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A visible light initiator system for the photoinduced cationic polymerization of epoxides is reported. It uses free radical promoted cationic polymerization the radical being generated from a visible light absorber. The developed system consists of an iodinated xanthene dye, a coinitiator and a diaryliodonium salt. Aromatic amines having low basicity and containing α-hydrogens are the preferred coinitiators for the polymerization of cyclohexene oxide. The system can efficiently photoinitiate the polymerization of certain cyclic ethers and can function at any wavelength of the visible spectrum depending on the dye's absorption spectrum and its oxidation/reduction potentials. Studies on photochemical reactions between each two of the three components and characterization of the polymer formed from cyclohexene oxide indicate that both the oxidative bleaching of the dye by the diaryliodonium salt and the reductive bleaching of the dye by the aromatic amine contribute to α–amino radical formation and oxidation of the α–amino radicals by diaryliodonium salts produces α–aminocarbocations which initiate the ring opening polymerization. Dye molecules are incorporated into the polymer in chain terminating processes.

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Photopolymerization of Cyclohexene Oxide - A Visible Light Initiating System and Mechanistic Investigations

by

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Photopolymerization of Cyclohexene Oxide
---A Visible Light Initiating System and Mechanistic Investigations

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Abstract

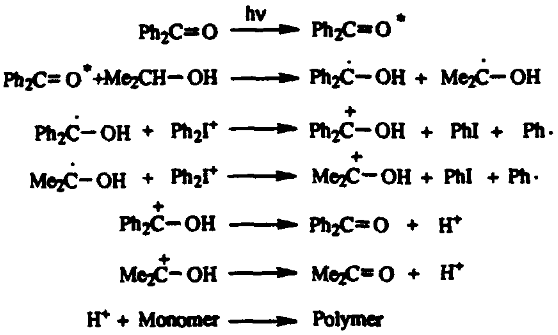
A visible light initiator system for the photoinduced cationic polymerization of epoxides is reported. It uses free radical promoted cationic polymerization the radical being generated from a visible light absorber. The developed system consists of an iodinated xanthene dye, a coinitiator and a diaryliodonium salt. Aromatic amines having low basicity and containing α-hydrogens are the preferred coinitiators for the polymerization of cyclohexene oxide. The system can efficiently photoinitiate the polymerization of certain cyclic ethers and can function at any wavelength of the visible spectrum depending on the dye's absorption spectrum and its oxidation/reduction potentials.

Studies on photochemical reactions between each two of the three components and characterization of the polymer formed from cyclohexene oxide indicate that both the oxidative bleaching of the dye by the diaryliodonium salt and the reductive bleaching of the dye by the aromatic amine contribute to α-amino radical formation and oxidation of the α-amino radicals by diaryliodonium salts produces α-aminocarbocations which initiate the ring opening polymerization. Dye molecules are incorporated into the polymer in chain terminating processes.

Introduction

It is of great interest to initiate the cationic ring opening polymerization of epoxides by visible light because visible light is cheap, safe and possesses higher penetrating ability towards many UV absorbing monomers and substrates. Unfortunately, few of cationic initiators[2] or sensitized cationic initiating systems[3] have been found to possess photosensitivity to visible light of above 450 nm.

Ledwith[4] first proposed the promotion of photoinduced cationic polymerization by photochemically generated free radicals. Benzoin derivatives (type I initiator) and benzophenone/isopropyl alcohol (type II initiator)[5] were used as absorbing chromophores, and oxidation of the formed free radicals by diaryliodonium salts gave cationic species which subsequently, apparently, initiated cationic polymerization. A typical example is given by Scheme 1.



$$Ph_2C{=}O \xrightarrow{hv} Ph_2C{=}O^*$$

$$Ph_2C{=}O^* + Me_2CH{-}OH \longrightarrow Ph_2\dot{C}{-}OH + Me_2\dot{C}{-}OH$$

$$Ph_2\dot{C}{-}OH + Ph_2I^+ \longrightarrow Ph_2\overset{+}{C}{-}OH + PhI + Ph\cdot$$

$$Me_2\dot{C}{-}OH + Ph_2I^+ \longrightarrow Me_2\overset{+}{C}{-}OH + PhI + Ph\cdot$$

$$Ph_2\overset{+}{C}{-}OH \longrightarrow Ph_2C{=}O + H^+$$

$$Me_2\overset{+}{C}{-}OH \longrightarrow Me_2C{=}O + H^+$$

$$H^+ + Monomer \longrightarrow Polymer$$

Scheme 1 Radical promoted cationic polymerization

Because of the easy access of a variety of UV radical photoinitiators, most work has been done only in UV source promoted cationic polymerization[6]. We reasoned that a visible light free radical initiating system, if carefully selected, might be used successfully to extend the curing wavelength for epoxy resins into the visible by a similar oxidation process. Since it is well known that halogenated xanthene dyes such as Eosin, Erythrosin, and Rose Bengal, in combination of electron donating coinitiators, act as efficient visible light photoinitiators for free radical polymerization of acrylic monomers[7] We explored the combination of the dye/coinitiators and onium salts as potential visible light initiating systems for cationic polymerization and report that a system consisting of a diaryliodonium salt, a N,N-dimethyl substituted aromatic amine and a halogenated xanthene dye is an efficient cationic photoinitiator for certain epoxy monomers. A mechanism of the initiation, based on detailed exploration of all the involved photochemical processes, is proposed.

Experimental Section

Materials. Cyclohexene oxide (Aldrich) was dried over calcium hydride, and then purified by fractional distillation under nitrogen. Rose Bengal, Eosin B, Erythrosin B, Rhodamine B, and methylene blue, and most aromatic amines (Aldrich) were used without further purification. RBAX (acetylated decarboxylated Rose Bengal)[8], TIHF (2,3,5,7-tetraiodo-6-hydroxyfluorone)[9] and DIEF (2,4-diiodo-6-ethoxyfluorone)[10] were gifts from SGL[11]. Diphenyliodonium hexafluorophosphate, diphenyliodonium hexafluoroarsenate, diphenyliodonium hexafluoroantimonate, diphenyliodonium tetrafluoroborate, 4,4'-dimethyl diphenyliodonium tetrafluoroborate, 4-methoxydiphenyl iodonium tetrafluoroborate, 3,3'-dinitrodiphenyliodonium tetrafluoroborate and triphenylsulfonium tetrafluoroborate were synthesized according to literature procedures[12].

Light Intensity of Sources. The light source used is a 450 W tungsten lamp equipped with 520 nm cutoff filters to eliminate UV irradiation. The emission spectrum of the filtered lamp was recorded using a Spex Fluorolog-2 fluorometer. Absolute light intensity was calibrated using a chemical actinometer, Aberchrome 999p[13], a photochromic fulgide whose quantum yield of bleaching is known at all wavelengths of its absorption ranging from 430 nm to 630 nm. The intensity of the light source measured is shown in Figure 1.

Polymerization. Polymerization initiated by the dye/coinitiator/onium salt system was carried out in a merry-go-round photolysis apparatus. At the center of the apparatus was a Sylvania 120V 500W tungsten filament immersion lamp, air cooled, placed into a double-walled quartz immersion well through which was pumped cooling water. The immersion well was put into a rectangular aluminum well with one window per side to which a glass filter was fixed. The entire apparatus was placed in a large thermostat water bath and the temperature controlled to within 1 °C. Suitable amounts of dye, coinitiator, onium salt and monomer were placed into a pruderies glass test tube and then sealed with a septum. Dry nitrogen gas was passed through the test tube slowly for several minutes to expel the oxygen trapped in the tube. The

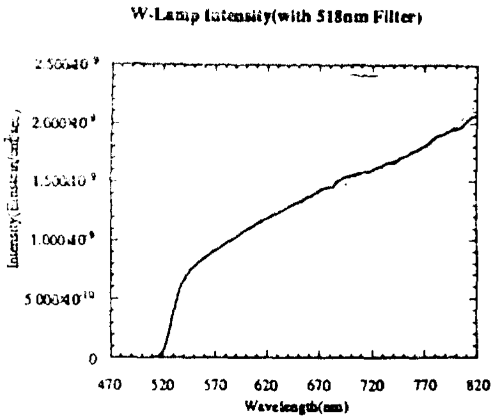


Figure 1 Light intensity of tungsten lamp with 518 nm filter

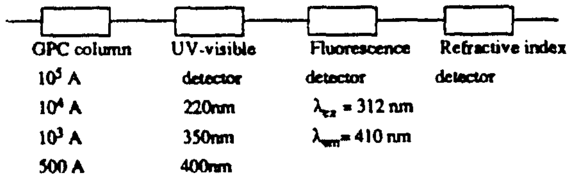
samples were then irradiated on the merry-go-round apparatus and tubes were withdrawn at regular time intervals. The polymerization was terminated by pouring the reaction mixture into methanol into which a small amount of ammonium hydroxide had been added. The precipitated polymer was isolated by filtration and washed with methanol. It was dried in the oven overnight at 90 °C. Percent conversion was calculated from the weight of the polymer obtained.

Molecular Weight Determination. Molecular weights of the polycyclohexene oxides obtained were measured using gel permeation chromatography (GPC). Four µ-Styragel GPC columns (10^5A, 10^4A, 10^3A, 500A) were connected to a Waters HPLC in the order of decreasing pore size to achieve maximum loading. A Waters Associates Differential Refractometer R-400 was used as the detector. HPLC grade THF was the eluent. The molecular weight standards were polystyrenes (PolySciences) with molecular weights of 4,000; 10,200; 17,500; 80,000; 160,000 and 410,000.

End Group Analysis. Fluorescence spectroscopy was used to identify the end groups in the polymer of cyclohexene oxide. N,N-Dimethylnaphthyl amine (DMNA), a compound with high fluorescence quantum yield, was used as the coinitiator. Both manual and GPC methods were used to separate the polymer and free initiator after polymerization.

In the manual method, polymer from cyclohexene oxide obtained through the bulk polymerization initiated by ethyl Erythrosin, diphenyliodonium hexafluoroantimonate (DPI), and DMNA was first dissolved in dichloromethane and then methanol was added drop by drop to precipitate the polymer. After filtration, the precipitate was dissolved again in dichloromethane and reprecipitated. This dissolution and precipitation was repeated 6 times to remove unreacted amine, DPI, and dye. The fluorescence spectrum of the purified polymer was recorded on the Fluorolog-2 fluorometer.

In the GPC method, the four µ-Styragel columns were connected to a HP1090 liquid chromatograph in the same order as that used for the MW determination. A diode array UV-visible detector, a HP 1046A programmable fluorescence detector and a Waters Associates Differential Refractometer R-400 were hooked to the end of the GPC column, Scheme 2. A solution containing 2% polymer in THF was used in GPC analysis.



Scheme 2 Scheme of instrumentation for end group analysis

The absorption, emission, and excitation spectrum of ethyl Erythrosin, DPI and DMNA was obtained using the HP8452 diode array UV visible spectrophotometer and the Fluorolog-2 spectrometer respectively. Three wavelengths were selected on the diode array detector. These wavelengths are 400 nm at which only bleached ethyl Erythrosin has absorption, 350 nm at which both the bleached xanthene dye and DMNA have absorption, and at 220 nm at which all the three main components of the initiator system have absorption. The excitation wavelength in the fluorescence detector is set at 312 nm which is the wavelength of the maximum absorption of DMNA. The emission was monitored at 410 nm. The solvent used is HPLC grade THF, and the rate of solvent flow is 1 ml/minute.

Results and Discussion

1. Effect of Xanthene Dyes on the Efficiency of Cationic Polymerization of Cyclohexene Oxide

As reported by Crivello and Lam[14], xanthene dyes such as Rose Bengal do not sensitize cationic polymerization of epoxy monomers in the presence of diaryliodonium salts. We have confirmed this in our initial study though we also found that the system bleaches rapidly upon irradiation with visible light[15]. Moreover, we find that addition of a small amount of an electron donor such as N,N-dimethylaniline causes the system to effectively initiate polymerization of cyclohexene oxide.

Table 1 gives certain of the dyes investigated and their physical parameters[16] as well as the percentage conversion of cyclohexene oxide to its polymer when they are used as reactants in a standard visible initiating system.

Table 1 Photopolymerization* of cyclohexene oxide (bulk) at 21°C with different dyes

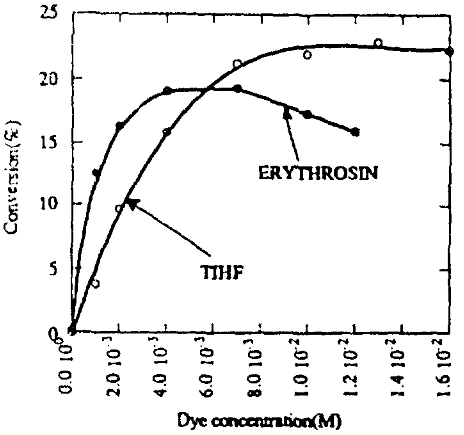
Dye	λ(nm)	Charge	ϕ_T	E_{ox}	Conversion(%)
Rose Bengal	548	-2	0.76	0.95	20.2
Eosin	514	-2	0.28	0.80	7.1
Erythrosin	525	-2	0.62	0.79	21.8
RBAX	492	0	< 0.87	~1.0	17.7
TIHF	538	-1	< 0.87	1.34	12.5
Methylene Blue	656	+1	0.58	1.17	4.6
Rhodamine B	556	+1	< 0.01	0.95	9.5

* Dye Concentration: $2x10^{-3}$ M
4,4'-Dimethyldiphenyliodonium tetrafluoroborate: $5x10^{-2}$ M
N,N-Dimethylaniline: $1.0x10^{-2}$ M
Irradiation time: 4 hours.

Erythrosin, with the lowest oxidation potential but bearing two negative charges, is the most efficient among these dyes, while Rose Bengal and RBAX are nearly as efficient. TIHF, with a high quantum yield of intersystem crossing but higher oxidation potential, is less efficient. Methylene blue, bearing a positive charge and a well known sensitizer of free radical polymerization[17], gives a very low conversion even though its absorption spectrum is in full overlap with the emission spectrum of the radiation sources used. Rhodamine B, a dye with high fluorescence yield (65%), also gives poor results.

Though it is hard to make an accurate comparison of the photosensitizing efficiency of such different dyes since the dyes have differing absorption band manifolds and extinction coefficients. By irradiating the sample for a long time we believe that we have made the absorption difference less important among the various factors which determine the photoefficiency of the dye. We conclude that iodinated xanthene dyes, usually with large quantum yields of intersystem crossing, longer triplet lifetimes, and lower oxidation potentials are better as initiators in the new system.

Figure 2 gives the concentration dependence of conversion of cyclohexene oxide initiated by TIHF and Erythrosin. Under the experimental conditions used there is no polymerization in the absence of dye, Figure 2. This is because both the diphenyliodonium salts and N,N-dimethylaniline have absorbance only in the UV region. At low dye concentration, Erythrosin brought about higher conversion than TIHF. Higher sensitivity of Erythrosin has also been found in the dye sensitized decomposition of diazonium salts[18]. At higher dye concentrations however, the efficiency of Erythrosin becomes lower than TIHF likely because Erythrosin bears two negative charges, one on the phenoxy oxygen of the xanthene ring, the other on the carboxy group of the 9-substituted benzene ring. It appears these negative centers function in the termination step of polymerization but are not important to the initiation step. Ethyl Erythrosin shows a much better solubility in the monomers studied, has only one negative charge and leads to much higher monomer conversion.



4,4'-Dimethyldiphenyliodonium tetrafluoroborate: $5x10^{-2}$ M;
N,N-Dimethylaniline: $1x10^{-2}$M;
Irradiation time: 4 hours.

Figure 2 Plot of conversion of cyclohexene oxide monomer vs. dye concentration .

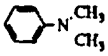
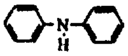
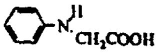
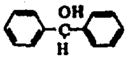
2. Effect of Coinitiators on the Efficiency of Cationic Polymerization of Cyclohexene Oxide

In most Type II radical initiators, it is radicals from the coinitiator that initiate polymerization[19]. Aliphatic and aromatic amines are coinitiators widely used in xanthene dye and thiazene dye induced free radical polymerization. However, the basicity of the amine is a major issue when these amines are used in a cationic polymerization system. Aliphatic amines, well known as terminators for cationic polymerizations are more basic than aromatic amines. Thus the pKas of most aromatic ammonium salts in aqueous solution are below 5 and can be as low as 2 or 3. (In comparison, the pKa of trimethylammonium is 9.76). Acridine orange[14], a reported sensitizer for cationic polymerization which bears two dimethylamino groups, provides direct evidence that an aromatic amine can be present in a cationic photopolymerization system without terminating the cationic chain. Thus, we included aromatic amines as potential coinitiators for the radical promoted cationic polymerization. Table 2 gives the conversion of cyclohexene oxide by using a series of coinitiators with decarboxylated Rose Bengal as the sensitizing dye.

No photopolymerization was observed when benzhydrol and isopropyl alcohol are used as a coinitiator. Benzophenone/isopropyl alcohol promoted cationic polymerization (Scheme 1) involves hydrogen abstraction from the alcohol by the excited benzophenone which has a triplet energy 68 Kcal/mole in the primary step. Since xanthene dye sensitizers have triplet energies as low as ~43 kcal/mole, hydrogen abstraction from an alcohol such as isopropyl alcohol is not a favorable path in producing radicals from the xanthenes.

Tertiary amines such as triethylamine and triethanolamine fail in initiating cationic polymerization as coinitiators in this system. As is well known, it is the basicity of the amine that prohibits cationic chain polymerization. Diphenylamine has a low basicity; the pKa value of the conjugate acid is 0.97 and this is much lower than acridine orange. It fails to initiate the polymerization of cyclohexene oxide since the stable α-amino radical can not be formed from it, indicating the necessity of the photogenerated radicals. In contrast, both N,N-dimethylaniline and N-phenylglycine are good coinitiators of cationic polymerization.

Table 2 Photopolymerization of cyclohexene oxide (bulk) at 21°C with different coinitiators

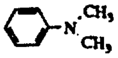
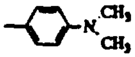
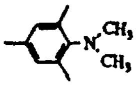
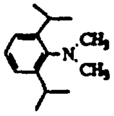
Coinitiator	Conversion(%)	Coinitiator	Conversion(%)
	18.0		<1
	15.9	$N(CH_2CH_2OH)_3$	0.2
		$N(CH_2CH_3)_3$	0.5
	0.7		0.1
	0.1	 $\overset{OH}{CH_3CHCH_3}$	0.02

* Decarboxylated rose bengal: $2x10^{-3}$M;
4,4'-Dimethyldiphenyliodonium tetrafluoroborate: $5x10^{-2}$M;
Coinitiator: $1x10^{-2}$M;
Irradiation time: 4 hours.

Summing all the data, we conclude that only aromatic amines with α hydrogens are capable of initiating the polymerization of cyclohexene oxide in this system. Aliphatic amines, aromatic amines without α hydrogen and non-amine hydrogen donors are incapable of initiation.

Based on this conclusion, we further explored several aromatic amines, all of which bear an α hydrogen. For a shortened irradiation time (1 hour), results are given in Table 3. 2,4,6,N,N-pentamethylaniline gives the highest conversion among these coinitiators. N,N-dimethylaniline is included in the table for comparison.

Table 3 Photopolymerization of cyclohexene oxide (bulk) at 21°C with aromatic amines containing α hydrogens

Coinitiator	Conversion(%)	Coinitiator	Conversion(%)
	9.8		8.9
	16.0		13.3

* Decarboxylated rose bengal: $2x10^{-3}$M;
4,4'-Dimethyldiphenyliodonium tetrafluoroborate: $5x10^{-2}$M;
Coinitiator: $1x10^{-2}$M;
Irradiation time: 1 hour.

Figure 3 is a plot of the cyclohexene oxide conversion vs. coinitiator (N,N-dimethylaniline) concentration. Without coinitiator, there is no polymerization under the experimental conditions. Conversion increases nearly linearly with coinitiator concentration, levels off and gradually goes down at higher concentration.

3. *Effect of Diaryliodonium Salts on the Efficiency of Cationic Polymerization of Cyclohexene Oxide*

We synthesized a variety of iodonium salts ranging from a common iodonium cation with different anions to a common anion with different onium cations. We also compared iodonium salts with a sulfonium salt. The experimental results are given in Table 4.

A dramatic difference is found in the initiation efficiency of the iodonium salt and the sulfonium salt. The dye/coinitiator system can accelerate diaryliodonium salt initiated cationic polymerization, but fails to accelerate the triphenylsulfonium salt initiated cationic polymerization. There is no selectivity based on the diaryliodonium salt if the counter anion is kept the same, for we observed similar conversions no matter what the nature of the substituent on the aromatic ring. Since both diaryliodonium salts and triarylsulfonium salts are efficient UV cationic initiators, the dramatic difference in their reactivity in the system investigated is related to substantial differences in the reduction potentials of the onium salts.

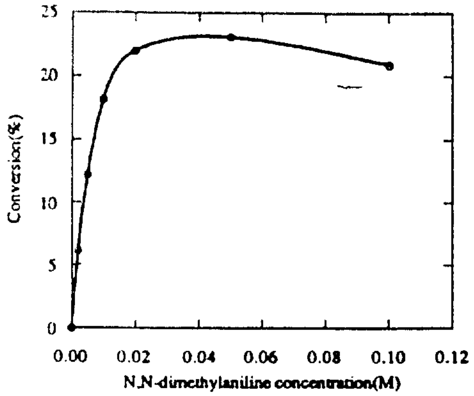
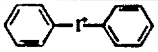
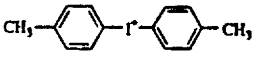
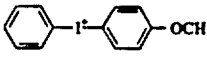
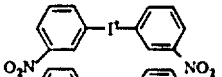
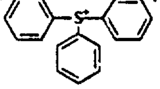
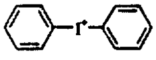
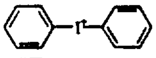
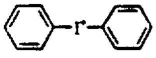
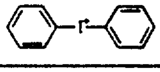


Figure 3 Plot of conversion of cyclohexene oxide vs. N,N-dimethylaniline concentration

Table 4 Photopolymerization of cyclohexene oxide (bulk) at 21°C with different onium salts

Iodonium salt Cation	anion	irradiation time(min.)	conversion (%)
	BF_4^-	240	16.6**
	BF_4^-	240	17.7
	BF_4^-	240	19.2
	BF_4^-	240	18.4
	BF_4^-	240	0.0
	BF_4^-	60	8.9**
	PF_6^-	30	>90
	AsF_6^-	~~15~~	100
	SbF_6^-	10	100

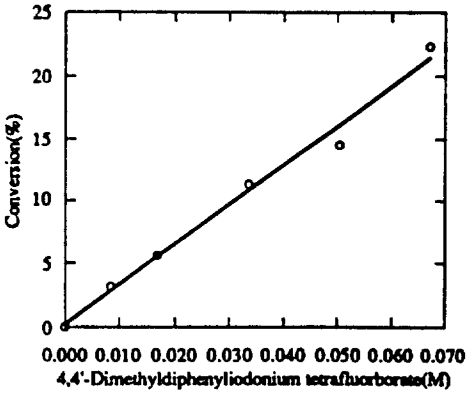
* Dye concentration: RBAX= $2x10^{-3}$M;
Diphenyl iodonium salt: $5x10^{-2}$M;
N,N-Dimethylaniline: $1x10^{-2}$M

** It was to our disadvantage that we found diphenyliodonium tetrafluorobate has poor solubility in monomer solution. A low concentration was used and the result was extrapolated to a comparable concentration. A linear conversion dependence on concentration has been found. See Figure 4.

Triphenylsulfonium salts have a reduction potential of ~ -1.2V (vs. SME)[20]. This is much lower than that of the iodonium salts, which is about -0.2 V (vs. SME)[21], meaning that iodonium salts are much more oxidative than are sulfonium salts. Substitution on the benzenering of iodonium salts does not, however, strongly influence the oxidation and reduction properties. 4-Methoxydiaryliodonium salts, which bear a strongly electron releasing substituent, have an oxidation potential of ~-0.186 while the 3,3'-dinitrodiphenyliodonium salt, which bears two strong electron withdrawing groups, has a reduction potential of -0.200 V [22]. This narrow range of the reduction potential parallels with the narrow range of conversions of monomer to polymer in our system so it is apparent that some key step in the initiation involves the iodonium salt in a redox reaction.

For diaryliodonium salts with different anions, we find exactly the same reactivity as for UV light initiated cationic polymerization: $SbF_6^- > AsF_6^- > PF_6^- > BF_4^-$· For the hexafluoroantimonate salt, cyclohexene oxide can be completely cured to solid polymer in 10 minutes visible light irradiation under well cooled conditions. (An explosive polymerization in several seconds may result if the solution is not suitably cooled.) We report the monomer conversion to be 100% in cases where the solid state polymer is formed, because a routine precipitation method cannot be used to measure the actual conversion. For hexafluorophosphate and hexafluoroarsenate salts the above monomer solution can be completely cured in less than 30 minutes irradiation. As to the tetrafluoroborate salt, the rate of polymerization is considerably slower, being less than 10% in one hour's irradiation. The order of reactivity $SbF_6^- > AsF_6^- > PF_6^- > BF_4^-$ reveals a cationic polymerization mechanism, even though some radical intermediates might be involved during the reaction.

Figure 4 is a plot of conversion of monomer vs. diaryliodonium salt concentration. The straight line obtained with the intercept equal to zero indicates that there is no polymerization in the absence of diaryliodonium salt.



RBAX: $2x10^{-3}$M;
N,N-Dimethylaniline $1x10^{-2}$M;
Irradiation time: 2 hours.

Figure 4 Plot of conversion of cyclohexene oxide vs. diaryliodonium salt concentration

Because the xanthene dye/electron donor coinitiator is a typical free radical initiating system[23], the fact that no polymerization occurs in the absence of iodonium salt indicates again that cyclohexene oxide is not polymerized via a radical process. All the polymer formed in the presence of the iodonium salt must be formed through a cationic mechanism. At constant dye concentration, a linear relationship between monomer conversion and onium salt concentration is strictly followed. Owing to the absence of absorption of the onium salt in the visible region of the spectrum, the initiating species can not be generated by the direct interaction of a photon with the onium salt but only through the interaction of the ground state onium salt with other species which is generated photochemically, for there is no polymerization without irradiation.

4. Characterization of Polycyclohexene Oxide

Figure 5 gives the molecular weights for a series of samples of polycyclohexene oxides polymerized under the same experimental conditions but with different irradiation times.

The molecular weight of polycyclohexene oxide does not change dramatically with irradiation time nor with conversion. The curves are indicative of the mechanistic character of the fundamental chain polymerization. Moreover, the living cationic polymerization is not so 'lively' in this system. High molecular weight at low conversion also indicates a back biting process (i.e. the oxygen in the polymer chain attacks the cationic center rather than the monomer to form a small ring) which is common in the polymerization of THF but is not thought to be an important process in the polymerization of cyclohexene oxide.

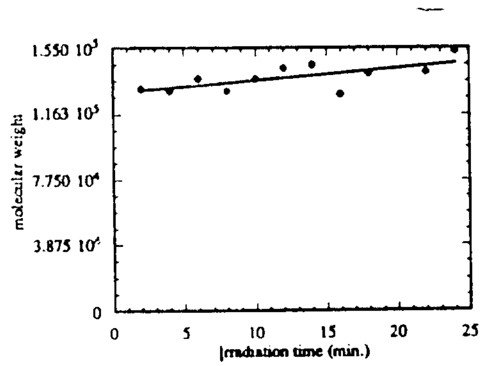


Figure 5 Molecular weight of polycyclohexene oxide obtained vs. irradiation time

The initiating species was investigated using multiple detection methods including absorption and fluorescence characterizing the end groups of the polymers formed. For a polymer with a molecular weight of around 10^5, fluorescence detection is sensitive enough to detect the signal from end groups in a polymer solution with concentration 10^{-3} - 10^{-4} g/liter if the end group is selected such that it has a high quantum yield of fluorescence. For this purpose, polymers were synthesized by using ethyl Erythrosin /DMNA/DPI as an initiator. DMNA absorbs at 312 nm and gives a fluorescence peak at 402 nm at low concentration in acetonitrile solution. Ethyl Erythrosin was totally bleached during the polymerization. Bleached ethyl Erythrosin has a broad absorption spectrum ranging from the UV to the 550 nm region. Excitation at 312 nm gives a weak emission with a maximum at 484 nm in acetonitrile solution. This weak emission may cause a small interference in the fluorescence determination of DMNA, but its maximum emission wavelength is different from DMNA's maximum emission wavelength. If the whole spectrum is recorded, the two emissions are easily differentiated. Diphenyliodonium salt and its decomposition products such as benzene or iodobenzene do not absorb at 312 nm, so their presence does not influence the determination of other components.

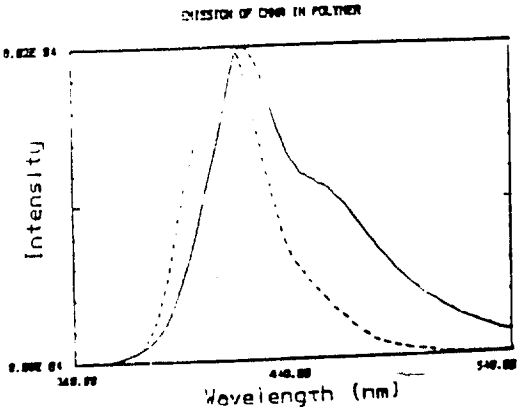


Figure 6 Fluorescence spectrum of polymer sample purified by the dissolution-precipitation method. Solid line: polymer solution; dashed line: DMNA

Figure 6 gives the fluorescence spectrum of a cyclohexene oxide polymer photoformed with ethyl Erythrosin/DPI/DMNA. The sample was purified by repeated dissolution in dichloromethane and precipitation from methanol solution until no substantial drop of fluorescence occurred after subsequent purification steps. The fluorescence peak (solid line) is basically the same as that derived from the fluorescence spectrum of DMNA in solution (dashed line), and the shoulder at long wavelength matches with the fluorescence spectrum of bleached ethyl Erythrosin. The polymer always remained yellowish, a typical color of the bleached dye, no matter how many times the sample is purified.

Figure 7 gives the normalized elution curves detected by the multiple detectors after GPC separation. Polymer was eluted from the column (retention time = 29.5 minutes) as indicated by the refractive index detector (curve 5).

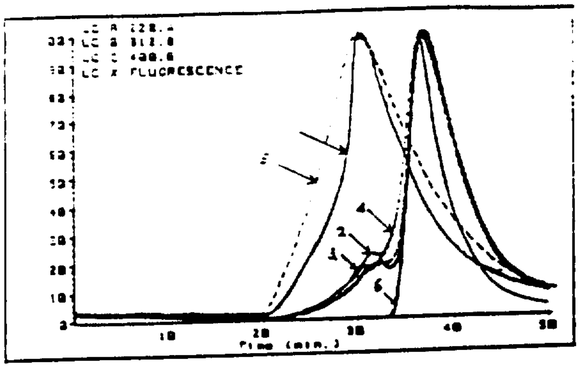


Figure 7 Normalized elution curves of the polymer sample initiated by ethyl Erythrosin/DMNA/DPI initiators.

Curve 1, 2, 3: absorption monitored at 400, 220, 350 nm;
Curve 4: fluorescence, λ_{ex}=312 nm; λ_{em}=400 nm;
Curve 5: refractive index detector response;
Curve 6: absorption and fluorescence of DMNA free molecules;
Elution solvent: THF; rate of flow: 1.2 ml/min.

Curve 1, the 400 nm absorption response from the diode array detector, has a retention time exactly the same as that of the polymer as indicated by curve 5, indicating that most of the 400 nm absorbing component(s) are incorporated to polymer molecules. Because only bleached ethyl Erythrosin absorbs through 380 nm to 550 nm in the system, we conclude that bleached dye molecules are connected to the polymer chain.

Curve 2 and 3 are the 200 nm and 312 nm absorption responses from diode array detector and curve 4 is the fluorescence signal at 400 nm. These curves have common peak positions indicating a retention time of 37 minutes. These peaks are attributed to unreacted small molecules such as unreacted DMNA, DPI, and formed photoproducts like benzene or iodobenzene. Both DMNA and DPI are in large excess and are not exhausted during photopolymerization. Thus they are eluted from the column as individual peaks. Control experiments show that unreacted DMNA gives elution curve expressed in Curve 6.

Comparison of the curves 2, 3, 4 with the curve 6 in Figure 7 discloses that in front of the large peaks curve 2, 3, 4, there are clearly distinct peaks which can be traced as far back as the starting point of the polymer peak. These peaks are caused by the 200 nm and 312 nm absorbing species, and 402 nm fluorescence emitting species.

By scanning the whole fluorescence spectrum at retention time 27.3 minutes, and comparing the spectrum with a sample thermally polymerized in the absence of ethyl Erythrosin, we find the main florescence species is from DMNA moiety rather than from the dye.

which indicates again the presence of DMNA in the polymer molecules.

5. Mechanism of Photoinitiation

Photochemical reactions between each two of the three components of the initiator system have been intensively studied. Irradiation of acetonitrile solutions of diaryliodonium salts and either ethyl Eosin or ethyl Erythroson[15,24] results in immediate bleaching of the dyes. The quantum yield of bleaching was found to be very close to the quantum yield of triplet formation, indicating that triplet formation controlled the efficiency of the photochemical reaction. Product analysis shows that phenyl radicals coupled and substituted on the aromatic nucleus of dyes (Figure 8) indicating the primary photochemical reaction is the electron transfer from the dye to the onium salt as expressed by equation 1 in Scheme 4.

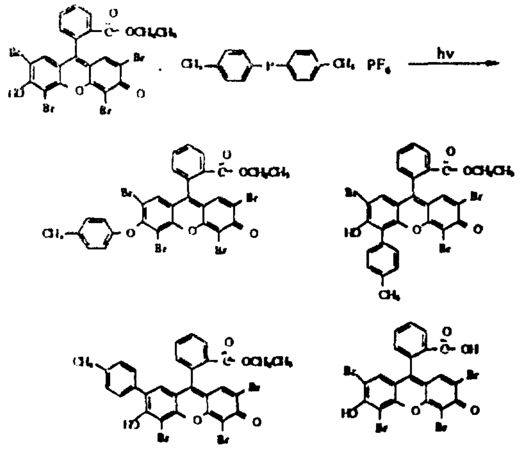
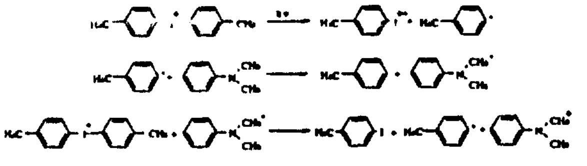


Figure 8 Products of the photochemical reaction between ethyl Eosin and iodonium salts

In contrast, irradiation of an acetonitrile solution of ethyl Erythrosin with N,N-dimethylaniline for an extended time does not cause the dye to bleach, although flash photolysis shows that the amine quenches the triplet states of the dye as efficiently as does the iodonium salt. This indicates both that the electron transfer and the back electron transfer (reaction 2 in Scheme 4) are very fast processes in the case of aromatic amine quenching of dye triplet.

Irradiation of an acetonitrile solution of a diphenyl iodonium salt with N,N-dimethylaniline[24] gives bis-(4, 4'-dimethylaminophenyl)methane as the main product and crystal violet, methyl violet, as well as the leuco forms of these dyes as minor products. This indicates that the α-amino radical is oxidized into α-aminocarbocation:

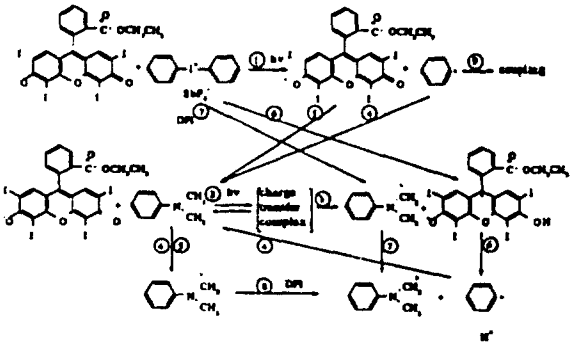


Scheme 3 Oxidation of α-aminoradicals by iodonium salts

End group analysis demonstrates that both the aniline and dye molecules are incorporated into the polymer.

Having considered all the possible reaction, we propose the mechanism of initiation as shown in Scheme 4.

Though we cannot rule out proton initiated polymerization in some small number of cases, it appears that the α-aminocarbocation is mainly responsible for initiation of cationic polymerization because the route of reaction 1 -> 4, 5 -> 8 is favored as compared to 2 -> 3 -> 6, 7 in which the back electron transfer hinders the free radical formation. Once the radicals are generated, a chain reaction between the diaryliodonium salt and [illegible] coinitiator, e. g. the N,N-dimethylamines, is triggered. Large quantities of reactive cations are produced, and an explosive polymerization results. The dye is incorporated into the polymer mainly by a termination process, although it is essential to the initiation step.



Scheme 4 Interaction diagram of ethyl Erythrosin/DPI/DMA upon visible light irradiation

Conclusion

The developed system consists of an iodinated xanthene dye, a N,N-dimethylaromatic amine coinitiator and an oxidative onium salt with a nonnucleophilic anion. The dye functions as a photon acceptor. Both the reductive bleaching of the dye by the amine and oxidative bleaching of the excited dye by onium salt contribute to generate α-aminoradicals. The onium salts are responsible for oxidizing some of the formed radicals to the carbocations, and the latter are responsible for the initiation of cationic polymerization. No polymerization occurs in the absence of any of the three components upon irradiation with visible light (>520 nm) under the described experimental conditions.

The system is unique in the following ways:

(1) The presence of the dye enables the sensitivity of the cationic initiator to be extended to a majority of visible wavelengths. Sensitivity can be easily adjusted by selecting xanthene dyes with the required absorption maxima.

(2) Aromatic amines, if of low basicity, do not always need be terminators of cation polymer chains. A nonnucleophilic amine can be a coinitiator for the polymerization of monomers containing reactive epoxy functions.

(3) The system is relatively stable in the dark, and reactivity can be controlled by selecting an aromatic amine coinitiator with both suitable basicity and oxidation potential. Substitution on the aromatic ring greatly influences the coinitiator's properties. The polymerization can be made very efficient by choosing suitable iodonium salts and coinitiators and an explosive polymerization can be achieved for the photopolymerization of cyclohexene oxide under certain conditions.

(4) As has been mentioned in the introduction, acridine yellow, and Setoflavin T have been found[14] to be efficient sensitizers for the cationic polymerization of some epoxides. These dyes absorb in the longer wavelength region of the spectrum, and also possess dimethylamino groups on their aromatic rings. Although both energy transfer and electron transfer sensitization have been proposed, we believe the sensitization process may involve similar reactions to those we have described. But the systems reported provide the freedom to select more efficient dyes, i.e. dyes with different absorption wavelengths and reactivity, more efficient donors, and reasonable ratios of their concentrations to reach maximum efficiency.

Acknowledgment

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