

# Birefringence of Injection-Molded Glassy Polymers During Relaxation and Recovery

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## Synopsis

Birefringence measurements have been made on six glassy polymers during stress-relaxation and recovery experiments at temperatures below  $T_g$ . Of the six polymers tested only one pair, poly(ethylene terephthalate) and a glassy polyamide ("Trogamid"), show a strong mutual resemblance in the behavior of birefringence under these conditions. The results are discussed with reference to molecular structure, and, although detailed interpretations are not offered, it is observed that the behavior is less complex for polymers which possess their most polarizable groups in the main chain or attached rigidly to it than for those polymers having polarizable side groups with relaxations which do not involve the main chain. All six polymers have been tested in injection-molded form, and the possible consequences of this are considered. The major differences observed to occur between the different materials do not appear to be related to processing, however, and some results obtained using specimens prepared in other ways are also presented to illustrate this.

## INTRODUCTION

Birefringence measurement provides a rapid, inexpensive, noncontact method for characterizing transparent polymer samples. Unfortunately, the results are far more difficult to interpret than to obtain. Birefringence is determined by the strain in the chemical bonds within the polymer, and hence by the stress, and also by the orientation of the chemical bonds. Separation of these two sources of birefringence can be very difficult when the stress and orientation are non-uniform, as is the case in an injection molding which contains a distribution of residual stresses and different states of orientation at different locations. A separation procedure has been developed by Saffell and Windle,<sup>1</sup> but it requires extremely careful execution of a rather lengthy procedure. When dealing with time-dependent changes in birefringence, the situation is much more complicated, for there may be several processes subdividing the "stress" and "orientation" contributions to birefringence. Stein and Tobolsky list the following "unit processes" which may contribute to time-dependent changes in stress or birefringence<sup>2</sup>: (a) chemical reaction; (b) viscous flow or diffusion; (c) crystallization; (d) release of distortion; (e) orientation of crystallites; (f) configurational changes; (g) macroscopic faults. Stein and Tobolsky indicate that they consider these to be the important processes, but do not claim the list to be exhaustive. There may be further complications because of the interactive nature of some of these processes. The relative contribution of different processes will vary from one polymer to another, and will be temperature-dependent. One of the ways of examining these phenomena is to measure birefringence during a stress-re-

TABLE I

Polymer	Manufacturer/grade	Molder <sup>a</sup>	Tool cavity <sup>b</sup>	Dimensions (mm)	Temperature (°C)			Machine pressure (MPa)
					Barrel	Nozzle	Mold (fixed/moving)	
PET	AKZO/A04-102	(a)	eg	152 × 10.6 × 4 <sup>c</sup>	265	270	<40	
PMMA	ICI/Diakon MG-102	(b)	eg	192 × 12.5 × 3.1 <sup>c</sup>	210/240	245	60/60	114
PA(G) <sup>d</sup>	Dynamit Nobel Trogamid	(c)	sg	216 × 12.8 × 3.3 <sup>c</sup>				
PS	BDH	(d)	eg	190 × 12.7 × 3.2	220/270	250	30	87
PC	Bayer/Makrolon 2603	(b)	eg	192 × 12.5 × 3.5 <sup>c</sup>	335/335	325	85/89	86
PES	ICI/Victrex 600P	(e)	eg	216 × 12.6 × 3.3 <sup>c</sup>	360		>150	

<sup>a</sup> (a) Provided by AKZO Chemie (U.K.) Ltd., Plastics Division, Hersham, Walton-on-Thames, Surrey; (b) produced by RAPRA, Shawbury, Shrewsbury on a Stubbe, SKM-76-110; (c) produced by PERME, Waltham Abbey, Essex; (d) produced at the University of Newcastle-upon-Tyne on a Butler-Smith 100/60; (e) provided by ICI Petrochemicals and Plastics Division, Welwyn Garden City, Herts.

<sup>b</sup> eg = end-gate; sg = side gate, 12 mm from one end.

<sup>c</sup> Bars produced as tab-ended tensile test pieces. The width dimension quoted refers to the gauge section.

<sup>d</sup> PA(G) is produced from dimethylterephthalate and trimethylhexamethylene diamine.

laxation test, and this is the method employed by Stein and Tobolsky.<sup>3,4</sup> Their measurements showed that the time-dependent changes in birefringence were quite different in different classes of polymers. They presented results for examples of the following groups of materials: crosslinked rubbers, linear amorphous rubbers, glassy polymers, plasticized poly(vinyl chloride)s, and semicrystalline polymers. They offered plausible explanations for the variations in behavior observed between groups of materials, but they also recorded variations within a single group which were less readily accounted for. Other studies of birefringence during stress-relaxation have been restricted usually to a single material and have concentrated primarily on the phenomenological aspects of the results.<sup>5-8</sup> Our own studies have included polystyrene (PS), polycarbonate (PC), poly(methyl methacrylate) (PMMA), poly(ethylene terephthalate) (PET), a glassy polyamide PA(G), and poly(ethersulphone) (PES), and, although all are normally termed "glassy polymers" in the range of test temperatures employed here (40–60°C for most tests), our results reveal marked differences in behavior between the different materials. This work has been conducted as part of a wider study on residual stresses and orientation in injection-molded polymers with the objective of investigating birefringence as a means of characterization, and some of the results obtained with PS, PC, and PES have been reported before.<sup>9,10</sup> The purpose of the current paper is to present previously published results on PMMA, PET, and PA(G), and to compare the results with those obtained with PS, PC, and PES, and with other data in the literature. A further feature of our studies is that for many tests birefringence is also followed during recovery on unloading the specimen following stress-relaxation, again with some unexpected results.

## EXPERIMENTAL

### Specimen Preparation

Details of the grades of materials and the molding conditions used are given in Table I. When using our own machine, we took the usual precautions to ensure no drift in conditions during a production run.<sup>11-13</sup> Batches of specimens provided by others were inspected between crossed polars on a light box and sets of specimens with visually identical birefringence patterns were selected for the experiments reported here.

### Stress-Relaxation and Birefringence Measurements

Stress-relaxation tests in uniaxial tension were conducted at closely controlled temperatures on rigs described previously.<sup>11,14</sup> The relative retardation was measured at a chosen location in the center of the specimen at intervals of time during the stress-relaxation test by identifying the characteristic color corresponding to the optical path difference caused by the double refraction of polychromatic light in the specimen. The fringe order and the sign of birefringence were determined using a quartz wedge compensator or a hand-held photoelastic rubber block sensitive to finger pressure. For measurements on specimens showing very small relative retardation (<200 nm), a retardation plate was interposed to displace the analyzed wave to a more sensitive region.

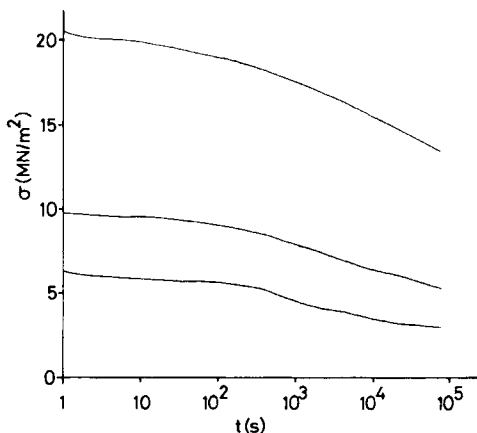


Fig. 1. Stress-relaxation of injection-molded PMMA at 40°C.

Tests on both PMMA and PET were conducted at 40°C, chosen because stress-relaxation proceeds at a measurable rate. After an extended period of stress-relaxation (usually 24 h), recovery experiments were conducted, leaving the specimen suspended in the test chamber, held still at 40°C, but with the lower grip decoupled, and birefringence measurements were recorded for a further extended period. PA(G) was tested at 40°C, 50°C, and 60°C, with most data collected at 50°C. The load cells used on the rigs are bidirectional and compression tests can be conducted by replacing the wedge grips used for tensile tests by flat-ended cylinders,<sup>12</sup> and measurements of birefringence during stress-relaxation in uniaxial compression were performed parallel to the bar axis on specimens approximately 12.5 mm high, cut from the gauge length of the injection moldings.

## RESULTS

### PMMA

Examples of the results of uniaxial tensile stress relaxation tests on PMMA are shown in Figure 1. Birefringence measurements recorded during these and other similar tests are shown in Figure 2(a). The initial birefringence, in the absence of any externally applied deformation, was very small and could not be separated from zero by our measurement technique. On applying a uniaxial tension, strong negative birefringence developed immediately. On continuing the test the magnitude of the birefringence fell, leveling off after a period of 1–3 h at a value dependent on the applied deformation. The decay in stress can be seen to occur at a different rate, as is confirmed on inspection of Figure 3, in which is plotted the ratio of birefringence to stress as a function of time.

The change in birefringence during recovery is shown in Figure 2(b). On releasing the specimen, there is an instantaneous positive jump in birefringence, consistent with its possessing a negative stress-optical coefficient as also demonstrated on loading for the stress-relaxation test.

The magnitude of the stress-optical sensitivity on unloading after the

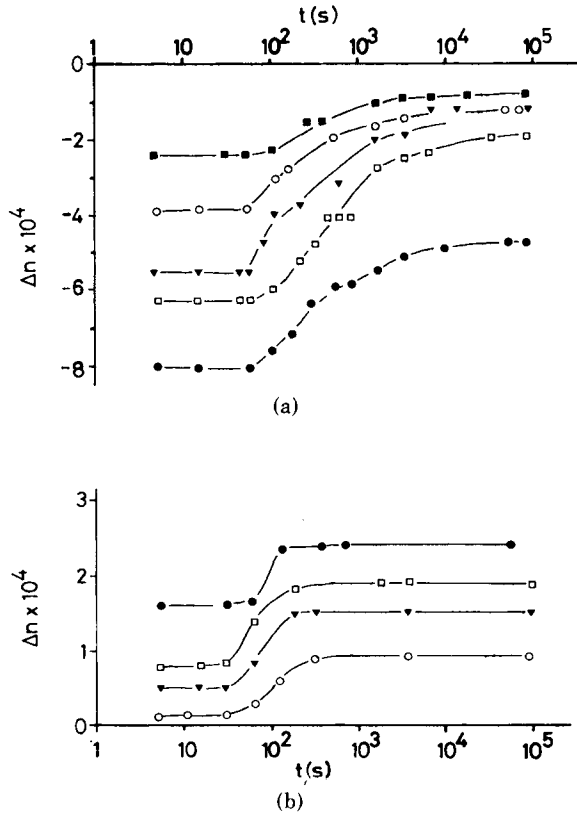


Fig. 2. (a) Birefringence measurements on PMMA during stress-relaxation at 40°C. (b) Birefringence measurements during recovery following stress-relaxation at different deformation levels. Note that the  $\Delta n$  scale is different in (a) and (b). Relaxation and recovery data obtained on the same sample are indicated by using the same symbol in (a) and (b).

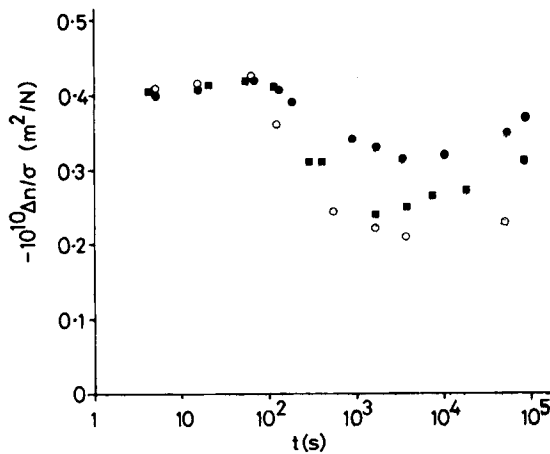


Fig. 3. Plots of  $\Delta n / \sigma$  against time obtained from three different relaxation tests on PMMA at 40°C.

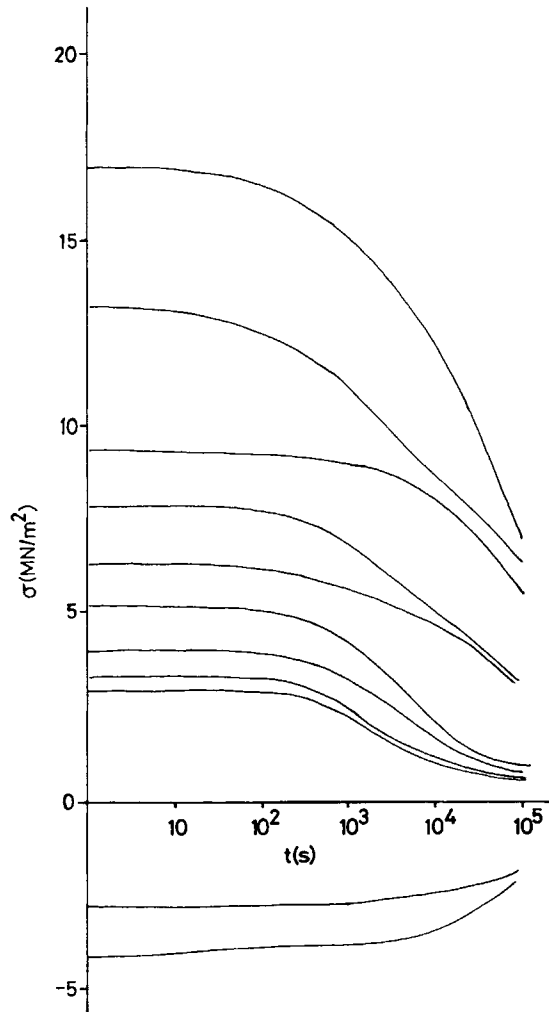


Fig. 4. Stress relaxation of injection-molded PET at 40°C obtained both in uniaxial tension (+ve) and uniaxial compression (-ve).

stress-relaxation test was fairly similar to that obtained on loading at the beginning of the test. The birefringence did not return to its original (zero) value on unloading, indicating that birefringence is not dependent only on stress in this material, but that the conformational changes occurring during relaxation must produce an additional contribution to birefringence.

Although it is expected intuitively that if the specimen continues to be undisturbed for a prolonged period after unloading, then some of the molecular rearrangements promoted by the deformation will be reversed and that birefringence will decay towards its original value, the results recorded during recovery on PMMA show the opposite effect. Figure 2(b) shows that the birefringence value became positive on unloading and then continued to climb to yet higher values.

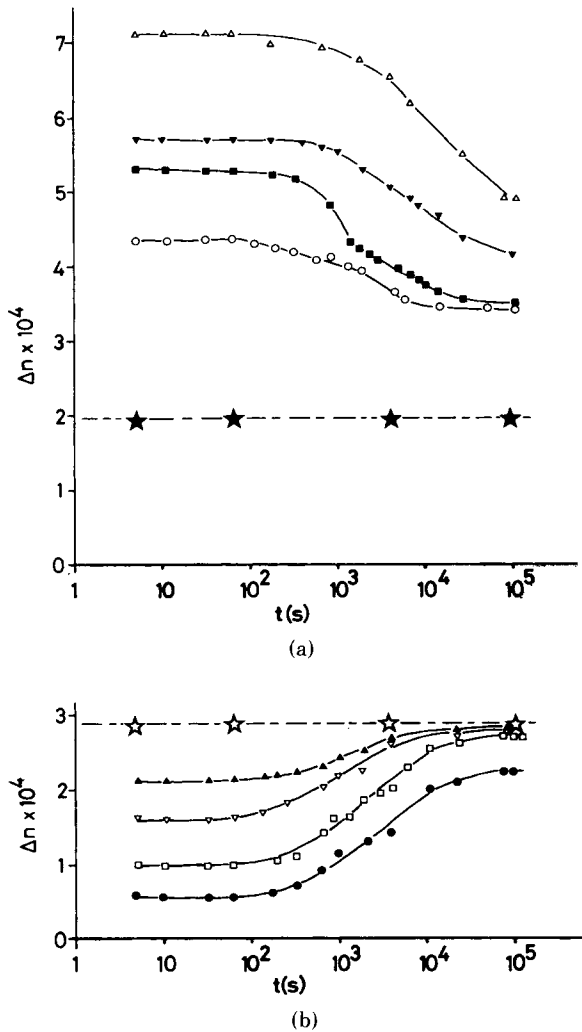


Fig. 5. (a) Birefringence measurements on injection-molded PET during tensile stress relaxation at 40°C at different deformation levels. The dashed line joins measurements taken at an equivalent site on an unstressed specimen. (b) Birefringence measurements on injection-molded PET during compressive stress relaxation at 40°C at different deformation levels. The dashed line joins measurements taken at an equivalent site on an unstressed specimen.

### PET

The results of uniaxial stress-relaxation tests both in tension and in compression (plotted as negative) on PET are shown in Figure 4. The corresponding plots of birefringence recorded during stress-relaxation are shown in Figures 5(a) (tension) and 5(b) (compression). In this case the specimens showed considerable birefringence in the as-molded state, and all birefringence measurements for a particular mode of loading (tension or compression) were obtained from part of the bar with a chosen value of birefringence in the unloaded state. This was easily accomplished because all of the bars were taken from the same

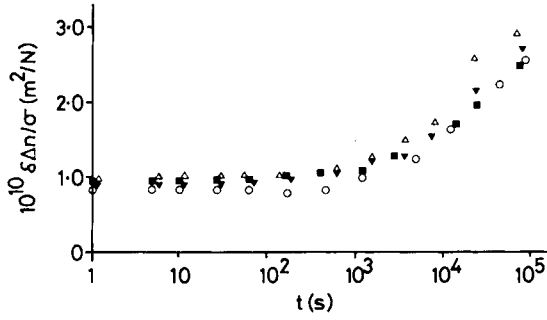


Fig. 6. Plots of  $\Delta n/\sigma$  against time obtained from four different tensile relaxation tests on PET at 40°C. The symbols used to represent the results of a particular test are the same as those used in Figure 5(a).

batch and in the as-molded state all showed the same birefringence distribution. The locations chosen, respectively, for tension and compression tests were different because it was convenient to start with a high unloaded value for birefringence in a compression test, in which the birefringence increment on loading was negative, whereas in tension a low unloaded birefringence value was preferred to minimize the total birefringence after loading since measurement becomes increasingly difficult beyond the fourth order.

In both tension and compression a positive stress-optical coefficient is evident, and in both cases the magnitude of the change in birefringence diminished as

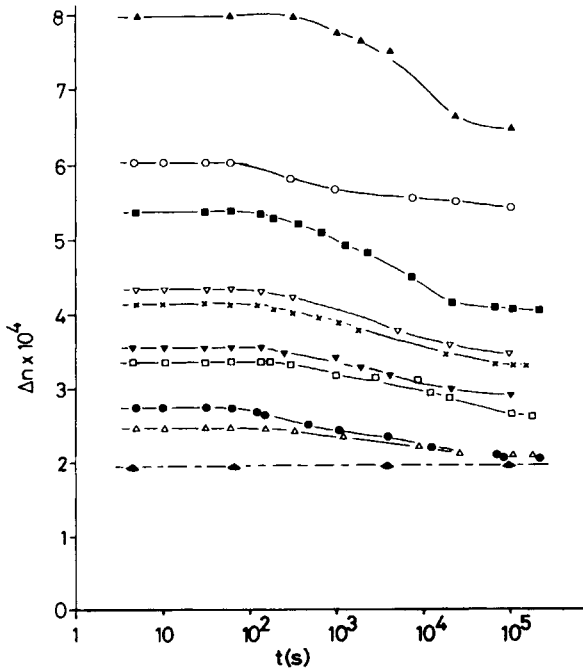


Fig. 7. Birefringence measurements on PET during recovery at 40°C after tensile stress relaxation at 40°C at different deformation levels. The dashed line indicates the level of birefringence found at an equivalent site in a specimen which was never subjected to deformation.



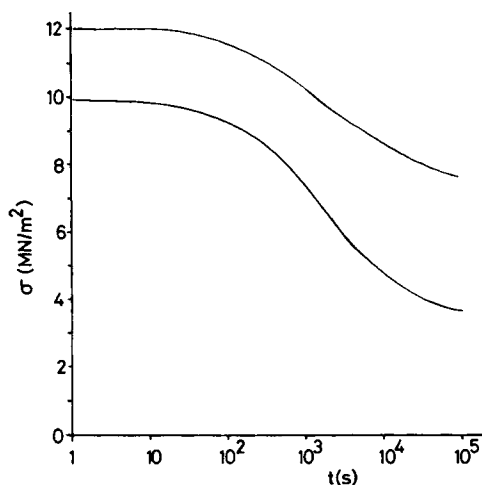


Fig. 8. Stress-relaxation of injection-molded PA(G) at 50°C.

stress-relaxation proceeded. In Figure 6 this change in birefringence (i.e., the instantaneous birefringence minus the value prior to loading), divided by the instantaneous value of the stress, is plotted against time and is seen to vary quite considerably.

On recovery following uniaxial tension stress-relaxation, the birefringence dropped to a value greater than the initial value (before applying the stress relaxation test deformation), and then continued to fall, appearing to approach this initial value for specimens tested at small deformations, but leveling off at a higher value in specimens stress relaxed at higher deformations (Fig. 7).

### PA(G)

Results of uniaxial stress relaxation tests on PA(G) are shown in Figure 8. The corresponding measurements of birefringence during these tests are shown in Figure 9, in which have also been plotted the measurements of birefringence recorded during recovery with time measured from the instant of unloading. A positive stress-optical coefficient is again obtained, but stress relief alone cannot account for the fall in birefringence observed during stress-relaxation for significant birefringence remains after unloading. This diminishes during recovery. The plot of  $\delta\Delta n/\sigma$  against logarithm of time (Fig. 10) has a similar appearance to that for PET, where  $\delta\Delta n$  is equal to the birefringence at time  $t$ , when the stress is  $\sigma$ , minus the birefringence before loading.

### PS, PC, and PES, and Summary of Results Using Injection Moldings

Data for PS, PC, and PES have been presented previously,<sup>9,10</sup> and the important features are shown schematically in Figure 11, which also includes PMMA, PET, and PA(G) for completeness. In this figure is illustrated the behavior of birefringence both in relaxation and in recovery after unloading following a stress-relaxation test. It is clear that the only pair of polymers with a strong mutual resemblance is PET and PA(G).

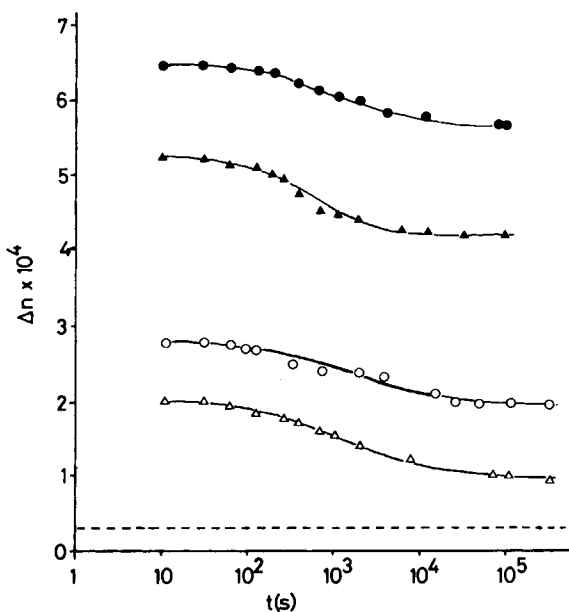


Fig. 9. Plots of birefringence against time for PA(G) at 50°C during tensile stress-relaxation (●, ▲) and subsequent recovery (○, △). Results obtained on the same specimen are indicated by symbols of the same shape, (e.g., ●, ○). The dashed line indicates the level of birefringence measured at an equivalent site in a specimen which was never subjected to deformation.

### Specimens Fabricated by Compression Molding

A limited test program using bars cut from a compression-molded sheet was conducted to provide a comparison with the studies of injection moldings. The polymers used were PC, PS, and PES. In both tensile stress-relaxation and recovery, PC gave results identical in form to those schematized in Figure 11, but with the initial birefringence (before applying the stress relaxation deformation) equal to zero instead of a significant positive quantity.<sup>9</sup> Similarly, compression-molded PES reproduced the behavior illustrated in Figure 11 in stress-relaxation<sup>10</sup> (no data was recorded for recovery). In the case of compression-molded PS specimens, the birefringence was zero in the as-prepared state, became positive on applying the tensile deformation, and then proceeded to fall during stress relaxation. On approaching zero birefringence again, the samples crazed and fractured soon afterwards.<sup>9</sup> It is therefore impossible to say whether the birefringence shows a fundamentally different time dependence to that found with injection moldings in which the value dropped, leveled off, and then began a second stage of negative change. Once crazes had developed, any measurements recorded during recovery would not be suitable for direct comparison with data obtained with the injection moldings. Samples cut from the same compression-molded sheet, but which were elongated approximately 4% to produce a level of birefringence similar to that found in the injection moldings, gave relaxation and recovery data broadly similar to that shown in Figure 11.<sup>9</sup>

In addition to these tests, some were conducted on a sheet of PET provided

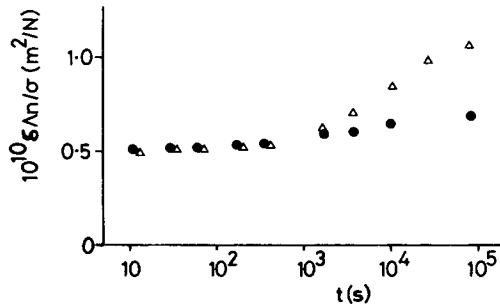


Fig. 10. Plots of  $\Delta n/\sigma$  vs. time during the tensile stress-relaxation tests on PA(G) from which the data in Figure 9 were obtained. Symbols of the same shape have been used to indicate a particular test in Figures 9 and 10.

by AKZO and stated to be extruded from the same grade of polymer (A04-102) used for the injection moldings. The as-prepared birefringence was zero. On testing samples cut both in the machine direction and in the transverse direction, it was found that the stress-optical coefficient was greater when the tensile deformation axis was perpendicular to the machine direction than when it was parallel to the machine direction. The interesting observation with this material was that the birefringence remained unchanged during tensile stress-relaxation (as with PC), but fell back to zero on unloading (a result not observed before). This implies that a much higher stress-optical coefficient obtains on unloading than on loading for the incremental change in birefringence is approximately the same magnitude in both cases, but the magnitude of the change of stress is much less after relaxation than in the original loading operation.

## DISCUSSION

From the summary presented in Figure 11 it is clear that the changes in birefringence that take place during stress-relaxation and recovery cannot be generalized for glassy polymers. Even though six polymers have been used, only one pair [PET and PA(G)] shows results which display a strong mutual resemblance on close inspection. Thus it is of great interest to investigate the origins of the differences in behavior. The first step is to consider which of the polymers display a pattern of behavior for which a relatively straightforward mechanism can be suggested. In support of this, it is convenient to consider the consequences of separating the total birefringence into a stress component  $\Delta n)_\sigma$  and an orientation component  $\Delta n)_\theta$  i.e.,

$$\Delta n = \Delta n)_\sigma + \Delta n)_\theta \quad (1)$$

In the simplest case,  $\Delta n)_\sigma$  would be proportional to the applied stress  $\sigma$  so that if stress relaxes, this component would change correspondingly, i.e.,

$$\Delta n)_\sigma(t) = a \sigma(t) \quad (2)$$

where  $a$  is a constant.

Suppose also that the relaxation by which stress is relieved causes the alignment of a polarizable bond, giving an orientation contribution to birefringence.

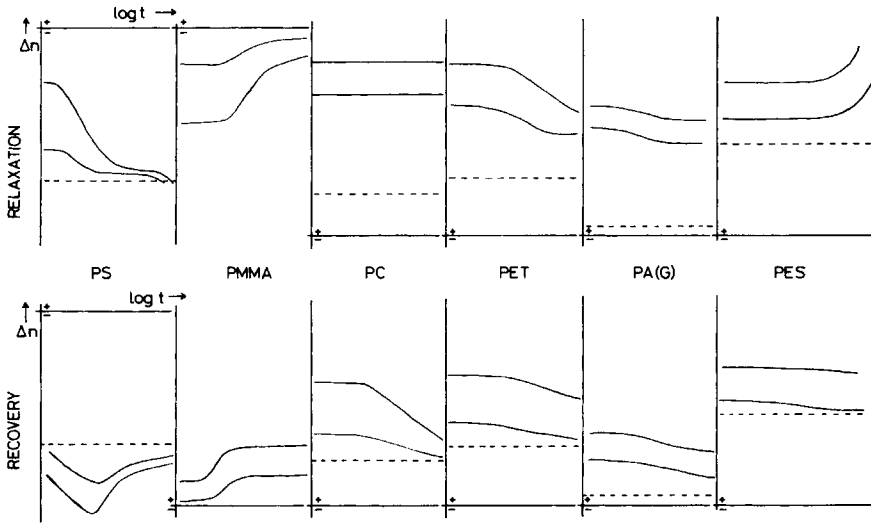


Fig. 11. Schematic representation of birefringence behavior in tensile stress-relaxation and subsequent recovery, summarizing the general features obtained with injection moldings produced from six different glassy polymers.

If this is the only relaxation mechanism operating, then the change in birefringence must be proportional to the fall in stress, i.e.,

$$\Delta n_{\theta}(t) = b[\sigma_0 - \sigma(t)] \quad (3)$$

where  $\sigma_0$  is the initial stress and  $b$  is a constant. This must therefore have the same time constant as  $\Delta n_{\sigma}$ , and from eqs. (1)–(3) can be derived the following:

$$\Delta n(t) = (a - b)\sigma(t) + b\sigma_0 \quad (4)$$

The only polymer for which this was found to be approximately true was PET, though PC can be considered a “special case,” as will be explained later. It must be recognized that the relative strengths of the two effects (stress and orientation) will be important in deciding the exact appearance of the birefringence vs. time plot. If the orientation effect is strong and in the opposite sense to the stress birefringent contribution, this might cause the birefringence to reach the as-molded level of birefringence long before stress decays to a negligible value. Alternatively, if the orientation produced birefringence of the same sense as that produced by the stress, the resultant change will be opposite to that corresponding to the diminishing stress level, and may even cause the departure of the birefringence from the as-molded value to increase in magnitude. In the case of polycarbonate the observation that the birefringence rose in deforming the specimen to a value which remained constant during stress relaxation is consistent with eq. (4) if  $a = b$ . There is no fundamental reason why  $a$  and  $b$  should be equal in the general case, and we do not have an explanation to offer for the result obtained with polycarbonate.

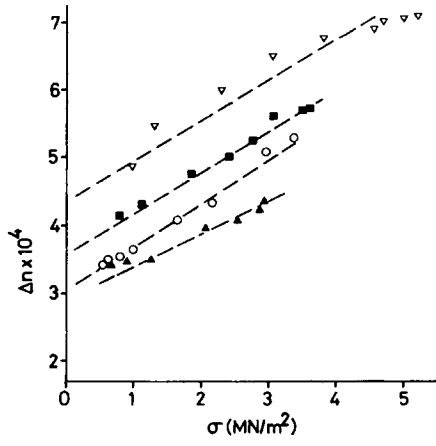
On further reference to eqs. (1)–(4), it can be seen that the ratio  $\Delta n/\sigma$  (or even  $\delta\Delta n/\sigma$  as employed here when the as-molded birefringence is nonzero) is of limited significance. If the ratio is constant, it would seem to indicate that birefringence

is produced by a stress-optical effect only, but it is difficult to see how any positive conclusion could be deduced from the results obtained here, and the main purpose of presenting the data in this manner is to afford comparison with the work of Stein and Tobolsky. Inspection of eq. (4) indicates that it would be more valuable to test a plot of  $\Delta n$  vs.  $\sigma$  for linearity. If the data show good linearity, it is possible that a simple mechanism of the kind outlined above may account for the observed behavior. Of the six materials examined here only PET shows reasonable linearity in the plot of  $\Delta n$  vs.  $\sigma$  [Fig. 12(a)], and even with this material the plot appears to be leveling off at low stresses. A more pronounced departure from linearity is displayed by PA(G) [Fig. 12(b)], and the data for PS, PMMA, and PES show even greater departures from linearity [Figs. 12(c), (d), (e)]. Since with PC the value of  $\Delta n$  remained constant for the duration of the stress-relaxation test, the  $\Delta n$  vs.  $\sigma$  plot would simply be a horizontal line, and is not included here.

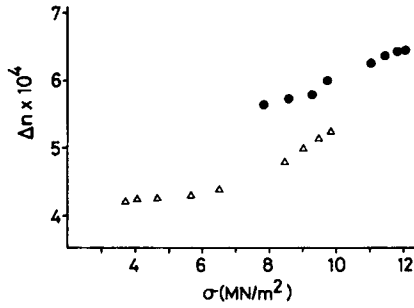
Whereas the absence of a straight line relationship between  $\Delta n$  and  $\sigma$  eliminates an explanation for the change in birefringence based on a single relaxation mechanism coupled with a stress optical effect with no orientational contribution, departure from linearity does not necessarily exclude the possibility of a single relaxation mechanism in which a change in the orientation contribution to birefringence is obtained. The reason for this can be explained as follows. In an injection-molded polymer the molecules will never show perfect orientation. Even when marked flow orientation is frozen-in, there will be segments of molecules lying in all directions, even though there may be a strongly preferred direction. If a sample undergoes stress-relaxation by a single molecular mechanism, then the extent by which the stress is relieved by an individual conformational change will depend on the orientation of the relaxing segment. If the relaxation is considered to be a stress-aided thermally activated event, then the reaction rate is also determined by the orientation of the relaxing element relative to the stress axis. In the special case of an isotropic amorphous solid, it has been shown that a single relaxation is predicted by the two-site theory,<sup>15</sup> but the time constant is different to that which would be obtained for a perfectly aligned sample undergoing the same molecular relaxation. A mixture of the two solutions for these two special cases would produce stress-relaxation less steep than exponential, indicating that the kind of intermediate orientation distribution expected to be found in an injection molding would also produce a less rational stress-relaxation behavior. This is not the point we wish to pursue here, however, but it does introduce the difficulty encountered when attempting to relate stress and birefringence relaxation data. The polarizability of a chemical bond is a highly directional property,<sup>16</sup> and the change in refractive index in a particular direction resulting from a conformational change will therefore depend on the orientation of the bond before and after the change takes place. A further complication is that each particular bond type has its own polarization ellipsoid. There is therefore no reason to expect that the summation of the changes in refractive index (and therefore in birefringence) averaged over a volume containing molecules, with segments undergoing relaxations from and into a distribution of orientation, will follow the same time dependence as the stress-relaxation which accompanies the same molecular conformational changes.

Thus the relaxation results do not give any clear indication of the source of birefringence for any of the polymers tested, with the possible exception of PET.

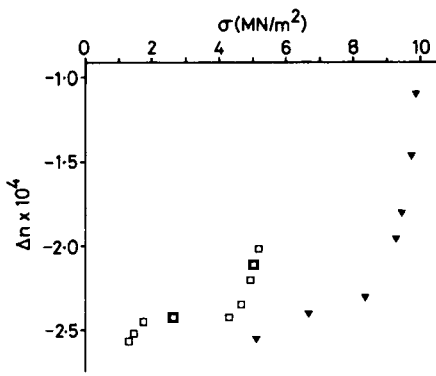
If the recovery results are taken into account, some further progress can be made in the analysis. The first observation is that as a general rule none of the injection-molded materials gave on unloading a birefringence value which was the



(a)

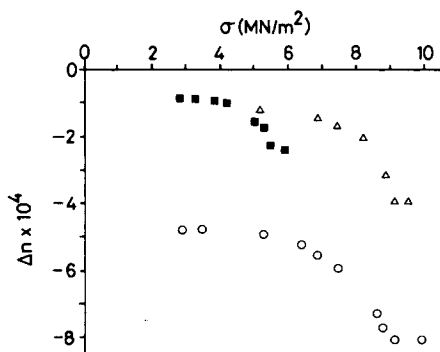


(b)

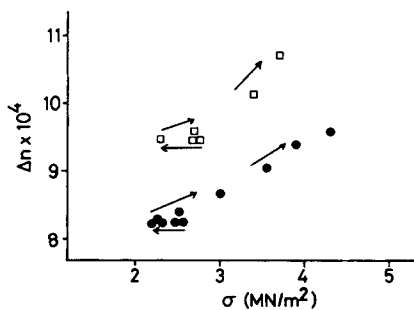


(c)

Fig. 12. Plots of  $\Delta n$  vs. stress obtained from data recorded in tensile stress-relaxation experiments on (a) PET at 40°C; (b) PA(G) at 50°C; (c) PS at 40°C; (d) PMMA at 40°C; and (e) PES at 60°C. Note that in (d) the results using symbol  $\circ$  have been shifted to the left and have been plotted as  $(\sigma - 10)$  MN/m<sup>2</sup>. In (e) the arrows indicate the order of data collection from small time to longer time.



(d)



(e)

Fig. 12 (continued from the previous page.)

same as that measured before stress-relaxation. PS and PMMA specimens tested at small extensions showed very small departures, but, even with these samples, subsequent changes in birefringence during the extended period of measurement conducted in the unloaded state indicated that a simple stress-optical effect could not be in operation alone. Indeed this was found to be generally true, for the birefringence of all six polymers changed during recovery, confirming that a simple stress optical effect cannot explain the observations. For PC, PET, PA(G), and PES, the change in birefringence on recovery reduced the difference between the value measured on unloading and that measured in the as-molded state prior to commencing the stress-relaxation test. Thus, in addition to the stress optical effect observed clearly on loading and unloading, it appears that an orientational bias develops during the period of stress-relaxation and produces some orientational birefringence. If, during recovery, conformational changes in the reverse direction take place, birefringence will change in the manner described, and this is the behavior we had anticipated. PS and PMMA do not follow the same pattern, however. With PS the birefringence in the as-molded state was negative and, on unloading after stress-relaxation, was found to be even more negative. During recovery the initial change was again in the negative direction, but the measured birefringence went through a minimum then began to climb again, eventually approaching the original as-molded value. With PMMA the operation of the negative stress-optical effect meant a positive change in birefringence on unloading. In most cases this took the value

into the positive domain and above the initial as-molded value ( $\sim 0$ ). On prolonged residence in the unloaded state, the birefringence became still larger, an unexpected result for which we do not offer any explanation at present.

No distinctly new modes of behavior were observed with compression-molded material (PS, PC, and PES), except that with PS specimens developed crazes and fractured during the stress-relaxation tests. With the extruded PET a small difference in stress sensitivity was noted when comparing specimens cut parallel and perpendicular to the machine direction, though the sheet showed negligible birefringence in the unstressed state. The surprising observation with these specimens was that the birefringence reverted to its original value on unloading after stress-relaxation, even though it remained constant during stress-relaxation. This contrasts with the hypothesis put forward above in which it is implied that, for a material for which the birefringence remains unchanged during stress-relaxation, an orientation contribution to birefringence must develop to compensate for the diminishing stress-optical part. This contribution should remain immediately after unloading and then proceed to decay during the period of recovery in the unloaded state.

Although it has been demonstrated that there are no general rules governing the birefringence behavior reported here and although, with the possible exception of PET, it seems that a single simple mechanism cannot be invoked to account for the observations, it is worthwhile reviewing the results, taking into consideration the molecular structures. It is perhaps hardly surprising that PS shows that the most complicated behavior for the most polarizable bonds are concentrated together in the phenyl residue which is present as a side group, attached rigidly to the main chain. As a consequence, any main chain relaxation must necessarily cause major changes in the orientation of this group and cause the birefringence to change, but in addition any motion independent of the main chain may also alter the birefringence. It is believed that the favored orientation of the phenyl residue relative to the local main chain carbon atoms may be influenced by the applied stress, giving rise to a relaxation with which will be associated a sensitive birefringence reaction, providing a second and (almost) independent source of birefringence change. Similarly, it is the ester side group in PMMA that provides the major source of birefringence. Again, it is expected that motion of or within this side group will be possible even at low temperatures<sup>17</sup> and will produce substantial changes in birefringence. Main chain conformational changes will also require movement of this group and will thus cause changes in birefringence. Such relaxations may be interactive, and the fact that the behavior of PMMA cannot be explained by a single mechanism is therefore not surprising.

The other polymers [PET, PC, PA(G), and PES] all have phenyl residues in the main chain. In addition, other strongly polarizable groups such as C=O are attached rigidly to the molecular backbone and can only take up new orientations as a consequence of main chain conformational changes. Therefore, the birefringence of these polymers can be expected to follow the events in the main chain more closely than is the case with PS and PMMA. PET appears to be "well behaved" with birefringence and stress approximately obeying a linear relationship during stress-relaxation. The PET observations can be accounted for if stress-relaxation takes place by an optically active conformational change so that, on releasing the stress, some birefringence remains as a consequence of the



conformational changes that occurred during stress-relaxation. The birefringence then proceeds to fall during recovery, presumably by reversal of the molecular conformational changes which took place during relaxation. PA(G) seems fairly similar to PET in its birefringence behavior during tensile stress-relaxation and recovery, though the lack of linearity in the  $\Delta n$  vs.  $\sigma$  plots for stress-relaxation shows that a single simple mechanism cannot account for the observations. With PC it seems that orientation must be the controlling factor and that the active changes must take place as soon as the deformation is applied. Stress-relaxation must then occur by conformational changes in optically inactive groups. These must partially stabilize the new main chain positions, for, on unloading, the birefringence does not return immediately to the unloaded value, but drops instantaneously by a large fraction of the original increment (obtained on loading), and then proceeds to recover slowly. Presumably, what is happening is that the conformational changes which took place during stress-relaxation are being reversed, allowing the main chain arrangement to revert back to its original state. The results obtained with PES are not very different from those for PA(G) if it is accepted that the increase in birefringence that takes place during a tensile test at constant deformation is connected with the corresponding increase in stress, thought to be a stress-accelerated aging effect.<sup>10</sup>

In the above discussion, no reference has been made to the thermomechanical history of the material. In the work reported here most of the studies have been on injection moldings, and it is important to consider the possible consequences of this for birefringence measurements, especially those performed during stress-relaxation as is the case here. These points can be itemized as follows:

(i) The moldings contain residual stresses which are commonly tensile in the interior and compressive near the surface.<sup>2,11-13</sup> As a consequence, the stress birefringence will be different at every point.

(ii) The frozen-in orientation depends on the shear stress during mold filling and on the rates of cooling and relaxation in the melt. The orientation birefringence will therefore be different everywhere.

(iii) Most of the material in an injection molding cools fairly rapidly. This is true even at the center of the molding except when very thick sections are used. The material at most locations will therefore cool through  $T_g$  sufficiently quickly to contain a substantial fractional-free volume<sup>18,19</sup> and will be a long way from its equilibrium state. It can therefore be expected to show marked aging, especially if heated to an elevated temperature (either when unloaded or while under an applied stress during a test).

The consequences of these features of an injection molding should now be considered. First, on measuring the birefringence of a bar, the value obtained is simply the mean value, averaged through the bar at the point of observation. By thinning the bar down (for example, by milling followed by polishing to restore optical clarity) and measuring the relative retardation successively at different thickness, the depth dependence of birefringence may be ascertained.<sup>1,11,12,20</sup> This kind of study confirms that very large variations in birefringence occur in a molded bar even at locations remote from corners, gates, etc., at which inspection between crossed polars reveals rapid changes. In polystyrene injection moldings, the birefringence changes very rapidly and changes sign at several places through the thickness of the bar.<sup>11,12,20</sup> It is not possible to combine this kind of depth-dependent measurement with the time-varying experiments under

examination in this paper. Therefore, it remains at present a matter for speculation whether the changes in birefringence promoted by the stress are occurring throughout the material or whether they are concentrated predominantly within the highly oriented skin or the less oriented core. (It must be remembered that the regions near the surface and within the interior respectively are not just different because of their states of orientation, but also because of their states of stress and their states of aging).

In the studies reported here the measurements on a particular batch of specimens (i.e., on each individual polymer) usually occupied a period of no more than 2 weeks and in the cases of PS, PMMA, and PA(G) it is most unlikely that significant aging could have taken place during this test period for the specimens had been in store for several months [and in the case of PA(G), several years] before commencing this particular program. The ages of the PET and PES batches were unknown, and the PC batch was believed to be only a few weeks old on commencing tests. This may be of significance, for, on attempting to repeat some of the measurements on polycarbonate after a lapse of 2 years, it was found that specimens from this same batch, which had therefore aged at room temperature for a further 2 years, showed a drop in birefringence during tensile stress-relaxation; this is to be compared with the results of the original tests in which no such drop was observed. Further details of this and other effects will be published in a future paper dealing with some aspects of weathering of injection-molded polymers.<sup>21</sup>

## CONCLUSIONS

The interpretation of birefringence measurements on glassy polymers such as PS and PMMA which contain strongly polarizable side groups is extremely complex, especially when these materials are loaded. Polymers containing polarizable groups within the main chain or rigidly attached to it tend to show less complex behavior, but interpretation is still not straightforward. Even in these materials it is often impossible to define either a time-independent strain-optical coefficient or a time-independent stress-optical coefficient that can be applied to both loading and unloading.

Although we have noted differences in the stress sensitivity of birefringence in samples prepared by different methods, the general behavior is material-specific and much less influenced by processing. This is even true when comparing injection moldings containing large variations in birefringence through the thickness and a large overall birefringence value with compression moldings which appear to be isotropic and have zero birefringence in the unloaded state.

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