Dielectric relaxation behaviour and the ductile/brittle transition of polycarbonate

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Injection moulded polydiancarbonate has been studied mechanically and dielectrically and compared with annealed and embrittled material. The two forms of polycarbonate differ by a factor of four in impact strength under plane stress conditions but there is no substantial difference in their low temperature dielectric β-relaxations. This contraindicates explanations of their different properties and of the toughness of polycarbonate exclusively in terms of local main chain motions. Approximately 17% of the total chain units are mobile in the glassy state. The β-process is resolved into two processes at low temperatures, and the molecular origins of these, and of the intermediate temperature relaxation at 80°C, are discussed.

INTRODUCTION

The polycarbonate of bisphenol-A has attracted considerable study[1] due to its excellent mechanical properties, notably its high impact strength and ductility below the glass transition temperature T_g. The high impact strength has been attributed to molecular motions of the main chain at low temperature[2–4]. A transition in bulk properties from the ductile to a relatively brittle form was first noted by Peilstocker[5], upon annealing the material at temperatures below T_g. He reported an increase in tensile yield stress and a decrease in ultimate elongation. Golden *et al.*[6] found that the tensile yield strength of polycarbonate was strongly dependent upon the annealing time for temperatures above about 90°C, and thereby a lower temperature annealing limit for the material was defined. The ductile/brittle transition was further characterized by Legrand[7], and also by Allen *et al.*[8] who established that the lower annealing limit is in the region of 80°C.

More recently, it has been shown by Williams[8] that there is a significant difference in impact strength between thick polycarbonate specimens, which undergo plane strain fracture, and thin specimens, which undergo plane stress fracture. A ductile/brittle transition in polycarbonate may thus be obtained not only by thermal annealing but also by increasing sample thickness.

The principal object of the present study was to compare the dielectric relaxation behaviour of unannealed and annealed polycarbonate in the glassy state and so to establish whether or not the difference in bulk properties of these two forms under plane stress conditions is reflected in their secondary molecular relaxation processes involving the main chain. This could contribute to an understanding of the toughness of the polymer.

EXPERIMENTAL

Injection moulding of samples

The polymer used in these experiments was GE Lexan 101, supplied in the form of pellets. These were dried for 12 h at 120°C in open trays under vacuum. Polycarbonate was injection moulded into discs, 11 cm in diameter using a side feed mould maintained at 90°C, and with a barrel temperature in the range 320° to 330°C. The molten polymer was injected into the disc-shaped mould from a point on its edge or circumference. Examination of the disc specimens under plane polarized light revealed minimal orientation in all but the periphery of the discs. The central portions of these discs were used to provide dielectric and impact test specimens. Dumb-bell shaped tensile test pieces having a gauge length of 5.4 cm and a cross-sectional area of 0.35 cm^2 were also moulded. All specimens were removed promptly from the moulds to avoid premature annealing.

Annealing

The 'as-moulded' specimens were referred to as polycarbonate A. Specimens of polycarbonate A were converted into the brittle form B by annealing under vacuum (less than 10^{-2} torr with a residual atmosphere of nitrogen) for 3 h at 120° ± 0.4°C. The samples were stored in a desiccator prior to study. The annealing process had no effect upon the dimensional stability of the sample discs. Neither was there any significant difference in the appearance of the discs under plane polarized light before and after annealing.

Impact and tensile testing

The samples for impact tests were all machined to uniform dimensions of 5 x 0.8 x 0.35 cm. The centrally located notch tip was 0.58 cm from the struck face. Samples were machined from each of the injection moulded discs in two directions: (a) parallel to a line drawn normal to a tangent at the point of injection and (b) perpendicular to this line. The Charpy impact tester was supplied by Tensometer Ltd. Tensile measurements were performed on specimens using a type 'E' Hounsfied Tensometer from which full stress—strain curves were obtained.

Table 1 Yield stress and ultimate strain for untreated polycarbonate (A) and annealed polycarbonate (B), at a strain rate of 1.4 cm/min

Sample	Temperature (°C)	Yield stress (MN/m^2)	Ultimate strain
A	23	56	0.66
B	23	63	0.40
A	43	53	0.59
B	43	59	0.43
A	80	39	0.60
B	80	47	0.39

Dielectric measurements

Sample discs of 3.5 cm diameter and 0.33 ± 0.003 cm thickness were studied in a three-terminal electrode cell. Metal foil was attached to the sample surface with a thin film of petroleum jelly to ensure good electrical contact between sample and electrodes. Measurements of the complex relative permittivity $\epsilon^* = \epsilon' - j\epsilon''$ of the samples over the frequency range 10 to 10^5 Hz were made using a General Radio Type 1621 capacitance measuring system. This system, which measures the dielectric properties as a capacitance C_p and a conductance G, has a maximum error of ±0.01% in these values. The relative values of ϵ' and ϵ'', at a given temperature, were thus known to at least ±0.01% accuracy. The absolute values of ϵ^* were measured to ±1% accuracy, the limiting factor being the planarity of the sample faces.

The temperature of the samples was controlled accurately by immersing the measuring cell in appropriate temperature baths. For temperatures between $-130°$ and $+30°C$ a Lauda ultra-Kryomat No. K120W was used, and these temperatures were accurate to ±0.01°C. For the range $+20°$ to $+200°C$ a silicone oil bath, accurate to ±0.2°C, was employed. A low temperature reading was also taken in liquid nitrogen.

RESULTS

Mechanical behaviour

The average impact test values for more than 15 samples of each material at 23°C are as follows. Polycarbonate A: 82 ± 6 kJ/m^2; annealed polycarbonate B: 18 ± 2 kJ/m^2. These results were independent of the direction (parallel or perpendicular) in which the impact samples were machined from the discs. This clearly reflects the embrittlement effect in the annealed material. Tensile measurements on these two forms of the polymer, over the range 20° to 80°C and at two rates of strain, 1.4 and 6.8 cm/min, established the consistently higher yield stress and decrease in ultimate elongation for polycarbonate B as shown in *Table 1*.

Dielectric behaviour

For all of the samples studied both permittivity, ϵ', and loss factor, ϵ'', values were determined as a function of frequency and temperature. Selected representative loss factor values are herein presented.

The general features of the dielectric loss peaks observable for polycarbonate A are illustrated at a single measurement frequency of 10 Hz in the temperature plane, in *Figure 1*. The broad loss peak at low temperature reflects the β-process. A narrower loss peak of greater magnitude

at higher temperatures, the α-process, is associated with the glass–rubber transition[9]. A low intensity intermediate loss process is also observable commencing at about 80°C and eventually merging with the α-process at higher temperatures. This intermediate loss process, however, is not apparent at higher measurement frequencies (10^3 to 10^5 Hz).

The same loss processes are also observable for the annealed polycarbonate B; the intermediate process being even less prominent. A comparison will now be made of the more detailed results for material A and material B. This is presented by considering respectively the three loss processes.

α-process. In *Figure 2* the α-process of polycarbonate A is shown by a plot of ϵ'' as a function of frequency, at three temperatures. Similar data were obtained at additional temperatures in this range: 143°, 149°, 155° and 161°C. The shape of the loss peak and behaviour with temperature is typical of the glassy polymers at their glass–rubber transi-
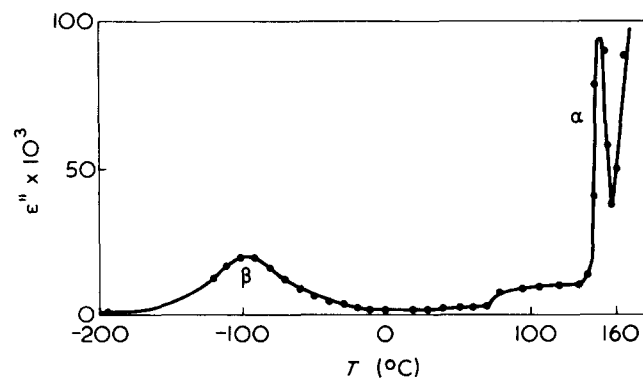

Figure 1 Dielectric loss factor, $\epsilon'' \times 10^3$, variation with temperature (°C) for polycarbonate A, at a measurement frequency of 10 Hz, showing α, β and 'intermediate temperature' loss processes

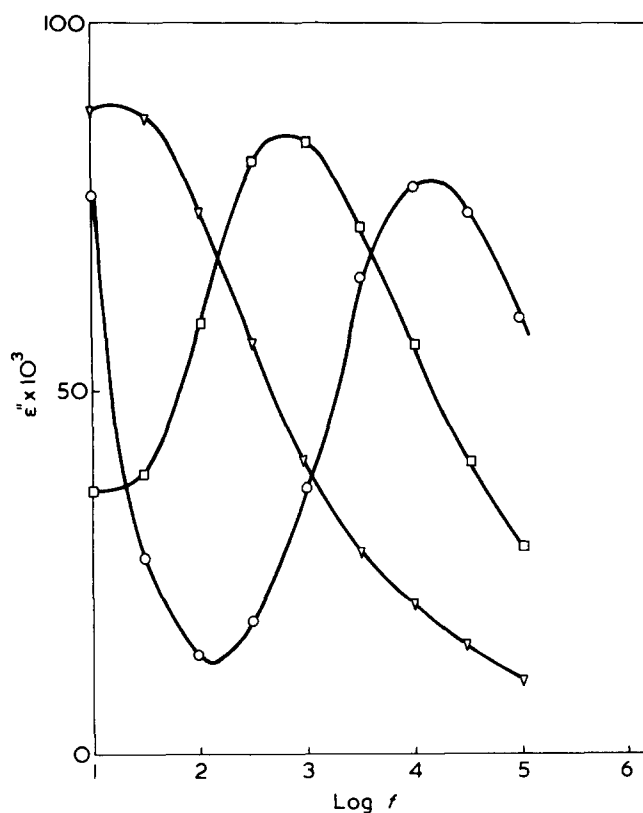*Figure 2* Dielectric loss factor, $\epsilon'' \times 10^3$, variation with log (frequency) for polycarbonate A, showing α-relaxation. ▽, 152°C; □, 158°C; ○, 164°C

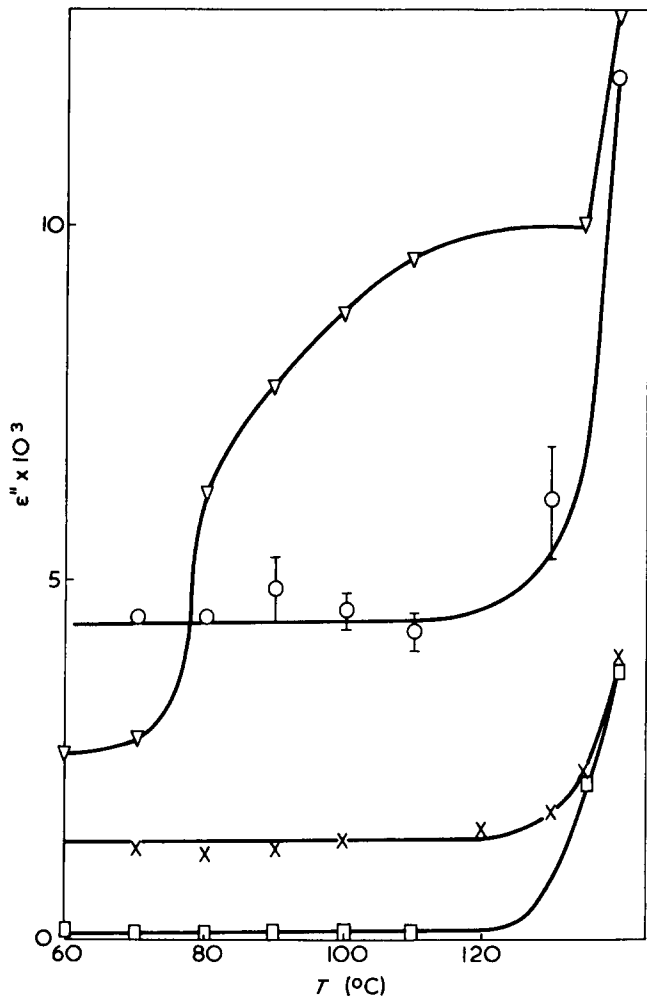**Figure 3** Dielectric loss factor, ϵ'' × 10^3, variation with temperature, showing 'intermediate temperature' relaxation. $\triangledown$, Polycarbonate A at 10 Hz; □, at 10^3 Hz; ○, polycarbonate B at 10 Hz; X, at 10^3 Hz

tion[9]. Virtually identical behaviour was observed at these same seven temperatures for the annealed polycarbonate B, in terms of the magnitude, shape and frequency/temperature location of the process. Consequently these results are not reproduced here.

'Intermediate' process. The 'intermediate relaxation' is shown in *Figure 3* at 10 and 10^3 Hz for both forms of polycarbonate. At the lower frequency, the loss process is approximately halved in magnitude on annealing material A to form B. At the higher frequency, the loss process has essentially disappeared in polycarbonate A, presumably being merged with the α-process. In the annealed material at 10^3 Hz the intermediate process is just apparent. Possibly the activation energy of the process is lower in the annealed state, and hence the loss-peak moves less rapidly with temperature to merge with the α-process.

β-process. Figures 4–7 show the β-loss peak in greater detail as a function of frequency. *Figures 4* and *5* present the data for the original material, and *Figures 6* and *7* refer to the annealed polycarbonate. It can be seen that there is no shift in the *frequency/temperature location* of the maxima of this family of loss peaks on annealing. However, there is some difference in the *magnitude* of the loss factor, at a particular temperature and frequency, between materials A and B. In particular, the maximum loss value is *lower* for the annealed sample. The percentage differences in peak areas for the two samples, normalized with

respect to the peak areas of material B, are obtainable from cross plots of these data as a function of temperature. Thus at a measurement frequency of 10^2 Hz, the peak area for the unannealed material is 8.6% larger; at 10^3 Hz, 6.9% larger and at 10^4 Hz, 4.9% larger. These aspects of our results are consistent with the observations of Müller and Huff[10] that the magnitude of the dielectric loss tangent of polycarbonate's β-process is reduced on annealing, but the frequency/temperature location of the peak is unchanged.

A further significant feature of *Figures 4* to *7* is the shape of the β-loss curves. These are markedly non-symmetrical about the logarithm of the frequency of maximum loss. The presence of more than one relaxation process is indicated. The asymmetry of the overall process becomes more pronounced as the temperature is decreased, and the shoulder on the high frequency side of the maximum is evidently a second, lower intensity, β-process. This may be distinguished as the 'β_2'-process from the parent 'β_1'-process. Comparison of *Figures 4* with *6*, and *5* with *7* shows that there is no substantial difference in the shape of these loss curves produced by annealing. The β_2-process has the same general character irrespective of this factor.

In *Figure 8* the Arrhenius plot summarizes the frequency/temperature location of these processes. The activation energy values are as follows: α-process, 800 kJ/mol; β_1-process 45 kJ/mol and β_2-process 10–30 kJ/mol. These activation energies (E), were obtained both from the Arrhenius plots, in the normal manner, and also from the area

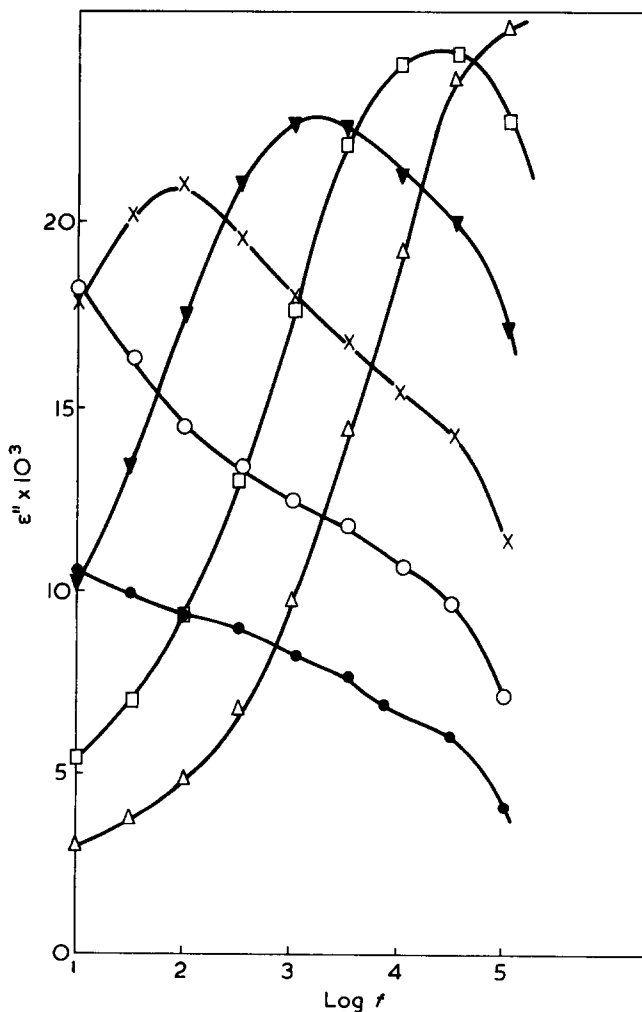
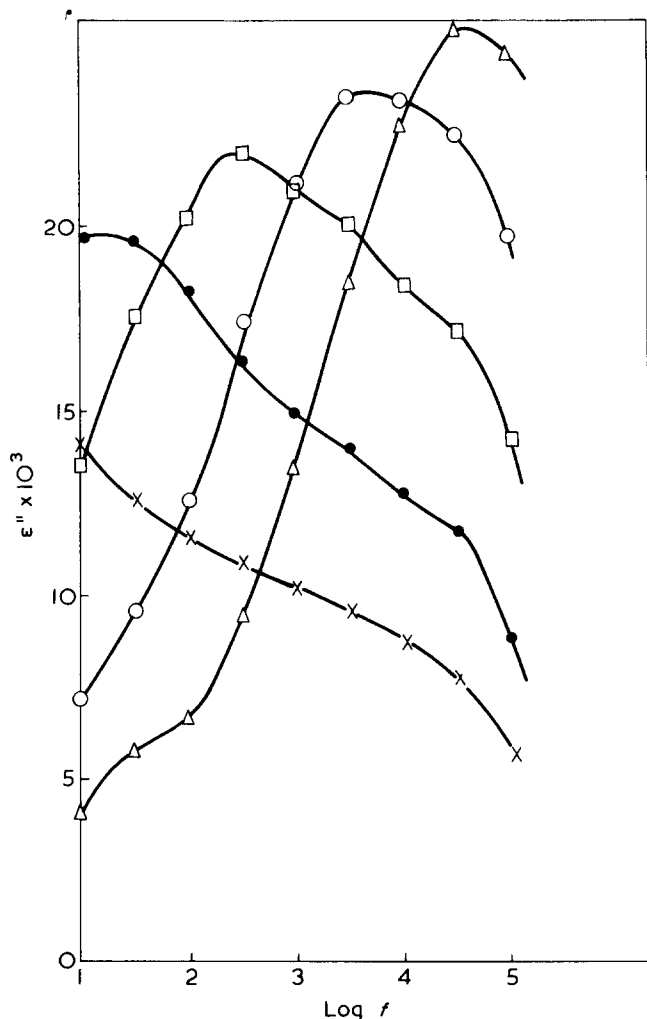**Figure 4** Dielectric loss factor, ϵ'' × 10^3, variation with log (frequency) for β-process in polycarbonate A. △, −25°C; □, −45°C; ▼, −65°C; X, −85°C; ○, −105°C; ●, −125°C

Figure 5 Dielectric loss factor, ϵ'' × 10^3, variation with log (frequency) for β-process in polycarbonate A. △, −35°C; ○, −55°C; □, −75°C; ●, −95°C; ✕, −115°C

These materials have been studied structurally by Wignall and Longman[15] using X-ray diffraction to determine the radial distribution function. Their results exclude explanations of the differing impact strengths of the A and B forms in terms of significant short-range reordering on annealing.

It has often been suggested that the toughness of a polymeric solid is in some way connected with the motion of chain segments in the glassy state below T_g. This concept has been reviewed by Heijboer[3] who concluded that a change in impact properties is only likely when a corresponding loss peak originates from movement within the main chain. Since polycarbonate lacks flexible side chains it satisfied Heijboer's criterion. Nielsen[2] and Tobolsky[4] have also attributed the toughness of polycarbonate to the presence of the β-process.

The explanation of the toughness of polycarbonate exclusively in terms of the β-process is sometimes supported by observations on the magnitude of the β-loss peak, as a function of temperature, relative to the α-loss peak. Such comparisons can be misleading, because the areas of the α and β regions of plots of $\epsilon''(T)$ are not a direct measure of the number of chain segments activated by these processes. The relative number of segments activated in the β and α-processes may be defined as $(S\mu^2)\beta/(S\mu^2)\alpha$, where S is the number of dipolar groups per unit volume, and μ is the resultant dipole moment of the repeat unit. This quantity
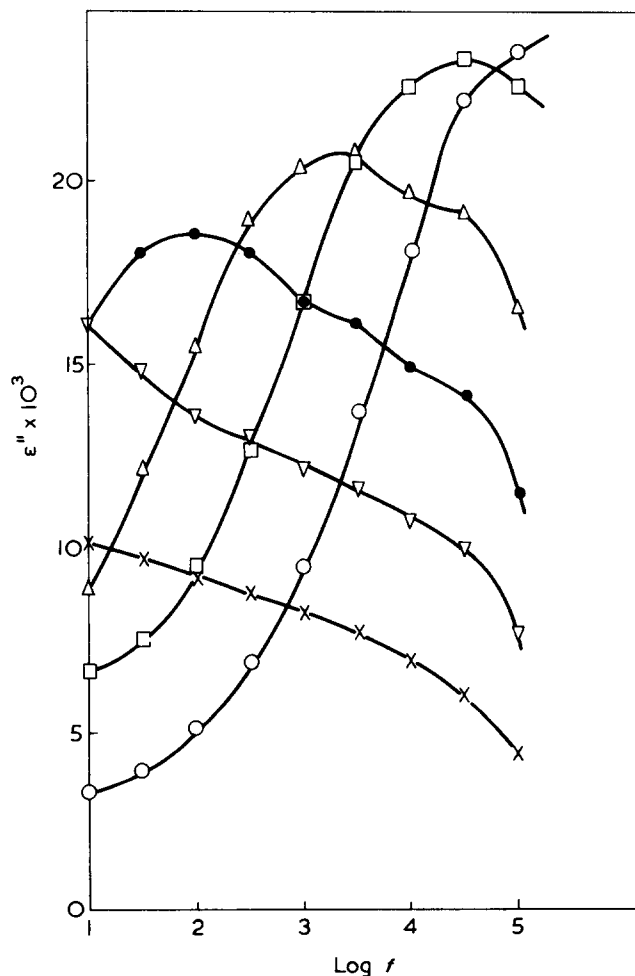
under the curve in a plot of ϵ'' versus T^{-1}, *Figure 9*, via the relationship:

$$\langle 1/E \rangle^{-1} = (\epsilon_0 - \epsilon_\infty)R\pi/2 \left[\int_0^\infty \epsilon'' d(T^{-1}) \right]^{-1}$$

where ϵ_∞ and ϵ_0 are the limiting high and low frequency permittivities, and R is the gas constant[11].

The additional data, from other workers, presented in *Figure 8* will be considered below.

DISCUSSION

Interpretation of the ductile/brittle transition in terms of the β-relaxation process

The dielectric relaxation behaviour of polycarbonate has been studied by several workers[10,12−14,21] notably by Matsuoka and Ishida. These latter workers investigated polycarbonate fabricated by compression moulding, whereas the present work is concerned with injection moulded material, including the annealed form. The general problem of the molecular explanation for the toughness of polycarbonate resolves, in the present investigation, into the particular question of the nature of the difference between polycarbonate A and B, at the molecular level.

Figure 6 Dielectric loss factor, ϵ'' × 10^3, variation with log (frequency) for β-process in polycarbonate B. ○, −25°C; □, −45°C; △, −65°C; ●, −85°C; ▽, −105°C; ✕, −125°C
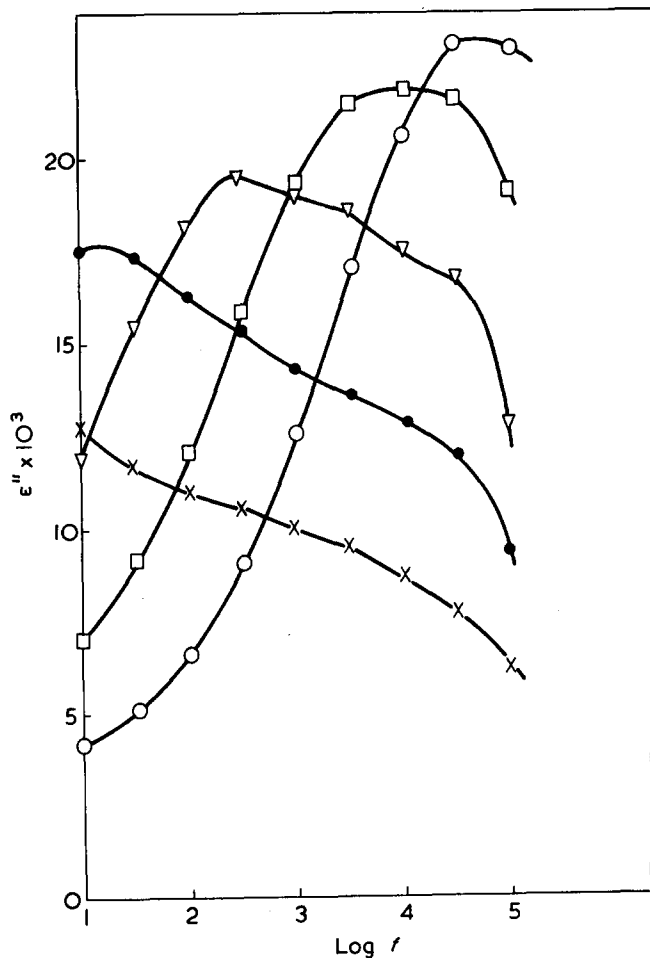
Figure 7 Dielectric loss factor, ϵ'' X 10^3, variation with log (frequency) for β-process in polycarbonate B. O, $-35°$C; □, $-55°$C; ▽, $-75°$C; ●, $-95°$C; X, $-115°$C

may be obtained from Onsager's equation[16]:

$$(\epsilon_0 - \epsilon_\infty) = \left[\frac{(\epsilon_\infty + 2)^2 \cdot \epsilon_0}{(2\epsilon_0 + \epsilon_\infty)} \right] \frac{4\pi}{9kT} S\mu^2$$

Since the term in square brackets is approximately unity, we obtain:

$$\frac{T_\beta(\epsilon_0 - \epsilon_\infty)_\beta}{T_\alpha(\epsilon_0 - \epsilon_\infty)_\alpha} \simeq \frac{(S\mu^2)_\beta}{(S\mu^2)_\alpha}$$

T_β and T_α are 205 and 434K respectively, the temperatures at which the β and α loss peaks occur, as measured at 10^3 Hz

$(\epsilon_0 - \epsilon_\infty)$ values may be obtained directly from permittivity measurements at T_β and T_α. Alternatively, as noted above[11], the product of activation energy and $\int_0^\infty \epsilon'' \, dT^{-1}$ is proportional to $(\epsilon_0 - \epsilon_\infty)$.

Thus we obtain from a ratio of β and α peak areas, in *Figure 9*, of 8:1:

$$(\epsilon_0 - \epsilon_\infty)_\beta/(\epsilon_0 - \epsilon_\infty)_\alpha = 0.45$$

and hence

$$(S\mu^2)_\beta/(S\mu^2)_\alpha = 0.21$$

Thus, despite the magnitude of the integrated β-loss peak,

the fraction of segments activated by this process is only approximately 0.21 of the number activated by the α-process.

An important result of the present work is the similarity observed between the frequency/temperature location, the shape and the magnitude of the β-loss peaks in type A and type B polycarbonate, despite the marked difference in impact strength. Thus the ductile/brittle transition, as manifested in the enhanced impact resistance of material A relative to the annealed form, cannot be explained in terms of a transition in, or substantial modification of the rate, or mode or intensity of chain backbone motions in the glassy state. Nevertheless, the lower, minimum impact resistance of the annealed (and embrittled) form of polycarbonate may result from such motions as are manifested in the β-process. The slight reduction of up to 9% in the magnitude of the process in material B is consistent with this hypothesis[3,4]. Generally speaking, however, a completely satisfactory quantitative correlation between loss
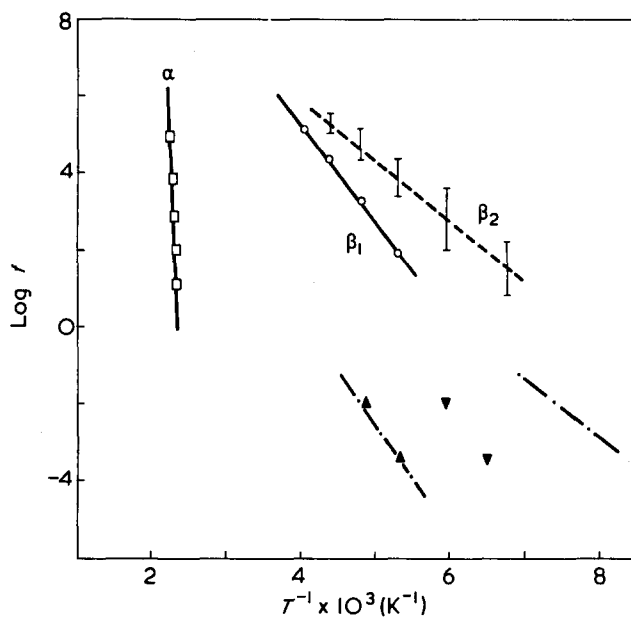

Figure 8 Log (frequency of maximum loss) variation with reciprocal temperature for polycarbonate. □, α-Relaxation; O, β-relaxation; — — —, β_2-relaxation; — · — · — · —, data of Aoki *et al.*[14]; ▲,▼, data of Locati *et al.*[4]
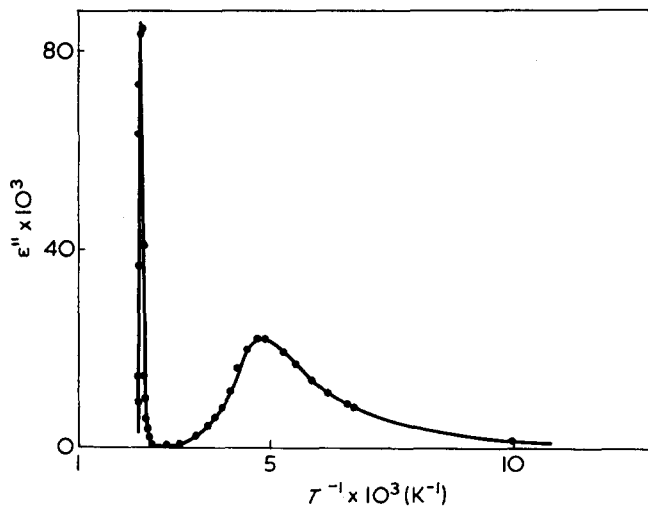

Figure 9 Dielectric loss factor, ϵ'' X 10^3, variation with reciprocal temperature for polycarbonate A, at 10^3 Hz
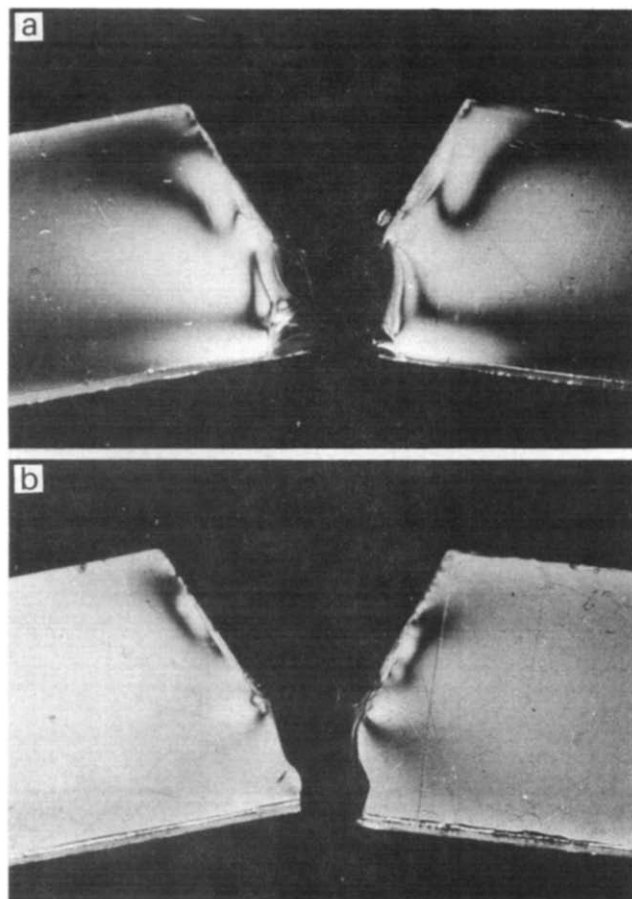
Figure 10 Photographs of broken Charpy test-peices, viewed in plane polarized light: (a) untreated polycarbonate; (b) annealed polycarbonate

peaks and ultimate properties of the polymer cannot be completely worked out, because, as Vincent[17] pointed out, the two types of measurement to be compared correspond to different regions of the stress—strain curve. More recent studies[18,19], of the surface characteristics of the A and B forms of polycarbonate, indicate that the difference between them is to be found positively in the production of a high density of surface crazes in the annealed material when the samples undergo permanent tensile deformation. Furthermore, when the broken Charpy impact test pieces are viewed in monochromatic plane polarized light, (*Figure 10*), then a reduction in the amount of plastic strain at the fracture zone is observed in the annealed sample, as compared with the unannealed material, as was observed previously by Adam *et al.*[27]. The volume of plastically deformed material is evidently a major factor in determining impact strength under plane stress conditions[27—29].

Molecular origin of the β-process

As already noted, since polycarbonate lacks flexible side chains the β-process must originate from some local motions of the main chain. A further general observation, made by several groups of workers[4,14] using a variety of techniques, is that the secondary β-relaxation of polycarbonate may be resolved into more than one process. The question then arises as to the distinct molecular origin of each of these processes.

In *Figure 8* the frequency—temperature locations of these multiple secondary processes are indicated. The main process we have observed corresponds to a process charac-

terized by many other workers[4,9]. The less pronounced lower temperature, β_2, process, has not been reported previously or emphasized as a distinct phenomena, in this polymer. Aoki and Brittain[14] have studied the dielectric behaviour of polycarbonate at very low frequencies. The loci of the two β-peaks which they observed are reproduced, and it may be seen that their lower temperature β-process is approximately correlated, by extrapolation, with our β-process. Their higher temperature β-process corresponds to the higher temperature peak observed by Locati and Tobolsky[4], using creep and shear stress relaxation studies. The lower temperature peak observed by these latter workers is uncorrelated in location with other published data.

Locati and Tobolsky[4], followed by Aoki and Brittain[14], have suggested that the lower temperature peaks they have observed are associated with the movement of the strongly dipolar carbonate groups, restricted, however, by the phenyl groups. If correct, this would indicate the same molecular origin for our β_1-process. Aoki and Brittain[14] attributed the higher temperature component of the β-relaxation to motion of the phenyl groups with cooperative motion of the carbonyl groups. These interpretations, however, have been challenged by Davenport and Manuel[20] on the basis of n.m.r. second moment measurements. They conclude that motion of the two methyl and the two phenyl groups as a unit is a necessary hypothesis. This interpretation parallels that of McCrum *et al.*[9], who questioned the possibility of independent local motions of the carbonate group, as this model for the β-process seems unable to account for the observed behaviour of the process with varying sample crystallinity[2,21].

The present observation of the resolution of the single β-process into two processes, β_1 and β_2, at lower temperatures, may be compared with the studies of Williams and Watts[22] on the resolution of a single (αβ) process into separate α and β-processes, by the reduction of temperature or the application of hydrostatic pressure. This was observed in many amorphous polymers. In general terms, the β-process was attributed to the partial randomization of dipoles in a range of fixed environments, followed by total relaxation of dipoles and environments in the α-process. The observed resolution of β into β_1 and β_2 peaks appears to be qualitatively consistent with a modification of this theory, wherein the β_2 and β_1 processes are interpreted respectively in parallel with the above model of the β and α relaxations. In particular, the total loss, integrated with respect to frequency, is approximately constant with temperature.

'Intermediate' and α-processes.

An intermediate loss peak, commencing at about 80°C in the temperature plane, has been observed by several workers[10,23,24], and Allen *et al.*[8] showed that the annealing process in polycarbonate proceeds rapidly above this temperature. This intermediate peak is small in magnitude and disappears on annealing or drawing the polycarbonate. Our results are consistent with the previous dielectric studies of Müller and Huff[10] and Krum and Müller[24], and the mechanical studies of Illers and Breuer[23]. Lunn and Yannas[25] observed a relaxation process in drawn polycarbonate film, the dichroic ratio being significantly time dependent above 80°C.

It is highly probable that this intermediate process is not at all characteristic of the equilibrium state of the polymer. It is evidently associated with stresses induced in the moulding or drawing of a specimen. It may therefore arise

primarily from the surface region of the material rather than from the bulk. Since the β-process is probably due to quite extensive local motion of the main chain, there is no reason why more extensive chain motion should not be activated at higher temperatures, particularly in regions of the material subject to frozen stresses.

Boyer[26], following the lead of Matsuoka and Ishida[12], has presented a plot of the temperature of secondary (β) transitions, for many linear polymers, as a function of the T_g of the polymer. This results in an approximately straight line relationship between these temperatures. It is suggested that for these polymers motion in the glassy state is of the same kind as at T_g but involves fewer consecutive monomer units along the chain. Thus the secondary process may be considered the remote precursor of the α-process. In the case of polycarbonate however, the very low temperature of the β-process does not fit on the approximate straight line observed for other polymers. However, if the 80°C temperature of the intermediate process is plotted as a function of T_g, then polycarbonate falls into the characteristic pattern of the other polymers. This may possibly lend some support for a view of the intermediate process as a proximate precursor of the α-process, in at least some regions of the unannealed polymer, involving motion of several repeat units of the polymer chain.

CONCLUSIONS

(1) The energy dissipated by the local main chain β-relaxation in the glassy state of polycarbonate is most probably a *contributory* factor to the toughness and impact resistance of the polymer under both plane stress and plane strain conditions. The ratio of groups activated respectively by the β and α processes is 0.21:1. Thus approximately 17% of the total chain units are mobile in the glassy state.

(2) The lack of substantial difference between the β-processes of unannealed and annealed polycarbonate shows that the ductile/brittle transition can not be straightforwardly explained in terms of changes in the rate or mode or intensity of local chain motions. For this reason, interpretation of the toughness of polycarbonate under plane stress conditions *exclusively* in terms of the β-process is also contraindicated.

(3) The dielectric β-relaxation in polycarbonate resolves into two processes, β_1, and β_2, at low temperatures. Suggestions have been made as to their possible molecular origins.

(4) The 'intermediate temperature' relaxation is some kind of precursor to the α-process, probably originating from regions of the unannealed polymer, such as surface zones, subject to frozen-in strains.

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