

## Optical Detection of Thermal Transitions in High Polymers

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### Synopsis

This report describes a series of recent experiments in which various thermal transitions including stress relaxations and glass transitions in high polymers were characterized by observing birefringence changes during heating and cooling. An automatic recording device employing a hot stage, polarizing microscope, photocell, and chart recorder was employed in these investigations. A general discussion of the utility and advantages of the technique of thermo-optical analysis (TOA) as well as its deficiencies is presented. Characteristic birefringence-temperature profiles of a number of amorphous and semi-crystalline polymers are included.

### INTRODUCTION

Birefringence, the property of having two indices of refraction, is a general characteristic of anisotropic materials and is the result of specific interactions between the electric field of an incoming light wave and the electronic structure of the sample. The detection of birefringence is possible, however, only when long-range correlations at least comparable to the wavelength of visible light exist. For example, chemical bonds are anisotropic since the electrons move more easily along the bond direction than perpendicular to it. In the absence of cooperative alignment, however, these molecular differences are canceled and no net birefringence is observed. If, in contrast, substantial molecular orientation is introduced, for instance, by the application of uniaxial stress to a polymeric material, the resulting birefringence is easily visible between crossed polarizers.

At least four independent phenomena can contribute to birefringence in high polymers<sup>1</sup>:

1. The preferential alignment of chain segments in one or several directions. This can be produced by application of shear stress above the glass transition temperature,  $T_g$ , of the polymer (hot drawing).

2. The bending or twisting of chemical bonds. This *distortional birefringence* arises from changes in the internal electric field of a glassy polymer resulting from the displacement of chain atoms from their equilibrium posi-

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tions. The distortional birefringence can persist after the removal of stress if deformation and yielding occur below  $T_g$  (cold drawing).

3. The coherent alignment of rather long chain segments resulting from crystallization. The optical effect is comparable to that obtained in (1), although the lateral packing density is generally different since it is determined by the unit-cell dimensions.

4. The presence of boundary regions such as the crystal-amorphous boundary in semicrystalline polymers or the domain boundaries in block copolymers or blends which are macroscopically isotropic. Such birefringence is often referred to as "form birefringence." Form birefringence arises from the distortion of the electrical field of the incident light near the interface in cases where the size or separation of domains is comparable to the wavelength of light. For example, the birefringence displayed by an unoriented semicrystalline polymer is made up of contributions from the presence of folded chain lamellae as well as from the distortions resulting from the presence of alternate crystalline and amorphous regions.

Deformation of a semicrystalline polymer will modify the contributions of these independent sources to the total birefringence by introducing changes in molecular order and orientation. This problem has been solved to within a good approximation for the case of spherulitic morphology.<sup>2</sup>

Obviously the magnitude of the birefringence,  $\Delta$ , is closely related to the physical state of the polymer as well as to its thermomechanical history. However, the quantitative evaluation of each of the several contributions to the birefringence often requires the use of considerable theory. Some of the correlations between the magnitude of  $\Delta$  and the degree of orientation are well known and have been extensively used in rheo-optical investigations and in crystallization studies. In other cases, such as those involving distortional and form birefringence, the theoretical interpretations remain only approximate.<sup>3</sup>

In spite of these difficulties, it was tempting to utilize birefringence changes as a means of investigating the thermal transitions and thermal histories of polymer samples. Such measurements appear to be both novel and useful. The detection of glass-rubber transitions in semicrystalline and amorphous homopolymers and copolymers is original and of great practical interest since conventional techniques such as dilatometry and calorimetry are often cumbersome and insensitive. The relationship of the glass-rubber transition to the birefringence is discussed qualitatively below. The contribution of crystallization or melting to the birefringence which is manifested by the appearance or disappearance of highly anisotropic regions will be considered later.

## BIREFRINGENCE AND THERMAL TRANSITIONS

It is well known that the glass-rubber transition does not involve appreciable structural changes. Therefore, in cooling an unrestrained, isotropic rubber below  $T_g$ , there is no reason to expect birefringence to develop. Conversely, on heating an isotropic glass no birefringence appears. This

is not true when the sample is strained or under stress, however, since both of these stimuli produce either orientational or distortional birefringence or both. The magnitude of  $\Delta$  is increased by an imposed stress or strain and reduced by thermal or Brownian motions of the chain segments which act to relax the orientation and diminish the birefringence. Consequently, the rate of decrease of  $\Delta$  in a strained sample during heating is related to the segmental mobility of the polymer and depends on both the temperature and free volume.

Since the glass transition occurs when the rate of configurational rearrangements contributing to the free volume and enthalpy are of the same order of magnitude as the rate of cooling,<sup>4</sup> the temperature coefficient of the rate of decrease of  $\Delta(d\Delta/dT)$  should decrease sharply at  $T_g$ . Although this statement corresponds to the kinetic definition of  $T_g$ , the measurement of  $d\Delta/dT$  versus  $T$  of a hot, drawn rubber is difficult and unattractive. An alternate method is available, however.

It was previously noted that a glassy sample may show two types of birefringence of the same or opposite sign.<sup>5</sup> These are classified as *orientational*, or *strain induced*, and *distortional*, or *stress induced*. One can expect the stress-induced birefringence to decrease much faster than the strain-induced birefringence (at least the anelastic fraction of strain involving long-range orientations) during heating. This occurs since the former involves only local motions of short segments which may still be effective in the glassy state while the latter involves cooperative motions of large chain segments which may be considered to be essentially "frozen in" in the glass. Thus the total birefringence may not drop to zero at  $T_g$ , but only at a higher temperature which depends on the relative magnitudes of the two relaxation processes and on the heating rate. Two cases may be envisaged:

1. If the glassy sample is heated under *constant strain*, the stress will drop rapidly near  $T_g$ . It may not drop to zero, however, since the rubber-like elasticity due to long-range chain orientation may persist and relax only at higher temperatures or, if the sample is crosslinked, may remain constant at some finite value. In any case, the relaxation of *stress birefringence* at  $T_g$  remains easily detectable.

2. If a cold-drawn, glassy sample is heated without restriction, the long-range orientation will disappear rapidly above  $T_g$  as the rubber contracts since rubbers in general have short recovery times. Consequently, the initial birefringence will drop to zero more rapidly in this case than in (1).

These are the basic premises for the detection of glass-rubber transitions by observing birefringence changes in amorphous polymers or in polymer systems containing an amorphous component. Since in glassy systems  $\Delta$  can arise from at least two sources and since its rate of decrease depends both on the temperature and on experimental conditions, one cannot predict "a priori" the exact correlation between birefringence changes and  $T_g$ . This has to be investigated experimentally.

For these reasons the thermo-optical analysis (TOA) of thermal transitions in polymers has been generally neglected. Preliminary experiments

have shown, however, that there are close correlations between birefringence changes and thermal transitions. Moreover, TOA seems to constitute a powerful tool for detecting these transitions and for investigating related phenomena especially in cases where other methods are extremely inefficient. Nevertheless, it has been found that the data must be analyzed with care and the experimental conditions must be carefully altered to determine the precise nature of the correlations since the proposed method is subject to many experimental artifacts which are discussed more fully below.

### EXPERIMENTAL ARTIFACTS

The direct measurement of  $\Delta$ , which, in a uniaxially oriented sample, is defined as the difference in the two primary indices of refraction, is often difficult or impossible. Therefore, instead of  $\Delta$ , it is more convenient to measure the intensity  $I$  of the light transmitted through an anisotropic sample held between crossed polarizers. This can be accomplished easily using a photocell whose output can be recorded as a function of temperature or time. A suitable instrument has been described in connection with isothermal crystallization studies.<sup>6</sup> Since, however,  $I$  is not directly proportional to  $\Delta$ , an exact correlation involves the use of rather complicated trigonometric functions. In the simplest case, a uniaxially oriented sample placed at a  $45^\circ$  angle between crossed polarizers,  $I$  is given as

$$I = I_0 \sin^2(\delta/2) \quad (1)$$

where  $I_0$  is the incident intensity and the retardation,  $\delta$ , is defined as

$$\delta = 2d \cdot \Delta / \lambda_0 \quad (2)$$

where  $d$  is the sample thickness and  $\lambda_0$  the wavelength of the light. As a consequence of approximating  $\Delta$  by  $I$ , one must be aware of the following difficulties:

1. Since  $I$  is a periodic function of  $\Delta$ , it may show maxima and minima even in the case of monotonically decreasing  $\Delta$  if the initial value of  $\delta$  is larger than  $\pi/4$ . Thus, if the  $I$ -versus- $T$  profile shows several maxima or minima, it should be verified that the number of extrema does not change when the thickness of the sample is reduced by half. If a change occurs, the thickness should be reduced until the number of maxima and/or minima becomes independent of  $d$ .

2. If a polychromatic light source is employed, errors may be introduced by the nonlinear chromatic sensitivity of the photocell. Again a sinusoidal variation is expected. This problem may in general be circumvented by employing a filter which is matched to the maximum sensitivity of the photocell.

3. Since  $\Delta$  is composed of contributions from four sources (see introduction) which may differ in sign, the algebraic sum of these contributions may increase or decrease or even pass through zero before the sample becomes isotropic. Although these variations reflect real structural changes in the

material, the measured extremes do not necessarily correspond directly to those of  $\Delta$  since  $I$  is a nonlinear function of the total birefringence. Such phenomena may be verified by employing the recommendations noted in paragraph (1) above.

4. Because the intensity of the transmitted light depends not only on  $\delta$  but also on the *scattering power* of the sample, changes occurring in the size and distribution of domains or crystallites may cause appreciable variations in  $I$ . A discussion of this phenomenon has been presented by Clough et al.<sup>7</sup> Again, these features are related to structural changes, but they disguise or mask other relaxation processes.

5. With block copolymers having a sharp molecular weight distribution within the blocks, specific *dispersion* and *interference* effects may be expected. The regular, almost crystallographically ordered domains of these materials<sup>8</sup> may produce unusual colors or contribute significantly to the measured intensity of the transmitted light.

6. In the case of severely stretched, unrestrained films, large changes in the thickness  $d$  may occur during heating as the sample relaxes. These changes will be reflected in changes in  $I$  as noted in eqs. (1) and (2). Simultaneous decreases in  $\Delta$  may be superimposed giving rise to secondary maxima and/or minima in the  $I$ -versus- $T$  curve. Biaxially stretched, unrestrained films may show more peculiar effects. In these cases, the experiments should be repeated with the sample held under constant strain. In all instances the effects of thermal expansion and thermal variations in the refractive index  $\eta$  may be neglected.

7. In addition to the aforementioned optical effects, one must be careful to avoid heating the sample so quickly that the relaxation processes lag behind their equilibrium values. This phenomenon is known as superheating and arises from the limited mobility of the chain segments in the condensed phase. It occurs both in glass-rubber transitions and in crystal-melt transitions. The use of heating rates of less than 20°C/min generally circumvents this problem.

Summarizing, it is noted that the observed optical effects reflect a combination of the artifacts introduced by measuring  $I$  rather than  $\Delta$  as well as effects resulting from true structural changes. Often careful visual examination of the sample during heating is necessary to interpret the results correctly. In other cases, experiments made on restrained and unrestrained films permit the qualitative separation of stress- and strain-induced birefringence.

## EXPERIMENTAL

The device used for the measurements is diagrammed schematically in Figure 1. Runs were made as follows:

A sample  $S$  held between coverslips or in a small jig (Fig. 2) was inserted in a Leitz hot stage mounted on a Zeiss polarizing microscope. Magnifications of 50–100 $\times$  were typically employed. Light was supplied by a 12-volt lamp operated from a transformer  $T_2$  at constant current  $A_2$ , and ob-

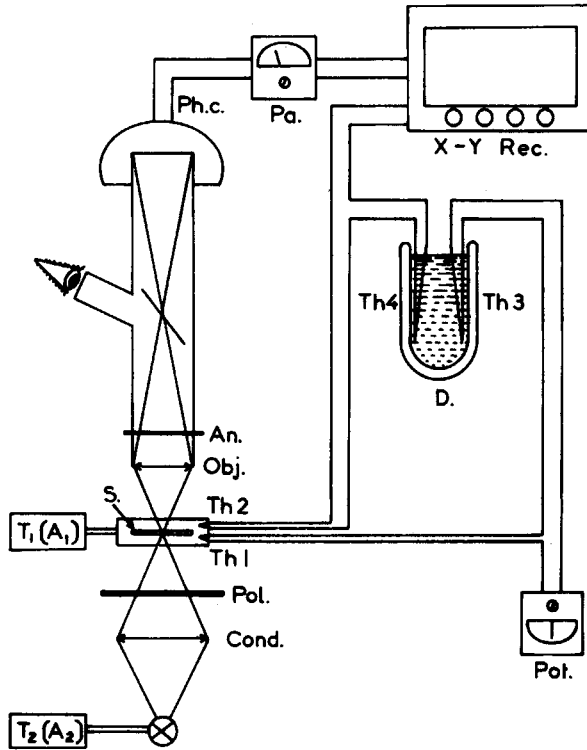


Fig. 1. Schematic diagram of thermo-optical analyzer (TOA).

servations were carried out with the specimens between crossed polarizers. The hot stage was controlled by transformer  $T_1$  operating at current  $A_1$ . Heating was accomplished stepwise by varying the power input to the hot stage. The heating rate was thus nonlinear but averaged about  $5^\circ\text{C}/\text{min}$ . Thermocouples Th 1 and Th 2 were used to monitor the hot stage tempera-

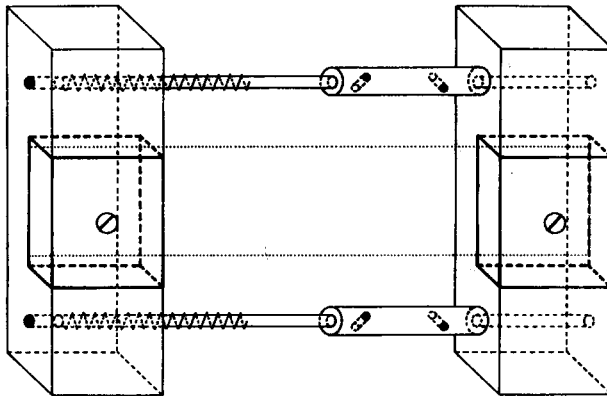


Fig. 2. Miniature stretching jig.

ture through leads to a Leeds-Northrup potentiometer and a Mosley X-Y recorder. Ice junctions were provided at thermocouples Th 3 and Th 4. The recorder Y scale was controlled by the output of a photocell Ph. c and its preamplifier Pa. A beam splitter and a triocular eyepiece allowed simultaneous visual observation of the sample during heating.

Samples were supplied as thin films and were generally isotropic. Birefringence was typically introduced by stretching or lightly scratching the material with a stylus before a run. In general, scratching was found to be a much easier and neater method of introducing localized orientation. In some cases the films were held at constant strain during heating by using the small jig diagrammed in Figure 2.

About 70 runs were made on various polymers including polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(dimethyl phenylene oxide) (PPO)\*, poly(diphenyl phenylene oxide) (P<sub>2</sub>O), three samples of poly(ethylene terephthalate) (PET), five samples of BPA polycarbonate (PCBA), two samples of polypropylene (PP), and a styrene-butadiene block copolymer (Shell Chemical Co. Kraton 101). The results are described below.

## RESULTS

Although all of the 15 samples examined showed quite different behavior, only seven will be analyzed here in some detail. In spite of their differences, these samples can be considered to be typical of the main classes of polymeric materials.

### Amorphous Polymers

PMMA and PS (Koppers Co. Dylene 8) were used as typical representatives of noncrystallizing atactic polymers.

Scratching the surface of PMMA does not produce appreciable birefringence since the stress-optical coefficient of this material is rather small, and the relatively mobile side chains are frozen in only at low temperatures. Thus, to obtain a measurable amount of birefringence, it was necessary to draw the samples at room temperature or above  $T_g$  followed by quenching.

PMMA #2 was *hot drawn* and was maintained unrestrained at room temperature for 50 hr prior to heating. Figure 3 shows an  $I-T$  plot for this sample during a heating (rate =  $\sim 5^\circ\text{C}/\text{min}$ ) and cooling cycle. The birefringence is seen to decrease monotonically during heating and reaches a minimum at  $92^\circ\text{C}$ , which is within a couple of degrees of the accepted  $T_g$  for this material.<sup>9</sup> No increase in  $\Delta$  can be detected during subsequent cooling.

PMMA #3 was *cold drawn* in the jig and was heated and cooled under constant strain. Figure 3 shows that this sample behaved much like the hot-drawn material. The zero  $I$  level is reached at a slightly higher temperature ( $\sim 100^\circ\text{C}$ ), however. This seems to be due to the retardation of

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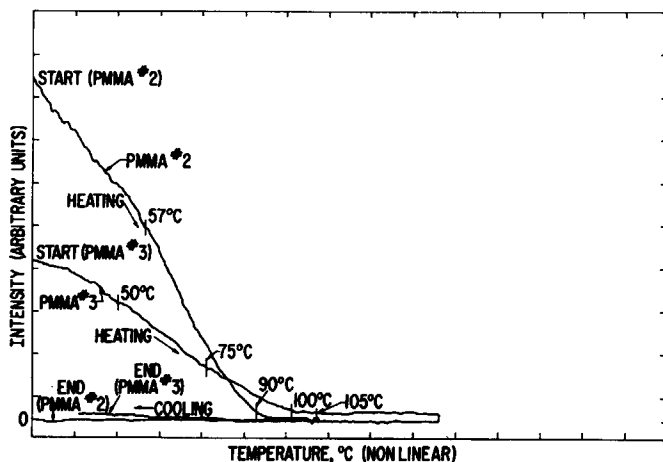


Fig. 3.  $I$ - $T$  plots for poly(methyl methacrylate): (#2) hot drawn and quenched; (#3) cold drawn and maintained at constant strain.

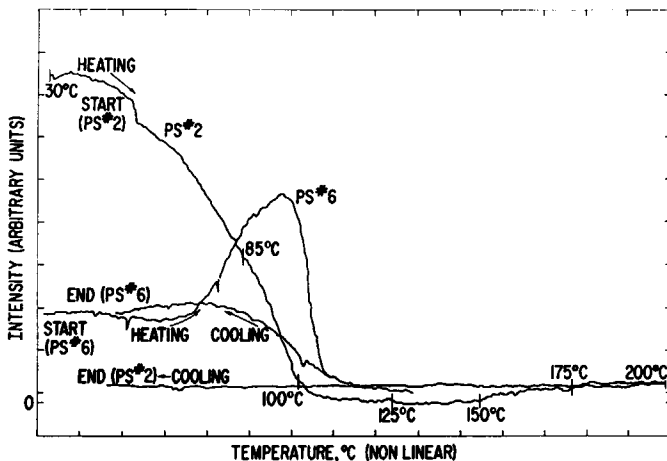


Fig. 4.  $I$ - $T$  plots for polystyrene: (#2) scratched and unrestrained; (#6) cold drawn and maintained at constant strain.

orientational recovery when the strain is kept constant. In polystyrene (see below), the retardation is much greater.

PS can be superficially oriented by scratching. Figure 4 shows an  $I$ - $T$  plot of such a sample (PS #2) during cycling between 25° and 200°C. The minimum in  $I$  occurs at 105°C, which is somewhat greater than the expected  $T_g$  of this material.<sup>9</sup> The slight increase in  $I$  between 105° and 200°C is unexplained. No increase in birefringence occurs during subsequent cooling.

PS #6 which was cold drawn and heated under constant strain shows somewhat different behavior.  $I$  increases rapidly above 65°C instead of decreasing and passes through a maximum at  $\sim 92^\circ\text{C}$  before dropping to



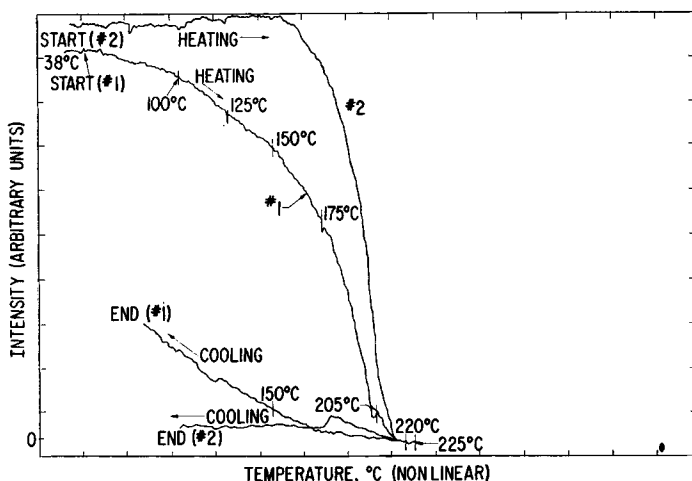


Fig. 5.  $I$ - $T$  plots for amorphous poly(dimethyl phenylene oxide): (#1) scratched and unannealed; (#2) scratched and annealed.

zero at about 125°C. In addition, the stress built up during subsequent cooling causes an increase in birefringence as room temperature is approached. This part of the curve is reversible. The origin of the maximum may be related either to the rather high value of the original retardation  $\delta$  or to the opposite sign of the stress-and-strain birefringence noted for polystyrene,<sup>10</sup> which in part balance each other in the initial state. On heating, the relaxation of the stress birefringence (-) leaves the orientational birefringence (+) unbalanced. Since the orientation persists above  $T_g$ , the minimum occurs at a somewhat higher temperature. Here,  $T_g$  is

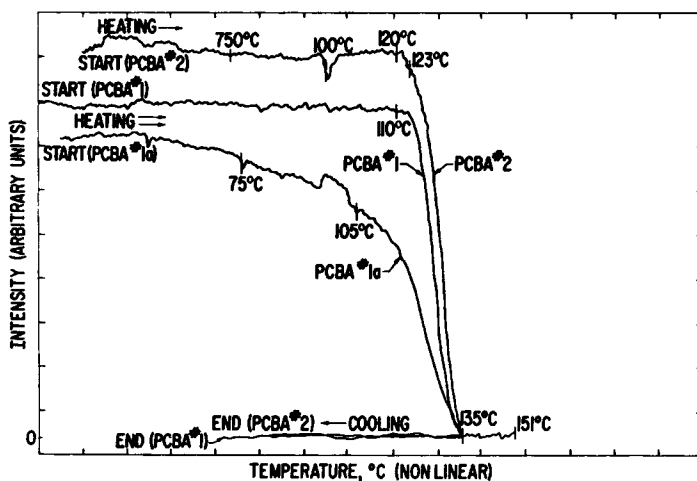


Fig. 6.  $I$ - $T$  plots for amorphous BPA polycarbonate: (#1) and (#2) as received (hot drawn, unrestrained); (#1a) scratched after melting at 150°C and cooling.

found near the maximum ( $\sim 92^\circ\text{C}$ ) where the stress birefringence is relieved.

Quenched samples of PPO resin and PCBA which do not crystallize thermally were found to behave much like the atactic materials. Figure 5 shows  $I$ - $T$  plots for scratched, unrestrained poly(dimethyl phenylene oxide) samples. The initial birefringence is found to decrease at an increasing rate until it reaches zero near  $T_g$  ( $210^\circ$ - $215^\circ\text{C}$ ).<sup>9</sup> The differences in the shapes of the two curves are the result of annealing sample #2 at  $160^\circ\text{C}$  prior to the run, whereas sample #1 was unannealed. The small increases in  $I$  during cooling are the result of stresses introduced by adhesion of the hot film to the coverslip. These disappeared on removing the film.

An  $I$ - $T$  plot for amorphous, uniaxially oriented PCBA is shown in Figure 6. Samples #1 and #2 were investigated as received and demonstrate the reproducibility of thermo-optical analyses on similar samples. The original intensity remains constant up to about  $155^\circ\text{C}$  and then decreases rapidly to zero near  $T_g$  ( $\sim 145^\circ\text{C}$ ). The samples remained isotropic during cooling.

The resulting isotropic PCBA samples can be made birefringent again by scratching, and the experiment can be repeated. Figure 6 shows a run using such a scratched sample. Although the curves are similar to those obtained earlier,  $I$  begins to drop slowly at about  $50^\circ\text{C}$  before dropping to a minimum at  $135^\circ\text{C}$ . The initial decay is obviously due to recovery processes which start at about  $50^\circ\text{C}$ , whereas the original, oriented films were stable to  $110^\circ\text{C}$ .

### Crystallizable Polymers

Two materials, PET and  $\text{P}_3\text{O}$ , are considered here. Both can be quenched from the melt to amorphous glasses and then thermally crystallized to produce a typical spherulitic morphology above  $T_g$ .

Figure 7 shows the  $I$ - $T$  profile of an amorphous, unoriented, scratched PET sample. As noted previously, some decay of birefringence occurs near room temperature, although  $I$  drops precipitously just before reaching a minimum near  $T_g$  ( $70^\circ\text{C}$ ).<sup>9</sup> The subsequent rise in  $I$  with increasing temperature is the result of crystallization. A small maximum is observed at  $110^\circ\text{C}$  as the scattering power of the spherulites increases and transmission is reduced. Further heating (not shown) results in a rapid disappearance of spherulites at  $240^\circ$ - $250^\circ\text{C}$  as melting occurs.  $I$  increases during slow cooling as melt crystallization commences. If this sample is again scratched and heated, the minimum in  $I$  is displaced to  $85^\circ\text{C}$ . This increase in the  $T_g$  of PET with crystallinity has been reported previously. In fact, in inhomogeneous semicrystalline-amorphous samples, a two-step decrease in  $I$  corresponding to the two  $T_g$  values can be observed.

The behavior of  $\text{P}_3\text{O}$  is similar to that of PET.  $I$  reaches a minimum at  $225^\circ \pm 5^\circ\text{C}$  ( $T_g$ ) and subsequently increases to a maximum at  $290^\circ\text{C}$  as

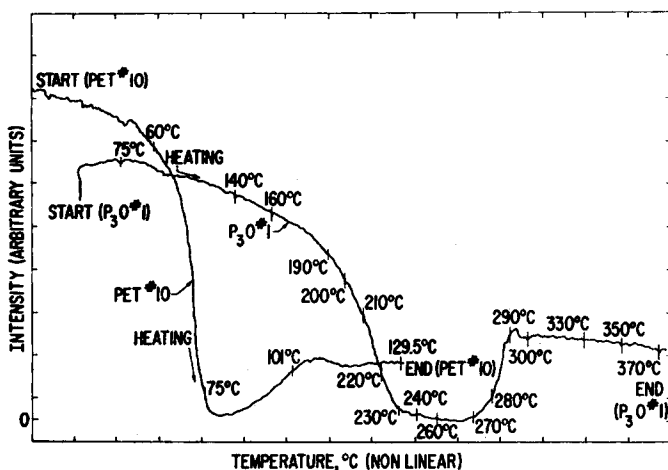


Fig. 7.  $I$ - $T$  plots for poly(ethylene terephthalate) (PET) and poly(diphenyl phenylene oxide) ( $P_3O$ ): (PET #10) scratched; ( $P_3O$  #1) scratched. (Note difference in temperature scale.)

crystallization occurs. Further heating to  $415^\circ\text{C}$  results in no change in  $I$ , with degradation occurring before melting is observed.

### Semicrystalline Polymers

Although some of the former polymers can be obtained and investigated as semicrystalline polymers, polypropylene is a typical example of a polymer that cannot be quenched to a completely amorphous glass. Two types of PP were investigated. The first was hot stretched uniaxially at  $150^\circ$  (PP #3), while the second was biaxially stretched under unbalanced strain.

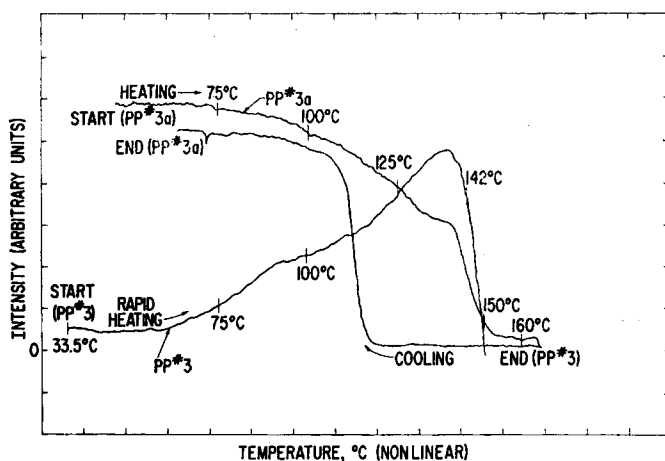


Fig. 8.  $I$ - $T$  plots for polypropylene: (#3) uniaxially drawn as received; (#3a) after melting on recrystallization.

The  $I$ - $T$  profile of PP #3 reproduced in Figure 8 shows a constant value of  $I$  up to 60°C, after which it increases to a maximum at 140°C. Repeated heating and cooling cycles (not shown) revealed that the observed increase in  $I$  was irreversible. Rapid melting commenced at 140°C, and the birefringence had decreased to zero by 160°C. The material recrystallized on cooling, showing a spherulitic structure which was substantially less birefringent than the original oriented film. (Note that the curve for sample PP #3 is displaced downward and expanded in Figure 8 with respect to the curves for sample PP #3a to allow inclusion on the same graph.) Heating the recrystallized film resulted in a monotonic decrease in  $I$ , with a pronounced shoulder at 140°C. Melting was complete by 160°C. Subsequent temperature recycling produced the same results.

These experiments demonstrate that the shape of the  $I$ - $T$  plots may vary markedly with initial orientation. The maximum observed on the first heating may have been the result of an initial optical retardation  $\delta$  greater than  $\pi/4$ , although varying contributions by sources of birefringence of different sign<sup>11</sup> such as those noted for samples PS #4 and PS #6 may also have been important.

The behavior of PP (biax.) (not shown) was more complicated than PP #3, showing two maxima in  $I$  at 148° and 158°C separated by a sharp minimum. In this critical temperature range the sample shrank dramatically although melting did not occur until 165°C. Surprisingly, remnants of the initial orientation persist up to 190°C. It is noteworthy that after complete melting (>190°C) and recrystallization, both polypropylene samples behaved identically.

## CONCLUSIONS

The proposed method for recording birefringence changes in thin polymer films by use of automated polarizing microscopy seems to supply a powerful tool for analyzing thermal transition phenomena such as glass transitions and stress relaxations. A number of advantages over conventional techniques are apparent:

1. Samples of a size less than 1 mg may be employed.
2. The instrument shows a very large signal-to-noise ratio and high sensitivity.
3. Multiple transitions resulting from several structural or conformational changes in the same sample may be detected.
4. Previous thermal treatments or orientation processes can be investigated.
5. Simultaneous observation of the sample during the experiment allows one to note important morphological changes.

Some limitations also exist:

1. The exact location of  $T_g$  is often rather crude. This deficiency may well be improved in more sophisticated apparatus, especially where programmed heating and cooling schedules are provided. Modifications of this type are currently being explored.

2. Some ambiguities in the interpretation of the  $I$ - $T$  plots remain. These may well be removed by systematically varying the preparation and analysis of given samples.

In spite of these difficulties, this method appears to be an extremely powerful tool for discovering new effects and for more thoroughly characterizing high polymers.

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