (S.D. Warren Co.).

P176. German 838,548, May 8, 1952 (Kalle, A.G.).

P177. U.S. 2,995,442, Appl. April 2, 1958 (Azoplate Corp.).

P178. U.S. 2,754,209, July 10, 1956 (Azoplate Corp.).

P179. British 836,341, June 1, 1960 (Kalle, A.G.); cf. German 1,053,930.

P180. U.S. 3,046,120, July 24, 1962 (Azoplate Corp.).

P181. German 281,454, Oct. 15, 1908 (Bakelite, G.m.b.H.).

P182. British 942,564, Nov. 27, 1963 (Kalle, A.G.).

P183. Belgian 641,004, June 9, 1964 (Kalle, A.G.).

P184. French 1,352,192, Feb. 14, 1964 (Nobel-Boxel S.A.).

P185. Czechoslovakian 94,515, Mar. 15, 1960 (by Z. Bukac).

P186. Belgian 620,344, Jan. 17, 1963 (Kalle, A.G.); cf. 599,939.

P187. German 1,022,005, Jan. 2, 1958 (Distillers' Co., Ltd.).

P188. U.S. 942,699, Dec. 7, 1909 (by L. H. Baekland).

P189. U.S. 2,696,437, Dec. 7, 1954 (Azoplate Corp.).

P190. Czechoslovakian 94,090, Feb. 15, 1960 (by Z. Bukac, et al).

P191. Czechoslovakian 99,639, May 15, 1961 and 100,548, Aug. 15, 1961 (by Z. Bukac and B. Obereigner).

P192. German 918,848, Oct. 7, 1954 and 1,075,950, Feb. 18, 1960 (Kalle A.G.); cf. British 852,946.

P193. U.S. 3,029,146, April 10, 1962 (Kalle, A.G.); cf. U.S. 2,975,053, March 14, 1961 (Azoplate Corp.).

P194. U.S. 3,050,387, Aug. 21, 1962 (Azoplate Corp.); cf. Belgian 620,660, Jan. 25, 1963 (Kalle, A.G.) and German 874,437, May 4, 1953 (Kalle, A.G.)..

P195. German 900,172, Dec. 21, 1953 (Kalle, A.G.).

P196. German 901,500, Jan. 11, 1954 (Kalle, A.G.).

P197. German 938,233, Jan. 26, 1956 (Kalle, A.G.).

P198. German 1,003,576, Feb. 28, 1957 (Kalle, A.G.); cf. British 788,975, Jan. 8, 1958.

P199. German 1,047,622, Dec. 24, 1955 (Kalle, A.G.).

P200. German 1,104,824, April 13, 1961 (Kalle, A.G.).

P201. German 1,118,606, Nov. 30, 1961 (Kalle, A.G.).

P202. British 830,386, Feb. 1, 1961 (Azoplate Corp.); cf. U.S. 2,994,609.

P203. British 784,672, Oct. 16, 1957 (Kalle, A.G.).

P204. U.S. 2,767,092, Oct. 16, 1956 (Azoplate Corp.).

P205. U.S. 2,859,112, Nov. 4, 1958 (Azoplate Corp.).

P206. U.S. 2,907,655, Oct. 6, 1959 (Kalle, A.G.); cf. German 933,012, Sept. 15, 1955, addn. to 931,288.

P207. U.S. 3,046,110, July 29, 1962 (Azoplate Corp.).

P208. U.S. 3,046,111-19, 3,046,121-24, 3,046,131, July 29, 1962 (Azoplate Corp.); cf. 3,050,389, Aug. 21, 1962, 3,061,435, Oct. 30, 1962, 3,102,809 Sept. 3, 1963, 3,106,465, Oct. 8, 1963, 3,110,596, Nov. 12, 1963 and 3,126,281, Mar. 24, 1964.

P209. German 876,202, May 21, 1953, 949,383, Sept. 20, 1956, 955,928, Jan.10, 1957, 1,120,273, Dec. 21, 1961 (Kalle, A.G.); cf. 901,129, Jan. 7, 1954, U.S. 2,890,115 (Jan. 10, 1957, cf. 2,887,467 (GAF Corp.) and British 816,382 (GAF Corp.). See also U.S. 2,959,482, Nov. 8, 1960, 2,667,415, Jan. 26, 1954 and 3,061,430, Oct. 30, 1962 (Azoplate Corp.); cf. German 1,086,555, U.S. Appl. Sept. 25, 1956.

P210. U.S. 2,063,631, Dec. 8, 1936 (Kalle, A.G.).

P211. U.S. 2,679,498, May 25, 1954 (Ditto, Inc.).

P212. U.S. 2,739,889, Mar. 27, 1956 and 2,810,341-2, Oct. 22, 1957 (Azoplate Corp.).

P213. Belgian 608,789, April 3, 1962 (Kalle, A.G.).

P214. U.S. 3,050,502, Aug. 21, 1962 (Polychrome Corp.).

P215. German 857,739, see U.S. 2,702,242, Feb. 15, 1955 and German 1,142,871, see Belgian 613,045, German Appl. Jan. 25, 1961 (Kalle,A.G.).

P216. U.S. 2,692,827, Oct. 26, 1954 (S.D. Warren Co.).

P217. U.S. 2,865,873, Dec. 23, 1958 (Litho Chemical and Supply Co., Inc.).

P218. U.S. 2,882,153-4, April 14, 1959 and 2,946,683, July 26, 1960 (Polychrome Corp.)

P219. German 1,091,433, addn. to 907,147, U.S. Appl. July 5 and 25, 1955 (3M Co.); cf. British 885,086, Dec. 20, 1961.

P220. Belgian 630565-6, Oct. 21, 1963, addn. to 613,045 (Kalle, A.G.); cf. British 401,898.

P221. Netherlands Application 280,797, Dec. 10, 1964 (3M Co.).

P222. U.S. 3,165,534, Dec. 29, 1964 (Harris-Intertype Corp.).

P223. Netherlands Application 6,410,224, March 8, 1965 (Polychrome Corp.); cf. U.S. 2,946,683.

P224. British 986,683, Mar. 24, 1963 (Kalle, A.G.).

P225. British 994,605, June 10, 1965 (S.D. Warren Co.).

P226. U.S. 2,729,562, Jan. 3, 1956 (E.I. duPont de Nemours & Co., Inc.)

P227. U.S. 2,778,735, Jan. 22, 1957 (S. D. Warren Co.).

P228. U.S. 2,826,501, Mar. 11, 1958 (Litho Chemical and Supply Co., Inc.).

P229. U.S. 2,937, , May 27, 1960 (Ditto, Inc.).

P230. U.S. 2,982,648, May 2, 1961 (GAF Corp.).

P231. Belgian 621,176, Nov. 20, 1962 (Kalle, A.G.).

P232. U.S. 3,085,008, April 9, 1963 (3M Co.).

P233. British 948,637, Feb. 5, 1964 (N.V. Lichtdruckpapierfabriek "de Atlas").

P234. U.S. 3,136,636, June 9, 1964 (3M Co.).

P235. German 1,169,467, Dec. 10, 1964 (Lithoplate, Inc.).

P236. U.S. 2,826,501, (Litho Chemical and Supply Co., Inc.).

P237. U.S. 1,762,033, June 3, 1930 and 2,100,063, Nov. 23, 1937 (Kalle A.G.); cf. British 454,137, Sept. 24, 1936 and 296,008, Aug. 22, 1927 and also 315,236, April 3, 1928.

P238. U.S. 3,189,451, June 15, 1965 (Azoplate Corp.).

P239. German 1,055,957, April 23, 1959, 1,059,766, June 18,1959, addn. to 1,072,478, Dec. 31, 1959 (Kalle, A.G.).

P240. U.S. 2,179,518, April 20, 1965 (Azoplate Corp.).

P241. U.S. 2,980,534, April 18, 1961 and 3,179,518, April 20, 1965, cf. British 861,871, Mar. 1, 1961 (Monsanto Chemical Co.).

P242. U.S. 2,673,151, (Pittsburgh Plate Glass Co.).

P243. German 1,067,307, Oct. 15, 1959 (Kalle, A.G.).

P244. U.S. 3,062,644, Nov. 6, 1962 (Azoplate Corp.).

P245. U.S. 3,136,639, June 9, 1964 (Lithoplate, Inc.).

P246. U.S. 2,994,608, German Appl. Feb. 25, 1955 (Azoplate Corp.).

P247. German 1,097,273, Jan. 12, 1961 (Kalle, A.G.).

P248. German 1,114,705, Oct. 5, 1961 (Kalle, A.G.).

P249. U.S. 2,722,512, Nov. 1, 1955 (E.I. duPont de Nemours & Co., Inc.).

P250. U.S. 1,241,738, Oct. 2, 1917 (by F. Klatte and A. Rollett).

P251. U.S. 2,367,600-1, Jan. 23, 1945 (E.I. duPont de Nemours & Co., Inc.).

P252. U.S. 2,760,863, Aug. 28, 1956 and 2,791,504, May 7, 1957, and German (1,031,130, May 25, 1958 (E.I. duPont de Nemours & Co., Inc.)

P253. U.S. 2,893,868, July 7, 1959, 2,902,365, Sept. 1, 1959, 2,923,673, Feb. 2, 1960, 2,929,710, Mar. 22, 1960, 2,948,611, Aug. 9, 1960,

P253. (cont'd.)
2,993,789, July 25, 1961, 3,198,633, Aug. 3, 1965, and British 815,277, June 24, 1959, 826,272, Dec. 31, 1959, 827,512, Feb. 3, 1960, 834,337, Appl. Aug. 3, 1957, 835,849, May 25, 1960, and 841,454, July 13, 1960, and German 1,104,825, April 13, 1961 (E.I. duPont de Nemours & Co., Inc.).

P254. German 956,992, Jan. 24, 1957 and 942,779, May 9, 1956, and U.S. 2,980,535, Oct. 6, 1958 (Feldmuehle Papier-und-Zellstoffewerke).

P255. U.S. 3,068,202, Appl. April 20, 1959, cf. Brit. 893,616, April 11, 1962, and U.S. 2,484,529, Oct. 11, 1949 (E.I. duPont de Nemours & Co.).

P256. U.S. 2,927,021, Mar. 1, 1960 (Horizons, Inc.).

P257. U.S. 3,046,126, July 24, 1962, cf. 3,046,110-24 (Azoplate Corp.).

P258. German 955,379, Jan. 3, 1957 (Kalle, A.G.).

P259. British 983,366, Feb. 17, 1965 (Union Carbide Corp.).

P260. U.S. 3,042,515-9, July 3, 1962, 3,046,125-6, July 24, 1962, 3,056,673, Oct. 2, 1962, 3,082,086, Mar. 19, 1963, 3,095-303, June 25, 1963, 3,100,703, Aug. 13, 1963, 3,102,027, Aug. 27, 1963, 3,102,109, Aug. 27, 1963, 3,102,810, Sept. 3, 1963, 3,106,466, Oct. 8, 1963, 3,112,200, Nov. 26, 1963, 3,113,024, Dec. 3, 1963, 3,121,632-3, Feb. 18, 1964, 3,154,416, Oct. 27, 1964, 3,164,467, Jan. 5, 1965, cf. Netherlands Appl. 6,410,585, Mar. 18, 1965 (Horizons, Inc.).

P261. French 1,302,010, Aug. 24, 1962, 1,302,610, Aug. 31, 1962, 1,303,075, Sept. 7, 1962, 1,313,083, Dec. 28, 1962, 1,313,761, Jan. 4, 1963, 1,314,392, Jan. 11, 1963 (Horizons, Inc.).

P262. British 955,029, April 8, 1964 and 959,033, cf. U.S. 3,140,948-9 and 3,147,117 (Horizons, Inc.).

P263. German 1,152,608, Aug. 8, 1963 (Horizons, Inc.).

P264. U.S. 2,997,391, Appl. April 22, 1957 and 3,081,168, Appl. Oct. 16. 1959 (Time, Inc.).

P265. German 954,127, Dec. 13, 1957 and 1,103,019, April 21, 1958 (Time,Inc.)

P266. British 875,378, Aug. 16, 1961, addn. to 767,912 (Time, Inc.).

P267. U.S. 3,029,145, April 10, 1962, 3,065,110, Appl. Aug. 27, 1959, 3,075,907, Jan. 23, 1963, 3,099,558, July 30, 1963, 3,101,370, Aug. 20, 1963, 3,110,592, Nov. 12, 1963, 3,118,767, Jan. 21, 1964, 3,130,050, April 21, 1964, 3,136,638, June 9, 1964, cf. U.S. 2,322,027, 3,147,116 and 3,147,119, Sept. 1, 1964 (GAF Corp.).

P268. German 1,106,172 May 4, 1961 (GAF Corp.).

P269. British 858,037, Jan. 4, 1961, 866, 631, April 26, 1961, 879,892, Oct. 11, 1961, cf. U.S. 3,041,172 and British 883,811, Dec. 9, 1961, 926,583 May 22, 1963, 937,387, Sept. 18, 1963, 984,456, Feb. 24, 1965(GAF Corp.)

P270. Belgian 622, 882, Sept. 18, 1963 and 638,336, Feb. 3, 1964 (GAF Corp.).

LIGHT-SENSITIVE STABLE-FREE RADICAL APPLICATIONS

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I want to talk about the extension of free radical technology through the applications of the chemistry of stable-free radicals. The technical aspects of many of the papers presented this week can be broadened by stable free radical chemistry. This will give us greater latitude in performance and choice of imaging processes.

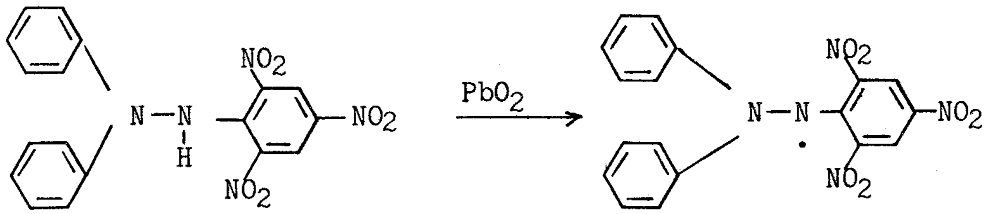
First, I will explain some of the chemistry of stable-free radicals. This will be followed by listing a number of applications using these chemicals, and finally, we will have some speculation and blue sky thinking on new ways to use this technology.

The stable-free radicals we are concerned with are those which have half lives measurable in months or years. That is, the content of unpaired electrons in a sample remains unchanged under normal conditions and is useful over a long period of time. This stability is due principally to the following properties.

1. Bulky groups provide steric hindrance to protect the unpaired electron.
2. Resonance stabilizes the electron system.
3. Interaction of the unpaired electron with orbitals of the shielding group also affects stability.

The chemistry of stable free radicals can be most easily described by studying the various classes of these materials.

We have found the following classes to be most useful in our work.



The hydrazyl group is an extremely large class of stable free radicals which contain an unpaired electron on a nitrogen atom. The size of the class is limited mostly by the chemist's ability to synthesize new hydrazines as starting materials. Let us see what can be done by using diphenyl picryl hydrazyl as a model.

We can start with the picryl component of the compound. This portion helps to stabilize the electron structure of the system as well as provides the hydrazyl radical a means of molecular complexing through pi or charge transfer bonding. Elimination of one or more of the nitro groups reduces the total stability of the system. Other groups such as halogens, aliphatics or acid groups can be added to the unsubstituted sites to change properties like color, reaction rates, stability, conductivity, and solubility. Salts can be prepared from the acid contining hydrazyls to provide unusual stable radical ions. These sites may also be used for other reactions such as condensations to give polyradicals or stable free radicals with more than one nitrogen containing unpaired electrons.

The phenyl groups on the nitrogen can be ring substituted or be replaced by bulky aromatic ring systems such as naphthyl, fluorene, or heterocyclic groups.

These substitutions will affect color and reaction rates. Some of the interesting properties of this class of radicals include:

1. High color content. These materials will give very intense colors at very low dilutions. These colors may vary from purple-black to red. Thus, they become useful in photo-bleach-out systems.

2. Many of the hydrazyls are photoconductors. This can be useful in photoelectrosensitive systems.

3. Hydrazyls as well as other stable free radicals can remove liable hydrogens from co-reactants under the influence of light.

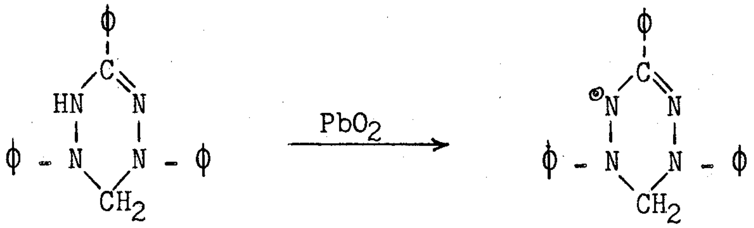
For example, DPPH irradiated with light at its absorption band of 520 m has been reduced to the hydrazine by the removal of hydrogen from cumene at a quantum yield of 1.3, cyclohexane at .57, methyl cyclohexane at .75 and toluene at .53. We may assume that the DPPH extracted a hydrogen and also scavenged part of the remaining fragments.

The hydrazyls are good photo-oxidizing agents for sulfides such as butyl disulfide, dimesityl disulfide, trimethylene disulfide and oxadithia cycloheptane.

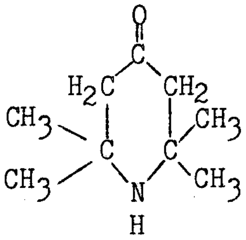
Another interesting property of hydrazyl and other stable free radicals is their ability to scavenge other free radicals and act as inhibitors in polymerization systems.

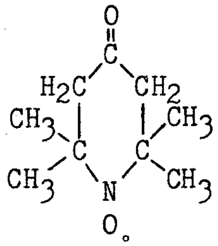
Hydrazyls as well as some of the other classes will also react with phenolic and aliphatic hydroxy groups and with amine compounds. Still another interesting property of several of the hydrazyls is their ability to change in magnetic field.

We have already mentioned the ability of many of these compounds to form charge transfer or pi complexes. This results in properties different from the parent compounds.

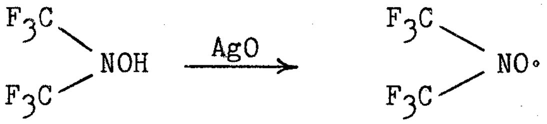


The verdazyls are a class of stable-free radicals very similar to the hydrazyls. The unpaired electron is on a nitrogen atom. Their colors are very intense and vary from green to almost black. They go through the same sort of photo oxidation reactions, and they are very reactive toward hydroxy and amino compounds. There are also a large number of stable radicals in this class. The phenyl groups may be substituted or replaced by other constituents, and polyradicals may be synthesized.

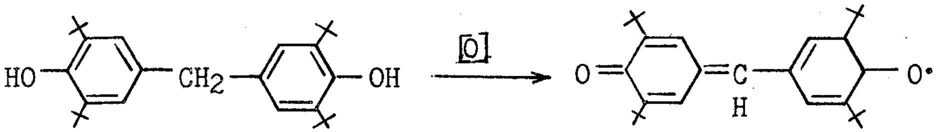




The nitroxides represent a very large class of stable-free radicals. I would like to use this slide of triacetone amine-N-oxide to show some unusual properties of stable-free radicals. Many reactions can be carried out with TAAO without affecting the unpaired electron. Physicals such as color, melting point, conductivity, solubility and so forth can be changed and we will still have an unpaired electron on the oxygen atom. In most cases, its ESR signal will remain approximately the same but its reaction rates with labile hydrogen and with other free radicals will be altered. As an example, the carbonyl group can be reduced to the hydroxide or to the hydrocarbon. This group will go through the normal reactions of ketones such as Grignard reactions which can place an unsaturated aliphatic group on this position for polymerization, formation of hydrazones, carbazones, carbamates and so on. The ring may be expanded with hydroxylamine to give the seven member homopiperazinone system. Thus, stable-free radicals can be chemically altered to give properties desirable for a specific end use. The heterocyclic nitroxide class can be 5-, 6-, or 7-member ring systems or can be fused ring heterocyclics such as carbolin-3-oxyl. The groups shielding the unpaired electron can be the same or different from one another. This class also includes polyradicals as well as the monoradical which has been described.

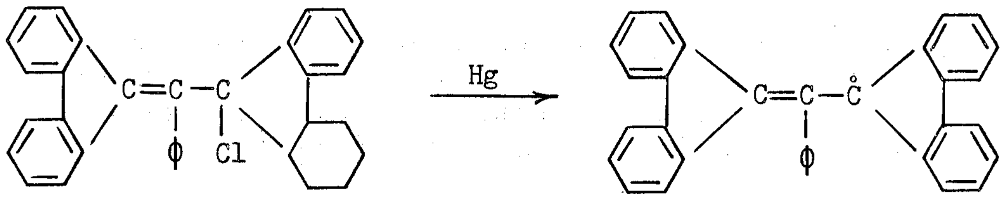


I will continue quickly with the other classes of stable-free radicals. This is an example of a di-substituted nitroxide-free radical. This particular compound is a purple gas and is extremely stable. There are many members of this class



The aroxyls represent a large well-known class of stable-free radicals. Many of these are well known as polymerization inhibitors and are also used to prevent the light degradation of films. Galvinoxyl and Coppinger's radical which replaces the methylene carbon with nitrogen are typical examples of stable-free radicals produced from bisphenol types of compounds.

Their colors generally vary from blue to yellow. We can also prepare polyradicals of this class.



The allyl carbon-free radicals are another class of materials which have received much attention recently. This particular form of carbon-free radical is quite stable and may be modified in the expected manner.

Another very large class of stable-free radicals includes the radical ions. The tetracyano quinodimethane or TCNQ complexes with organic bases and alkali metals form one important group of this class. These materials are very intensely colored blue-black to green-black compounds. They also offer another interesting way of forming radical ion polymers. TCNQ will complex with basic polymers such as polyvinyl pyridine to give polymeric stable-free radical ions.

Another class of stable-free radicals are those obtained by X-ray irradiation of clathrate and inclusion molecular complexes.

Let's now speculate on what we can do with this chemistry. First, we should assume that we can prepare a stable-free radical image in a coating, on a film, or in a polymeric media. This can be done. Now what are the possible uses we can find for this stable-free radical image.

1. A direct positive from positive or positive from negative photocomposition can be obtained based directly due to the color formation available in free radical chemistry.

2. The stable-free radical image will provide a differential in conductivity for electrostatic or electrochemical development.

3. The image area is chemically different from the surrounding light struck areas so that chemical means can be used to develop the image.

4. The image area will have a different solubility than the surrounding areas so that printing plates, printed circuits, and so forth, can be produced.

5. The image area can have different wetting properties than the surrounding areas so we can think of lithographic plates.

6. The conductive image area is stable so that electrostatic printing plates can be developed.

7. Additional physical treatment such as a second light exposure heat or passage of current may greatly amplify the quantum yield.

8. Using polyradicals as an example, the first photo product using up the first unpaired electron will result in a system having a different absorption spectrum and a different reaction rate. This may be useful for multiple compositions or multicolor effects. This also offers the possibility of multi-color lithography from one plate.

9. The stable-free radical imaging process can be useful for producing photosensitive adhesive compositions. These may be used as adhesives per se or for transfer to paper and powder or chemically developed to give a duplicating process from a single adhesive plate.

In conclusion, you can be sure that Management Research Laboratories, Inc. is making its best effort to bring these applications out of the speculation classification. MRL has already announced the development of a dry photo-bleach-out process, a non-pigmented photoelectrosensitive copy process of the Electrofax type, and a photoelectrosensitive plate process somewhat similar to the Xerox duplicating process.

I am sorry I am unable to give the chemistry or procedure for imaging stable-free radical systems at this time. At present, security measures prevent us from discussions of this type.

DETERMINATION OF THE EFFECTIVENESS OF A PHOTORESIST*

Dr. Walter Kornfeld**

Present technology of integrated circuits calls for an every-growing number of photomasking steps which for some devices may come up to seventeen. As a matter of fact, we face the only technique which interferes this many times with the manufacture of a device. It stands, therefore, to reason that the quality of the photoresist will largely determine the quality, the yield and the reliability of the product.

The first objective in evaluating a photoresist is to find an optimum exposure time. A correct amount of photons will create the number of crosslinks necessary to give the best performance in resolution, definition and etch resistance of the resist.

The adjustment of the exposure time for geometries with openings and islands in the micron range presents a serious problem. Figures 1 and 2 show such features in the repeating pattern of a mask. Overexposure will cause the openings to close while underexposure does not permit a sufficient polymerization of the islands.

Because of the small ratio of polymerized resin volume to surface area attacked by the developer spray, the islands require more exposure time than do large exposed fields to withstand the solvent spray. To make the problem more severe, the transparent areas in the opaque field of the mask intended to give small islands after etching the substrate are very often indistinct or clouded. An even longer exposure time becomes necessary to provide enough light through the apertures to induce sufficient polymerization. Non-uniformity in the intensity of the light source and uneven contact with the mask contribute to the problem.

One could try to eliminate these causes by improving the mask or the performance of the light course. On the other hand, one could also change the composition of the resist and/or modify the resist processing steps. Thus, the effects of light scattering, refraction and the mask defects could be conveniently minimized. The latter approach was chosen for this study.

An evaluation technique providing numerical results has been developed. The evaluation is done by counting the fraction of "acceptable" patterns obtained at different exposure times and after etching through 1 micron of silicondioxide. Figure 3 shows such a pattern at 400X. The term "fraction acceptable" is defined as the ratio of number of features acceptable to number of features counted.

In the present example, those sets containing both satisfactory triplets of holes and triplets of islands, are counted as acceptable. This number is then

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*Work on this study was supported by Motorola SPD, Phoenix, Ariz., and by Wright-Patterson AFB under Contract AF33(615)-3566.

**The author is now with Westinghouse M.E.D., Baltimore, Md.

plotted against exposure time, resist formulation, light path or other significant parameters.

The resist under observation is Kodak Metal Etch Resist which has been centrifuged to remove all particulate matter, e.g., the fraction with the highest molecular weight. In view of the small patterns the resist films have to be as thin as possible. This is accomplished by dilution and by using a high spinning speed.

Figure 4 shows the performance of centrifuged KMER, which has been diluted 1:8 and spun at 10K rpm., before and after etch. As is shown, there is no exposure time at which an etched pattern can be achieved. The very high pinhole count indicates a far too small sensitizer concentration to permit efficient polymerization. Due to the same defect and the relatively thick films, the energy does not reach the substrate. The features are only superficial and cannot be etched.

When sensitizer is added to the original concentration of 2.5 per cent, and when dilution ratio is changed, an extraordinary improvement takes place. Utilizing the evaluation technique described above, one can determine easily what the optimum formulation is. This is illustrated by Figure 5. Exposure time, spinning speed and light path length have been kept constant. The table shows the different compositions. No. 956 having been diluted 1:12 and containing 8 per cent of sensitizer excels.

Figure 6 shows that for the formulation 956, an optimum distance from the light source can be fixed at 13 inches. If the light intensity at this geometry is measured, it is possible to adjust the performance of most other sources and to correct the fading energy supply of older lamps.

Figure 7 provides information about the sensitivity to small exposure increments of the formulation 956. The timing device can be adjusted to these conditions.

SUMMARY

The effectiveness of a photoresist to resolve simultaneously holes and islands in the micron range can be numerically determined. This is done by counting the fraction of developed and etched "acceptable" patterns across an oxide wafer. The development of a resist formulation and the establishment of optimum exposure conditions are greatly assisted by this evaluation method. (Author)

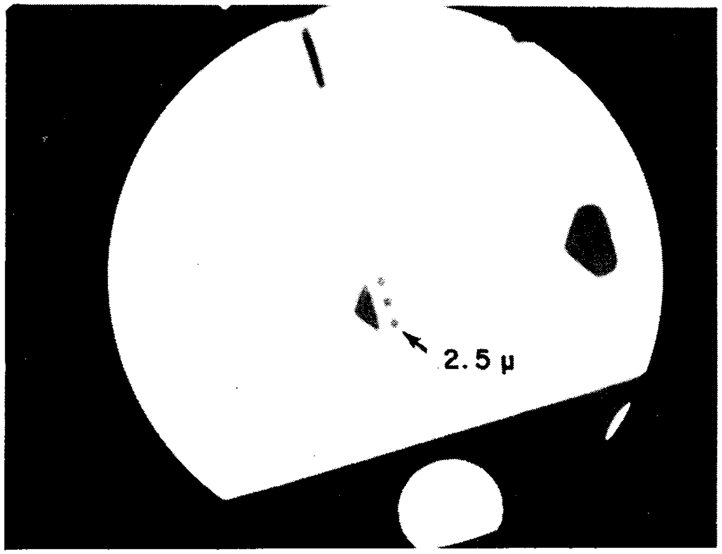

FIGURE 1: Repeating Pattern of a Mask Feature "Holes"

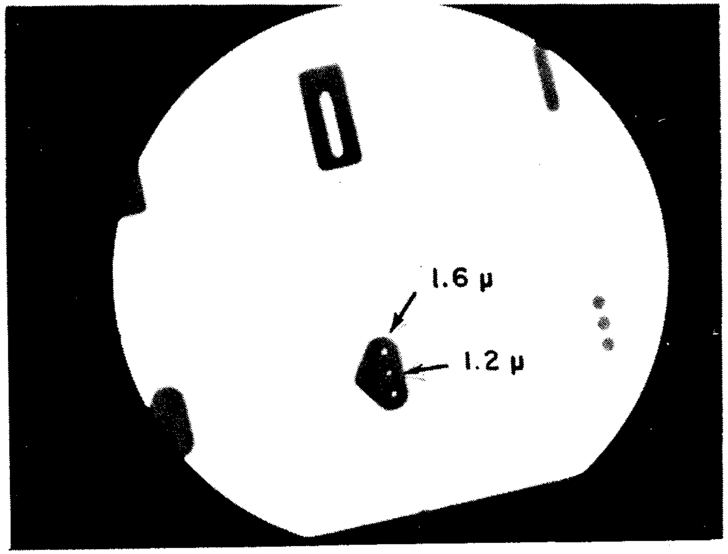

FIGURE 2: Repeating Pattern of a Mask Feature "Islands"

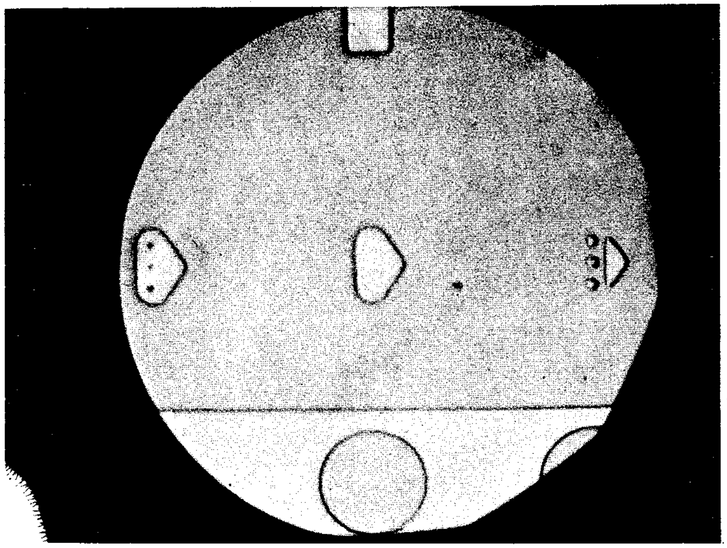

FIGURE 3: Repeating Test Pattern Etched Through 10,000
A Silicon Dioxide

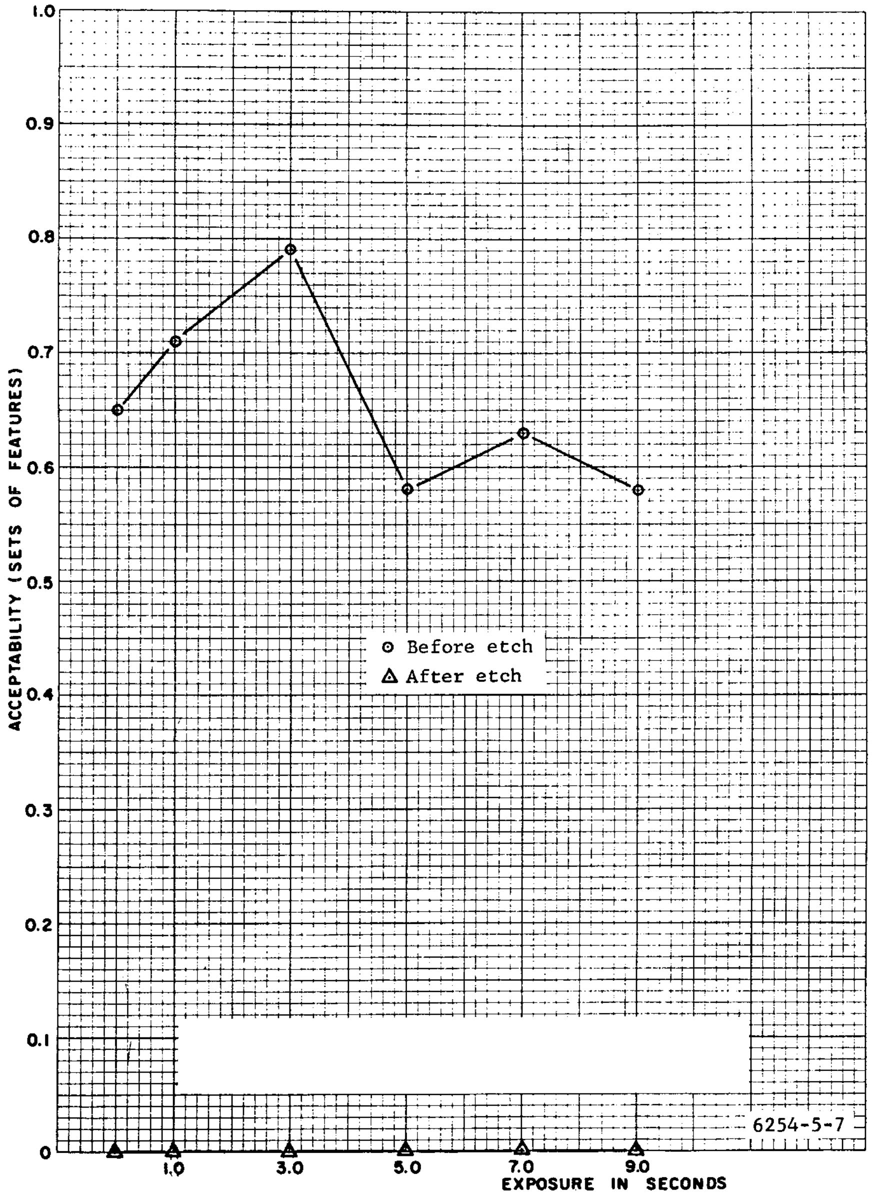

FIGURE 4: Lot No. 950, 2.5% ABC Dilution 1:8, Spin Speed 10K rpm, U.V. Path Length 13 Inches

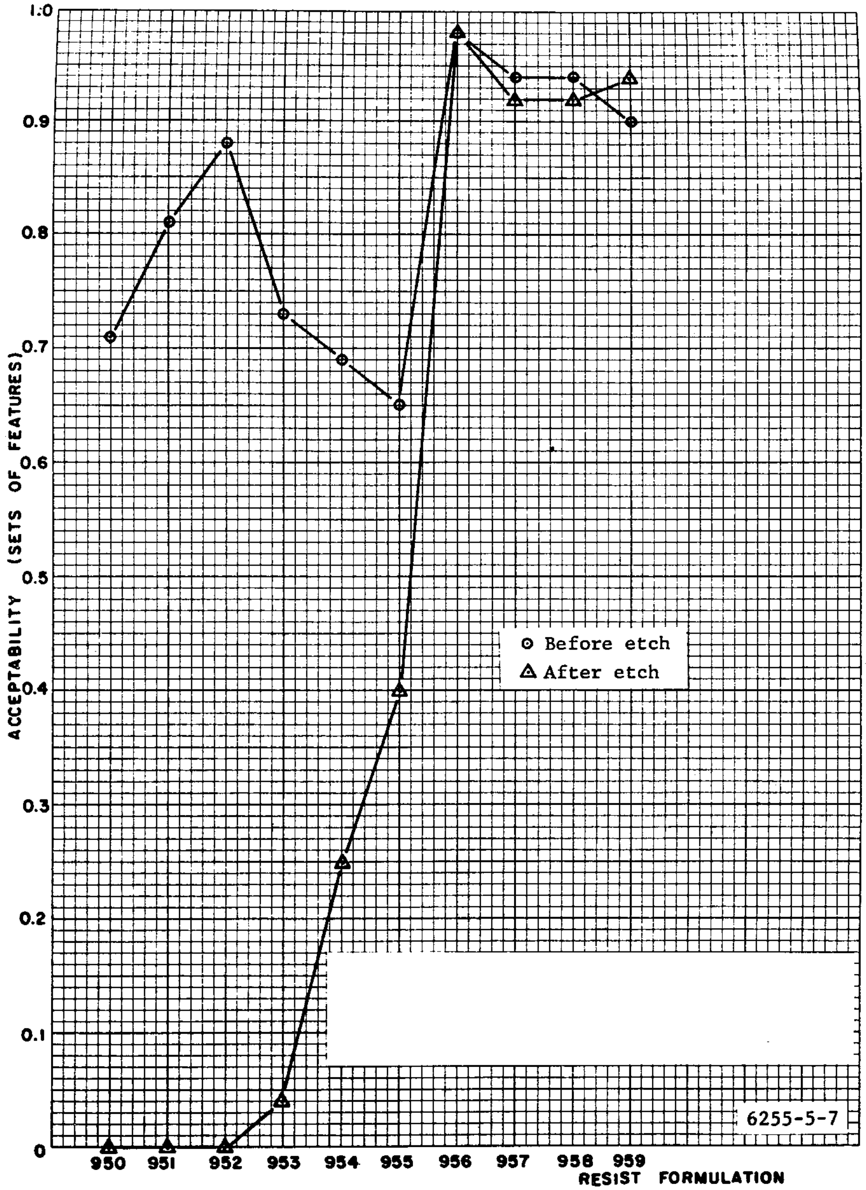

FIGURE 5: Various Resist Formulations (KMER Based) Exposure 1.0 Second, Spinning Speed 10K rpm, U.V. Path Length 13 Inches

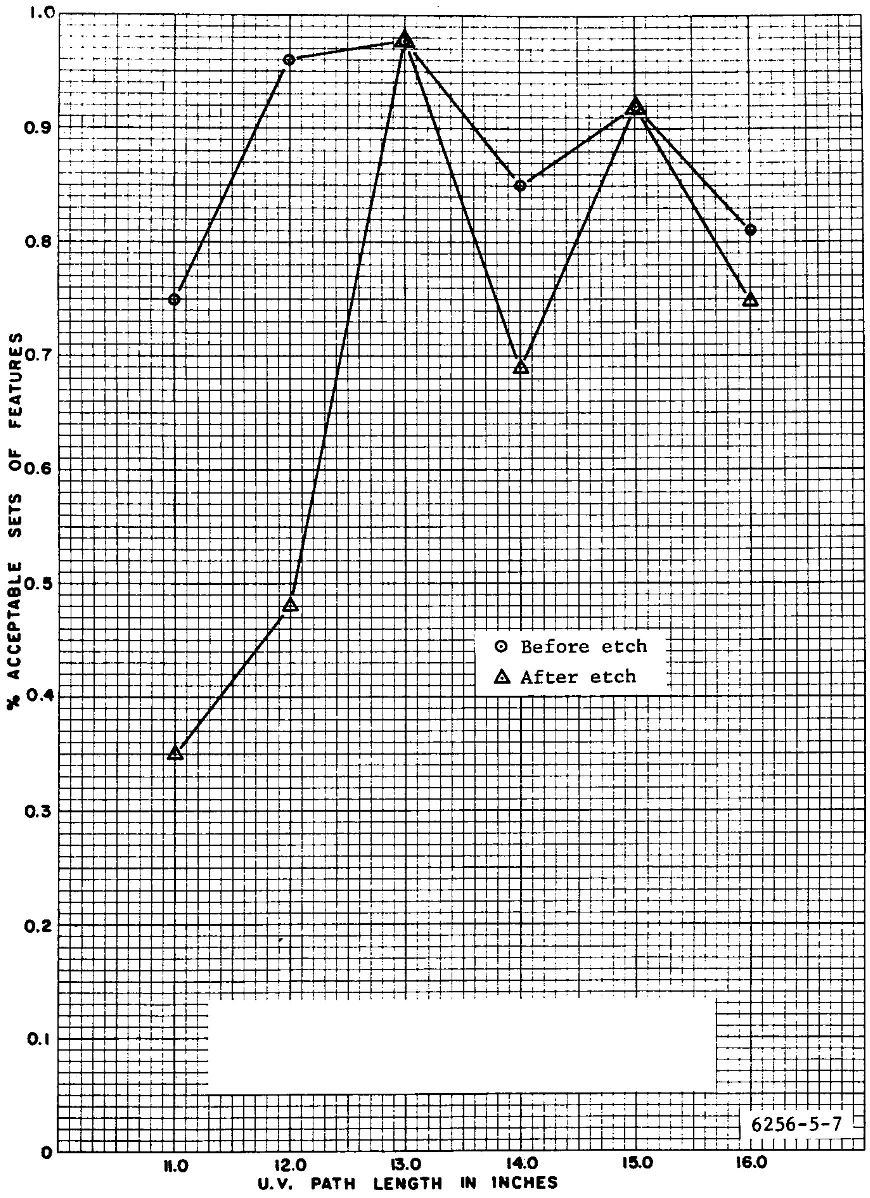

FIGURE 6: Exposure of No. 956 From Different Source Distances, Spin Speed 10K rpm, Exposure time 1 Second

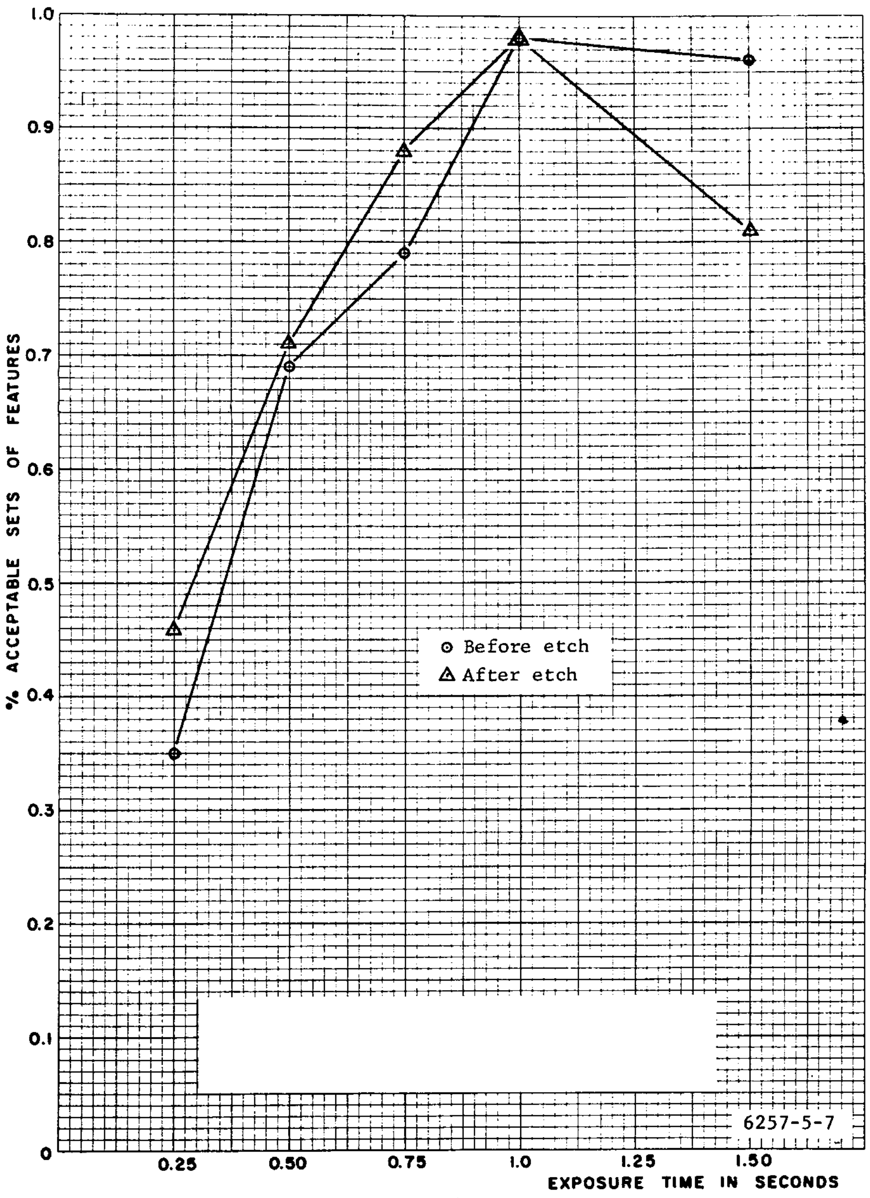

FIGURE 7: Exposure of No. 956 to Small Time Increment, Spinning Speed 10K rpm, U.V. light Path 13 Inches

INITIATION FEE MUST BE ATTACHED FOR PROCESSING.

SOCIETY OF PLASTICS ENGINEERS, INC.

65 Prospect Street, Stamford, Conn. 06902
348-7528 AREA CODE 203

MEMBERSHIP APPLICATION

PLEASE PRINT OR TYPE

Executive Office Use Only
I.D. No. ______
Ack. ______
Elected ______

I hereby make application for ☐ admission into ☐ reclassification within ☐ reinstatement in the Society of Plastics Engineers, Inc. in the grade of membership indicated below for which I believe I am qualified. (See instructions or reverse side.)

Grade	Initiation Fees	Annual Dues	Foreign Dues
☐ Senior Member	$10.00	$20.00	$17.50
☐ Member	10.00	20.00	17.50
☐ Affiliate Member	10.00	20.00	17.50
☐ Student Member	None	5.00	5.00

I wish to affiliate with the ______ section.
(Geographical location. See listing on reverse side.)

Applicants Full Name ______ (First) (M.I.) (Last) (Citizen of) (Birthdate)

Please fill in both addresses and **CHECK THE ONE TO WHICH YOUR MAIL SHOULD BE ADDRESSED.**

☐ **BUSINESS:** Company Name and Division: ______
Position ______
Address ______ City ______ State ______ Zip Code ______

☐ **HOME:** Address ______ City ______ State ______ Zip Code ______

REFERENCES The By-Laws require the names of three references who are familiar with your work. One of them should be a member of the Society. Assistance in providing member-references, when needed, will be given on request.

1. ______ Address ______
2. ______ Address ______
3. ______ Address ______

STATEMENT OF COLLEGE WORK

Years Attended		Institution	Major and Minor	Degree	Experience Credits See reverse side
From	To				
				Total Education Experience Credits	

RECORD OF QUALIFYING EXPERIENCE IN PLASTICS

Dates				Give your title, name and location of employer, and name of immediate superior for each position. List in chronological order. Describe duties fully and state briefly any important engineering work you have done in in each position. If space is not sufficient, use a separate sheet.	Time in years and months
From		To			
Mo.	Yr.	Mo.	Yr.		
				Total qualifying years of experience.	
				Total education and qualifying experience credits.	

I certify that the statements made in this application are correct. I agree, if elected, to be governed by the Constitution and By-Laws of the Society, and to promote the objective of the Society.

NATIONAL CREDENTIALS COMMITTEE USE ONLY

Approved (Signature) ______ **Date** ______

Approved (Signature) ______ **Date** ______

______ Date of Application

______ Signature in ink.

COMPLETING THE APPLICATION

Grade of Membership . . .

Membership grades are based on experience credits which are earned as follows:

1. **Experience credits earned for education.**

Doctorate in science or engineering subject:	**6 credits**
Masters in science or engineering subject:	**5 credits**
Bachelors in science or engineering subject:	**4 credits**
Other degree in non-science or non-engineering subject:	**2 credits**

Maximum credits allowable for education shall be six (6).

When filling in the "Statement of College Work" on the reverse side of this application, please place the corresponding number of credits earned in the right-hand column.

2. **Experience credits** for qualifying experience in plastics or plastics engineering are earned at the rate of one (1) per year, e.g. 5½ years of qualifying experience = 5½ credits. *Please detail carefully the engineering skill required for* ***each position*** *to help the Credentials Committee judge experience as "qualifying."*

When filling in the "Record of Qualifying Experience in Plastics" on the reverse side, please place the amount of time spent in each position (in years and months) in the right-hand column.

When you have determined the number of credits which you believe you have earned consult the following membership grade requirements. Indicate on the reverse side the grade of membership for which you believe you are qualified.

GRADE	REQUIREMENTS
Senior Member	Minimum of twelve (12) experience credits and maintained continuous membership in the Society for a minimum of two (2) years.
Member	Minimum of six (6) experience credits
Affiliate Member	Less than six (6) experience credits
Student Member	Regularly enrolled student (full- or part-time) in a course of study in plastics and between the ages of 16 years and 26 years, inclusive.

THIS PORTION MUST BE COMPLETED FOR PROCESSING OF YOUR APPLICATION.

Please check off the principal activity of your company under either Manufacturing or Non-Manufacturing.

MANUFACTURING

1. ☐ Electrical & Electronic Machinery, Equipment & Appliances
2. ☐ Motor Vehicles and Equipment
3. ☐ Transportation Equipment (except Motor Vehicles)
4. ☐ Professional, Scientific and Controlling Instruments, Photographic & Optical Goods, Clocks
5. ☐ Iron, Steel & Nonferrous Metals & Machinery (except Plastic & Electrical Machinery)
6. ☐ Fabricated Metal Products and Housewares
7. ☐ Finished Apparel Products
8. ☐ Food and Tobacco Products
9. ☐ Toilet Preparations, Drugs and Insecticides
10. ☐ Paints, Varnishes and Industrial Chemicals (except Plastic Raw Materials)
11. ☐ Petroleum, Coal, Rubber, Stone and Glass Products
12. ☐ Musical Instruments, Toys, Sporting Goods, Athletic Goods, Ordnance & Smokers' Supplies
13. ☐ Jewelry and Fashion Accessories
14. ☐ Furniture and Finished Wood Products
15. ☐ Leather and Leather Products
16. ☐ MANUFACTURING, other than above. Please specify ____

17. ☐ Plastics Custom Molders, Extruders, Laminators, and Fabricators
18. ☐ Plastic Materials
19. ☐ Producers and Processors of Textiles, Lumber, Paper, Oils, Dyes, Chemicals, etc. used in Manufacture of Plastics
20. ☐ Plastic Machinery

NON-MANUFACTURING

21. ☐ Government: Federal, State, Municipal and Foreign; Officers of the Armed Forces
22. ☐ Advertising Agencies, Sales Consultants and Sales Engineers
23. ☐ Libraries, Schools, Colleges and Trade Associations
24. ☐ Consultants and Research Organizations, Architects, Engineers, Designers, Chemists
25. ☐ Transportation Operating Companies
26. ☐ Retail Stores
27. ☐ Exporters, Importers, Distributors, Jobbers, Wholesalers and Manufacturers' Agents
28. ☐ Doctors, Lawyers and other Professionals
29. ☐ NON-MANUFACTURING, other than above. Please specify

30. ☐ Packaging & Containers
31. ☐ Aerospace
32. ☐ Construction Materials

MEMBERSHIP APPLICATION

SOCIETY OF PLASTICS ENGINEERS, INC.
65 Prospect Street, Stamford, Conn. 06902
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