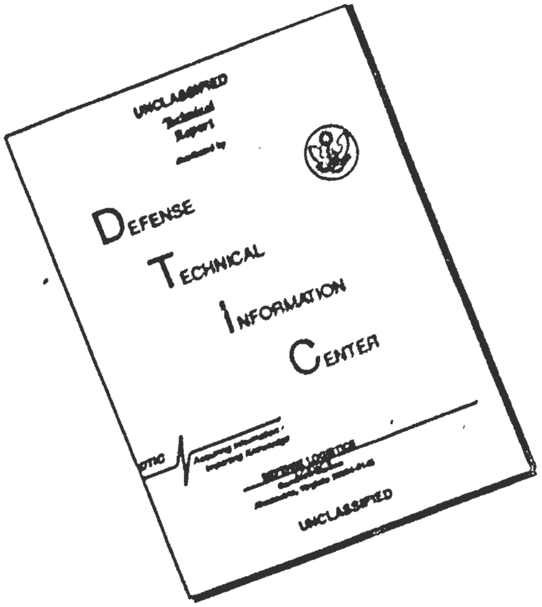

TECHNICAL REPORT
69-42-CE

# COLD DRAWING IN CRYSTALLINE POLYMERS

by

R. D. Andrews

Stevens Institute of Technology
Hoboken, New Jersey

Contract No. DA19-129-AMC-1001(N)

October 1968

UNITED STATES ARMY
NATICK LABORATORIES
Natick, Massachusetts 01760

Clothing & Personal Life Support Equipment Laboratory
C&PLSEL-57

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# FOREWORD

Many of the high-strength polymeric materials of interest to the U.S. Army are of a semicrystalline type. The drawing and yielding behavior of such polymers is of interest both in the strengthening of fibrous materials and in the analysis of their mechanical properties in use.

The four polymers of primary interest in this study were Nylon 6, polyethylene terephthalate, polyacrylonitrile and polyvinyl chloride. The first two are important crystalline textile polymers. Polyacrylonitrile, also important as a textile material, is of interest both for its less perfect type of crystallinity and for its transparency. The fourth material, polyvinyl chloride, is only slightly crystalline and possesses special properties because of this micro-crystallinity.

The major research effort was on the yielding properties of Nylon 6. The presence of a plasticizer such as phenol was found to eliminate the characteristic yield peak and neck leading to uniform and homogeneous stretching. Removal of the plasticizer raised the properties (such as modulus), but the yield peak continued to be absent. In general, the work has led to a greater understanding of the mechanism of yielding in polymers and the role of both the crystalline and the amorphous regions in the process.

The work under this Contract DA19-129-AMC-1001(N) was conducted from 15 June 66 to 15 Sept 1967 at Stevens Institute of Technology under the direction of Professor R. D. Andrews, Department of Chemistry and Chemical Engineering. The U.S. Army Project Officer was Mr. Roy C. Laible and the Alternate Project Officer was Mr. Anthony Alesi, Materials Research Division, Clothing & Organic Materials Laboratory (currently redesignated as the Clothing and Personal Life Support Equipment Laboratory).

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# Abstract

In this investigation of the plastic yield (or cold-drawing) phenomenon in crystalline polymers, most of the work was carried out on Nylon 6, although polyethylene terephthalate (PET), polyacrylonitrile (PAN) and polyvinyl chloride (PVC) were also studied. Absorption of plasticizers (water, alcohols, phenol) in Nylon 6 produced changes in the crystalline structure as well as plasticizer action; these two effects must therefore be carefully distinguished. Changes in the crystalline structure were followed by changes in the infrared spectrum. Dynamic mechanical and thermogravimetric analysis (TGA) measurements were carried out on the polymer before and after treatment. The effects of plasticizer and temperature were investigated in both stress-strain and creep tests. The stress-strain curve of Nylon 6 can be decomposed into two components; one of these is affected by the plasticizer, and probably can be related to the amorphous phase. Phenol treatment produces a total disappearance of the yield peak in the stress-strain curve and a simultaneous disappearance of neck formation.

The drawing of amorphous PET was studied under dead-load creep conditions. This polymer showed an unusual behavior in that the neck formation would sometimes initiate at very high strains (above 50 percent elongation). The drawing of PAN under the same creep conditions indicates that a progressive structure change takes place in this polymer when temperature varies through the range of $70^{\circ}$-$160^{\circ}$C. (which spans the glass transition region). The birefringence-strain relation for PAN is also unusual, and a possible two-phase structure is hypothesized for this polymer, based on these results.

Creep drawing of plasticized PVC was also measured. The concept of plastic yield as a stress-induced glass transition seems relevant in this case, just as in the case of unplasticized PVC. The birefringence-strain relation for this polymer was of a more normal form than was observed for PAN. Measurements were made of the temperature dependence of orientation birefringence in PVC containing different amounts of plasticizers (dioctyl phthalate, dioctyl adipate, tricresyl phosphate). The different plasticizers produced very different effects in this type of experiment.

## 1. Introduction

The present project was set up as an extension and continuation in the area of crystalline polymers of previous studies of the plastic yield phenomenon carried out on glassy, amorphous polymers. Final reports (1,2) have already been published on the two projects devoted to glassy polymers. The previous studies were carried out at the Massachusetts Institute of Technology, and the present project was conducted at the Stevens Institute of Technology.

Some initial exploratory studies of the yield (or "cold drawing") behavior of crystalline polymers indicated that the behavior of crystalline polymers was surprisingly similar to the behavior of glassy, amorphous polymers, despite the great difference in their structure and morphology. This would indicate that some caution is needed in setting up theories of the yield process in crystalline polymers which are based on such concepts as slip planes and dislocations in the crystalline phase. It is tempting to postulate such mechanisms because they represent a direct analogy (or duplication) of the theory which has been developed to explain the phenomenon of plastic yield in metals. A review article on the possible application of dislocation and slip concepts to the plastic yield of crystalline polymers has been published recently by Predecki and Statton (3), and they have also proposed (4) a dislocation mechanism for plastic deformation in polyethylene. Dey (5) has also recently published an interpretation of plastic flow rates in nylon in terms of dislocation motion.

It is known that drawing or plastic yield in crystalline polymers breaks up the existing crystalline structure and produces a new and rearranged type of crystalline structure in the drawn state. This has been demonstrated by the work of Peterlin and co-workers (6,7,8), who have shown by electron microscope studies that in polyethylene, drawing breaks up the spherulites and breaks the lamellae into small fragments which finally line up in ordered rows perpendicular to the axis of extension as the sample becomes highly drawn. The reason for the peculiar nature of the ordering in the final drawn state is not yet understood.

In any definitive study of the drawing behavior of crystalline polymers, it is of course necessary to define the crystalline structure and the changes of crystalline structure as completely as possible. The use of X-ray measurements is almost essential, and other techniques such as infrared and electron microscope studies of thin sections can also be very useful. Birefringence measurements are of some general value, but it is difficult to give this kind of data detailed interpretation in the case of crystalline polymers. The method becomes more useful for polymers with lower degrees of crystallinity.

The present investigation must be regarded as an exploratory study in the area of crystalline polymers, the purpose of which was to gain some feeling for the nature of the problems involved, and some of the phenomena which are encountered. Since this was a new area of research activity at Stevens, it was necessary to build up equipment and facilities. It was necessary, for example, to construct temperature chambers (air thermostats) suitable for measurements of drawing under dead-load creep conditions. A special temperature control box was also constructed to surround a specimen when its stress-strain curve was measured on the small Instron testing machine. The air-pressure clamping system of the Instron machine also required modification (replacement of gaskets and rubber tubing with Viton rubber) for use into a higher temperature range. Some special glass tubes in which creep experiments could be carried out in controlled atmospheres were also constructed, but these were not used in the studies reported here. It was also necessary to order cathetometers, optical equipment for making birefringence measurements, and other supplementary equipment. Fortunately, infrared equipment was already available and ready for use. Therefore, principal reliance was placed on infrared data as a means of identifying crystal structure changes in the studies reported here. Some use was also made of birefringence measurements.

Other changes of strategy were made as the study progressed. The original research plan involved an emphasis on comparative studies of polymers of different types. However, it became increasingly evident that the best progress could be made by a more intensive study of a single polymer, or a small number of polymers. An intensive study was therefore made of Nylon 6. One reason for this choice was the importance of nylon in synthetic fiber applications, and the importance of the drawing process in the manufacture of such synthetic fibers. Another valuable feature of this polymer is its sensitivity to moisture and other solvent and plasticizer effects. The effects of phenol treatments, for example, were investigated in some detail. Some comparative studies were, however, made with amorphous polyethylene terephthalate (PET) and with polyacrylonitrile (PAN) and polyvinyl chloride (PVC), in which the crystalline nature is less pronounced. The phases of the research which were not completed within the time limits of the present project have not been abandoned; it is still intended to carry these studies through as soon as possible within another framework (such as student research projects).

## 2. Nylon 6

Samples of a Nylon 6 type polymer (polycaprolactam) were obtained in the form of a 5-mil commercial film, designated by the trade name Capran 77C. Rectangular strips were cut from this film with a razor blade for use in the experiments.

### a. Effect of Temperature

Stress-strain curves for the Nylon 6 film at different temperatures are given in Figure 1; the samples used here were original film without any modifying treatments. A progressive decrease of stress level with increasing temperature is seen, as well as a development of irregularities in the drawing region of the curve in the middle of this temperature range. A progressive disappearance of the initial yield peak with increasing temperature is also noted.

The drawing behavior at different temperatures was also studied in creep experiments under dead load. This type of experiment has also been reported by Bender and Williams (9) for unoriented Nylon 66 filaments, and by Ender and Andrews (10) for preoriented polystyrene. A constant (initial) stress of 12,700 psi was employed, and experiments were carried out at temperatures of $70^{\circ}$, $75^{\circ}$, $80^{\circ}$, $90^{\circ}$ and $110^{\circ}$C. The results are presented in Figure 2, in which percent elongation is plotted vs. log time. The drawing region of the curve (corresponding to neck formation and propagation) is normally seen as a fairly abrupt increase in elongation over a short region of log time. This effect can be seen clearly only at the beginning of the $80^{\circ}$ curve. At higher temperatures, this elongation has already taken place before the first measurement could be made, and therefore cannot be seen. At lower temperatures ($70^{\circ}$ and $75^{\circ}$), no such abrupt (and large) increase of elongation is seen. After the drawing

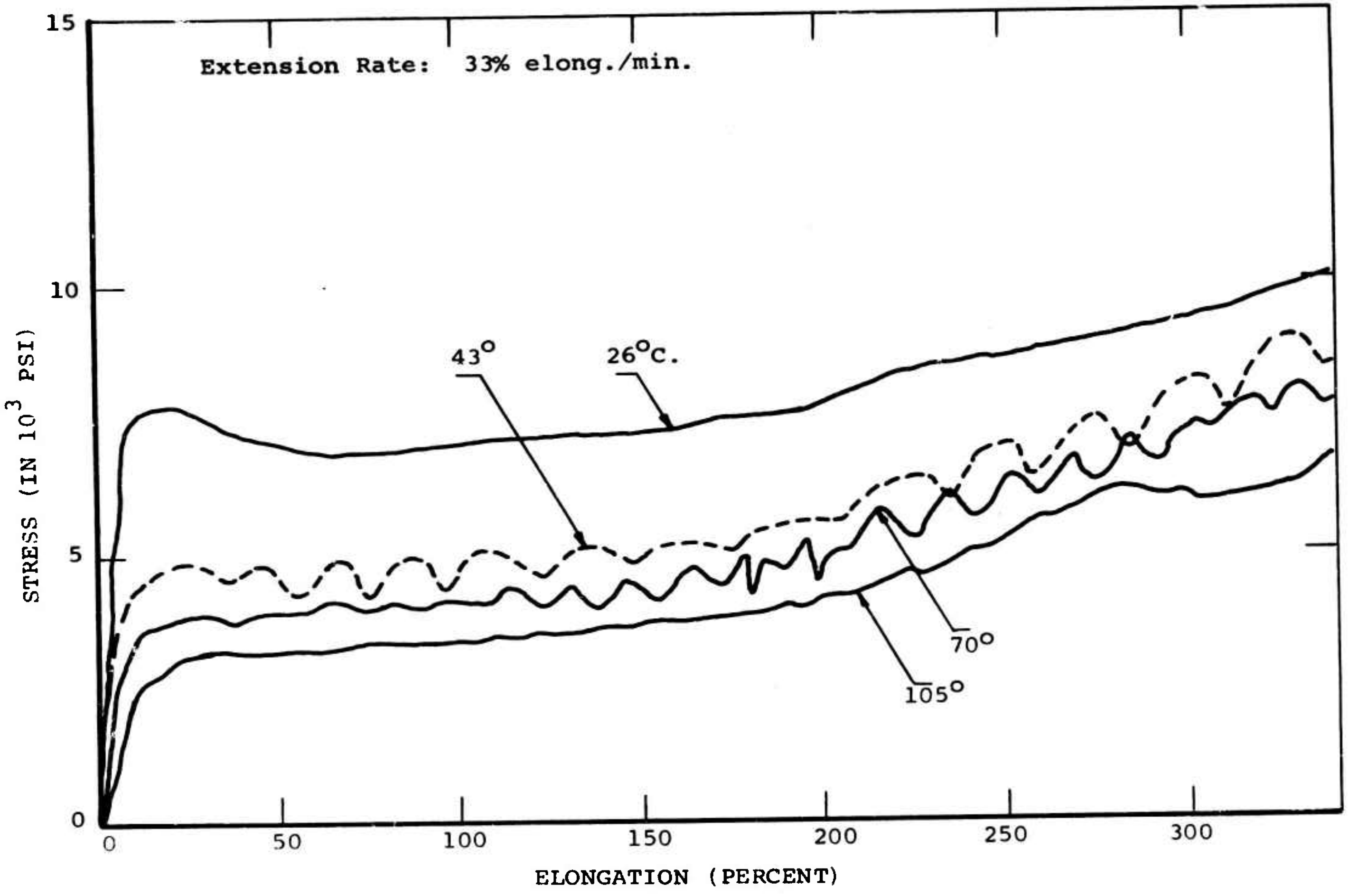

Figure 1. Stress-Strain Curves for Nylon 6 Film (5 mil) at Different Temperatures

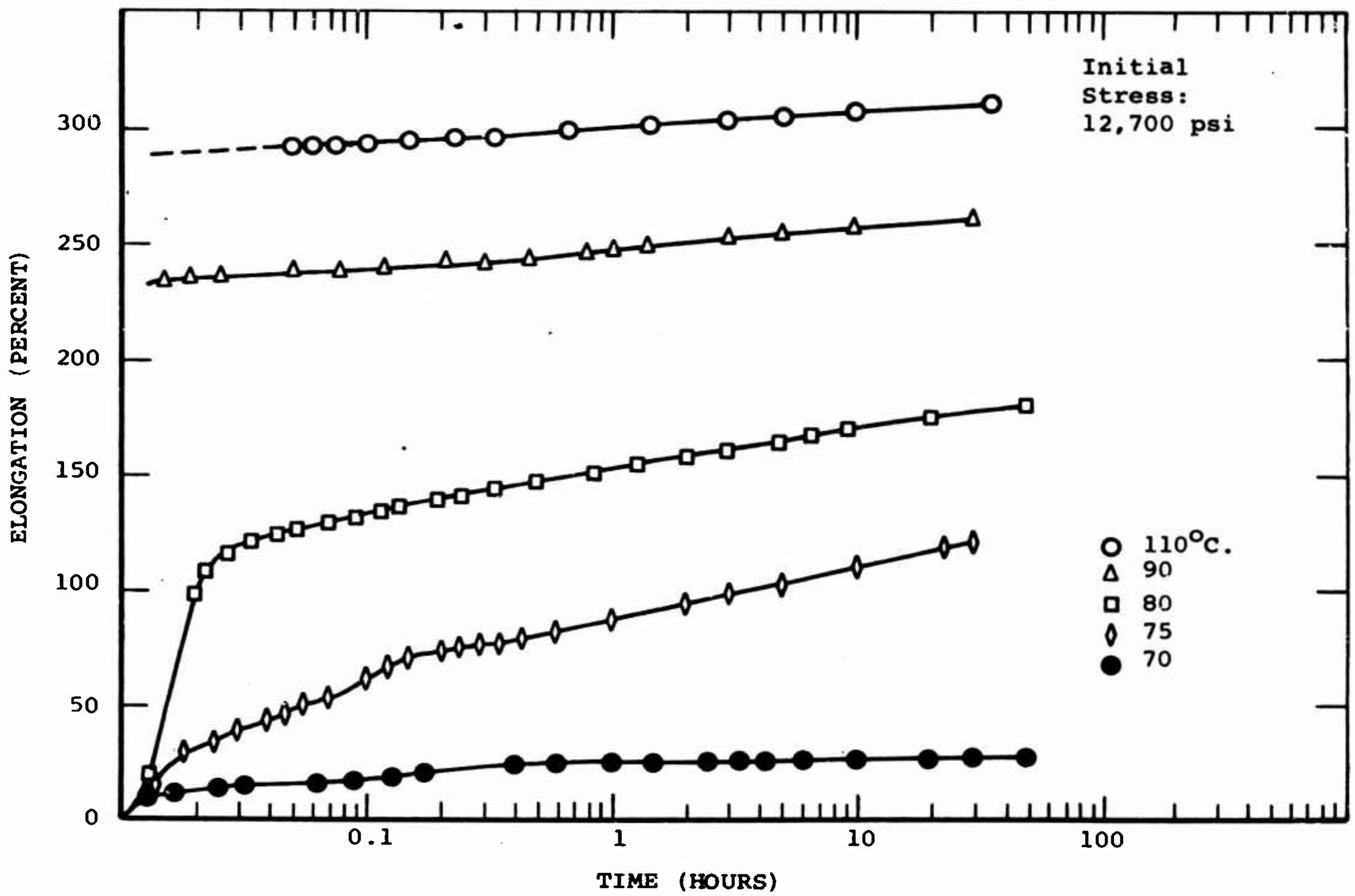

Figure 2. Effect of Temperature on Dead Load Creep Drawing of Nylon 6 Film (5 mil)

region, there is a further gradual increase of elongation with log time. A striking feature of these curves is the large change in degree of extension at long times for the different temperatures (from 25 percent at 70° to more than 300 percent at 110°); this extension at long times is essentially equivalent to the "draw ratio" at each temperature. No indication of this difference in final elongation seems to be given by the stress-strain curves in Figure 1.

### b. Effect of Absorbed Moisture

Humidity conditioning (in the range 0 percent - 100 percent R.H.) was carried out by storing samples in sealed desiccators with various mixtures of water and sulfuric acid in the bottom, at room temperature. It was found that water content had reached equilibrium in these 5-mil samples after 30 hours of conditioning (as determined by weight changes), and conditioning was therefore carried out for at least this length of time before the samples were used in the drawing experiments. Samples exposed to 100 percent R.H. picked up about 6 percent water, and samples at 0 percent R.H. lost about 2 percent water (based on total sample weight), in comparison to their original state of equilibration with the outside atmosphere. Some recent X-ray studies by Boukal (11) have indicated that the lattice spacing of the crystalline regions of Nylon 6 change reversibly by absorption and desorption of water, and also that the mechanism of deformation in both the amorphous and crystalline regions changes when water is absorbed.

The drawing experiments were carried out at room temperature. It was particularly desired to get an idea of the magnitude and nature of the humidity effect in this nylon polymer. Experiments were carried out both at constant strain rate (on the Instron machine) and under dead load conditions, and the results are presented in Figures 3 and 4.

The samples used in the constant-strain-rate tests were 0.5 inch wide and 1.5 inch in length (distance between clamps) and the crosshead speed used was 0.5 inch/min.; this gave an elongation rate of 33 percent elong./min. in all cases. Stress is calculated on the basis of original cross-sectional area, and elongation is calculated from the distance between clamps. The curves in Figure 3 show that humidity conditioning produces changes of appreciable magnitude in the stress-strain curve. The primary effect is on the level of the yield stress and the drawing stress. Both the yield stress and the drawing stress decrease progressively with increasing moisture

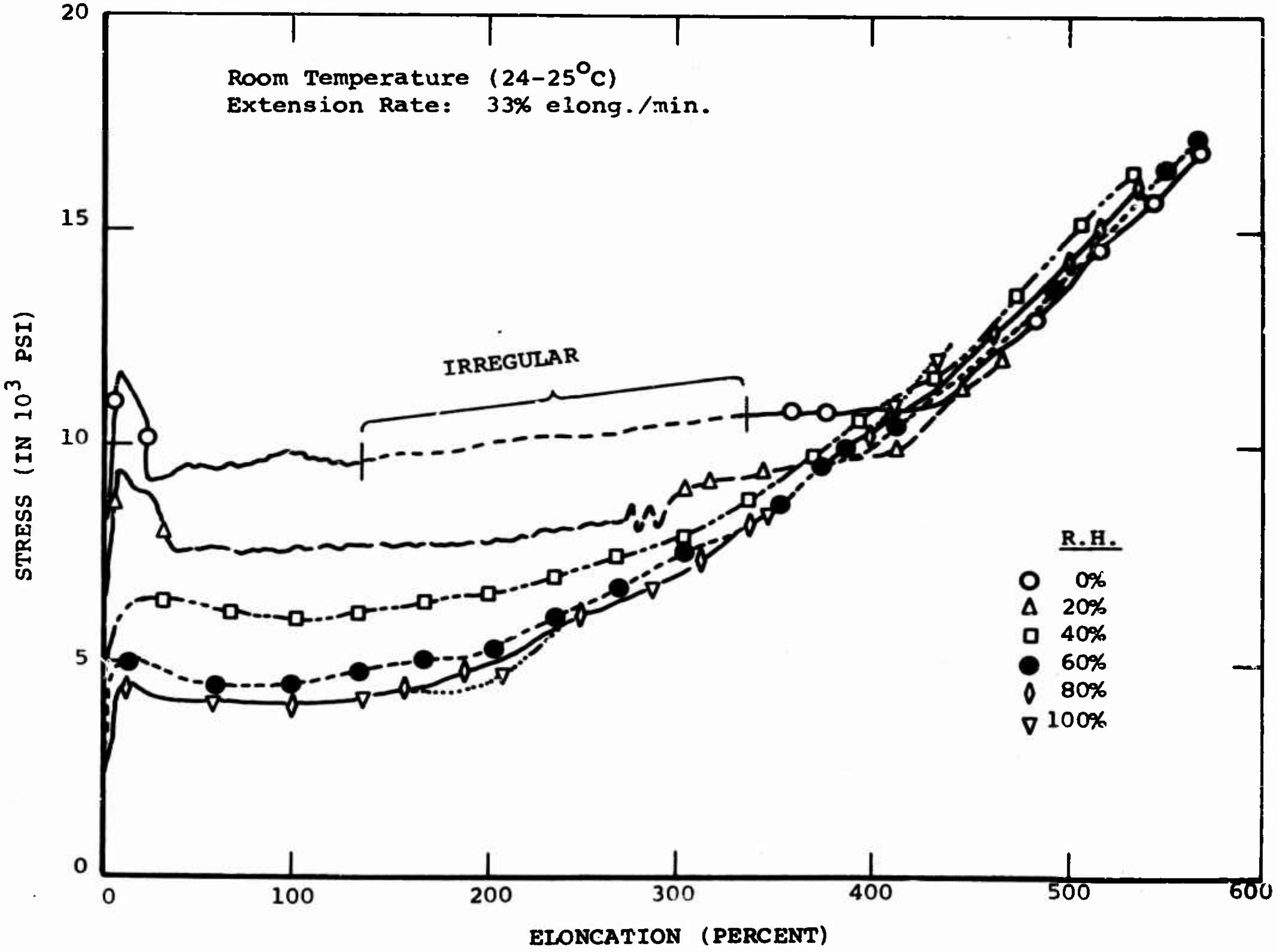

Figure 3. Stress-Strain Curves for Nylon 6 Film (5 mil) with Different Humidity Conditioning

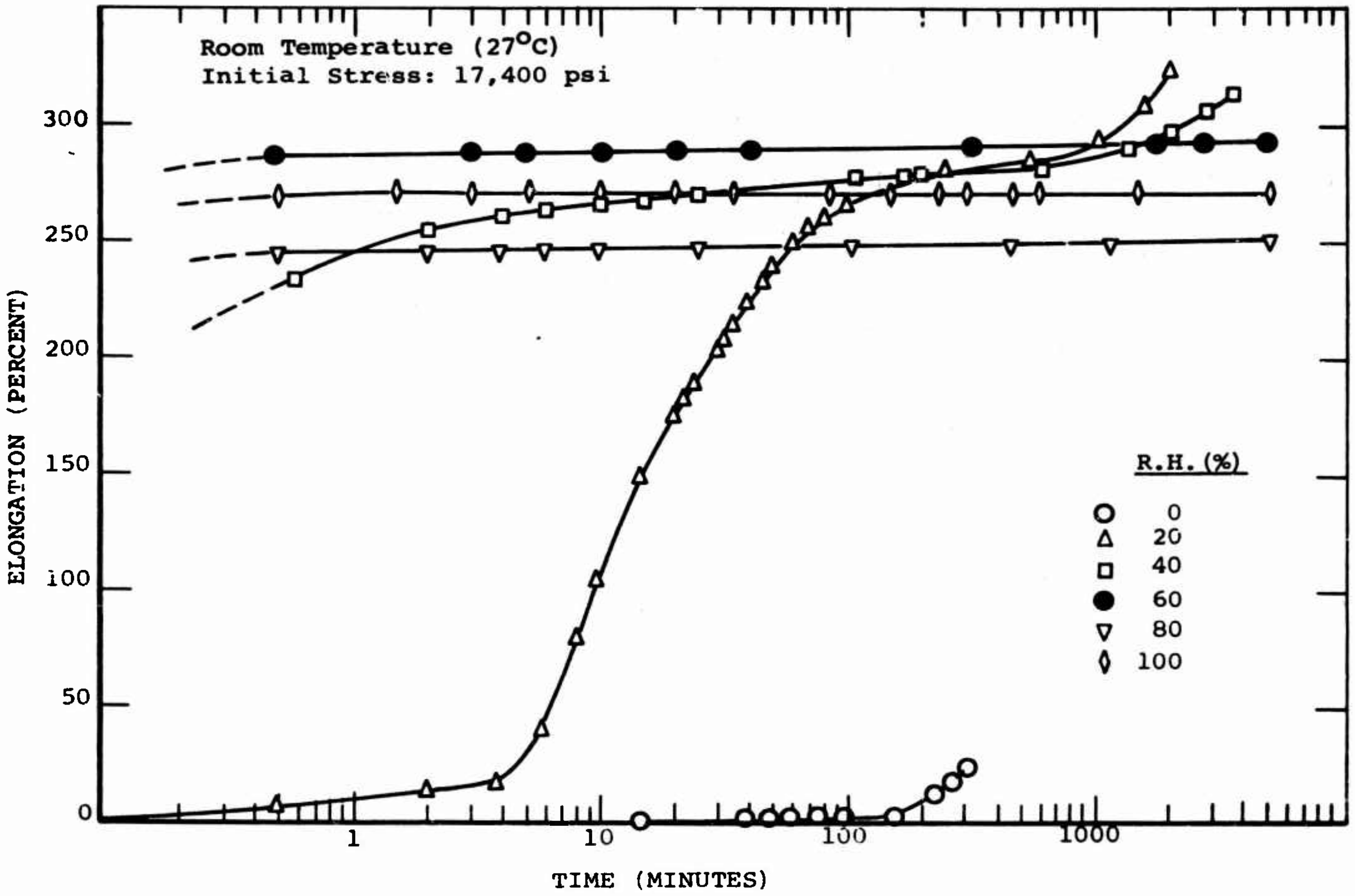

Figure 4. Dead Load Creep Drawing of Nylon 6 Film (5 mil) with Different Humidity Conditioning

content, though the effect may finally reach saturation (there is little difference between the 80 percent and 100 percent R.H. curves).

The general impression obtained in looking at this family of curves is that the drawing (or neck propagation) region represents a path of transition between two envelope curves roughly identical for all specimens: the first envelope is the elastic region for the undrawn polymer (before necking or yield has taken place), and the second envelope has the appearance of a corresponding elastic curve for the drawn polymer (after neck propagation has been completed). This pattern of curves is very similar to that which has been reported by Yumoto (12) for Nylon 6 monofilaments at different humidities, indicating that the behavior of filaments and film is not greatly different. This structural interpretation has also been discussed in a recent journal article (13).

In addition, the magnitude of the drop in stress, when the neck forms, becomes progressively less with increasing moisture content. This is very similar to the effect of increasing temperature. Visual observation of the samples indicates that the neck also becomes less localized and more diffuse with increasing moisture content. One section of the drawing region of the curve for 0 percent R.H. is denoted as "irregular"; in this region a very peculiar effect was observed in which the stress oscillated regularly back and forth between two stress values--higher and lower, respectively, than the mean dotted curve drawn--and the sample showed alternating transparent and white opaque bands (perpendicular to the length and evenly spaced, in a sequence of 20 or 30) as the neck propagated along the specimen. This behavior does not seem to be completely reproducible, and cannot be explained at the present time. The same effect has also been reported by Hookway (14) in stress-strain curves of Nylon 66 filaments; he uses the term "lacunose drawing" to describe this sort of curve. This effect may also be related to the irregularities in the stress-strain curve in a certain temperature range noted in connection with Figure 1.

The experiments of drawing under dead load are shown in Figure 4. The strip samples used in these experiments were 0.25-inch wide and 2.0 inches long (distance between clamps) and the initial stress applied (calculated on original cross-sectional area) was 17,400 psi in all cases. Length measurements were made visually using a cathetometer. Again a very large effect of absorbed moisture on the drawing behavior is seen. The formation and propagation of a neck could be seen clearly only in the 20 percent R.H. sample. The samples at higher R.H. drew so quickly that the length changes could not be followed; after this, no significant further extension took place during the remainder of the experiment (i.e., up to about 3 days) in the samples with highest moisture content (60 percent, 80 percent, 100 percent R.H.), though the magnitude of the final extension does not seem to vary systematically with percent R.H., as would be expected. The samples at 20 percent and 40 percent R.H. show a further extension, or second region of creep at the long-time end; this should be investigated further. No definite neck could be seen in the 0 percent R.H. sample as far as the experiment was carried out, but the difference in "delay time" (for onset of yield or necking) between the 0 percent and 20 percent R.H. curves can be estimated from the incomplete curve shown.

The experiments reported here are not ideal experiments, for two reasons. First, the room temperature did not remain strictly constant; and second, the moisture content of the specimens did not remain constant during an experiment. Although the conditioned specimens were in equilibrium in the desiccator, they immediately began to pick up or lose moisture when they were removed for use in an experiment, as could be readily verified by measuring their weight change. This problem can be solved only by using an atmospheric enclosure for the specimen during the drawing experiment, or by using a plasticizing agent less volatile than water.

### c. Effect of Absorbed Alcohols

One of the major objectives of the present contract was the study of plasticizer effects on the drawing behavior of crystalline polymers, as a means of determining the relative roles of the crystalline and amorphous regions in the drawing process. The ideal plasticizer would be one which entered the amorphous regions as a completely miscible solvent, without affecting the crystalline regions, and remained permanently without volatilization. This would allow a selective plasticization of the amorphous regions. As noted above, the volatility of water, and rapid moisture pick-up from the atmosphere in dried samples, was a serious problem, since the composition of the sample did not remain stable during the drawing experiments.

To investigate some of the alternatives to water as a plasticizer, a series of alcohols was tested. These should also act as hydrogen-bonding type plasticizers, and the results are given in Table I. Strips cut from the sheets of Nylon 6 (as received, without additional pretreatment) were immersed in the pure liquids at room temperature and sample weight followed as a function of time until equilibrium absorption was reached (equilibration was complete within 30 hours in all cases).

The second column of Table I indicates that the equilibrium absorption of the seven alcohols shows considerable variation, and that the behavior is fairly complex. (Further studies have indicated some revision of the numerical values given here, so that these results should be regarded as only approximate.) Except for a slight reversal in the case of methanol and ethanol, the aliphatic alcohols show a systematic decrease in absorption with molecular size (the negative value reported for amyl alcohol probably represents a slight extraction of the sample--presumably of the lowest molecular weight components). The absorption of cyclohexanol is also very low. However, the absorption of benzyl alcohol, which is an even larger molecule, is very high--significantly higher even than methanol. This cannot be due simply to the ring structure because of the behavior of cyclohexanol, but must be a result of the presence of the aromatic ring. This would suggest that phenol must also be an effective plasticizer. This is true, and has been known for some time. Phenol is much more effective than benzyl alcohol, and is absorbed so strongly that it will actually dissolve nylon, indicating that it attacks the crystalline as well as the amorphous regions. It was found that 5 percent, 3 percent and even 1 percent solutions of phenol in carbon tetrachloride would dissolve strips of Nylon 6 immersed in them for an extended period of time, as the phenol progressively entered the polymer. The distribution coefficient of phenol between carbon tetrachloride and polymer is greatly in favor of the polymer.

The loss of absorbed solvent was also measured during subsequent stress-strain experiments. The time required for the stress-strain test is indicated in the third column of Table I and the corresponding weight loss in the fourth and fifth columns (as total weight loss during the stress-strain experiment, and as average rate of weight loss, calculated as percent of original sample weight per minute, respectively). The most suitable plasticizer from this list would appear to

## TABLE I

## ABSORPTION AND DESORPTION OF DIFFERENT ALCOHOLS

## BY NYLON 6 FILM AT ROOM TEMPERATURE

| Solvent | Percent increase in wt. after equilibrium was reached | Period of stress-strain experiment (minutes) | Percent wt. loss (based on original sample wt.) during the experiment | Average rate of wt. loss (percent per minute) |
|---|---|---|---|---|
| Methanol | 12.60 | 11.45 | 7.39 | 0.64 |
| Ethanol | 13.26 | 9.35 | 3.81 | 0.41 |
| Butanol | 2.95 | 10.70 | 0.88 | 0.82 |
| Amyl alc. | - 0.60 | 2.00 | 0.60 | 0.30 |
| n-Hexyl alc. | 0 | 2.80 | 0 | 0 |
| Benzyl alc. | 44.80 | 4.45 | 3.82 | 0.86 |
| Cyclohexanol | 0.35 | 2.25 | 0.35 | 0.16 |

be benzyl alcohol, because of the large degree of absorption and low rate of volatilization, and the absorption behavior of this alcohol was therefore investigated in more detail, as indicated in Table II.

In these experiments (Table II), both temperature and solvent concentration were varied. The absorption seemed essentially unaffected by temperature, in the range of room temperature to 100°C. However, the amount of benzyl alcohol absorbed at equilibrium was found to depend significantly on the concentration of benzyl alcohol in the solvent (mixtures with cyclohexanol containing 10 percent, 50 percent and 100 percent benzyl alcohol were used). Solvent mixtures of this sort can therefore be used to introduce controlled amounts of plasticizer into the sample, and the distribution of plasticizer should be uniform (macroscopically, disregarding the difference in distribution between crystalline and amorphous regions) through the specimen, since equilibrium was reached. It remains to be demonstrated that the plasticizer remains in the amorphous regions and that the crystalline structure has not been disturbed. X-ray studies are required for this purpose.

Stress-strain curves for samples containing the different absorbed alcohols are shown in Figure 5. Major changes in the nature of the stress-strain curve are seen here. The height of the yield peak and drawing stress seems to decrease systematically with the amount of alcohol absorbed, regardless of the chemical nature of the alcohol. The final region of the stress-strain curve does not seem to be affected, however, and the curves converge to a final "envelope" curve, very much like the samples subjected to humidity conditioning (Figure 3).

There also seems to be a second effect of the absorbed alcohols--an effect on the elongation at break. Curiously enough, it is the alcohols which were least absorbed (amyl and n-hexyl alcohols and cyclohexanol) which produce the greatest reduction in the elongation at break. This is an effect on fracture rather than yield. (It was found in later experiments that this fracture was also affected by the method of cutting the strip sample, and could be eliminated by an improved method of sample cutting.)

## TABLE II

## ABSORPTION AND DESORPTION OF BENZYL ALCOHOL BY NYLON 6 FILM AT DIFFERENT TEMPERATURES AND DIFFERENT CONCENTRATIONS

| Temp. (°C) | Composition of immersion liquid | Percent increase in wt. after equilibrium was reached | Period of stress-strain experiment (minutes) | Percent wt. loss (based on original sample wt.) during the experiment | Average rate of wt. loss (percent per minute) |
|---|---|---|---|---|---|
| 23 | Benzyl alcohol (Pure) | 46.07 | 8.20 | 5.15 | 0.63 |
| | Benzyl alcohol and cyclohexanol (50:50) | 27.05 | 9.60 | 3.16 | 0.33 |
| | Benzyl alcohol and cyclohexanol (10:90) | 2.62 | 11.20 | 0.51 | 0.05 |
| 60 | Benzyl alcohol (Pure) | 45.40 | 21.00 | 23.10 | 1.10 |
| | Benzyl alcohol and cyclohexanol (50:50) | 23.15 | 24.10 | 9.27 | 0.38 |
| | Benzyl alcohol and cyclohexanol (10:90) | 2.55 | 23.80 | 1.83 | 0.08 |
| 100 | Benzyl alcohol (Pure) | 44.98 | 30.50 | 35.64 | 1.17 |
| | Benzyl alcohol and cyclohexanol (50:50) | 25.75 | 32.30 | 17.85 | 0.55 |
| | Benzyl alcohol and cyclohexanol (10:90) | 1.78 | 31.40 | 2.49 | 0.08 |

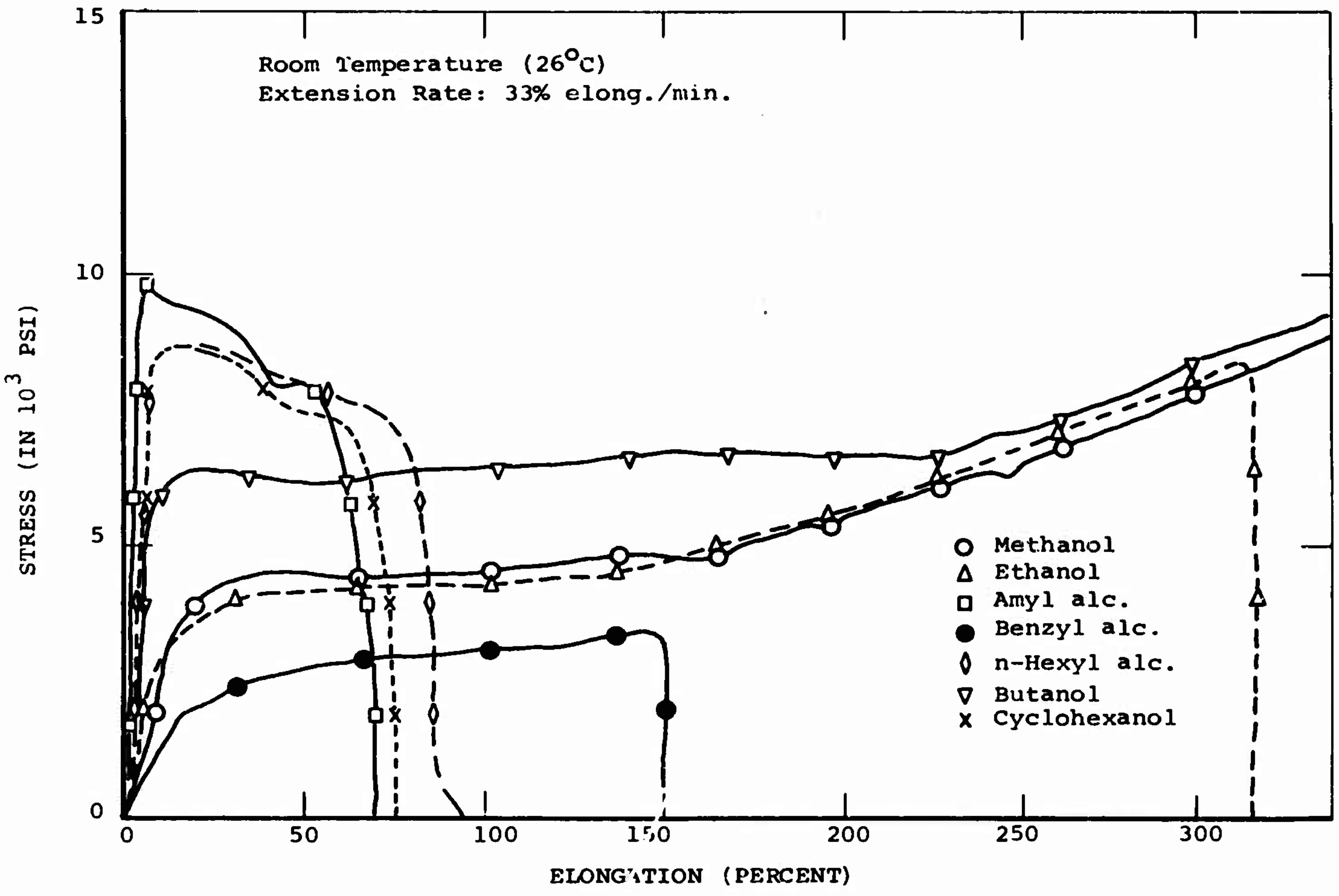

Figure 5. Stress-Strain Curves for Nylon 6 Film (5 mil) Soaked in Different Alcohols

### d. Effect of Phenol

Detailed studies were carried out on the effects of phenol, which has a very strong plasticizer action, and can even be a solvent for nylon. Some of the effects of a combination of phenol treatment and drawing on the structure and state of order in Nylon 66 have been discussed in a recent paper by Sakuma and Rebenfeld (15). Treatments with water and with benzyl alcohol and (benzyl alcohol)/(cyclohexanol) mixtures were also included for comparison. Benzyl alcohol is strongly absorbed by the Nylon 6 (but less strongly than phenol), whereas cyclohexanol is not absorbed. Water is mildly absorbed. Phenol and benzyl alcohol are less volatile plasticizers than water, and this adds to the convenience of their use. Infrared measurements were also carried out in connection with these plasticizer studies.

The effects of different plasticizers could be readily distinguished by running stress-strain curves on film samples after treatment. These tests were run at room temperature on a table model Instron machine, at an extension rate of 100 percent/min. The film samples used were one inch in width, with a one inch length between sample clamps. The use of such a square sample might seem somewhat questionable, because the sample would be subjected to some degree of biaxial stress, rather than pure tension. However, this was checked using samples of different length/width ratios, and it was found that the stress-strain curve for such a square sample did not differ greatly from the curve obtained for a "long" strip (large length/width ratio).

A comparison of stress-strain curves for the original nylon film and for samples treated with various agents is shown in Figure 6. In all cases the prior treatments were carried out until equilibrium absorption had been attained. The curve for the original (untreated) film is shown as a dashed line, for convenience of comparison. The phenol treatment was carried out using an 0.25 molar solution (approximately 1.5 percent by weight) in carbon tetrachloride. The other treatments were with the pure solvents and solvent mixtures, as indicated. The changes in the stress-strain curve seem to correlate fairly well with the amount of plasticizing agent absorbed, regardless of its chemical nature. This also seemed to be the case for the series of alcohols investigated previously.

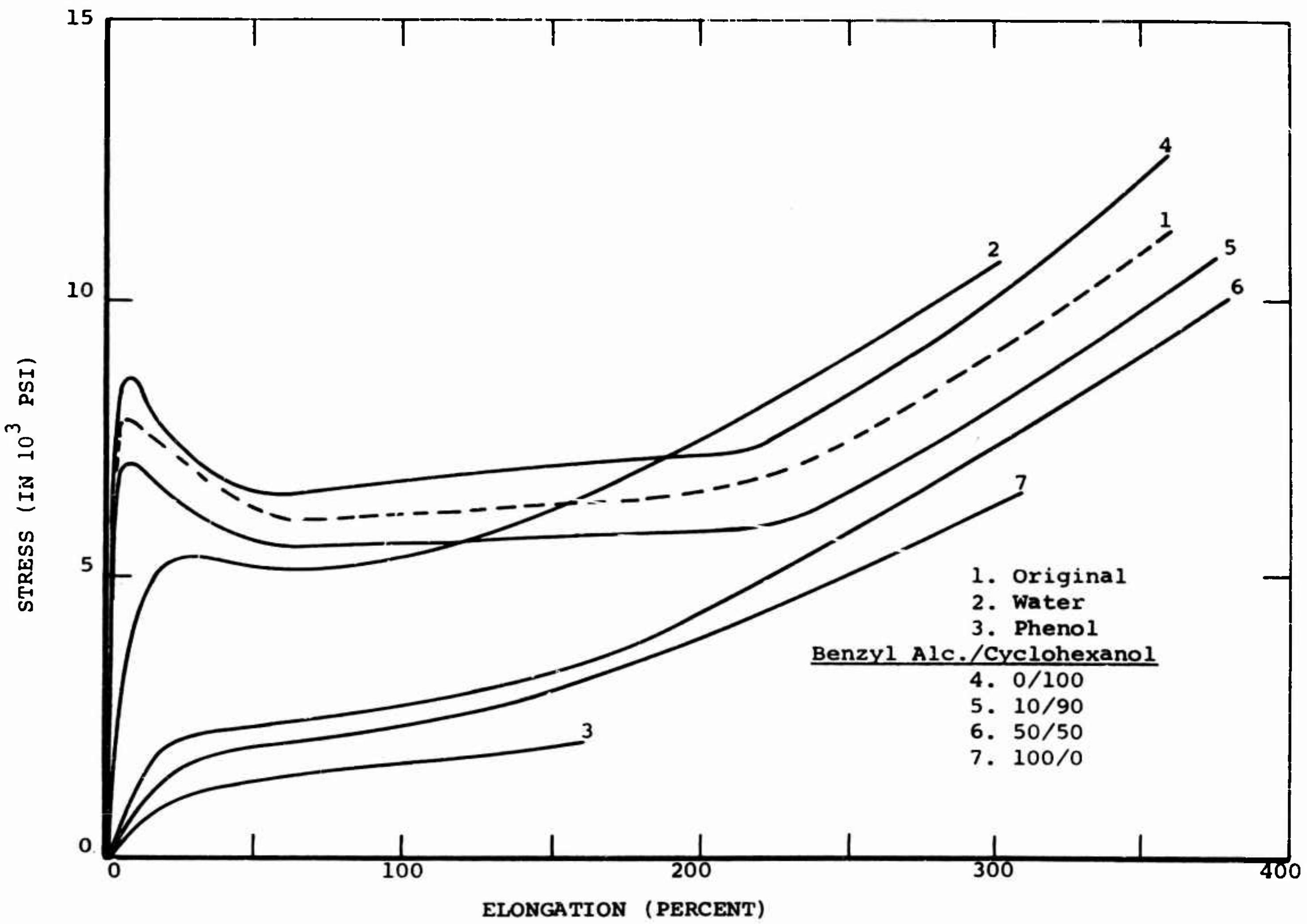

Figure 6. Stress-Strain Curves for Nylon 6 Film (1 mil) Soaked in Different Liquids

The curve in Figure 6 for the sample treated with water seems slightly different from the curves for the samples treated with the (benzyl alcohol)/(cyclohexanol) mixtures; the essential difference seems to be that the "plateau" region of the curve is shorter, indicating that the draw ratio for this sample is less. From the data in Tables I and II, it is estimated that the weight gain from the treatments in the four (benzyl alc.)/(cyclohexanol) mixtures, numbered 4-7, would be 0.4, 2.6, 27 and 46 percent,respectively. The amount of water absorbed (after soaking in liquid water) was about 5 percent and the amount of phenol absorbed was about 70 percent. The sample treated with pure cyclohexanol actually shows an <u>increase</u> in yield stress and stress level throughout the curve; this may be due to the extraction of the approximately 2 percent of absorbed water normally present in the polymer, or extraction of other low molecular weight components which would similarly act as plasticizers.

It should also be noted that complete stress-strain curves were obtained for the samples treated with pure benzyl alcohol and pure cyclohexanol. Premature fracture was obtained in similar curves shown in Figure 5. The difference in behavior is undoubtedly related to the different method of sample preparation employed. The present samples were cut from 1 mil film with scissors whereas the previous samples were cut from 5 mil film with a razor blade; this latter procedure is believed to have produced cracks on the edges which led to the premature fracture. Samples cut from the 1 mil film with a razor blade showed such premature fracture due to the growth of an edge crack.

It is clear from Figure 6 that the largest effect is produced by the phenol treatment. The curve for this sample (#3) shows the greatest decrease of stress level, and also a complete disappearance of the "yield peak" ordinarily seen at a few percent elongation. Observation of the sample itself during the stress-strain test showed that no neck formation took place as the sample extended; the stretching was completely uniform and homogeneous. It is interesting and significant that neck formation can be eliminated in this way. This could provide a helpful experimental approach to the problem of why neck formation takes place during cold drawing.

It seemed desirable to study this effect of phenol treatment in somewhat greater detail. In particular, it seemed of interest to study the effect of repeated phenol treatments. After the phenol has been absorbed, it is possible to extract it again by immersion of the sample in 1 molar aqueous sodium hydroxide solution. Stress-strain curves for samples subjected to a sequence of phenol treatments and extractions are shown in Figure 7. The curves with phenol absorbed in the sample seem essentially identical, and the same is true of the samples from which the phenol has been extracted. However, there is a major difference between the curve for the original polymer and the curve after the phenol treatment and extraction. After extraction of the phenol, the modulus is increased (compared to the polymer with the phenol in), but the yield peak continues to be absent and the sample shows no neck formation during drawing. The yield peak and neck formation seem to be directly associated.

It is evident that some major change in the polymer has taken place during the first phenol treatment. It is also clear that in studying the effect of plasticizer on mechanical properties, the proper comparison to make is not between the original polymer and the polymer with the plasticizer absorbed (as is usually done) but between the polymer with plasticizer absorbed and the polymer with plasticizer extracted. This allows the pure plasticizer effect to be observed, rather than a combination of the effects of plasticizer and structural change.

### e. Infrared Studies

In investigating the effects of solvent treatment further, infrared measurements were made on untreated and treated polymer samples. These measurements required the use of 1 mil film; 5 mil film gave too much absorption. All measurements were made on a Perkin-Elmer Model 21 spectrometer. The infrared measurements confirmed the structure change noted above in connection with phenol treatments, and it seems clear that this represents essentially a change in crystalline form. The plasticizer gives the molecules the mobility they need to re-crystallize in a more perfect type of crystalline lattice.

There are at least two major crystalline forms of Nylon 6, which have been called the $\gamma$-phase and the $\alpha$-phase. The $\gamma$-phase is the less perfect form which is produced by rapid quenching from the melt; the $\alpha$-phase is produced by subsequent solvent or plasticizer treatments or annealing.

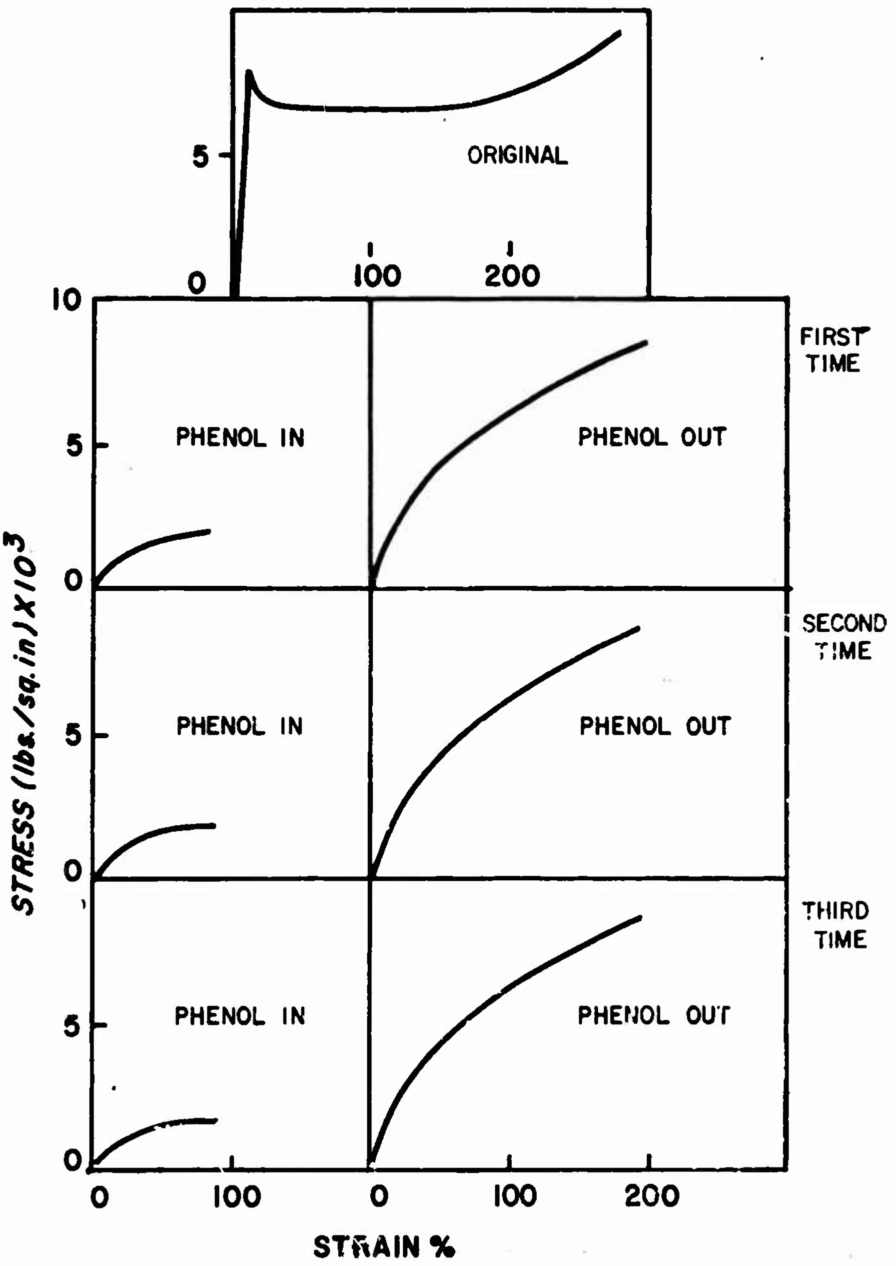

Figure 7. Effect of Repeated Phenol Treatments

A brief discussion of these different forms has been published by Roldan and Kaufman (16), and additional discussions were also held with Dr. Roldan (Central Research Laboratory, Allied Chemical Corp., Morristown, N. J.). The structure of the $\gamma$-phase has also been discussed recently by Bradbury, Brown, Elliott and Parry (17). There is also amorphous material present. A $\beta$-phase has been postulated to exist in oriented (drawn) polymer, though there is some controversy over this. Apparently it is possible to re-convert the $\alpha$-phase to the $\gamma$-phase by iodine treatment of the polymer (17).

A few of the infrared results are shown in Figures 8-10. Curves showing the effect of phenol treatment and subsequent extraction are presented in Figure 8, for the region 9-13 microns. A comparison of the absorption curves for the original and phenol-treated samples shows that several new absorptions have appeared in the phenol-treated sample. Some of these absorptions are absorptions of the phenol molecule --i.e., the peaks at 9.37, 10.03, 11.34 and 12.30 microns. The other four bands in the treated specimen--at 9.75, 10.42, 10.80 and 12.03 microns--are nylon absorptions. Assignments of these nylon bands have been given by Sandeman and Keller (18); they assign the first three to in-plane vibrations of the amide group, and the fourth (at 12.03 microns) to a $-CH_2$-rocking frequency. These would be crystalline vibrations of the $\alpha$-phase. It is seen that when the phenol is removed, the new nylon absorptions remain. A comparison of the curves before treatment and after phenol extraction shows the considerable structural change which has taken place in the polymer. Measurements of the changes in the spectrum vs. time of treatment in the phenol solution indicated that equilibrium absorption was attained very rapidly --within 5 minutes.

Curves are presented in Figure 9 for film samples which were heated in boiling water and annealed by heating to 210°C. The sample heated in boiling water was heated for a period of about 25 minutes. The sample annealed to 210°C was taken through a sequence in which the sample was placed in an oven at 100°C, the oven heated to 210°C, and the sample allowed to remain at 210°C for 10 minutes, after which it was removed to the outside to cool. These curves show the development of the same four new nylon bands which were seen in Figure 8, but to a lesser extent. The structure change produced by these treatments is therefore of the same nature as produced by the phenol treatment (transformation of the

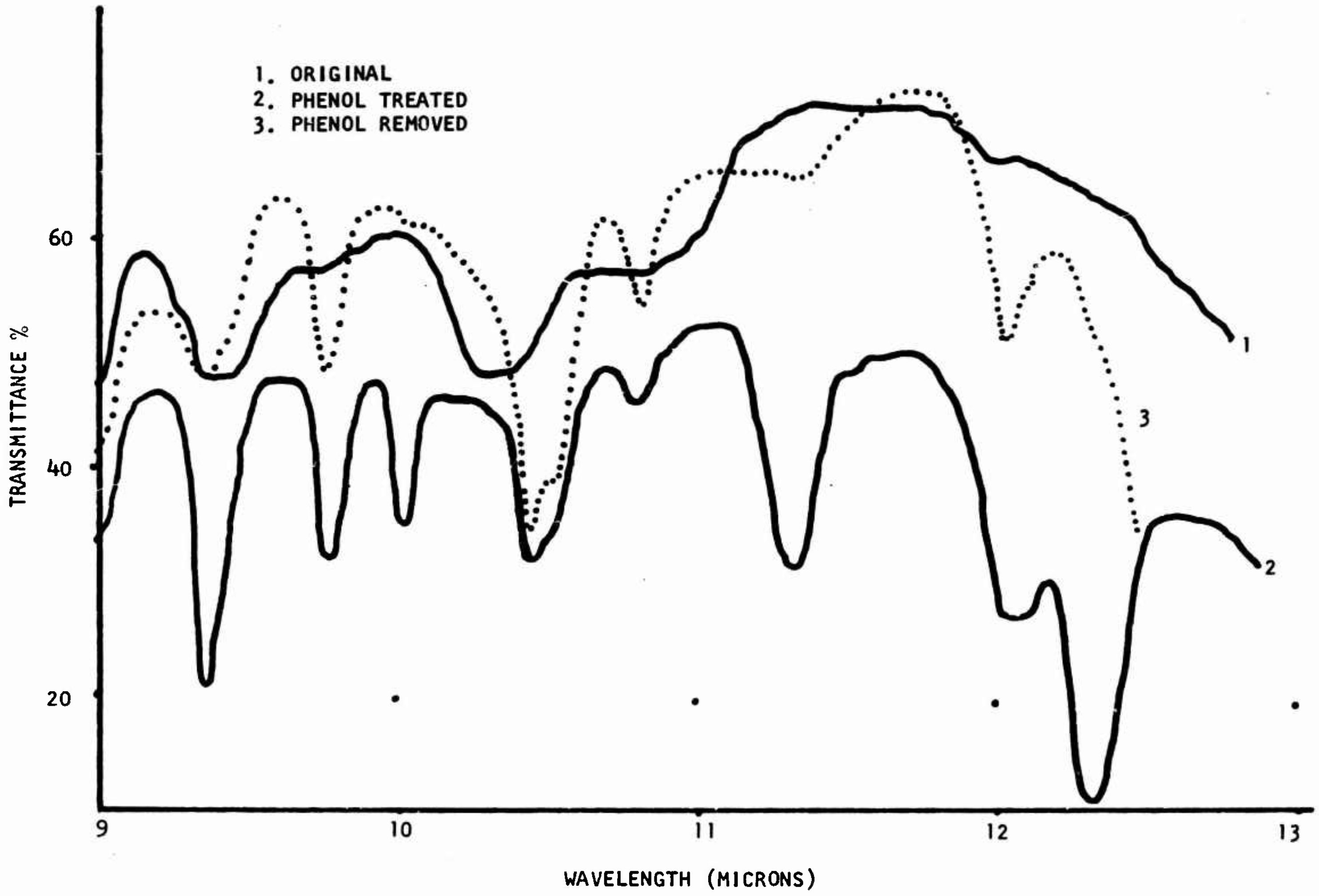

Figure 8. Infrared Spectra for Nylon 6 Film Before and After Phenol Treatment

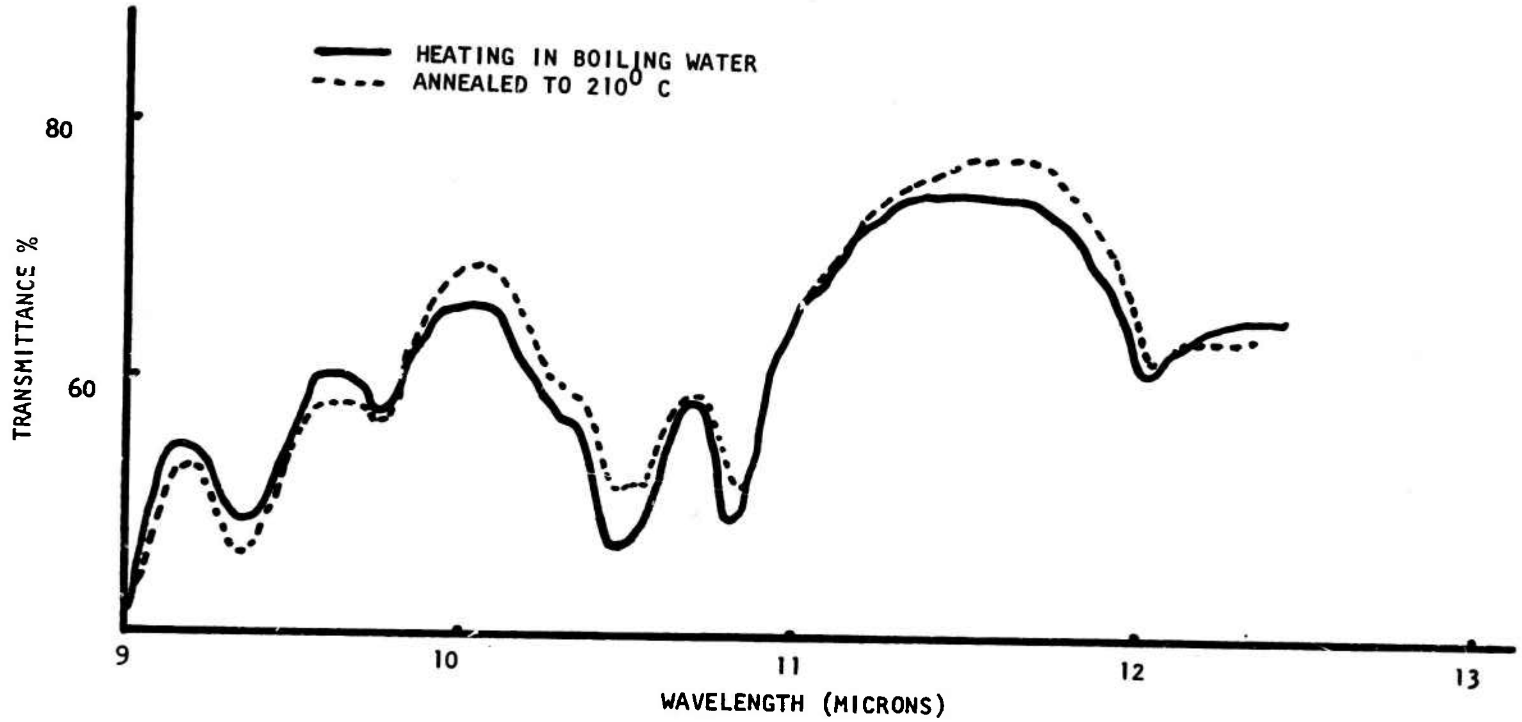

Figure 9. Infrared Spectra for Nylon 6 Film After Water and Annealing Treatments

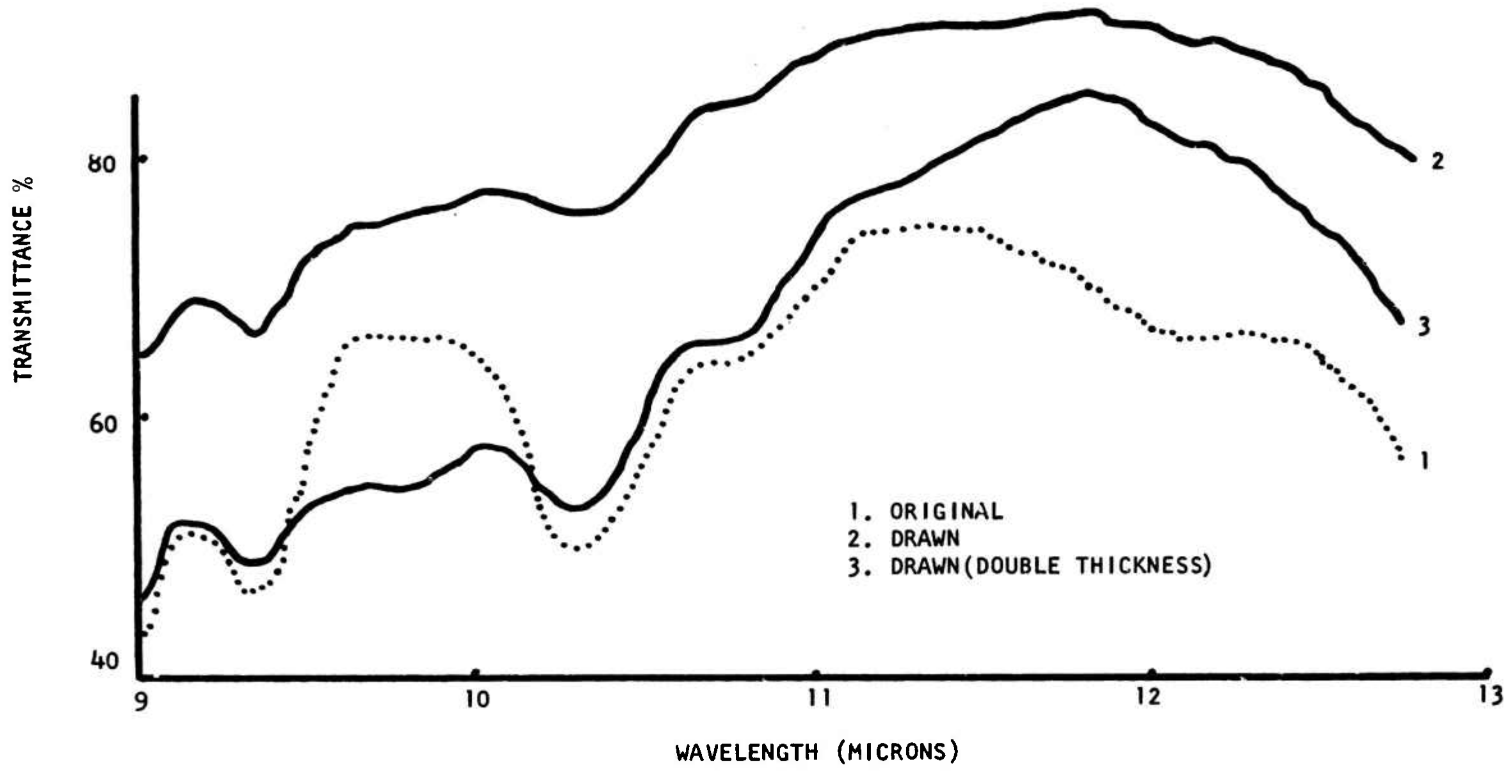

Figure 10. Infrared Spectra for Nylon 6 Film Before and After Drawing

$\gamma$-phase to the $\alpha$-phase), but has not proceeded as far. The effect of benzyl alcohol absorption is also in the same direction as the phenol treatment but to a lesser degree. The degree of change varies with benzyl alcohol concentration in the (benzyl alc.)/(cyclohexanol) mixtures in the way that would be expected. Cyclohexanol by itself, which shows negligible absorption, produces no change whatever in the original spectrum.

The curves in Figure 10 show the effect of drawing the original untreated film. Since drawing decreases the thickness of the film, the absorption of the film decreases throughout the spectrum as a consequence. The absorption curve of a double thickness of the drawn film is, therefore, also shown, since the general level of absorption is more nearly equal to that of the original film, and comparisons can more easily be made. No detailed interpretation of the curve for the drawn polymer will be proposed here; however, it is clear that the effect of drawing on the infrared spectrum is very different from that of phenol treatment or the other annealing treatments described.

### f. Dynamic Mechanical Measurements

Very helpful additional information on the effects of plasticizer treatments can be obtained by use of dynamic mechanical and thermogravimetric (TGA) measurements. Some measurements of this type were carried out at the Bell Telephone Laboratories, Murray Hill, N. J., through the kind cooperation of Dr. Shiro Matsuoka, Mr. John Daane, and Dr. W. L. Hawkins.

The particular usefulness of dynamic mechanical measurements is in identifying transitions in a polymer as a function of temperature and frequency. These appear as a drop in the curve of storage modulus (E') and as a peak in the curve of loss modulus (E") or loss tangent (tan $\delta$), when plotted vs. temperature or log frequency. It is important to see the way in which the transitions are shifted by plasticizer treatment, in order to obtain a more detailed picture of the nature of the plasticizer action. This also helps in the interpretation of stress-strain data--particularly of stress-strain data at different temperatures (above and below the various transitions).

The apparatus used for the dynamic mechanical measurements was the Vibron Model DDV-II Tester. Measurements were made over the temperature range from room temperature down to -150°C, at a single frequency (110 cycles/sec). The significant transitions could be seen in this temperature range, though a still broader temperature range might be desirable in future measurements. Cooling was achieved by use of a liquid nitrogen spray; temperatures below -150°C are therefore possible to attain. The samples used were strips of 1 mil film 0.5 cm in width and 2.5 cm in overall length. Masking tape was put on the ends of the strip to aid in clamping, and the length of sample between clamps was about 2.0 cm. This instrument subjects the sample to a sinusoidal tensile strain which is well within the linear viscoelastic range, and tan $\delta$ (which is equal to $E''/E'$) is read directly from the instrument.

The effect of absorbed moisture was primarily examined in these measurements. The untreated film was compared with samples of film soaked in water and dried in an oven at 50°C. The results are shown in Figures 11, 12 and 13, which show curves of $E'$, $E''$ and tan $\delta$ vs. temperature. From the curves of $E''$ and tan $\delta$, the presence of three transitions in this temperature range can be seen: one near room temperature, one at about -60°C and the other near -140°C. The transition near room temperature ($\alpha$) is frequently specified as the glass transition, and the low-temperature transition near -140°C is the $\gamma$-transition which is seen in polyethylene and other polymers (such as Nylon 6) containing ethylenic sequences in the backbone or side groups (19). The nature of the $\beta$-transition at -60°C is less clear. A compilation and discussion of the mechanical and dielectric loss peaks in nylon (and many other) polymers has been given in a useful new book by McCrum and co-authors (20).

From the results shown here, it is evident that the position of these transitions (temperature of the loss peak) is significantly shifted by absorbed water. The shift in the room temperature transition seems greater than is the case for the -60°C transition. The data are not complete enough for the -140°C transition to show the magnitude of the shift for this transition. Some difficulties were encountered previously at Bell Laboratories in obtaining reproducible dynamic mechanical data on Nylon 6 in experiments above room temperature. The same was found to be true in some preliminary experiments above room temperature with our samples. This is probably due to absorption and desorption of moisture by the sample as the temperature

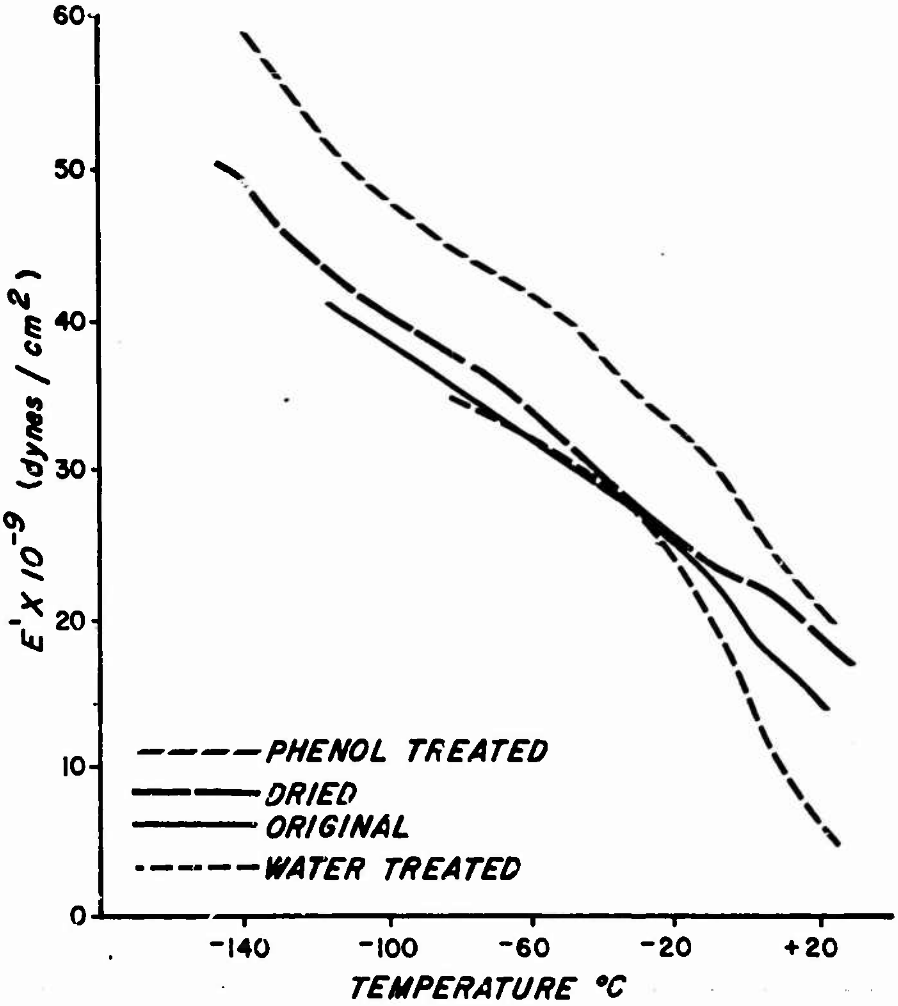

Figure 11. Dynamic Storage Modulus vs. Temperature for Nylon 6 Film

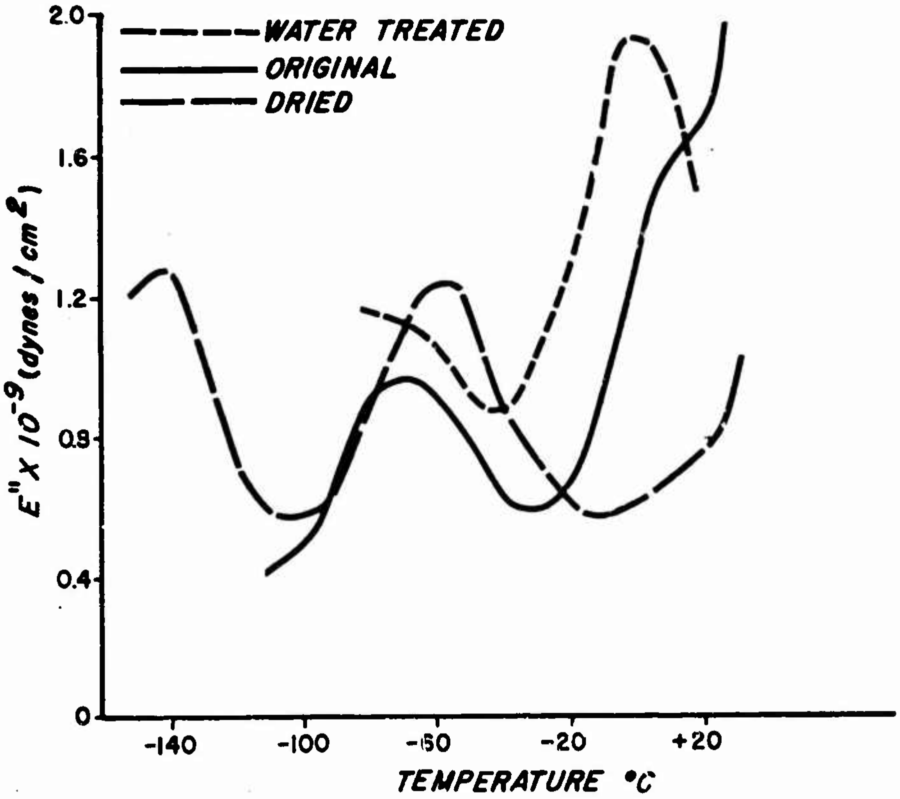

Figure 12. Dynamic Loss Modulus vs. Temperature for Nylon 6 Film

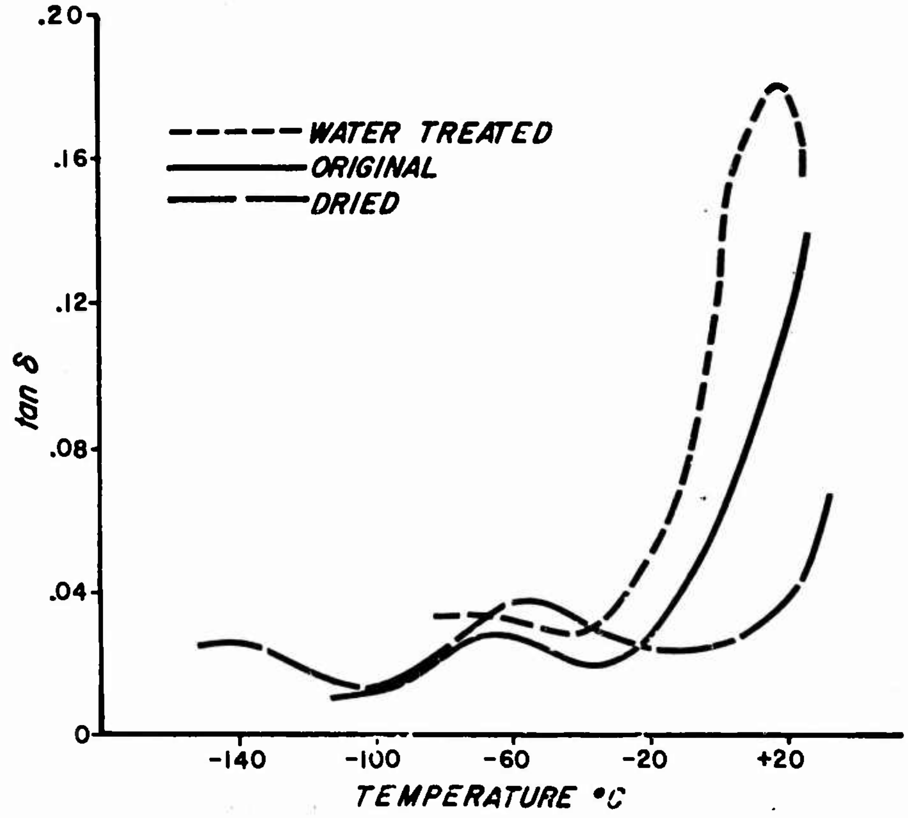

Figure 13. Dynamic Mechanical Loss Tangent for Nylon 6 Film

is changed during the experiment. Therefore, the good results presented in Figures 11-13 are undoubtedly due to the fact that the samples were never heated above room temperature. In the work of Deeley et al. (21), curves of tan $\delta$ vs. temperature for a dried Nylon 66 sample showed no $\beta$ peak, suggesting that the presence of this peak is related to the presence of absorbed water. However, Kawaguchi (22) studied a series of polyamides, all dried over $P_2O_5$ for a month, and found that all these dried nylons exhibited the $\beta$ peak. Our results are thus in agreement with Kawaguchi's, since we see the $\beta$ peak in our dried sample.

The storage modulus (E') curve for a phenol-treated sample is also included in Figure 11 (this sample was soaked in an 0.25 molar phenol/$CCl_4$ solution until equilibrium absorption was attained, as in previous work). This curve is higher than the other curves throughout the temperature range, which can be explained by an enhanced crystallization of the film produced by the phenol treatment. The other three curves, however, do not show a regular vertical displacement correlating with the amount of absorbed water. The curves intersect at a common value at about -30°C, and show a divergence at temperatures above and below this value. The modulus values at room temperature differ considerably, and in the order expected from the amount of absorbed water. The differences are larger at room temperature than at lower temperatures.

### g. Thermogravimetric Measurements

Thermogravimetric (TGA) measurements were carried out on a sample of original (untreated) film, a film sample soaked in water, and a sample treated with phenol by soaking in a phenol/$CCl_4$ solution as described above. The results are shown in Figure 14, in which total sample weight is plotted vs. temperature. A temperature scan from room temperature up to about 500°C was used, with a heating rate of 15°C/min. The samples were heated under a nitrogen atmosphere.

The original film showed a weight loss of 2.7 percent between room temperature and 300°C, and most of this weight loss occurred at temperatures significantly above 100°C, indicating a very diffuse and elevated "boiling point" for this absorbed water. The sample soaked in water showed a weight loss of only 3.7 percent in the same temperature range, which is not much greater than that of the original film. This low value may be a result of water loss from the sample while it

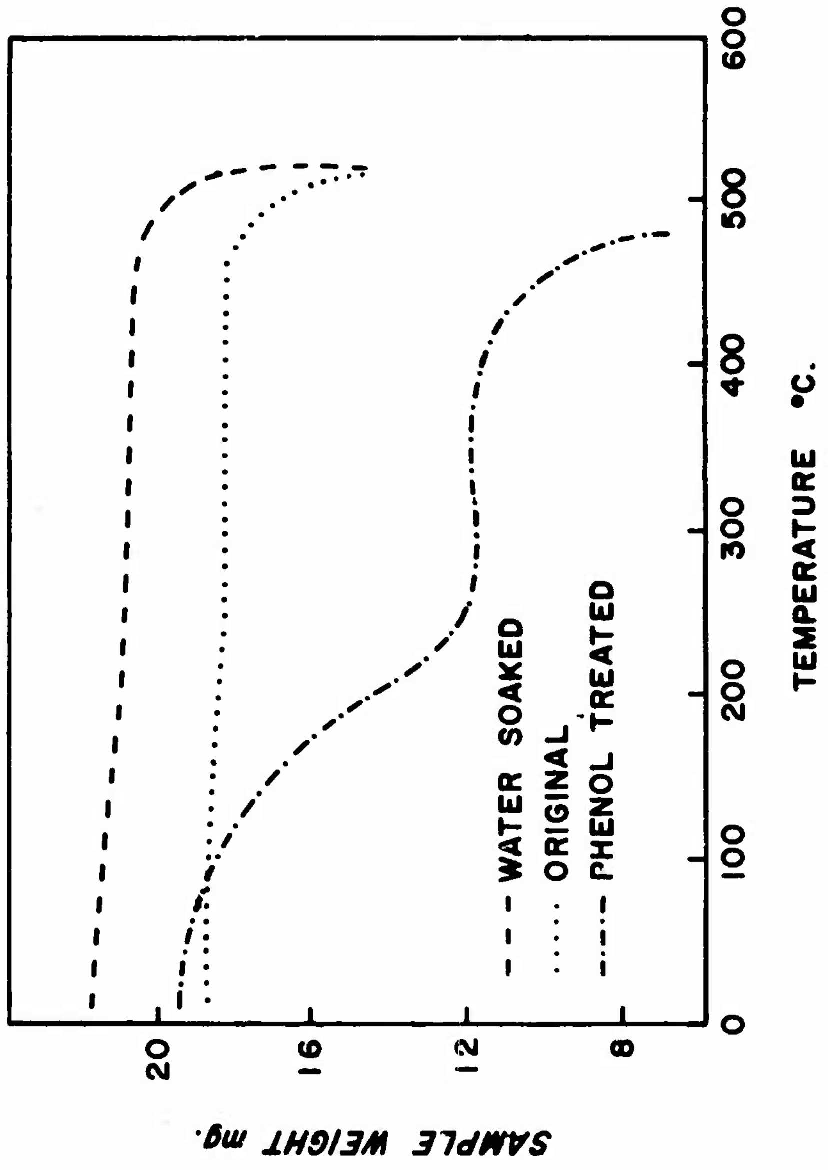

Figure 14. Thermogravimetric Analysis (TGA) Curves for Nylon 6 Film

is being prepared for the TGA analysis. A measurement of sample weight immediately after removal from water indicated a 4.7 percent weight gain, as compared to the original sample. Addition of this weight gain to the 2.7 percent measured above would give a total water content for the soaked film of 7.4 percent, which is a much more reasonable value. It is interesting that the soaked sample showed the onset of weight loss well below 100°C, in contrast to the behavior of the original film. This could be explained if there was more than one type of absorbed water (more and less strongly bound); other evidence in the published literature points to this same conclusion.

The phenol-treated sample showed a 38.5 percent weight loss between room temperature and 300°C. This took place gradually in the range of 70 - 240°C, again indicating a very diffuse "boiling point" for the absorbed plasticizer. (It is also of interest that the onset of high-temperature degradation takes place at a lower temperature in the sample containing phenol than in the samples containing absorbed water). A direct weighing experiment showed that the phenol-treated film had a weight increase of 70.5 percent (based on untreated sample weight); this would convert to a weight loss of 41.3 percent based on the treated sample weight. This agrees fairly well with the 38.5 percent value measured in the TGA experiment; some sublimation of phenol may have taken place during preparation of the sample for the TGA measurement, which would account for the small remaining discrepancy.

### 3. Polyethylene Terephthalate

The mechanical properties, oriented states, and drawing behavior of PET have been studied over a period of years by Ward and coworkers at the Imperial Chemical Industries (ICI) Fibers Division in England. (See, for example, a recent publication by Allison and Ward (23).) This particular polymer is an interesting one in that it can be quenched into an amorphous state because of its sluggish crystallization rate. It can then be crystallized to varying degrees by annealing treatments. Fibers of this polymer prepared by melt spinning are normally amorphous; they are later oriented and crystallized by a hot-drawing treatment.

It was not possible to carry out an extensive study of PET during the present research program. However, some preliminary data were obtained on the drawing behavior of this polymer under dead-load creep conditions. The polymer used was an amorphous film sample, specially prepared to avoid crystallization*. Creep experiments were carried out at different load levels at four different temperatures (60°, 70°, 80° and 90°C), and the results will be reported in detail elsewhere. Typical results (for 70°C) are shown in Figure 15, where the creep curves are plotted as log compliance vs. log time. The general pattern of curve shapes at different stress levels is very similar to that which has been found (24) for PVC in the same type of experiment.

A very unusual feature of these curves is the fact that neck formation sometimes takes place at very high strains. The point of neck formation is indicated on the curves in Figure 15 at the three highest stresses by an arrow at the left side of the curve. Since these curves are plotted with compliance as ordinate, the actual elongations involved are not immediately evident. However, neck formation sometimes took place after homogeneous creep to elongations of greater than 50 percent. This is very unusual, since neck formation usually takes place at elongations of the order of 5 - 10 percent.

## 4. Polyacrylonitrile

Some results on the drawing behavior of PAN have already been presented in a previous report (2). However, data on the drawing of PAN under dead-load creep conditions had not been previously obtained, and therefore some measurements of this type were made in the present study. The film samples used were obtained from the Sohio Research Laboratories in Cleveland. They were solvent-cast and had some degree of biaxial orientation. The film was given a pre-treatment of boiling in water for 30 minutes to remove residual solvent and provide some annealing.

Results of the creep measurements are shown in Figure 16. Creep was measured at a series of stresses at four different temperatures (70°, 100°, 120° and 160°C) which spanned the

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*Supplied by the Fuji Photo Film Co. of Japan

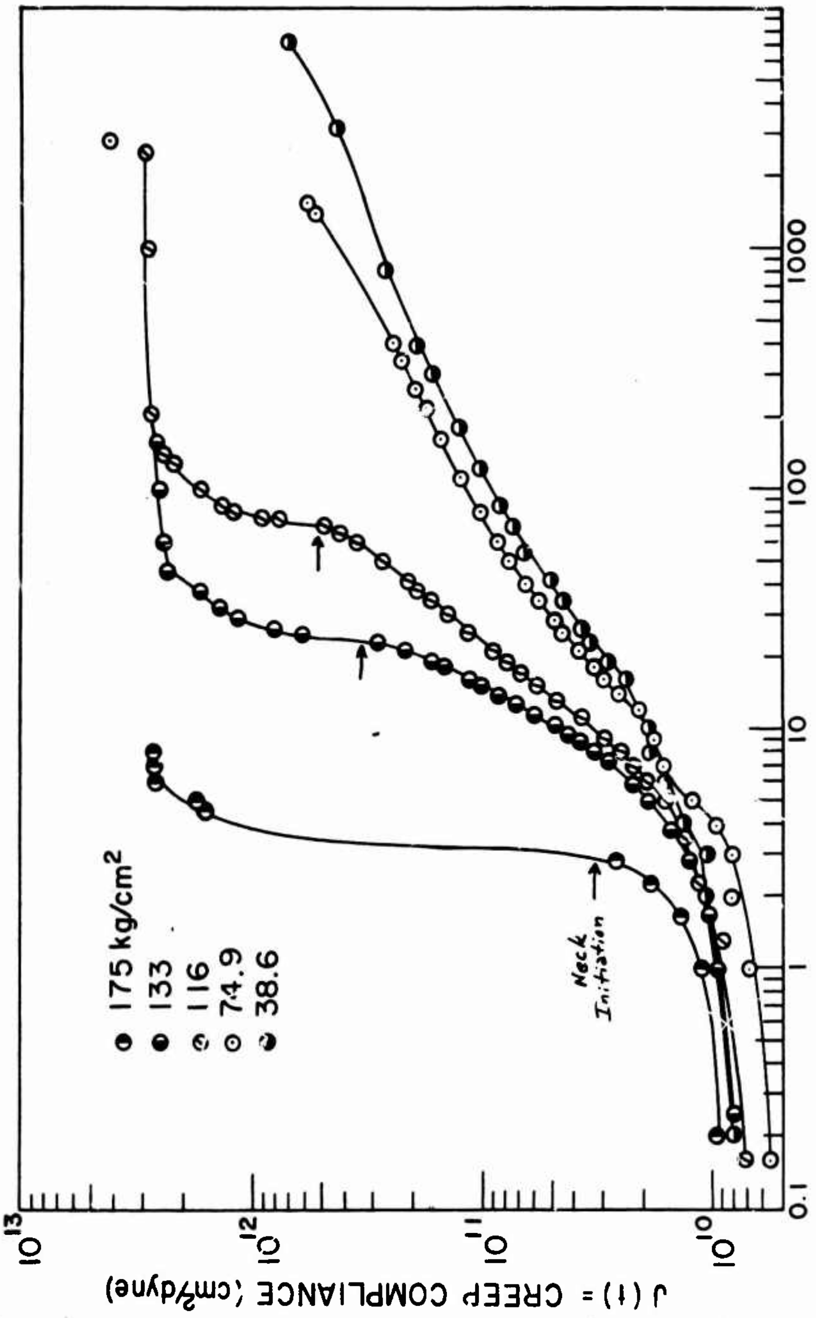

Figure 15. Creep Curves of Polyethylene Terephthalate for Different Initial Stress Levels at Four Different Temperatures

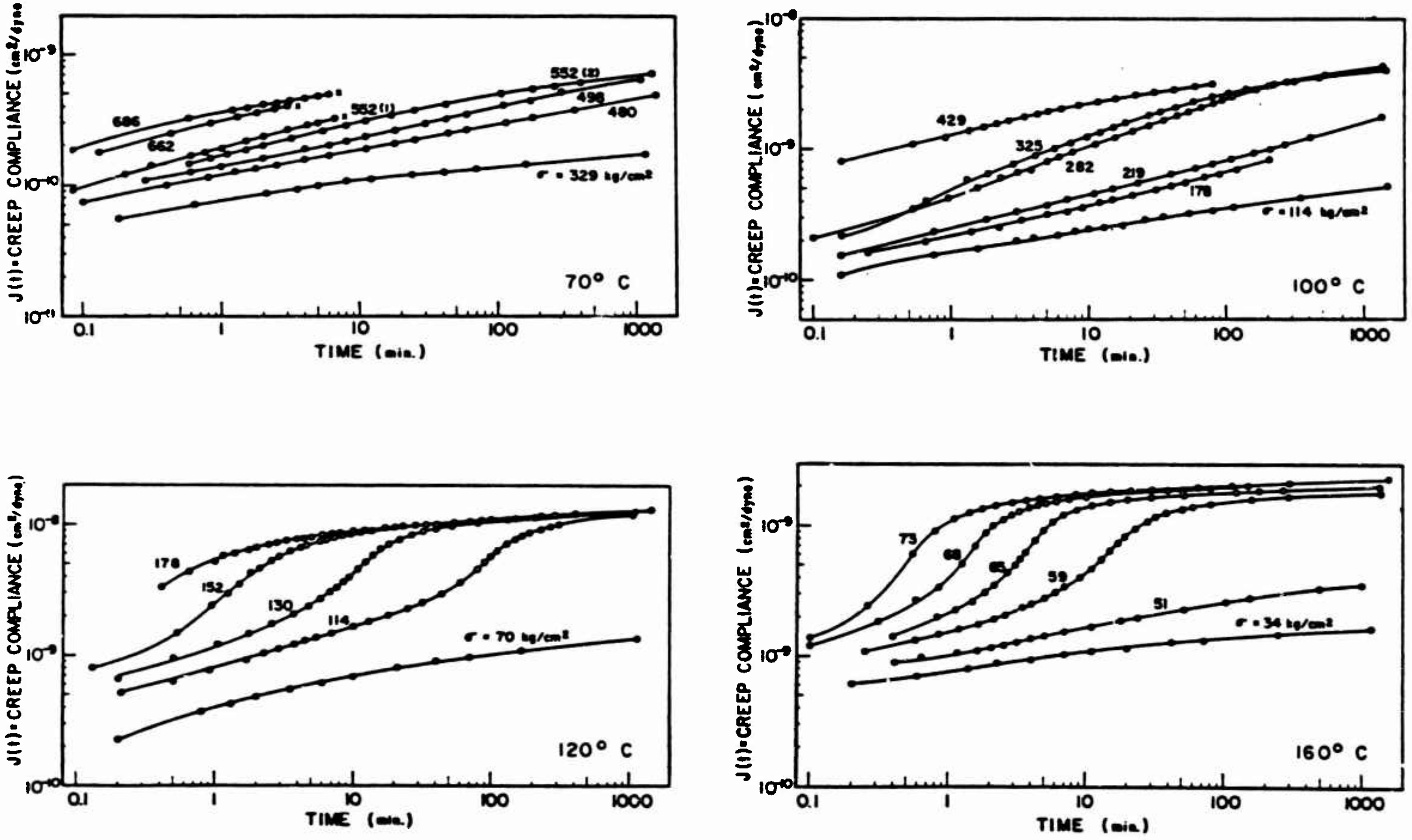

Figure 16. Creep Curves of Polyacrylonitrile for Different Initial Stress Levels at Four Different Temperatures

range of the two glass transitions of this polymer (located at about 90°C and 140°C). Two general results are seen from these curves. First, the magnitude of the compliance attained increases with increasing temperature. Second, the curves become increasingly S-shaped with increasing temperature, and thus become more like the curves observed for PVC (24). It would appear that some sort of basic structure change is taking place in this material over the temperature range covered here; the change seems gradual and no effect of two transitions is seen. No neck formation was seen in any of the creep curves reported here; the drawing was always homogeneous. It is still regarded as "drawing" because of the magnitude of the elongations obtained.

Some recovery experiments were also carried out following the creep experiments. It was observed that the recovery curves were not the reverse of the creep curves, as would be the case for viscoelastic (retarded elastic) creep. Also, a large amount of the creep was not recovered. If the recovery experiment was carried out at a higher temperature than the preceding creep experiment, more of the elongation could be recovered; this effect was greatest if the original creep experiment was at a lower temperature. The conclusion from these experiments was that the creep is not of the usual viscoelastic type, but is due to some mechanism of structure change in the material, such as breaking and formation of some type of cross-links.

Measurements of birefringence changes during the creep experiments were also made. The results have been plotted as birefringence vs. elongation, and average curves for the different temperatures are shown in Figure 17. These curves have a very curious shape. The curves at 120°C and 140°C seem to show two distinctly different regions: first, a region of very rapid increase of negative birefringence with elongation, then a region of more gradual increase. The height of the rapid-rise region decreases with increasing temperature. The curves show considerable similarity to birefringence-elongation curves obtained from stress-strain tests by Kimmel and Andrews (shown in Figure 55 of Ref. 2). These results can be interpreted (25) in terms of orientation of a solid state structure consisting of a combination of rigid rod-like structures and coiled amorphous chains (something like the fringe-micelle picture used formerly to represent crystalline polymers). The initial rapid-rise

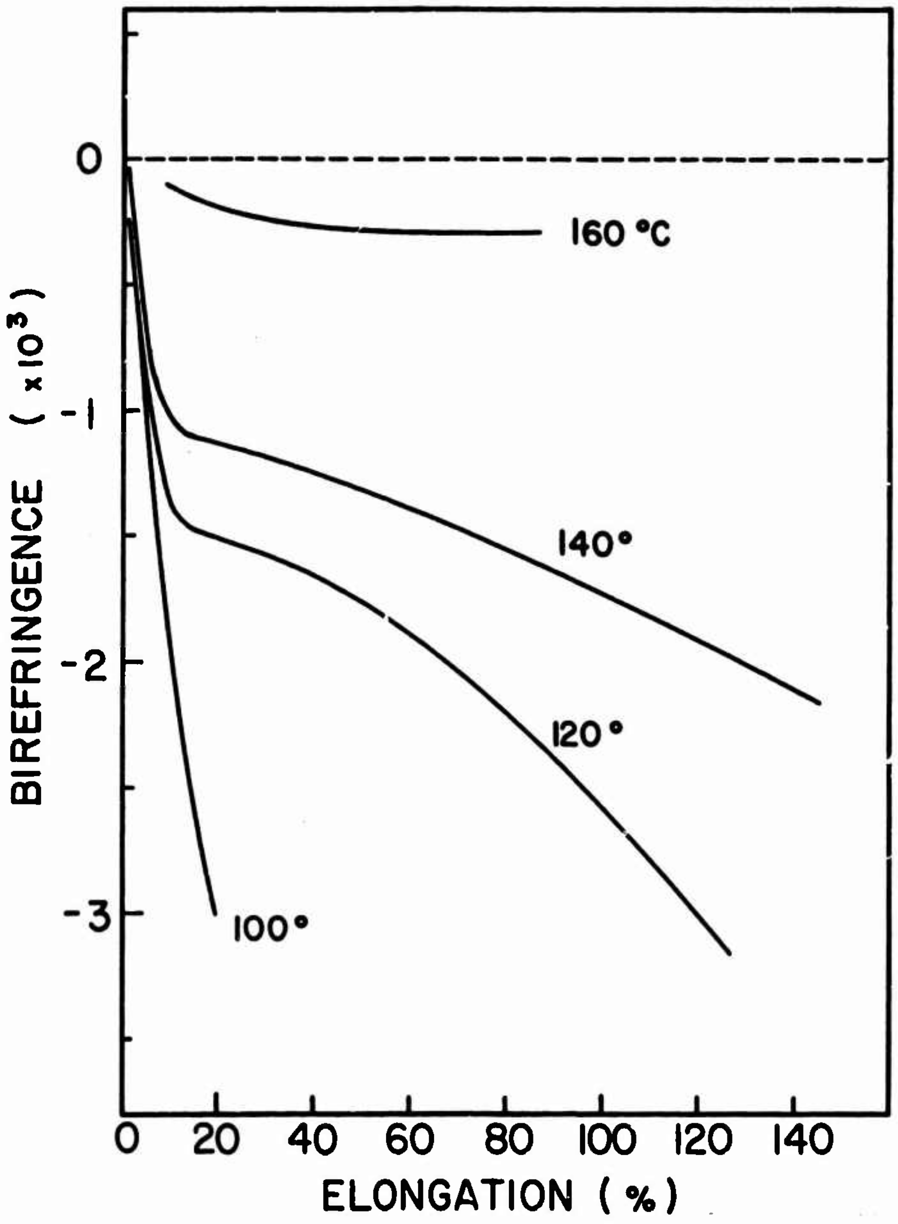

Figure 17. Birefringence-Strain Curves for Polyacrylonitrile at Four Different Temperatures

region presumably corresponds to orientation of the rod-like structures, and the more gradual increase to the orientation of coiled amorphous chains. The rod-like structures are probably domains in which chains are associated by dipole-dipole bonding; the presence of such structures in PAN and their dissociation in the neighborhood of 140°C has been concluded from a previous investigation (26).

## 5. Polyvinyl Chloride

Some studies of dead-load creep drawing of plasticized PVC homopolymer have been carried out to supplement similar data already obtained (24) on unplasticized PVC homopolymer. Creep curves at different stresses at a fixed temperature (-20°C), plotted as log compliance vs. log time, are shown for a polymer containing 0.3 weight fraction of dioctyl phthalate (DOP) in Figure 18. The glass transition temperature of the polymer has obviously been shifted downward by the plasticizer (cf. the data for unplasticized polymer in Ref. 24). However, the general shape and pattern of the curves remains similar to that of the unplasticized polymer, suggesting that no radical structure change has taken place as a result of introducing the plasticizer. Birefringence measurements were made during creep experiments at different temperatures; these gave a plot of birefringence vs. elongation as shown in Figure 19. The results at the different temperatures correspond closely and the form of the curve is not unusual in any way. This is a fairly normal type of behavior and contrasts with the behavior of PAN as shown in Figure 17.

One other type of birefringence measurement was also carried out (26) on unplasticized and plasticized PVC: the measurement of the temperature dependence of orientation birefringence. This type of measurement has been investigated extensively in previous work of Hammack and Andrews (28-30). Results for unplasticized homopolymer at different percent extensions (introduced by previous hot-stretching above the glass transition), plotted as fraction of the birefringence value at room temperature vs. temperature, are shown in Figure 20. The shape of the curve is the same for the different extensions and is essentially a straight line. The slope of similar curves was measured for plasticized samples containing different weight fractions of dioctyl adipate (DOA), DOP and tricresyl phosphate (TCP), and this slope is plotted vs. plasticizer weight fraction in Figure 21. The most important result here is that the

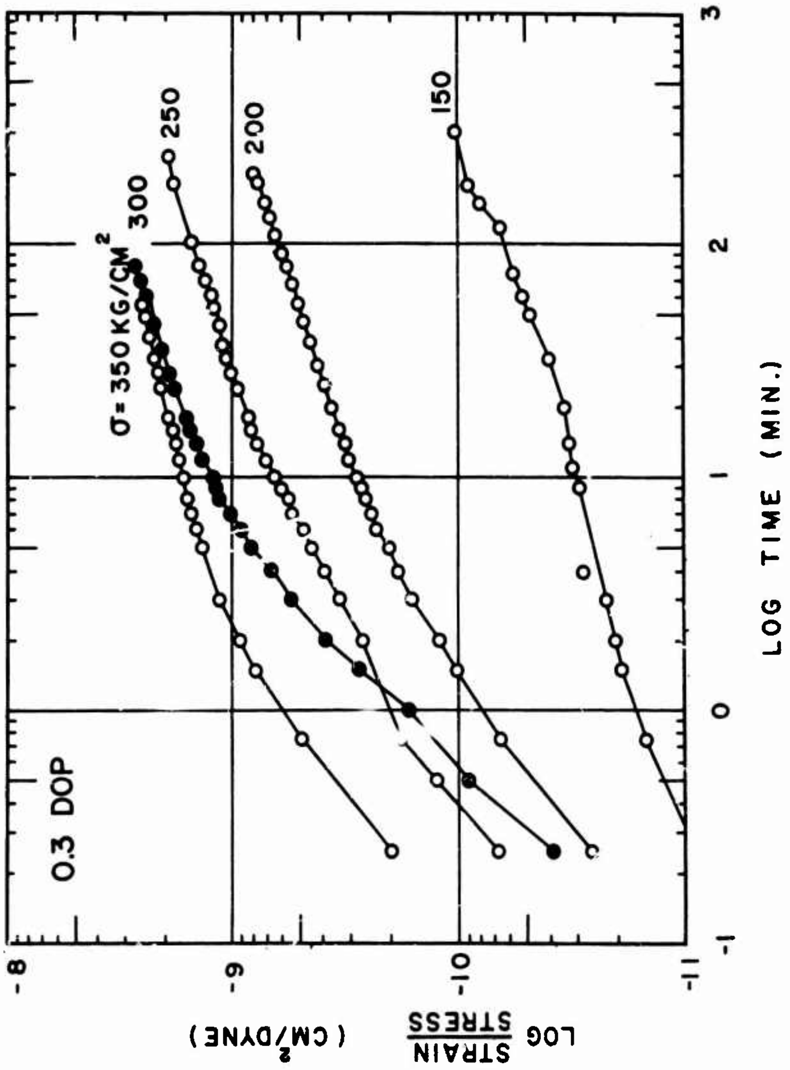

Figure 18. Creep Curves of Plasticized Polyvinyl Chloride (containing 0.3 weight fraction DOP) at Different Stress Levels at a Constant Temperature (-20°C)

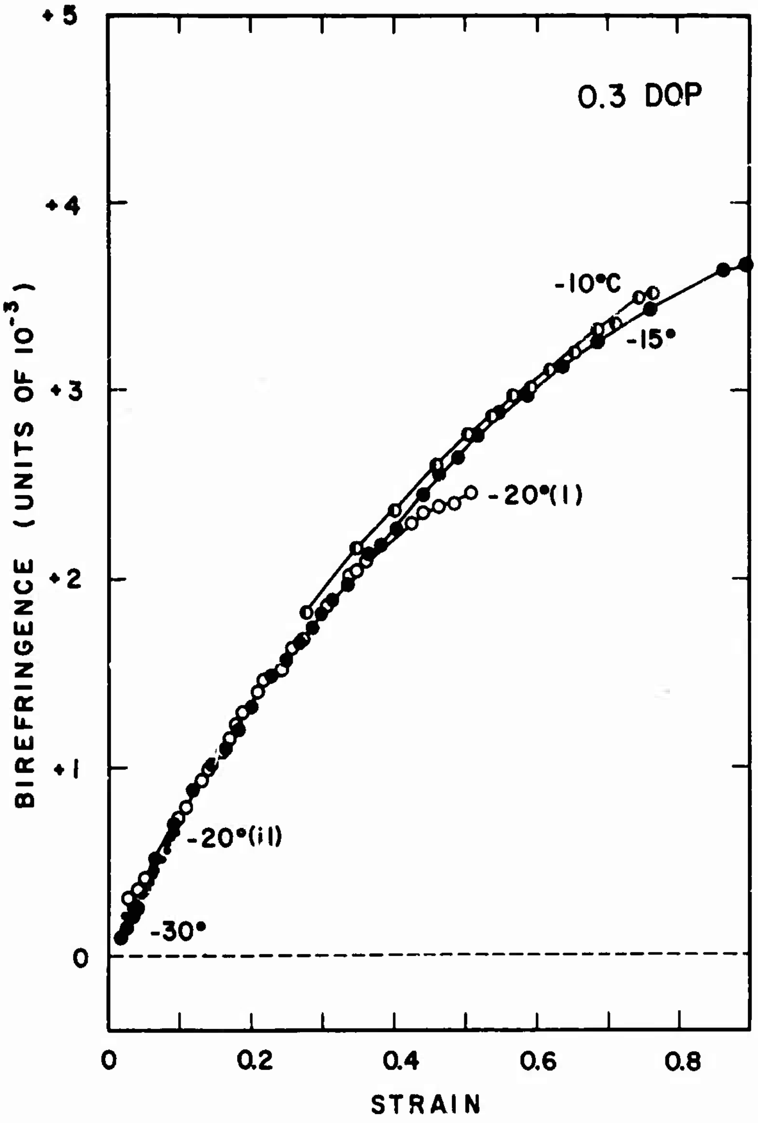

Figure 19. Birefringence-Strain Relation for Plasticized Polyvinyl Chloride (containing 0.3 weight fraction DOP) at Different Temperatures

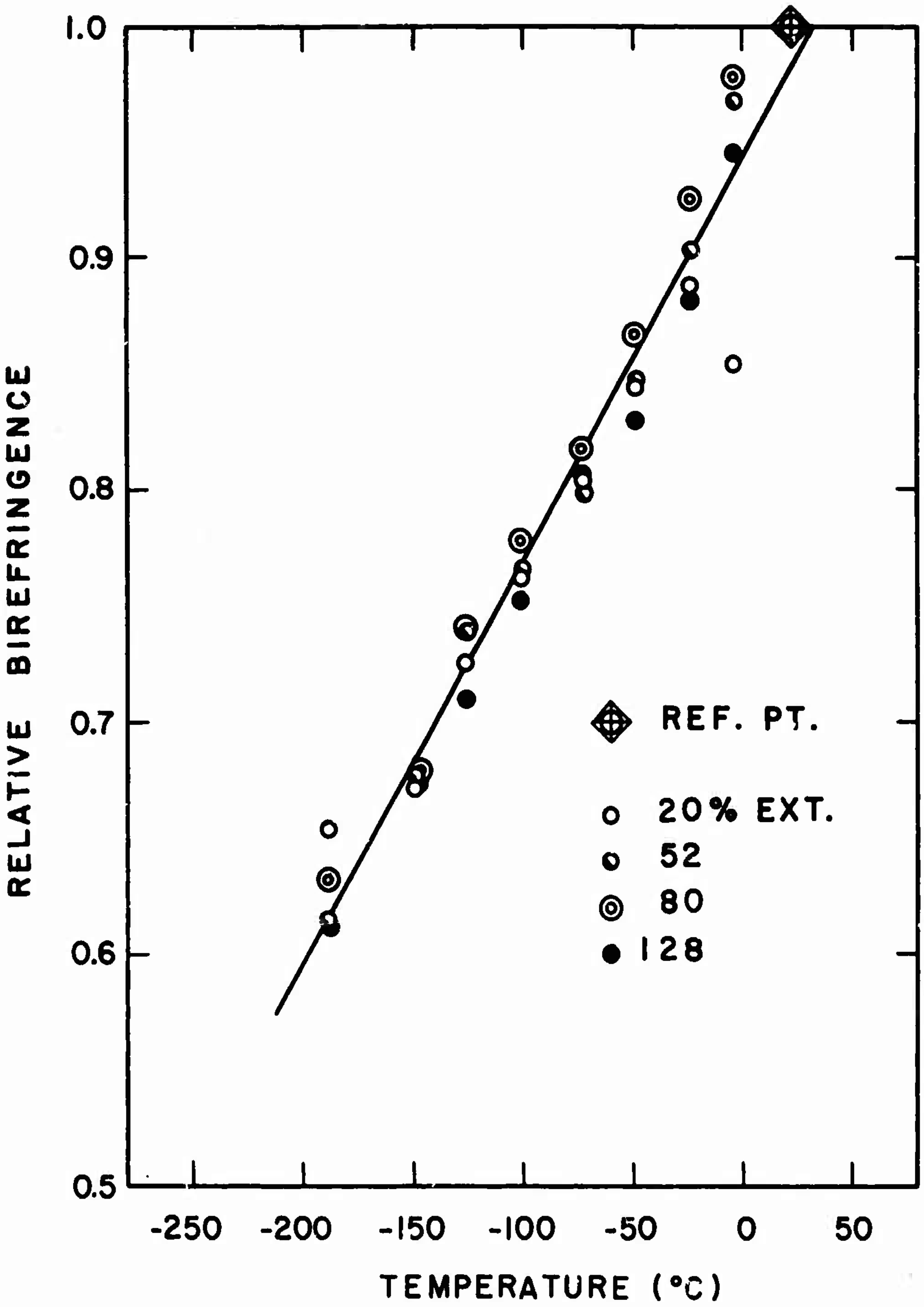

Figure 20. Temperature Dependence of Orientation Birefringence of Unplasticized Polyvinyl Chloride at Four Different Temperatures

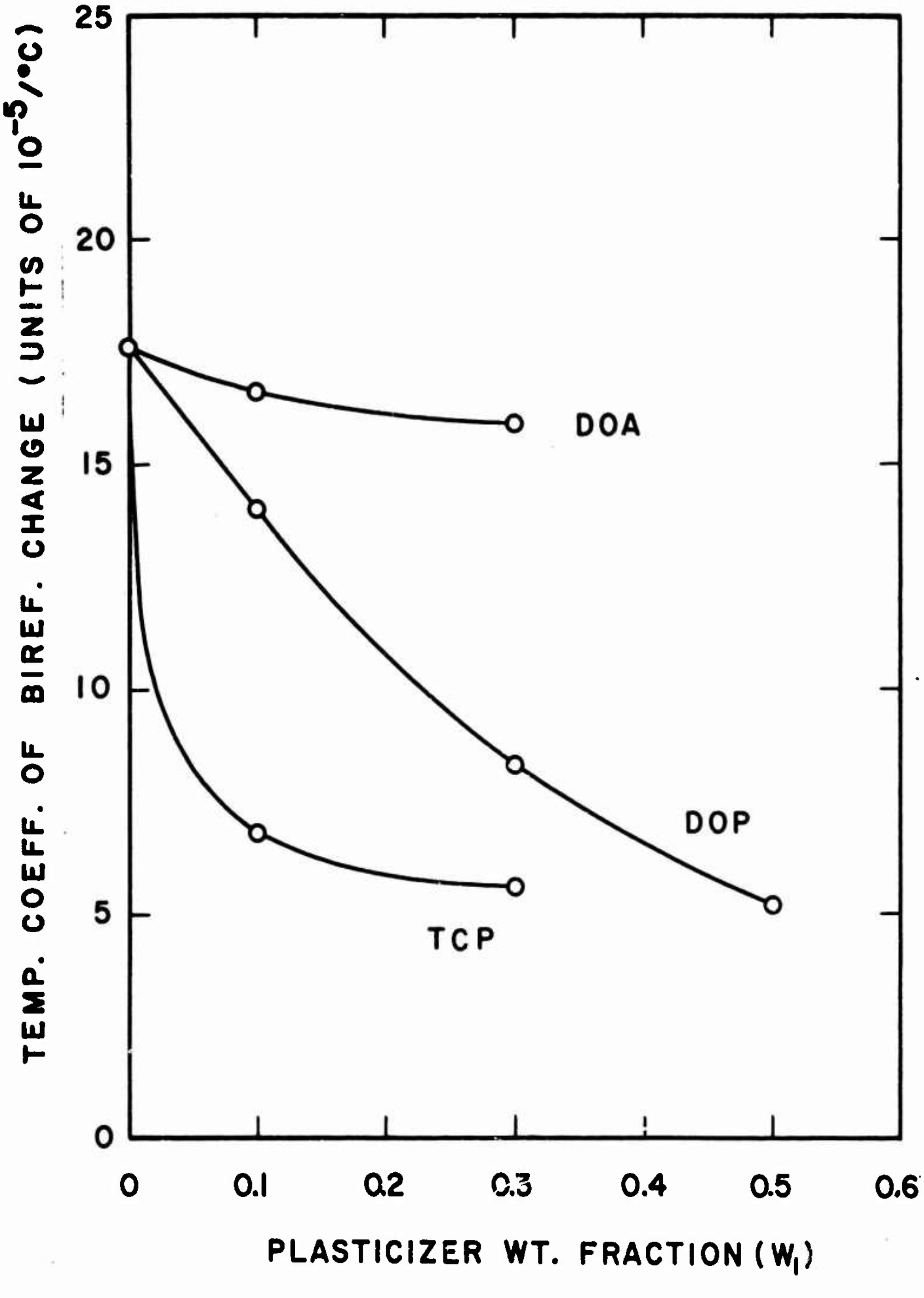

Figure 21. Coefficient of Temperature Dependence of Orientation Birefringence vs. Plasticizer Content for Polyvinyl Chloride Containing Three Different Plasticizers

different plasticizers have a very different effect on this optical parameter. This suggests that there is some type of structure change with temperature in these materials which shows up in a more sensitive way in this type of measurement than in the creep curves.

## 6. Conclusions and Recommendations

In addition to the detailed conclusions which have been presented, one broad conclusion can be drawn from this general exploratory study. A detailed understanding of the mechanism and nature of the drawing process for crystalline polymers is a subtle and complex problem which is not easily solved. The characterization of the structure of these polymers is in itself a difficult problem, since these polymers can be highly crystalline (Nylon 6), paracrystalline (PAN) or slightly microcrystalline (PVC). This means, in turn, that a few simple comparisons of polymers with different degrees of crystallinity or of polymers which crystallize on drawing (as was originally planned in this project) will probably not lead to any useful results or conclusions. It appears that only studies carried out in some depth will give results of value.

One of the specific results of value in the present study is the considerable variety of behavior encountered in regard to neck formation. Neck formation was found in some cases but not in others, and in one case (PET) could be observed to initiate at very high elongations. Studies around the borderline where neck formation does or does not take place should lead to some useful conclusions as to the basic criterion for neck formation (which is still not properly understood).

The other specific point most needed in future studies is the extensive use of X-ray measurements in connection with the type of experiments reported here. A correlation could perhaps be established between X-ray and infrared data, so that the latter (which are quicker and easier) could be used as a routine method but in a more meaningful way. A detailed analysis of the structure changes taking place during the various stages of drawing, and when drawing takes place under different conditions (of temperature and absorbed solvent, for example), could be achieved in this way, and such information is very necessary.

The exploratory goals of the present study were successfully achieved, however, and the future work required represents simply an extension and continuation of the lines of investigation developed here. Such a continuation of several aspects of the present study is planned in future research work.

## 7. Acknowledgments

Grateful acknowledgment is extended to several of the people involved in this investigation. Mr. V. A. Lathiya and Mr. S. R. Shoney served as research assistants; they did much of the work of equipment construction, and carried out the studies of humidity effects and alcohol treatments of Nylon 6.

The data on phenol treatments of Nylon 6 and the stress-strain, infrared, dynamic mechanical and thermogravimetric properties of the treated samples were obtained by Dr. J. Rubin, who was at the time holder of a PIA (Plastics Institute of America) Postdoctoral Fellowship at Stevens Institute.

The data on polyethylene terephthalate and polyacrylonitrile were obtained by Mr. H. Okuyama, who was a research visitor at Stevens from the Fuji Photo Film Company in Japan. The data on PVC were obtained by Mr. Y. Kazama, who was a research visitor at Stevens from the Kao Soap Company in Japan.

Our samples of Nylon 6 film (Capran 77C) were obtained from Allied Chemical Corp., Morristown, N. J., through the kindness of Mr. George Koo. The PAN film was furnished to us by the Sohio Research Laboratories in Cleveland, Ohio. The amorphous PET film was obtained from the Research Laboratories of the Fuji Photo Film Co. in Ashigara, Japan. The PVC polymer used in making solvent-cast films (SCC-676) was furnished to us by the Stauffer Chemical Co.

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13. ABSTRACT

In this investigation of the plastic yield (or cold-drawing) phenomenon in crystalline polymers, most of the work was carried out on Nylon 6, although polyethylene terephthalate (PET), polyacrylonitrile (PAN) and polyvinyl chloride (PVC) were also studied. Absorption of plasticizers (water, alcohols, phenol) in Nylon 6 produced changes in the crystalline structure as well as plasticizer action; these two effects must, therefore, be carefully distinguished. Changes in the crystalline structure were followed by changes in the infrared spectrum. Dynamic mechanical and thermogravimetric analysis (TGA) measurements were carried out on the polymer before and after treatment. The effects of plasticizer and temperature were investigated in both stress-strain and creep tests. The stress-strain curve of Nylon 6 can be decomposed into two components; one of these is affected by the plasticizer, and probably can be related to the amorphous phase. Phenol treatment produces a total disappearance of the yield peak in the stress-strain curve and a simultaneous disappearance of neck formation.

The drawing of amorphous PET was studied under dead-load creep conditions. This polymer showed an unusual behavior in that the neck formation would sometimes initiate at very high strains (above 50 percent elongation). The drawing of PAN under the same creep conditions indicates that a progressive structure change takes place in this polymer when temperature varies through the range of 70° - 160°C. (which spans the glass transition region). The birefringence-strain relation for PAN is also unusual, and a possible two-phase structure is hypothesized for this polymer, based on these results.

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|---|---|---|---|---|---|---|
| | ROLE | WT | ROLE | WT | ROLE | WT |
| Tests | 8 | | | | | |
| Cold drawing | 8,6 | | | | | |
| Nylon 6 | 9 | | 7,9 | | | |
| Polyethylene terephthalate | 9 | | 7 | | | |
| Polyacrylonitrile | 9 | | 7 | | | |
| Polyvinyl chloride | 9 | | 7 | | 9 | |
| Water | 6 | | | | | |
| Phenols | 6 | | | | | |
| Alcohols | 6 | | | | | |
| Crystal structure | 7 | | | | | |
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| Stress-strain curve | | | 10,8 | | | |
| Birefringence | | | | | 7 | |
| Strains | | | | | 6 | |

## Abstract (cont'd)

Creep drawing of plasticized PVC was also measured. The concept of plastic yield as a stress-induced glass transition seems relevant, just as in the case of unplasticized PVC. The birefringence-strain relation for this polymer was of a more normal form than was observed for PAN. Measurements were made of the temperature dependence of orientation birefringence in PVC containing different amounts of plasticizers (dioctyl phthalate, dioctyl adipate, tricresyl phosphate). The different plasticizers produced very different effects in this type of experiment.