Time-dependent birefringence in glassy polymers during stress–relaxation and recovery

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The birefringence of polystyrene and polycarbonate have been measured during uniaxial stress relaxation tests. The birefringence of polystyrene shows an instantaneous positive increment on applying a tensile deformation; during stress relaxation the value showed a time-dependent change in the negative direction and the total birefringence eventually became more negative than the value measured prior to the deformation. On unloading, the overall trend was for the birefringence to change towards the level measured in the as-prepared sample prior to deformation but an initial departure in the opposite direction was observed. With polycarbonate, the birefringence changed instantaneously on applying the deformation and remained steady during stress relaxation. On unloading the birefringence fell instantaneously by an amount less than the increment observed on applying the deformation. Thereafter the birefringence continued to fall, approaching the original value with a time constant similar to that governing stress relaxation. These results are interpreted with reference to the molecular structures, in particular the location of the highly polarizable aromatic rings.

Keywords Mechanical behaviour; birefringence; polystyrene; polycarbonate; stress relaxation; tensile deformation; recovery

INTRODUCTION

Birefringence is commonly used as a measure of molecular orientation in glassy polymers. There are many examples in the literature of good correlation between birefringence and those fabricated variables which are expected to influence molecular orientation. Similarly good correlation has been reported between birefringence and properties expected to be orientation-dependent. Several examples for polystyrene are given in ref. 1, showing birefringence plotted against nominal draw ratio, length reversion ratio, maximum shrinkage stress and modulus for a series of drawn samples. In most studies of this kind, a single fabrication or testing parameter is changed in producing each set of data and under these conditions the prospects for obtaining monotonic relationships are inevitably enhanced. What is less certain is that a particular measurement of birefringence can be taken to signify an unique state of molecular orientation. This is particularly questionable in polystyrene in which the highly polarizable phenyl groups provide a large fraction of the total birefringence[1–7]. In this case main-chain conformation will not alone determine the level of birefringence, and any analysis based, for example, on the theory of rubber elasticity, must also take into account the orientation of the phenyl side groups with respect to the main-chain. Detailed consideration of this factor is presumably required to explain apparently contradictory observations reported in the literature, some of them originating in the same laboratory. For illustration we will briefly review some of the work on the time-dependence of birefringence of polystyrene under load. Strong time dependence was found by Kolsky[8] when recording birefringence under constant load. Similarly significant time-dependent changes in birefringence were recorded by Gurnee *et al.*[9] for extruded polystyrene at 40°C both in creep and stress relaxation. In the same study[9] they found that the relaxation modulus and the birefringence showed similar time-dependence to one another at elevated temperatures (104°–115°C). On the other hand, Andrews and Rudd[10] reported that time effects with polystyrene were negligibly small at 24°C and the same is implied in the companion paper describing work at lower temperatures using unoriented polystyrene[5]. Similarly, time effects were largely absent with compression-moulded specimens of polystyrene (and some other polymers), except just after application or removal of the load[6].

Evidence supporting the hypothesis that the main-chain conformation does not alone determine the magnitude of birefringence has been obtained from annealing studies. Considerable reduction in the level of birefringence in injection-moulded bars was found at temperatures lower than that at which shrinkage measurements indicated the presence of significant molecule backbone conformation changes[11,12]. This result could not be explained in terms of changes in residual stresses on annealing[11,12].

In the experiments reported here we have monitored birefringence during stress relaxation tests and also during subsequent recovery after unloading. We have used polystyrene (i) cut from compression-moulded sheet, (ii) drawn near to T_g, and (iii) injection-moulded as straight bars. Observations were also made on

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Table 1 Injection pressure and temperature and mould temperature conditions

Polymer	Injection pressure (MPa)	Injection temperatures (°C) Nozzle/Zone 2/ Zone 1	Mould temperatures (°C) Fixed/moving plate
Polystyrene BP KLP 35	87	280/270/220	30/30
Polycarbonate Makrolon 2603	86	325/335/335	85/89

polycarbonate both in compression-moulded and injection-moulded form. The time-dependent behaviour of polystyrene and polycarbonate have been found to be quite different.

EXPERIMENTAL

Specimen preparation

Polystyrene. Three forms of polystyrene specimens were employed in this investigation, all prepared from the same grade of general purpose injection-moulding material, supplied in the form of granules by BDH.

(i) Compression moulded specimens were produced in the form of plaques 3.9 mm thick. The mould containing the granules was allowed to heat up for a few minutes in the press which had been pre-heated to 170°C, then the pressure was applied for 5 min before rapidly cooling by running cold water through the platens. Specimens of dimensions 162 mm × 12 mm × 3.9 mm were cut from the plaques and polished to remove surface flaws and to provide sufficient clarity for the optical measurements.

(ii) Oriented specimens were produced by drawing or stretching compression-moulded bars (as (i)) using a J. J. Lloyd tensile testing machine with a cross-head speed of 50 mm min^{-1}. The material was heated to approximately 100°C prior to deformation and cooled rapidly with a cold air blast. The draw ratio was estimated by areal reduction. Results reported here were obtained on specimens for which only a small extension was applied ($\sim 4\%$), as this produced a level of birefringence comparable to that obtained in the injection-mouldings.

(iii) Injection-moulded bars measuring 190 mm × 12.5 mm × 3.17 mm were produced on a Butler-Smith 100/60 reciprocating screw machine using conditions shown in *Table 1* and taking our usual precautions to ensure no drift in conditions during the production run[11–13].

Polycarbonate. Two types of polycarbonate specimen were used in the investigation.

(i) Compression moulded plaques were produced in the same manner as with polystyrene, using a moulding temperature of 260°C. The material used was 'Lexan' in the form of granules and was carefully pre-dried in a vacuum oven before moulding. Specimens were cut into the form of straight bars measuring 192 mm × 12.5 mm × 3.6 mm and polished as before.

(ii) Injection-moulded specimens were provided by RAPRA in the form of dumb-bell shaped ASTM tensile test bars 192 mm long and with a gauge length cross section of 12.5 mm × 3.6 mm. The material used was Makrolon 2603 and moulding conditions were as shown in *Table 1*. The mouldings were inspected on a light box between crossed polars prior to testing and it was found that the birefringence patterns were almost identical throughout the batch.

Some specimens measuring 12.5 mm × 12.5 mm × 3.6 mm were cut from the gauge length of the bars to be used for compression testing.

Stress relaxation and birefringence measurement

Stress relaxation tests in uniaxial tension were conducted at closely controlled temperatures on rigs described previously[11,14]. The relative retardation was measured at a chosen location in the centre of the specimen at intervals of time during the stress relaxation test by identifying the characteristic colour 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 analysed wave to a more sensitive region. Colour photographs were taken on some specimens to obtain information at very short times (~ 1 s) after the application of the deformation.

Most tests on polystyrene were conducted at 40°C, for reasons given before and also to afford comparison with the previous work[11]. Some further tests were made at 25°C, 60°C, and 80°C. Polycarbonate was tested at 60°C, at which temperature relaxation proceeded at a reasonable rate for our purposes, with a few experiments at 80°C and 90°C. After an extended period of stress relaxation (usually 24 h) recovery experiments were conducted, leaving the specimen suspended in the test chamber held at the same controlled temperature as in stress relaxation but with the lower grip decoupled, and birefringence measurements were continued for a further extended period.

The load cells used on the rigs are bi-directional (Pye Ether UF2) making conversion for compression testing a simple matter of replacing the wedge grips used for tensile testing by flat-ended cylinders[11]. Since the compression specimens are much shorter than the tensile bars close temperature control is even more vital with these tests. Stress relaxation of polycarbonate in uniaxial compression was conducted at 60°C.

Layer removal tests

The layer removal procedure for determining the residual stress distribution in rectangular parallelipipeds described by Treuting and Read[15] and applied to polymer sheets and mouldings by Peiter[16–18], Bürkle[19] and So and Broutman[20] has been used in our laboratory in several studies and our experimental procedures have been described previously[11–14,21,22].

RESULTS

Birefringence during stress relaxation in uniaxial tension

Polystyrene at 40°C. Measurements of birefringence during stress relaxation tests in uniaxial tension on polystyrene in all three forms are shown in *Figures 1–3*, in which are also displayed examples of the stress relaxation characteristics; further details on the stress relaxation of injection moulded polystyrene are reported

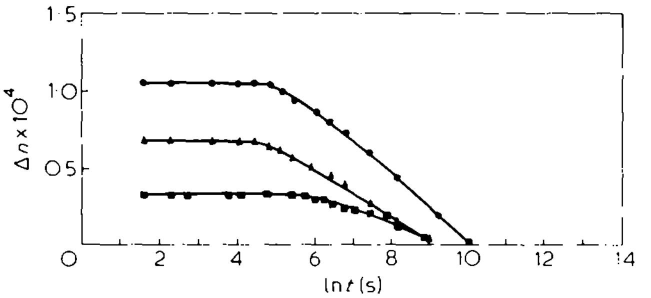

Figure 1 Birefringence of compression-moulded polystyrene as a function of time for specimens tested at 40°C under stress relaxation conditions with an initial stress of 14.5 MN m^{-2} (●); 8.5 MN m^{-2} (▲); and 5.4 MN m^{-2} (■)

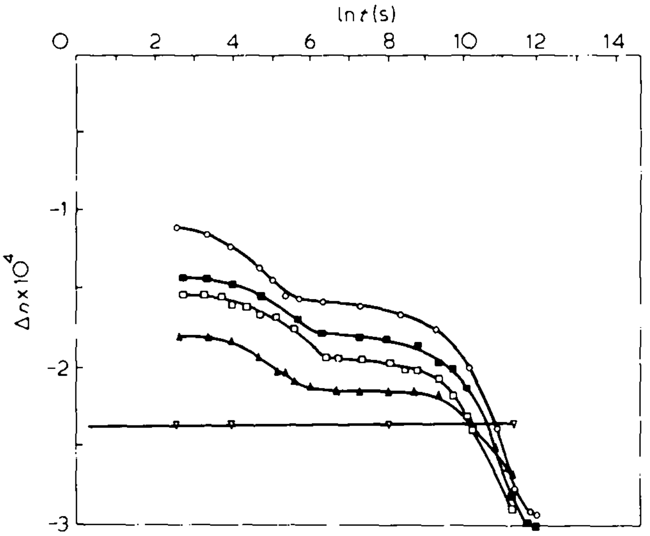

Figure 2 Birefringence of drawn polystyrene tested at 40°C under stress relaxation conditions with an initial stress of 15 MN m^{-2} (○); 10.3 MN m^{-2} (■); 9.3 MN m^{-2} (□); 6.6 MN m^{-2} (▲). Also shown are results for a bar held at 40°C with zero applied load (▽)

elsewhere[11–13]. An immediate change in birefringence in the positive direction (when referred to the stress axis) was recorded in each case, followed by a time-dependent change in the opposite (negative) direction. The initial sensitivity appeared to be greatest for the injection-moulded specimens and least for the compression-moulded specimens (*Figure 4*).

A most interesting discovery was that the birefringence did not level off at the initial value obtained with the as-prepared specimen nor at some value intermediate between the as-prepared value and that obtained immediately after applying the deformation. Instead the magnitude of the change in birefringence during stress relaxation exceeded the instantaneous change on applying the deformation so that at long times the birefringence became more negative than in the as-prepared state.

Polycarbonate at 60°C. On testing polycarbonate in both forms (compression-moulded and injection moulded), it was found that the birefringence rose immediately to a steady value on applying the deformation and remained almost unchanged during prolonged testing, while the stress fell by approximately one third, (*Figure 5*). The stress sensitivity was greater than that for polystyrene (*Figure 6*) and we were unable to measure birefringence at the highest stresses used in this programme because of the high levels of retardation.

Birefringence during recovery after stress relaxation

Polystyrene at 40°C. On unloading polystyrene at the completion of a stress relaxation test the immediate change was in the negative direction, sending the total level even more negative than in the as-prepared specimen. Thereafter a further negative increment was observed to develop in the first few minutes, followed by a change in the opposite direction, and a gradual climb towards the initial as-prepared value, (*Figures 7* and *8*).

Polycarbonate at 60°C. On unloading polycarbonate the recovery of birefringence towards the value measured before application of the deformation was partly instantaneous but contained a substantial time-dependent component with a time constant similar to that observed for the relaxation of stress at constant deformation during the first part of the loading programme, (*Figures 9* and *10*). The instantaneous change in birefringence on removing the load has been plotted against the final stress in the stress relaxation test in *Figure 11*.

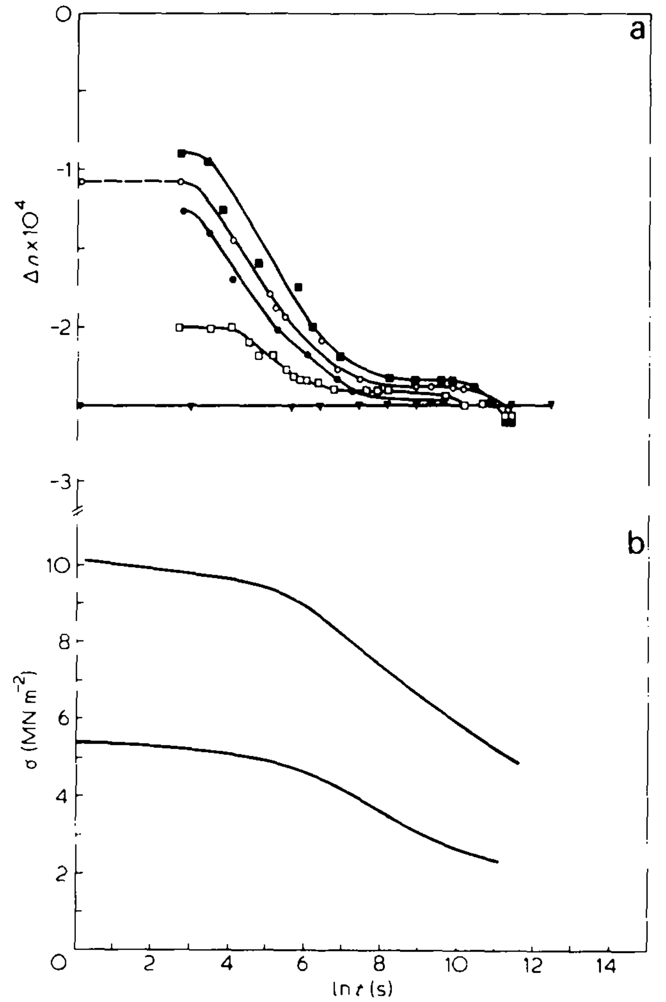

Figure 3 (a) Birefringence of injection-moulded polystyrene tested at 40°C under stress relaxation conditions with an initial stress of 14.3 MN m^{-2} (■); 10.3 MN m^{-2} (○); 10.1 MN m^{-2} (●); 5.4 MN m^{-2} (□). Also shown are results for a bar held at 40°C with zero applied load (▼) (b) Examples of stress relaxation characteristics from these specimens

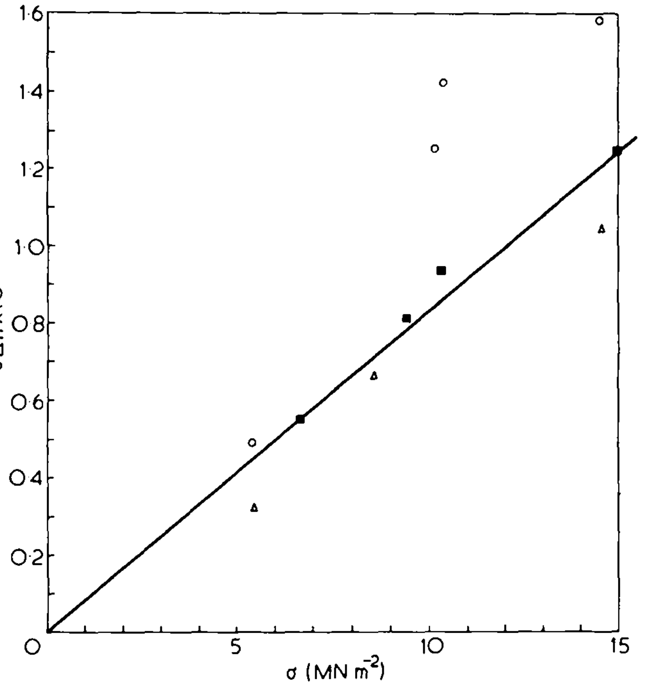

Figure 4 Initial change of birefringence ($\delta\Delta n$) observed in tensile stress relaxation experiments plotted against the corresponding initial applied stress: compression-moulded specimens (△); drawn specimens (■); injection-moulded specimens (○). The line is drawn for guidance only and is approximately the best line for drawn specimens. Compression moulded specimens appear to be the least stress-sensitive and injection-mouldings the most sensitive

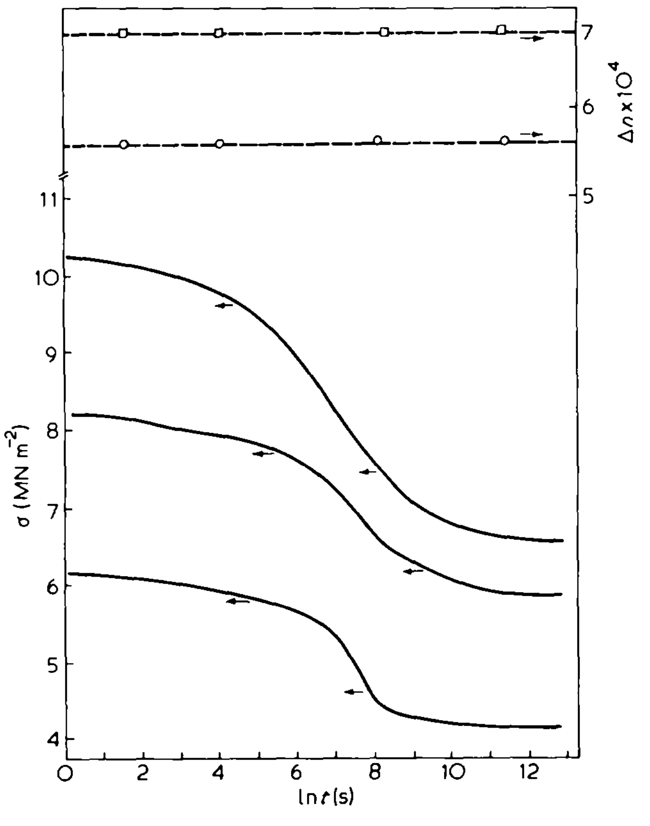

Figure 5 Stress relaxation of injection-moulded polycarbonate tested at 60°C at initial stresses of 6.15 MN m^{-2}, 8.2 MN m^{-2} and 10.3 MN m^{-2}, (lower), and corresponding measurements of birefringence for the test having initial stress 6.15 MN m^{-2} (○) and 8.2 MN m^{-2} (□) (upper)

Effect of temperature

Birefringence changes during stress relaxation/recovery tests on polystyrene at 25°C, 60°C and 80°C are shown in *Figures 12* and *13*. The birefringence of undeformed specimens was also monitored for extended periods and was found to be temperature dependent but not time dependent. These results are also shown in *Figures 12* and *13*.

The birefringence of undeformed polycarbonate increased slightly with temperature. Results obtained under load at 80°C and at 90°C did not show any marked departure from the behaviour at 60°C (*Figure 14*).

Birefringence under uniaxial compressive stress relaxation conditions

Polycarbonate. The change in birefringence for a compressive load was in the opposite sense to that found

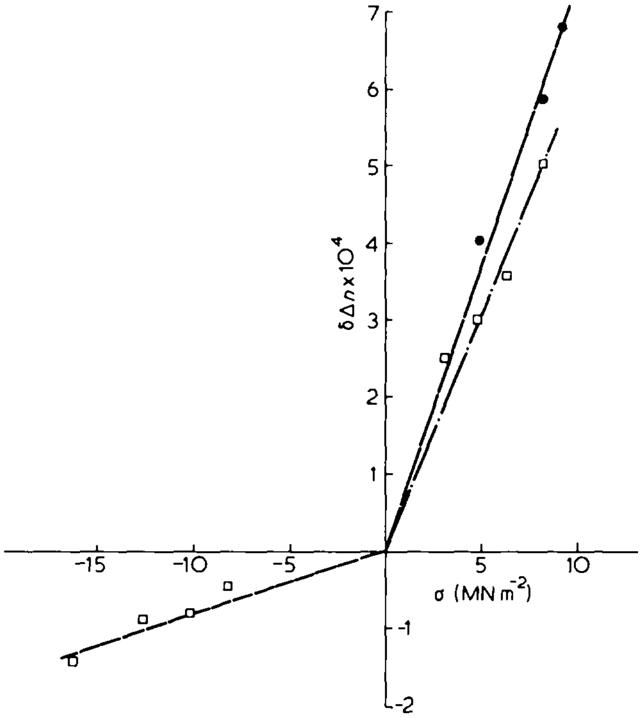

Figure 6 Change in birefringence produced on stressing polycarbonate specimens at 60°C. Compression-moulded specimens (●); injection-moulded specimens (□). The results obtained from injection-moulded specimens in compression, (plotted as negative), indicate a much smaller stress sensitivity than that observed in tension

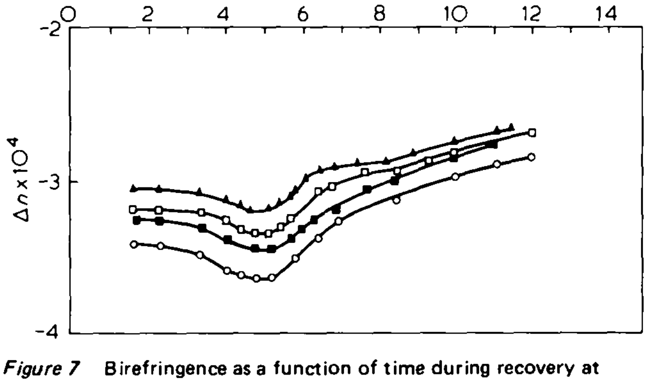

Figure 7 Birefringence as a function of time during recovery at 40°C of drawn polystyrene specimens unloaded after stress relaxation experiments at 40°C at initial stresses of 15 MN m^{-2} (○); 10.3 MN m^{-2} (■); 9.3 MN m^{-2} (□); and 6.6 MN m^{-2} (▲)

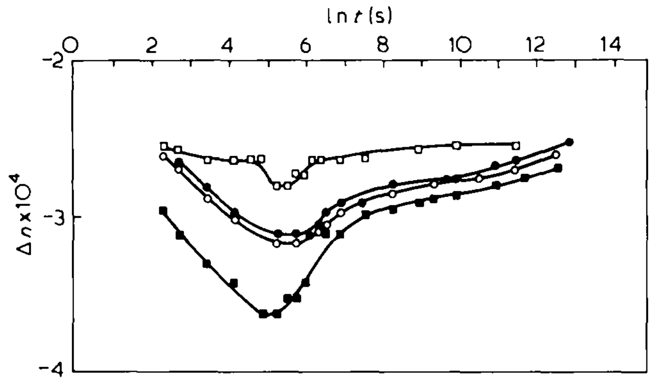

Figure 8 Birefringence as a function of time during recovery at 40°C of injection-moulded polystyrene specimens unloaded after stress relaxation experiments at 40°C at initial stresses of 14.3 MN m^{-2} (■); 10.3 MN m^{-2} (○); 10.1 MN m^{-2} (●); 5.4 MN m^{-2} (□)

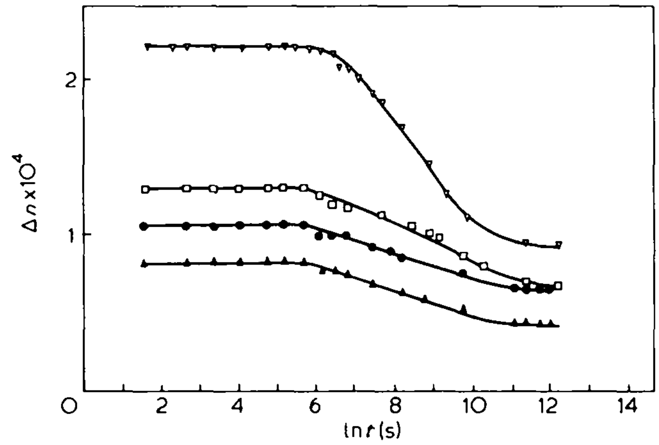

Figure 9 Birefringence as a function of time during recovery at 60°C of compression-moulded polycarbonate specimens unloaded after stress relaxation experiments at 60°C at initial stresses of 16.5 MN m^{-2} (▽); 9.0 MN m^{-2} (□); 8.2 MN m^{-2} (●); and 4.9 MN m^{-2} (▲)

in tension. The stress-optical coefficient was considerably smaller however (*Figure 6*). Recovery of birefringence after unloading followed a similar pattern to that observed in tension with a large instantaneous change followed by a stationary period lasting about 2 min, leading into the second recovery phase (*Figure 10*). For specimens subjected to modest deformations, corresponding to a stress $\lesssim 10$ MN m^{-2}, recovery was almost complete within an hour. At higher deformations, the birefringence seemed to approach a limiting value different from the initial value measured before applying the loading programme.

Stress relaxation analysis

In order to provide comparison with earlier studies[11-14] we have analysed the stress relaxation data for injection-moulded polycarbonate by the procedure of Kubát and Rigdahl. For this analysis the steepest slope of each σ vs. ln$t$ plot for a series of nominally identical specimens is plotted against the initial stress, σ_0, for the test, ('KR plot'). The results are shown in *Figure 15*.

The original Kubát and Rigdahl analysis was based upon a power law, the index of which can be obtained from the slope of the KR plot[23]. Although we have questioned the validity of the power law[24,25] the index, n, derived in this manner may be a useful characteristic for moulded polymers[12-14] and has been found from *Figure 15* to be 19.6. The intercept of the KR plot line with the σ_0 axis has been called the 'internal stress parameter', ($=\sigma_i$), by Kubát and Rigdahl[23], and is claimed to be indicative of the state of residual stresses within the specimen[23,26-28]. In addition to the residual stress state it is evident that structural and state parameters also have a marked influence on the value of σ_i obtained in this way, and it

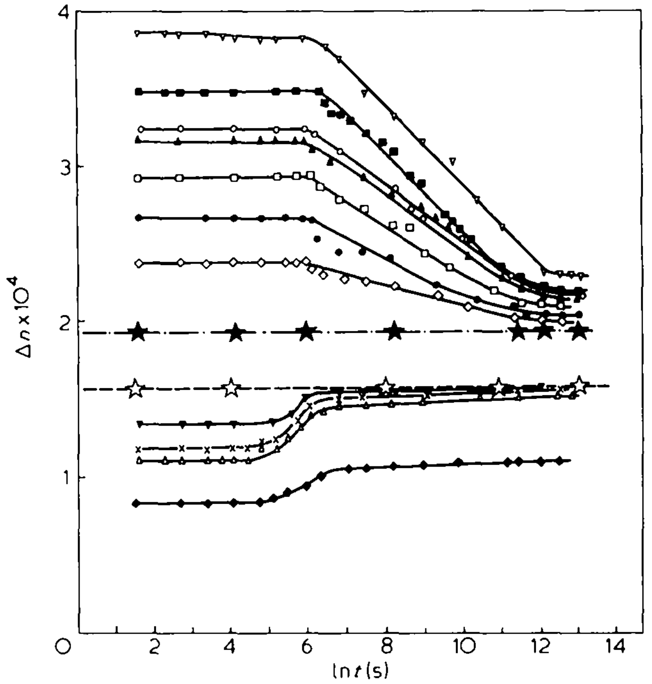

Figure 10 Birefringence as a function of time during recovery at 60°C of injection-moulded polycarbonate specimens unloaded after stress relaxation experiments in tension at 60°C at initial stresses of 16.8 MN m^{-2} (▽); 14.6 MN m^{-2} (■); 9.0 MN m^{-2} (○); 8.2 MN m^{-2} (▲); 6.15 MN m^{-2} (□); 4.8 MN m^{-2} (●); 3.05 MN m^{-2} (◇); and after stress relaxation experiments in compression at 60°C at initial stress levels of 16.5 MN m^{-2} (♦); 12.6 MN m^{-2} (△); 10.3 MN m^{-2} (X); 8.2 MN m^{-2} (▼). Shown also are measurements of birefringence in undeformed bars under zero stress at 60°C: from a sample from the batch used for tensile experiments (★) and also from a sample from the batch used for the compression experiments (☆)

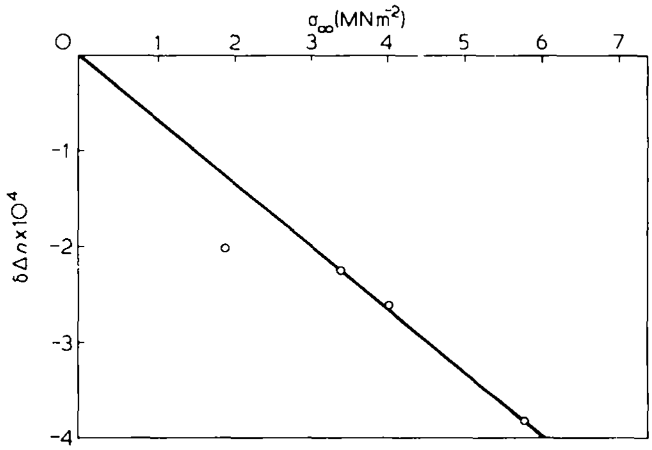

Figure 11 The instantaneous change in birefringence ($\delta\Delta n$) on unloading polycarbonate injection-moulded bars after tensile stress relaxation tests at 60°C plotted against the final stress, σ_∞, just prior to unloading

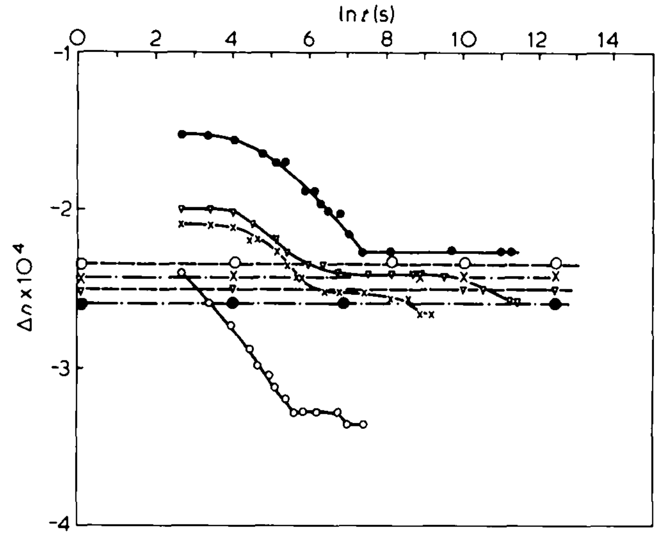

Figure 12 Birefringence of injection-moulded polystyrene as a function of time during stress-relaxation tests at 80°C (○); 60°C (X); 40°C (▽); 25°C (●). (Initial stress ≈5.4 MN m^{-2} in each case). Measurements of birefringence taken from undeformed specimens at the same temperatures are represented by the corresponding large decals and joined by broken lines. Results at 40°C (▽) are those already shown in *Figure 3*

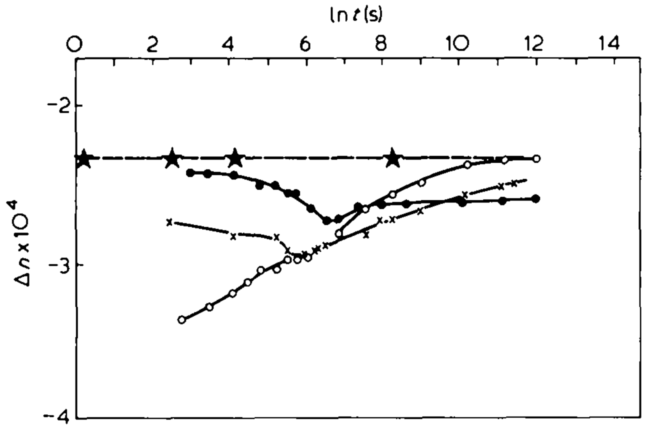

Figure 13 Birefringence of injection-moulded polystyrene as a function of time during recovery after unloading the stress relaxation specimens for which data is presented in *Figure 12*, maintaining the same temperature for the duration of this phase of testing, i.e. 80°C (○); 60°C (X); 25°C (●). (Results at 40°C can be found in *Figure 8*: *c.f.* initial stress 5.4 MN m^{-2}.) Also shown are measurements of birefringence at 80°C for an undeformed specimen (★). Results for undeformed specimens at other temperatures are not shown to avoid confusion: they may be found in *Figure 12*

cannot be used as a significant characteristic in isolation. The value obtained here is -0.8 ± 0.2MN m^{-2}.

Insufficient stress relaxation experiments were conducted on the other batches of specimens to produce a worthwhile analysis of this kind.

Layer removal experiments

Results from layer removal experiments on polycarbonate are shown in *Figures 16* and *17*. Tensile stresses are found in the interior and compressive stresses near to the surface with both compression-moulded and injection-moulded samples. The magnitude of the residual stresses are much higher in the injection-moulded sample than with the compression-moulded sample. This is because the cooling rate obtained in injection-moulding is much more rapid than that in compression moulding, even when forced cooling is applied by running water through the platens of the press, because of the high thermal capacity of the platens.

The results of layer removal experiments on injection-moulded polystyrene have been reported previously[12,13].

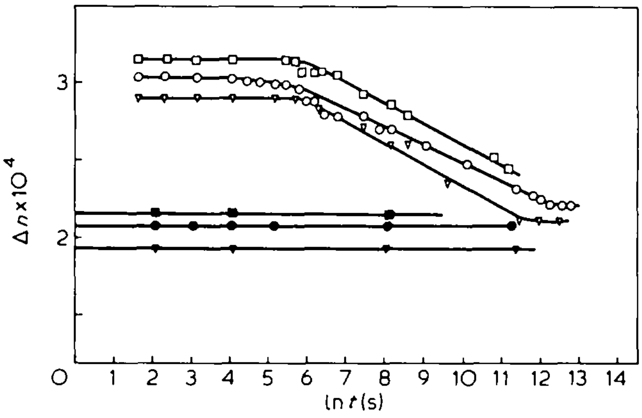

Figure 14 Birefringence as a function of time during recovery of injection-moulded polycarbonate specimens unloaded after stress relaxation experiments and maintained at the test temperature: 60°C (▽); 80°C (○); 90°C (□). The solid symbols denote measurements on unloaded specimens maintained at the corresponding temperatures

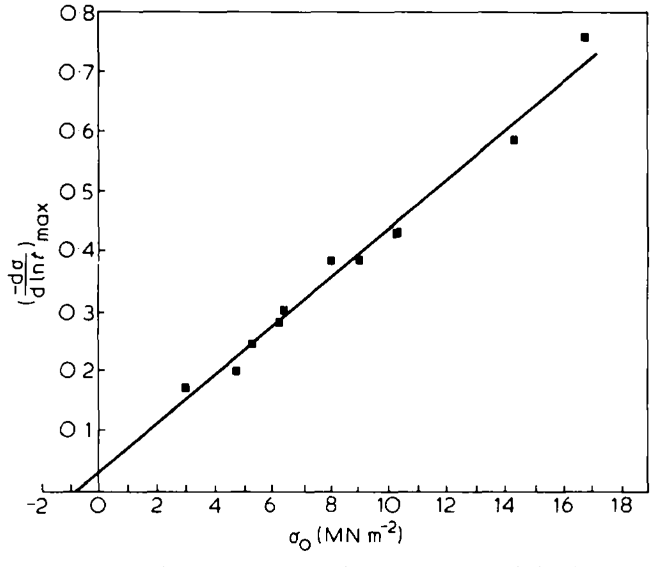

Figure 15 Kubát and Rigdahl plot for injection-moulded polycarbonate tested in tensile stress-relaxation at 60°C

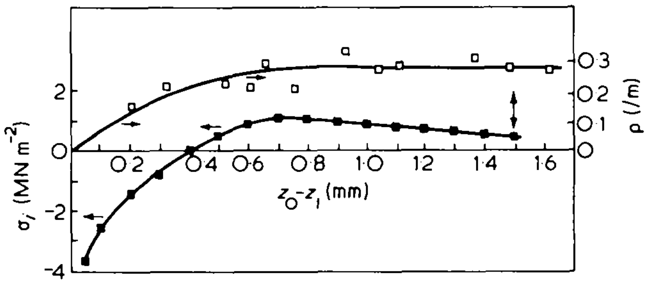

Figure 16 Layer removal analysis from compression-moulded polycarbonate sheet showing curvature (ρ), *versus* amount of material removed (z_0–z_1); and the computed residual stress σ_i, as a function of position within the bar. The surface of the bar is at (z_0–z_1) = 0, and the vertical arrow marks the centre of the bar

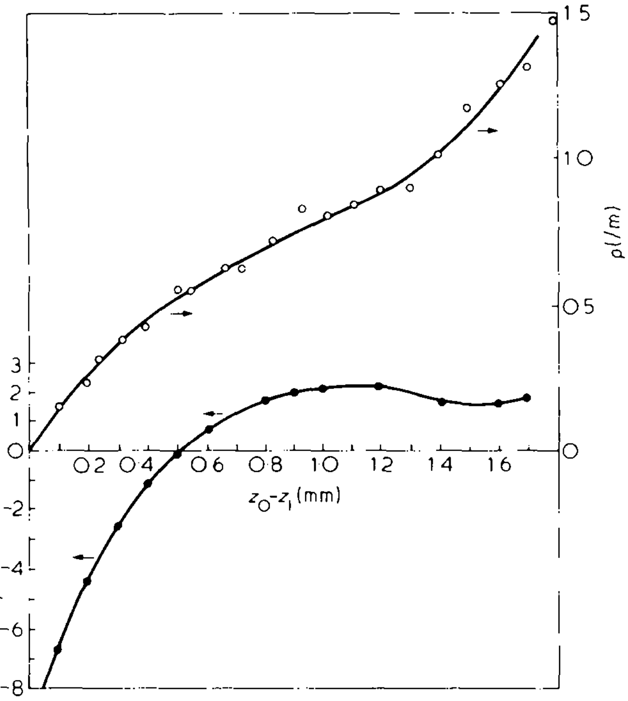

Figure 17 Layer removal analysis from an injection-moulded polycarbonate bar showing ρ and σ_i *versus* (z_0-z_1) as before

DISCUSSION

The value of σ_i found for the polycarbonate injection-mouldings from the KR analysis at 60°C was -0.8 ± 0.2MN m^{-2}. Although it has been predicted that σ_i for injection-mouldings will usually be negative[26] our own studies have often yielded positive values[13,14,21]. A magnitude of less than 1 MN m^{-2} is quite normal in our experience.

The layer removal results confirm that at all locations except those very close to the surface of the specimen the contribution to the net stress from the applied deformation will be much greater than that from the residual moulding stresses for all of the samples examined. We therefore consider that we are justified in analysing our results simply with reference to the measured applied stress, though we are in the process of making a closer examination of the influence of residual stress on the time dependence of birefringence changes on annealing bars in the unstressed state and will report on this at a later date. The difference in stress sensitivity in tension and in compression respectively will need to be taken into account in making this analysis.

The most interesting results obtained in the current study are those of polystyrene birefringence because of the apparently anomalous behaviour both in stress relaxation and recovery. These results are by no means unique, however. Studies of the retraction of oriented polystyrene monofilaments at elevated temperatures showed results analogous to our own recovery experiments, with a reversal of the sign of birefringence being produced after prolonged annealing[29,30]. The decay of the magnitude of birefringence was much more rapid than the decrease in the length of the monofilaments, a result similar to that obtained in studies of polystyrene injection-mouldings in this laboratory[11,12]. Another example of reversal of the sign of birefringence during recovery has been reported by Andrews and Kazama[31], working with annealed solvent-cast plasticized poly(vinyl chloride).

The explanation of these results is by no means straightforward. It is first to be recognised that the orientation of the highly polarizable phenyl groups will largely determine the birefringence characteristics of polystyrene. This has long been known and discussion, including some quantitative analysis can be found in the literature[2-7,32]. The question now arises as to what extent the orientation of the phenyl groups is decided by the molecular backbone orientation. The most favoured attitude for a phenyl group attached to a backbone carbon atom in an all-*trans* sequence will be with the normal to the plane of the phenyl group parallel to the (local) axis of the molecular backbone. This will of course only be true for an isolated molecule and inter-molecular effects will impose significant modification. For molecules in most solidified non-crystalline polymers long sequences of all-*trans* conformation are the exception rather than the rule, and strong intra-molecular influences will also be present. This alone would not cause any great difficulty in analysis as long as a description of molecular backbone orientation distribution could be found that showed a unique correlation with phenyl group orientation distribution. Experimental observations indicate that this is unlikely to happen, however. On annealing injection-mouldings at temperatures below T_g it is found that substantial changes in birefringence are brought about under conditions causing negligible shrinkage[11,12,33]: almost no effect is found up to 80°C with polystyrene[11,12,34] so that the separation of molecular backbone conformational changes, (indicated by shrinkage) and birefringence changes has not always been evident because of the rather narrow temperature range in which it is revealed. The observations cannot be accounted for by explanations invoking residual stresses[11,12]. It seems, therefore, that the distribution of phenyl group orientation can be modified under stress or on heat-treatment without large-scale changes in molecular backbone conformation.

With both mechanically oriented and injection-moulded polystyrene the birefringence changes during stress relaxation appear to be governed by two processes with quite different relaxation times. The initial time-dependent change in birefringence that takes place following the instantaneous jump that accompanies the application of the deformation seems to correspond to stress relaxation coupled with a positive stress-optical coefficient. The value of birefringence for the as-fabricated state is approached, but not reached, during this phase of the programme, and the rate of change of both stress and birefringence becomes very small. While the rate of change of stress continues to diminish a second process that causes further negative increments in birefringence begins to operate. We propose that this is an orientation effect, and that the stress is causing re-orientation of phenyl groups into directions with their normals more parallel to the stress axis, as is the case in a polystyrene melt for which a negative stress-optical coefficient is consequently produced. On removal of the stress the recovery stage begins with the birefringence moving instantaneously to a value showing a negative departure from the initial as-fabricated value of even greater magnitude. According to our hypothesis this jump corresponds to the release of the tensile stress, (coupled with the positive stress-optical coefficient), and the total incremental change from the initial unloaded state to the final unloaded state corresponds to the orientation that took place during stress relaxation. Time-dependent recovery towards the original state would explain the final part of the unloaded characteristics, but the hump after approximately 2 min is not easily accounted for. We could speculate that this is connected with regions of transverse orientation (thought to occur in injection-mouldings[35] at least), showing effects opposing those associated with regions possessing longitudinal orientation and possibly governed by different time constants as their thermo-mechanical history will be different, giving different states of ageing[36,37], but this could not be easily tested.

The decay of birefringence observed with compression-moulded samples under stress relaxation did not enter a second stage. At stresses large enough to produce significant changes in birefringence during the period of observation the tests on compression-moulded material could not be continued for as long as those on polystyrene in different states because the test-pieces fractured on prolonged deformation, following gradual initiation and growth of crazes. It is therefore not known whether the two-stage decay of birefringence observed with the mechanically oriented and with the injection-moulded polystyrene is connected with the presence of orientation prior to testing.

The development of greater negative birefringence in polystyrene under stress relaxation conditions proceeds more rapidly at higher temperatures (*Figure 12*). This is consistent with our proposal that the change in birefringence is caused by a relaxation process involving reorientation of phenyl groups. The recovery behaviour is similarly temperature sensitive, with the specimen tested at 80°C showing almost complete recovery of the birefringence value held prior to the deformation within 24 h of unloading (*Figure 13*).

With polycarbonate none of the anomalies found with polystyrene are reproduced. The birefringence changes instantaneously on deforming then remains unchanged, within the precision limits of our experiment, throughout a stress relaxation test. The change in birefringence that is associated with the molecular conformational changes that occur and which allow the stress relaxation, therefore exactly balances the change that must accompany the reduction in stress. On releasing the stress the conformational component remains and is found to decay according to a time constant similar to that which governs stress relaxation. The instantaneous change in birefringence has been plotted against the relaxed stress just prior to unloading and is found to give a similar stress optical coefficient to that obtained from the loading results, thus adding confidence to this interpretation (compare *Figures 6* and *11*).

We believe that our results emphasize the importance of taking into consideration side group motion independent of main chain motion when interpreting birefringence measurements on polymers with highly polarizable side groups. We would expect similar anomalies to occur with poly(methyl methacrylate) as have been observed with polystyrene, though the effects may be somewhat masked by the fact that stress and orientation both cause negative birefringence in this material[38-40].

In view of the importance of side group orientation in determining birefringence and the fact that main chain conformation is not the sole determinant of side group orientation it is unfortunate that many of the detailed computations of molecular orientation in injection mouldings have been compared to birefringence data obtained on polystyrene[41-50]. In these computations it is aimed to assess the extent to which molecular orientation produced during flow is retained on cooling in the mould, but the effect of secondary relaxations associated with side groups is not accounted for.

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