

Aliphatic polyesters as models for relaxation processes in crystalline polymers:

2. Dielectric relaxation in copolymers of adipic acid with 1,6 and 2,5-hexanediols

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(Received 25 January 1983; revised 4 April 1983)

Linear aliphatic polyesters are interesting model systems for studying relaxation processes in crystalline polymers because they show both γ and β relaxations in a prominent way whereas in many highly crystalline linear polymers (LPE, POM etc.) the β process is suppressed and, unlike branched polyethylene which also has a prominent β process, the polyesters have no chemical structural complications due to branches. To study the hypothesis that variations in the appearance of the β (glass-rubber) relaxation are due to varying degrees of immobilization of long-range segmental motion in the amorphous fraction by the presence of the crystal phase measurements are made of dielectric relaxation in a series of the title copolymers that span the crystallinity range of zero (homopolymer with 2,5-hexanediol) to $\approx 60\%$ (homopolymer with 1,6-hexanediol). The data are analysed in terms of the effect of degree of crystallinity on both kinetic parameters (activation energies and relaxation width) and equilibrium parameters (dipole correlation factor deduced from relaxation strength). In the latter case special care is taken to properly assess composite mixture effects on the relaxation strength. The shape of the β process is extremely sensitive to the degree of crystallinity, broadening greatly with the onset of the presence of crystallinity and increasing in broadness with increasing degree of crystallinity. Although less sensitive than the width, the β relaxation dipole correlation factor depends on crystallinity also, the availability of chain configurations within the amorphous fraction being noticeably reduced in the crystalline specimens. The γ process kinetic parameters are relatively insensitive to the presence of the crystal phase, a behaviour consistent with a localized motion mechanism. The γ relaxation strength correlates with the process having an amorphous phase origin if it is assumed that the 2,5 diol units contribute less to relaxation strength than the 1,6 diol units; a result also consistent with the localized motion concept.

Keywords Aliphatic polyesters; dielectric relaxation; crystal phase; amorphous phase; relaxation strength; relaxation width

INTRODUCTION

Semi-crystalline polymers with simple linear chains, as is well-known, may show up to three prominent relaxation processes (α , β , γ in descending temperature at constant frequency)¹. The highest temperature process, α , is associated with the crystal fraction¹⁻⁶, the β with the glass-rubber relaxation in the amorphous fraction^{1,2} and the γ has largely an amorphous fraction origin^{3,7-10} although it has sometimes supposed to have a crystalline component as well². The γ process is often conjectured to involve molecular motions of much more localized character than the long-range generalized segmental motions associated with the glass-rubber relaxation^{11,12}. Unfortunately, the situation is in some respects more complicated than described and there appears to be considerable uncertainty with respect to the origins of the relaxations in a given polymer. This uncertainty arises largely because the relative prominence or even occurrence of the three processes varies greatly from polymer to polymer. The α crystalline process certainly does not occur in all such polymers (aliphatic polyamides and aromatic polyesters would be examples). However, based on what is known about the nature of the requisite

molecular motions in polymer crystals¹³, the process would be expected often to lie unobservable above the crystalline melting point or in the case of dielectric measurements sometimes simply not be dielectrically active. Perhaps more perplexing, however, is the variation in prominence of the β relaxation amongst various crystalline polymers. In some highly crystalline polymers of simple structure (linear polyethylene, polyoxymethylene) it is not a prominent feature relative to the α and γ processes. This lack of prominence has led some to propose that the γ process is, therefore, the glass-rubber relaxation^{10,14}. This could be regarded as merely a semantic argument (if T_g is to be associated by definition with the most prominent amorphous phase relaxation). However, the question has a strong conceptual bias to it, as many would like to associate T_g with a glass-rubber transition where generalized segmental motion occurs. It is important, therefore, to establish why the β process is suppressed in some highly crystalline polymers such as linear polyethylene and the γ process has the same character in these polymers as it does in those that do show a prominent β process. A reasonable hypothesis for the former is that the presence of the crystalline fraction immobilizes to a lesser or greater

degree the amorphous one. This could be explained in kinetic terms by the interconnections (loops, loose folds, tie chains) presenting increased barriers to conformational change that compared to an unconstrained amorphous phase could slow and broaden the relaxation. The crystal fraction could also immobilize the amorphous material in an equilibrium sense. These topological entities as well as the simple presence of the crystal surface would remove conformations from availability and, thus, not all of the configurational states accessible to an unconstrained chain would be accessible to many amorphous segments in a semi-crystalline polymer. Clearly, the kinetic effects would be evident in measured relaxation parameters such as central relaxation time and broadness and shape parameters. The equilibrium effects would be evident in relaxation strength. Surprisingly, although it is known that crystalline β relaxations tend to be broad, there is little quantitative information describing the broadness and its variation among different polymers or in the same polymer under variations in crystallization conditions. There is much less information available on the degree of suppression of the relaxation strength in semi-crystalline polymers. Thus, it has not been established whether lack of prominence of the β relaxation is due to just an extreme broadening effect or whether the relaxation strength has decreased also. The purpose of the present series of papers is to measure relaxation parameters in a family of semi-crystalline polymers of simple linear structure where both the β and γ processes are prominent enough to characterize the relaxation parameters of both reasonably well. The linear aliphatic polyesters behave in many respects in a manner similar to polyethylene. Some of the crystal structures are similar to PE, there are no strong specific interchain forces such as those arising from hydrogen bonding in polyamides. In fact the melting points are considerably lower than in PE, a property that led to their neglect despite being the first condensation polymers of well known¹⁵ and characterized^{16,17} structure. In their relaxation behaviour¹⁸⁻²⁰ the process is almost indistinguishable in its time-temperature behaviour from that in PE. The β process appears to be similar to that in branched polyethylene (BPE) but without the possibility of ambiguity in interpretation because the structures are completely linear and no flexible side groups are present. It is not clear yet to what extent an α process can be detected^{18,19}. It is clear, however, that the low melting points interfere with the possible observation. Here, therefore, the α designation is reserved for a possible α crystalline process and to preserve a notational correspondence between obviously similar processes in PE and other polymers β and γ are used as the labelling for the processes studied.

The scarcity of quantitative information about the relaxation parameters, especially relaxation strengths, characterizing the amorphous fraction in semi-crystalline polymers is in part due to fundamental problems with respect to their determination. It is important to establish the relaxation strength of the amorphous phase (but as it behaves in the semi-crystalline environment). Measurements on the bulk specimens however refer to the semi-crystalline composite. It is non-trivial to 'back-out' the separate phase properties from bulk properties. It is necessary to obtain suitable data against which various composite models for semi-crystalline polymer behaviour

can be tested. One of the few examples is the availability of data on mechanical relaxation in LPE over a wide crystallinity range⁷ for such model assessment. In the present work it has not been possible to vary the crystallinity of aliphatic polyesters significantly by varying crystallization conditions or through annealing. However, in accordance with the observation that the condensation of sebacic acid with 2,5-hexanediol gives an amorphous polymer²⁰, variation from completely amorphous to $\approx 60\%$ crystallinity can be effected by copolymerization of adipic acid with two isomeric diols, 1,6-hexanediol and 2,5-hexanediol, in varying ratios. The homopolymer with the first diol which is designated 6-6 polyester is highly crystalline ($\approx 60\%$). The homopolymer of the second diol, designated 6B-6 is completely amorphous (a behaviour no doubt enhanced by stereo irregularity of the 6B diol) and copolymers of low 6B content are of intermediate crystallinity. In the present paper results are presented of the measurement of the dielectric relaxation behaviour of a series of these polymers covering this crystallinity range for the purpose of providing information about the effect of the crystalline phase on amorphous phase relaxation processes, by (a) reliably determining bulk specimen relaxation parameters and (b) properly interpreting bulk specimen parameters in terms of separate phase properties. This plan is not completely without difficulties as there are some effects of chemical structure variation distinct from crystallinity variation; the main one being that the glass temperature of the 6B-6 amorphous homopolymer is slightly higher than that of the amorphous fraction in the 6-6 homopolymer.

EXPERIMENTAL

The polyesters were synthesized in the laboratory by polymerization of dimethyl adipate with a slight total mol excess of 1,6-hexanediol and 2,5-hexanediol. The approximate desired composition of a copolymer was attained by setting the starting mol ratio of the diols. The actual composition was determined by mass balance on the starting monomers and the resulting polymer are distilled excess diols (the distillate being analysed by gas chromatography). Further details of the synthesis may be found in the Ph.D. dissertation of P. A. Aylwin²¹. The resulting molecular weight of the various samples were established by gel permeation chromatography to be between 20 and 30 kg mol⁻¹. The samples were given designations based on their nominal starting mol ratios of diols, i.e. '60/40' means 60 mol per cent 1,6-hexanediol and 40 mol per cent 2,5-hexanediol. The actual composition of the samples are given in *Table 1*.

The crystallinities of all of the specimens determined from heats of fusion and density are listed in *Table 1*. The heat of fusion of the crystal phase was taken as 151 kJ kg⁻¹ (which is the value determined for the 6-6 homopolymer²²) and assumed to be independent of the composition. The crystal density was taken as 1222 kg m⁻³²². The amorphous density of the 6-6 homopolymer was taken as 1096 kg m⁻³ and that of the 6B-6 homopolymer 1076 kg m⁻³²². The amorphous density of a copolymer was estimated as the mol fraction average of the 6-6 and 6B-6 homopolymer values.

The dielectric measurements were made in a three-terminal parallel plate cell on specimens 6-6, 90-10,

Table 1 Characterization of samples

| Sample designation | Sample composition (% 1,6-hexanediol) | Melting temperature ^a | | ΔH_f (kJ kg ⁻¹) | Crystallinity, ΔH_f (%) | Crystallinity, density (%) |
|--------------------|---------------------------------------|----------------------------------|---------------|-------------------------------------|---------------------------------|----------------------------|
| | | T_{m1} (°C) | T_{m2} (°C) | | | |
| 6-6 | 100 | 59 | — | 90.0 | 60 | 57 |
| 90-10 | 90.1 | 52 | — | 65.7 | 43 | 45 |
| 80-20 | 81.9 | 38 | 45 | 54.4 | 36 | — |
| 70-30 | 74.6 | 30 | 40 | 42.7 | 28 | 32 |
| 60-40 | 59.9 | 24 | 32 | 28.4 | 19 | 23 |
| 50-50 | 50.0 | — | — | 0 | 0 | 0 |
| 6B-6 | 0.0 | — | — | 0 | 0 | 0 |

^a As determined by d.s.c. Some of the samples exhibited a double melting peak T_{m1} , T_{m2}

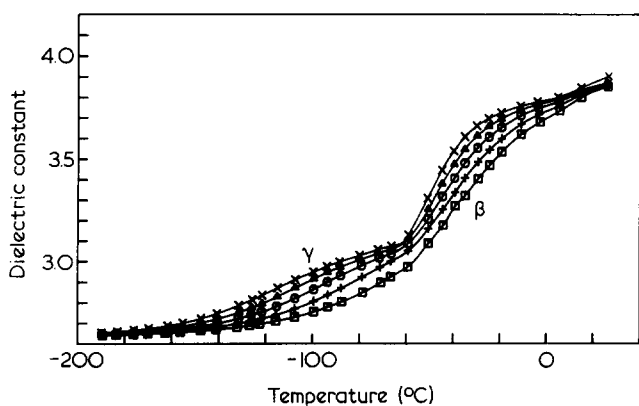


Figure 1 Experimental data for dielectric constant of semi-crystalline 6-6 homopolymer versus temperature. Isochronal scans at x 10 Hz; Δ , 100 Hz; \circ , 1 kHz; +, 10 kHz; \square , 100 kHz

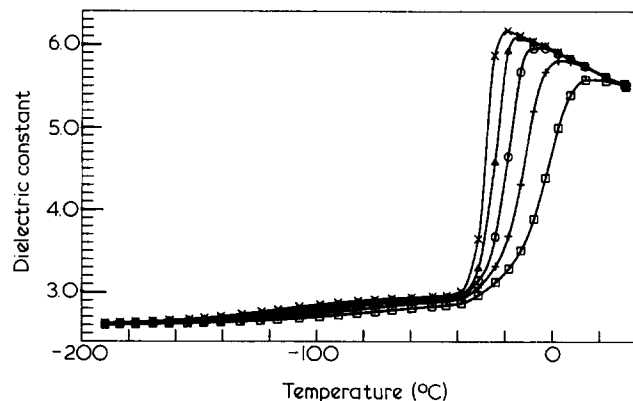


Figure 3 Experimental data for dielectric constant of amorphous 6B-6 homopolymer versus temperature. See Figure 1 for frequencies

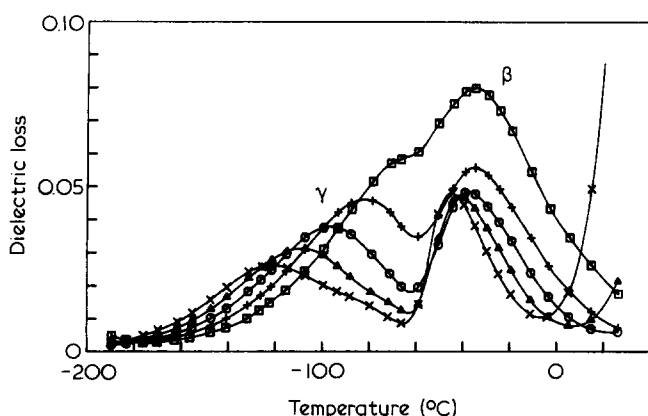


Figure 2 Experimental data for dielectric loss factor of semi-crystalline 6-6 homopolymer versus temperature. See Figure 1 for frequencies of isochronal scans

80-20, 60-40 and 6B-6 using methods previously described³. The measurements were made isothermally at five decade frequencies from 10 Hz to 100 kHz. The crystalline specimens (≈ 50 mm diam. discs) were compression moulded in a platten press between sheets of aluminum foil. They were kept in the press under pressure until it had slowly cooled from 10°C above the melting point to room temperature. In the 6-6 and 90-10 specimens the foil was stripped off and gold electrodes evaporated on. In the lower melting samples the foil adhered tightly and was left in place. The completely amorphous 6B-6 specimen was a viscous liquid at room temperature and was heated and poured into the cell. The latter was modified by addition of an acrylic plastic

annular ring surrounding the electrodes to provide containment. The low-temperature electrode was placed on top and slowly released to avoid an air pocket between the sample and the electrode. Measurements made on the melts of 6-6, 5-7 and 6-10 homopolymers also used the acrylic ring for confinement although the specimens were loaded as solids.

RESULTS AND DATA FITTING

Although the data was obtained in isothermal mode it is best displayed isochronally plotted against temperature. Only part of the experimental data is shown here. The homopolymer extremes are illustrated in Figures 1 and 2 for 6-6, and Figures 3 and 4 for 6B-6. Interpretation of the data is best made through comparisons among the specimens of the phenomenological parameters that characterize the relaxation processes. To accomplish this the Havriliak-Negami (HN) equation²³ was fitted to the data. This equation is a generalization of the Cole-Cole function²⁴, which accommodates symmetrical broadening of a loss peak, and the Davidson-Cole function²⁵ which describes skewing of the process. Here, there are multiple overlapping (γ , β) loss processes so the specimen complex dielectric constant, ϵ^* , is the sum of two HN functions:

$$\epsilon^* = \epsilon_U + (\epsilon_R - \epsilon_U)_1 (1 + (i\omega\tau_1)^{\alpha_1})^{-\beta_1} + (\epsilon_R - \epsilon_U)_2 (1 + (i\omega\tau_2)^{\alpha_2})^{-\beta_2} \quad (1)$$

where subscripts R, U refer to relaxed and unrelaxed dielectric constants, τ to central relaxation time, α to the width parameter, β to the skewness parameter, ω to

angular frequency and subscripts 1 and 2 to the two relaxation processes ($1 = \gamma$, $2 = \beta$) present.

Isothermal fits were made interactively using a computer terminal that displayed a calculated Argand diagram of ϵ'' plotted against ϵ' along with the experimental points. Values of ϵ_R , ϵ_U , $\bar{\alpha}$, $\bar{\beta}$ for the process being fitted were adjusted to give a good fit of the calculated Argand diagram to the experimental points. At each temperature an estimate of the contribution from the process not being adjusted was calculated from temperature dependency equations for its parameters and added to the calculated values for the process being adjusted. The τ value was found by explicitly solving equation (1) for τ at each frequency using the experimental ϵ^* on the l.h.s. and the chosen ϵ_R , ϵ_U , $\bar{\alpha}$ and $\bar{\beta}$ on the r.h.s. (and the calculated estimates of the contribution to ϵ^* of the process not being adjusted). Constancy of τ with

frequency in one Argand plot was also taken as a criterion of proper choices of ϵ_R , ϵ_U , $\bar{\alpha}$ and $\bar{\beta}$. The parameters at a number of temperatures for a given process were then fitted to temperature dependency equations of the following forms:

$$\epsilon_U^0 = \epsilon_U^0 + s_U(T - T_0) \quad (2a)$$

$$\epsilon_R = \epsilon_R^0 + s_R(T - T_0) \quad (2b)$$

$$\bar{\alpha} = \bar{\alpha}_0 + \bar{\alpha}'(T - T_0) \quad (2c)$$

$$\bar{\beta} = \bar{\beta}_0 + \bar{\beta}'(T - T_0) \quad (2d)$$

$$\log \tau = A/(T - T_\infty) + B \quad (2e)$$

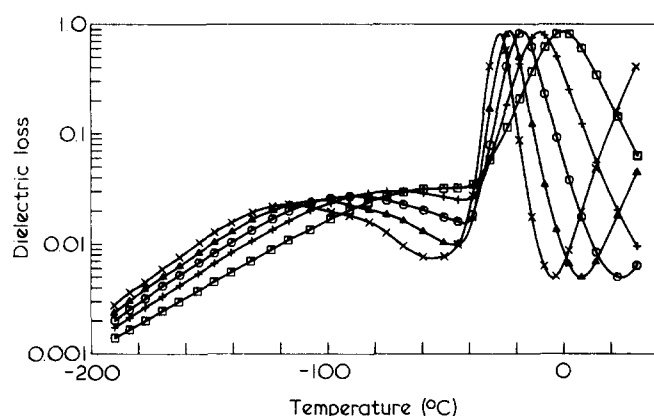


Figure 4 Experimental data for dielectric loss factor of amorphous 6B-6 homopolymer plotted logarithmically versus temperature. See Figure 1 for frequencies. Log plot is used because of greater disparity between loss values of γ , β processes compared to Figure 2

Several iterations of fitting the γ and then the β process were carried out. The sets of parameters determined for the γ process for each of the samples are listed in Table 2 and those for the β process in Table 3.

A typical result of the fitting is shown in Figures 5 and 6 where the dielectric constant and loss curves calculated from equations (2a)–(2e) and the parameters of Tables 2 and 3 are compared with the experimental results for the 80–20 copolymer.

Several further comments on the fitting are appropriate. All of the specimens began to show conductance loss at high temperature and low frequency, as evidenced by upswing of the loss factor. No attempt was made to accommodate this in the fitting. In the crystalline samples some upswing in dielectric constant is also noticed. This is perhaps associated with interfacial polarization accompanying the conductance process. Finally, in all of the specimens the loss versus temperature plots at the lowest frequency (10 Hz) indicate a resolution of the γ process into two processes, with a small feature appearing between the main γ process and the β process.

Table 2 Relaxation spectra for the γ process^a

| Sample | ϵ_U | | ϵ_R | | $\bar{\alpha}$ | | | $\log \tau$ | | |
|--------|----------------|-------|----------------|--------|------------------|-----------------|---------------|-------------|-------|------------|
| | ϵ_U^0 | S_U | ϵ_R^0 | S_R | $\bar{\alpha}_0$ | $\bar{\alpha}'$ | $\bar{\beta}$ | A | -B | T_∞ |
| 6-6 | 2.64 | 0.0 | 3.01 | 0.001 | 0.269 | 0.0027 | 1.0 | 2514 | 18.87 | 0.0 |
| 90-10 | 2.67 | 0.0 | 3.02 | 0.0012 | 0.263 | 0.0022 | 1.0 | 2368 | 18.30 | 0.0 |
| 80-20 | 2.62 | 0.0 | 3.01 | 0.0011 | 0.261 | 0.0024 | 1.0 | 2470 | 18.82 | 0.0 |
| 60-40 | 2.72 | 0.0 | 3.16 | 0.0 | 0.246 | 0.0019 | 1.0 | 2733 | 20.20 | 0.0 |
| 6B-6 | 2.63 | 0.0 | 2.92 | 0.0006 | 0.226 | 0.0010 | 1.0 | 2444 | 17.82 | 0.0 |

^a Parameters for equation (2) of text. $T_0 = 173$ K

Table 3 Relaxation spectra for the β process^a

| Sample | ϵ_U | | ϵ_R | | $\bar{\alpha}$ | | | $\log \tau$ | | | T_g^b |
|--------|----------------|--------|----------------|---------|----------------|-----------------|---------------|-------------|-------|------------|---------|
| | ϵ_U^0 | S_U | ϵ_R^0 | S_R | $\bar{\alpha}$ | $\bar{\alpha}'$ | $\bar{\beta}$ | A | -B | T_∞ | |
| 6-6 | 3.06 | 0.0010 | 3.85 | -0.0018 | 0.132 | 0.0016 | 1.0 | 783.0 | 17.76 | 180 | 224 |
| 90-10 | 3.08 | 0.0012 | 4.01 | -0.0008 | 0.176 | 0.0028 | 1.0 | 590.3 | 15.00 | 182 | 221 |
| 80-20 | 3.07 | 0.0010 | 4.25 | 0.0 | 0.218 | 0.0034 | 1.0 | 550.0 | 13.81 | 180 | 220 |
| 60-40 | 3.16 | 0.0 | 4.75 | 0.0 | 0.343 | 0.0022 | 1.0 | 802.2 | 15.73 | 170 | 221 |
| 6B-6 | 2.95 | 0.0006 | 6.62 | -0.014 | 0.802 | 0.0010 | ^c | 687.7 | 13.83 | 190 | 240 |

^a Parameters for equation (2) of text. $T_0 = 223$ K

^b T_g is defined here as the temperature at which $\log \tau = 0$

^c For this sample, $\bar{\beta} = 0.359$, $\bar{\beta}' = 0.0025$

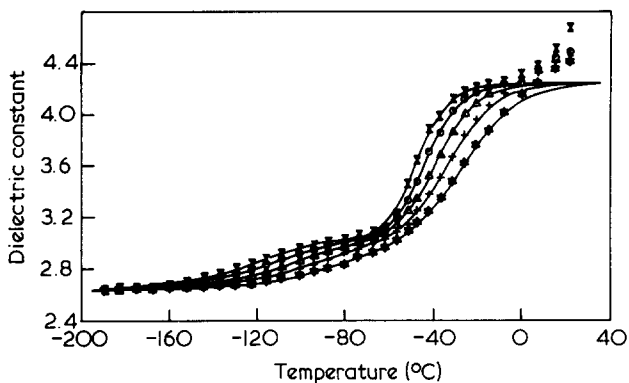


Figure 5 Phenomenological data-fitting. Dielectric constant of 80-20 copolymer versus temperature. Points are experimental, curves are calculated using equation (1) of text and parameters of Tables 2 and 3. x, 10; O, 100; Δ, 1000; +, 10 000; *, 100 000 Hz

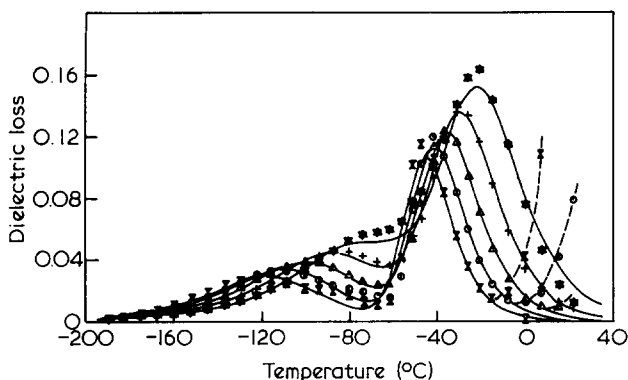


Figure 6 Phenomenological data-fitting. Dielectric loss factor of 80-20 copolymer versus temperature. Points are experimental, curves are calculated using equation (1) of text and parameters of Tables 2 and 3. Dashed curves are high temperature conductance loss not fitted. x, 10; O, 100; Δ, 1000; +, 10 000; *, 100 000 Hz

There has been no attempt to include this in the fitting and the γ process has been treated as a single process. Measurements of the dielectric constants of 6-6, 5-7 and 6-10 homopolymer melts are summarized in Table 4. No dispersion loss was detected and these represent unrelaxed values.

DISCUSSION

The β relaxation

The results verify that the β relaxation indeed has an amorphous phase origin. Although interpretation of relaxation strengths is considered later, it is noteworthy here that when the bulk specimen values are plotted against crystallinity as shown in Figure 7, it is evident that the process is associated with the amorphous fraction.

To establish the effects of crystallization on chain dynamics by examining the central relaxation time behaviour, the $\log \tau$ values (both the individual values from the final cycle of isothermal fits and the curves calculated from equation (2e), and the parameters of Table 3) for the β process are compared for the various samples via a $1/T$ plot in Figure 8. The predominant feature is simply a result of the fact that the chemical structure of the chain is changing along with crystallinity. The glass temperature of the 6B-6 homopolymer is some 15° higher

than that of the amorphous fraction in the 6-6 homopolymer (Table 3). The $\log \tau$ curve for 6B-6 is significantly above (at larger τ) that for the 6-6 homopolymer. However, there are other noteworthy effects. At high temperature (decreasing $1/T$ in Figure 8) there is a progression in the copolymers towards longer τ with increasing 6B content, no doubt due to the chemical

Table 4 Dielectric constant of homopolymer melts^a

| Polymer | ϵ_R^0 | S_R (°C ⁻¹) | Δ (°C) |
|---------|----------------|---------------------------|---------------|
| 6-6 | 4.95 | -0.010 | 60-80 |
| 5-7 | 4.95 | -0.012 | 60-80 |
| 6-10 | 4.27 | -0.080 | 75-100 |

^a Listed are the dielectric constants measured at 10 kHz and 75°C along with the temperature coefficient (S_R) and the temperature interval over which the measurements were made (Δ)

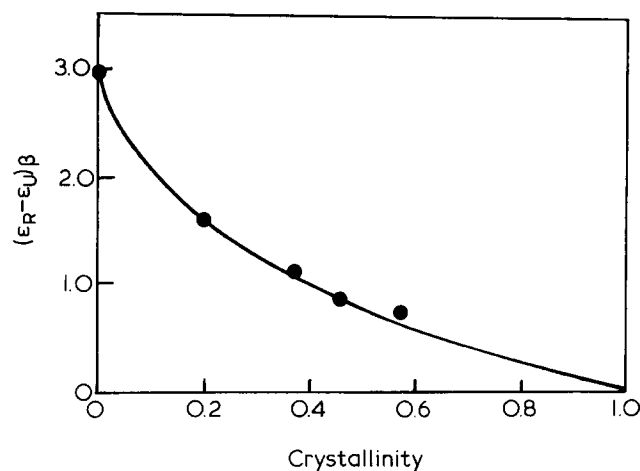


Figure 7 Relaxation strengths of β process versus crystallinity (data from Table 3 at 0°C)

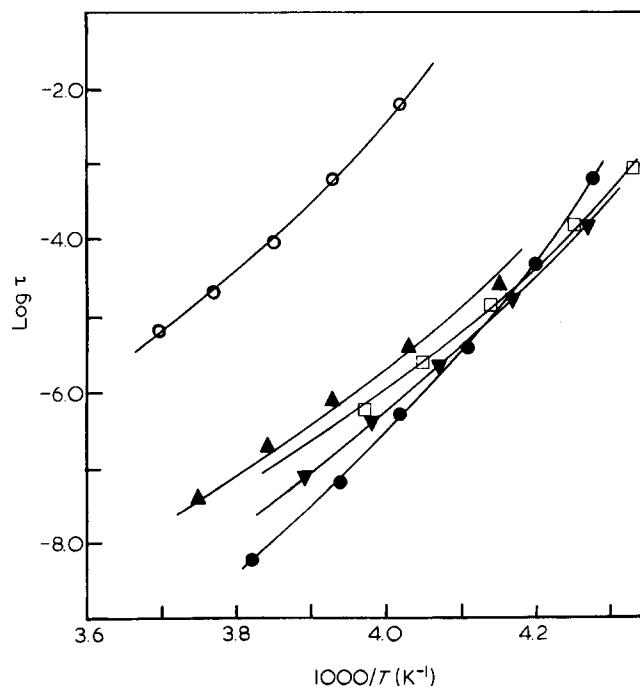


Figure 8 Central relaxation time versus $1/T$ for β process (O, 6B-6; Δ, 60-40; □, 80-20; ◀, 90-10; ●, 6-6). Curves are calculated from parameters of Table 3, points are from isothermal fits of ϵ'' versus ϵ'

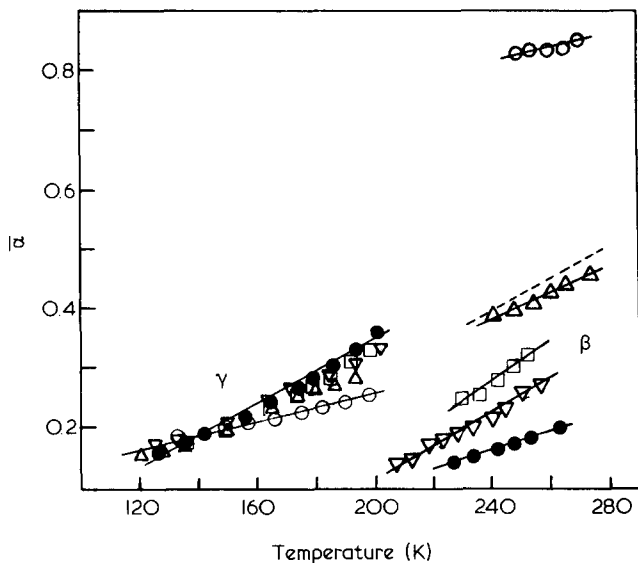


Figure 9 Width parameter $\bar{\alpha}$ versus temperature (○, 6B-6; △, 60-40; □, 80-20; ▽, 90-10; ●, 6-6) for both γ and β processes. Curves are calculated from parameters of Tables 2 and 3. Points are from isothermal fits of ϵ'' versus ϵ' . For all samples except 6B-6, skewness parameter $\bar{\beta}=1$. For β process for 6B-6, $\bar{\beta}$ is shown as dashed curve

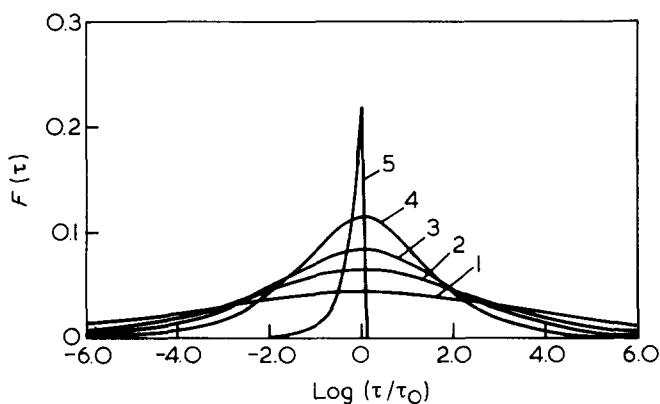


Figure 10 Distribution of relaxation times for the β process versus $\log \tau/\tau_0$ at 250K. Calculated from the parameters of Table 3. (1=6-6; 2=90-10; 3=80-20; 4=60-40; 5=6B-6)

structure effect on glass temperature. However, there is also an opposite progression of slopes. In fact the 6-6 homopolymer curve crosses over those for the copolymers, probably a result of the opposing tendency for the more highly crystalline polymers to show increased constraints on amorphous segment motion. Thus, a hypothetical non-crystalline 6-6 homopolymer would probably have a $\log \tau$ curve that would merge with the actual one at high temperature but possess a lower slope and be far below it (at smaller τ) at low temperature.

Considering the effect of crystallization on relaxation width, the β relaxation in 6B-6 homopolymer has a shape behaviour very similar to the glass-rubber relaxation in other completely amorphous polymers^{23,26}. The relaxation is relatively narrow and its shape dominated by the skewness parameter ($\bar{\beta} \approx 0.4-0.5$) but with a value of $\bar{\alpha}$ slightly less than one (0.8-0.9). In the crystalline polymers the process is more broad and is dominated by the symmetric broadening parameter $\bar{\alpha}$. It was not necessary to invoke in the curve fitting a value of $\bar{\beta} < 1$ in any of the crystalline samples (all of the copolymers and 6-6 homo-

polymer). The $\bar{\alpha}$ parameters for all of the samples are plotted against temperature in Figure 9 (the $\bar{\beta}$ parameter of the 6B-6 homopolymer is also shown). From this it is evident that the β relaxation is extremely broad in the crystalline samples. The width is temperature dependent, the process becoming narrower with increasing temperature. There is a progression through the samples with the process narrower in the less crystalline specimens. However, the largest effect is the onset of crystallization in going from completely amorphous 6B-6 homopolymer to the 60-40 copolymer ($\approx 20\%$ crystallinity). To illustrate the profound differences between the relaxation shapes of the crystalline and amorphous polymers, the relaxation time distributions for the copolymers and homopolymers are compared in Figure 10. The distributions were calculated from the formulae given by HN²³, using the parameters in Table 3. The same temperature (250 K) is used for all, but they are displayed relative to the central relaxation time τ , which is different among the polymers at the same temperature. In summary it appears that the act of crystallization has significant influence on the broadness of the relaxation associated with long-range segmental motion in the amorphous fraction.

The γ relaxation

Here, the effects of crystallization are established by considering the phase origin. The bulk specimen relaxation strengths for the γ process are plotted against crystallinity in Figure 11 which appears to show that there is not an obvious correlation between the process and either phase content. However, it seems unlikely that the process is not at all phase specific and a much more plausible interpretation that provides considerable evidence in favour of the suggestion of localized molecular motion is easily constructed. It has often been suggested that the process involves conformational transitions that are possible only in certain chemical structures, linear aliphatic sequences of a certain minimum size being one specific hypothesis¹¹. The fact that the γ process is weakest in the 6B-6 homopolymer supports this idea as it

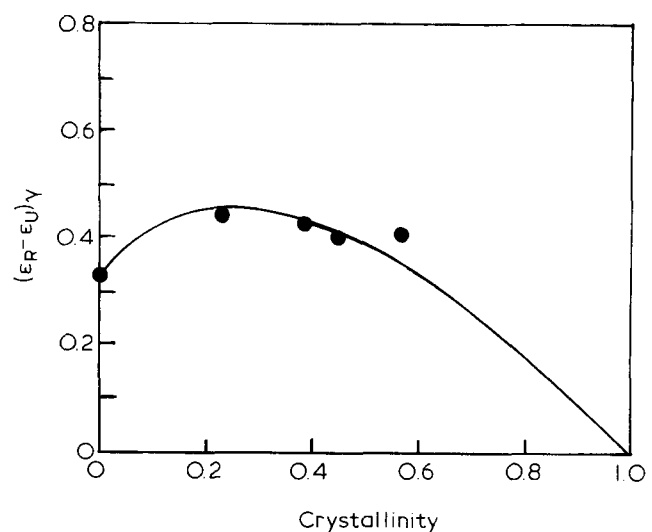


Figure 11 Relaxation strength of γ process versus crystallinity (data from Table 2 at -60°C). The curve is calculated from equation (3) of text and assumes that the relaxation occurs only in amorphous fraction and that 6-6 units contribute 2.5 times the strength of 6B-6 units

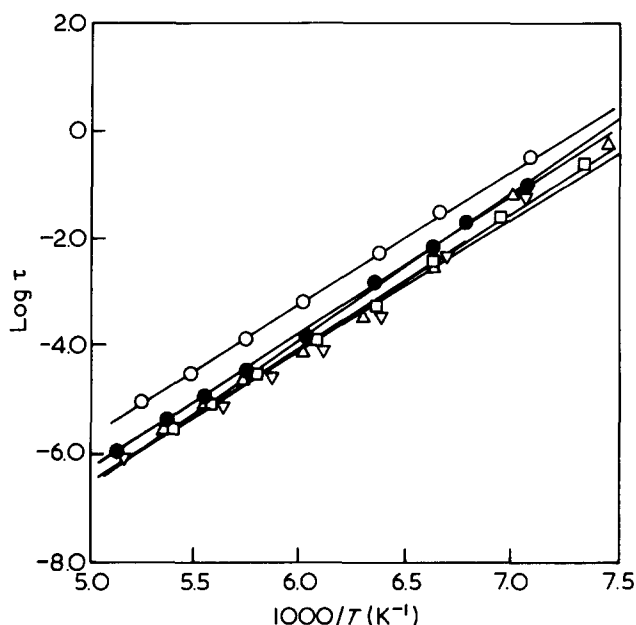


Figure 12 Central relaxation time versus $1/T$ for γ process. (\circ , 6B-6; \triangle , 60-40; \square , 80-20; ∇ , 90-10; \bullet , 6-6). Curves are calculated from parameters of Table 2, points are from isothermal fits of ϵ'' versus ϵ'

has the minimum number of appropriate sequences if it is true that the 2,5-hexane linkages are not admissible of the motion. The opposing effects of chemical unit content and crystallinity are easily quantified in a simple model. It is assumed that relaxation strength contributions can be assigned locally to chain structural units and a strength \bar{S}_B is assigned to a 6B-6 unit. If it is also assumed that the 6B-6 units are completely excluded from the crystals and that the overall strength is the sum of all of the strengths of units in the amorphous fraction only, then the total strength S ($=(\epsilon_R - \epsilon_U)_\gamma$) divided by the total number of units N (6-6 plus 6B-6) in the whole sample is given by:

$$S/N = \bar{S}_A((1-X) - P_B) + \bar{S}_B P_B \quad (3)$$

where X is the degree of crystallinity and P_B is the chemical composition of the copolymer expressed as the fraction of B (6B-6) units in the total of A (6-6) and B units (i.e., $P_B = 0.40$ for the 60-40 copolymer). As N is to a good approximation independent of chemical composition and crystallinity in these isomeric specimens, the r.h.s. of equation (3) should represent relaxation strength variation with X and P_B under these assumptions. The relation between X and P_B has been established experimentally (Table 1) and as $N\bar{S}_B = 0.33$ is directly experimentally available from the 6B-6 homopolymer, this is effectively a one-parameter equation. The solid curve in Figure 11 was calculated using $\bar{S}_A = 2.5\bar{S}_B$ and a plot of X versus P_B constructed from Table 1. The calculated curve reasonably reflects the measured relaxation strength behaviour. If the 6B part of a 6B-6 unit contributed nothing to S_B but the 6 diol units in 6-6 contributed slightly more than the 6 acid units, then the indicated \bar{S}_B/\bar{S}_A ratio appears reasonable.

In considering the dynamics associated with the γ process, the $\log \tau$ temperature behaviour is Arrhenius in nature, in contrast to the Vogel or WLF character of the β process. As seen in Figure 12, there is little effect of crystallization or chemical structure on the activation

parameters, the activation energies being 45–50 kJ mol⁻¹. With respect to the relaxation breadth, symmetric ($\bar{\alpha} < 1$) broadening and no skewing ($\bar{\beta} = 1$) accounts for the relaxation shape. The γ process is extremely broad (as shown in Figure 9 where the $\bar{\alpha}$ parameters are plotted) for all samples, not just the crystalline ones, and the process sharpens with increasing temperature. Although there seems some tendency for increasing temperature dependence of $\bar{\alpha}$ as crystallinity increases, the salient feature is that the breadth is much less dependent on crystallinity for the γ process than for the β process.

Another noteworthy feature is that an isochronal plot of ϵ'' versus temperature for the γ process in polyethylene and in the linear polyesters is skewed in the sense that the low-temperature side has a slowly decreasing 'tail'. This tail is sometimes postulated to be the result of a poorly resolved additional process occurring in the crystal fraction. Actually this tail is a phenomenological feature resulting from the narrowing of the γ process as temperature increases (increasing $\bar{\alpha}$ with temperature, Figure 9). In the polyesters an additional process is becoming resolved at low frequency (10 Hz), but the lesser process occurs at higher temperature, not lower, and is not involved in the shape of the low-temperature tail. Furthermore, the added feature in the γ process found here occurs in all of the specimens, crystalline and non-crystalline.

In summary, the marked independence of activation parameters and relaxation width on the presence or degree of crystallization together with the dependence of relaxation strength on chemical constitution as well as crystallinity are strong evidence for a localized motion origin of the γ process. The behaviour with respect to activation energy and relaxation width is very similar to that found previously for dipole decorated polyethylenes where widely varying crystallization conditions and presence or absence of branching have little effect on the width parameters for the γ relaxation³. The low-temperature tail in PE is also obviously due to the narrowing of the process with increasing temperature. The only noteworthy difference in the γ processes in PE and polyesters is the extra process becoming resolved between the γ and β at low frequency in the latter polymers.

Relaxation strength and correlation factor

One of the major aims of this study is to attempt to establish whether the crystal fraction suppresses amorphous relaxation in an equilibrium sense by removing configurational states of amorphous segments that are available in unconstrained chains. Probably the best way to express this effect would be in terms of the dipole correlation factor, g . For a single-phase system it probably can be calculated with useful accuracy from the measured relaxed and unrelaxed dielectric constants (ϵ_R, ϵ_U), the dipole number density \bar{N} and the dipole moment of the relaxing unit μ_0 using the Kirkwood-Onsager equation²⁷:

$$\epsilon_R - \epsilon_U = \left(\frac{3\epsilon_R}{2\epsilon_R + \epsilon_U} \right) \left(\frac{\epsilon_U + 2}{3} \right)^2 \frac{4\pi\bar{N}\mu_0^2 g}{3kT} \quad (4)$$

This equation has sometimes been applied to two-phase semi-crystalline polymers by still identifying ϵ_R and ϵ_U

Table 5 Amorphous-phase dielectric constant ϵ_1 , calculated from lamellar mixture bounds (6–6 polyester homopolymer as an example)

| Temperature (°C) | ϵ_2 | ϵ_R (measured) | ϵ_1 (upper) ^a | ϵ_1 (lower) ^b |
|---------------------------------|--------------|-------------------------|-----------------------------------|-----------------------------------|
| -100 (γ process) | 2.771 | 3.01 ^c | 3.345 (3.32) | 3.345 (3.39) |
| -20 ($\gamma + \beta$ process) | 2.721 | 3.80 ^d | 5.564 (5.24) | 5.604 (7.92) |

^a Using equation (7) together with equations (5) and (6) of text (the values in parentheses are calculated from equation (5) directly). Upper refers to upper bound equation

^b Using equation (8) together with equations (5) and (6) of text (the values in parentheses are calculated from equation (6) directly). Lower refers to lower bound equation

^c From Table 2

^d From Table 3

with the specimen measured values but taking $\bar{N} = N_a/V$ where N_a is the number of amorphous dipoles (if the process is supposed to have that origin) and V as the specimen volume. This expedient ignores the discontinuities in dielectric constant across the polar, non-polar phase boundaries and can only be correct if the phase dielectric constants are very similar, which in turn implies $\epsilon_R \approx \epsilon_U$. The best way to resolve this problem is to treat the semi-crystalline polymer as a macroscopic two-component mixture and attempt to reliably assign values to the macroscopic dielectric constant of each phase from the bulk specimen measured value. Once this is done then the Kirkwood–Onsager equation can be used to calculate the correlation factor from the dielectric constant of the desired phase. As the dielectric constant of the non-polar, non-relaxing phase can usually be estimated reliably, the problem really reduces to backing-out the dielectric constant of the polar phase from measurements on the bulk specimen. This is not straightforward because the relations for forming the dielectric constant of a mixture from the components are known only under a few simple circumstances (such as dilute suspension of spheres²⁸). Recently, however, it has been shown²⁹ that for semi-crystalline polymers of lamellar local structure, reasonably tight bounds on the mixture dielectric constant can be derived. In fact here the restrictions are sufficient to retrieve the amorphous phase dielectric constant from the bulk one without uncertainty. If horizontal and vertical direction dielectric constants appropriate to lamellar structures are formulated as:

$$\epsilon_H = (1 - X)\epsilon_1 + X\epsilon_2 \quad (5)$$

$$1/\epsilon_V = (1 - X)/\epsilon_1 + X/\epsilon_2 \quad (6)$$

where ϵ_1 and ϵ_2 are the amorphous and crystal phase dielectric constants respectively and X is the degree of crystallinity, then for:

$$\epsilon(\text{upper}) = (2\epsilon_H + \epsilon_V)/3 \quad (7)$$

$\epsilon(\text{upper})$ is an upper bound to the mixture constant in a macroscopic randomly oriented sample²⁹. Similarly for

$$1/\epsilon(\text{lower}) = (2/\epsilon_H + 1/\epsilon_V)/3 \quad (8)$$

$\epsilon(\text{lower})$ is a lower bound. For the specimens here, values of ϵ_1 calculated from $\epsilon(\text{measured}) = \epsilon(\text{upper})$ using

equation (7) via equations (5) and (6), and ϵ_2 and X do not differ significantly from values of ϵ_1 calculated from $\epsilon(\text{measured}) = \epsilon(\text{lower})$ using equation (8). The crystal dielectric constant is assumed to be isotropic and was calculated from the specimen unrelaxed dielectric constant using a density correction. The Clausius–Mosotti relation for the crystal dielectric constant ϵ_2 is:

$$(\epsilon_2 - 1)/(2\epsilon_2 + 1) = Pd_2/M \quad (9)$$

where P is the molar polarization, d is the density and M the molecular weight of the polarizable unit. Similarly for the unrelaxed specimen dielectric constant ϵ_U :

$$(\epsilon_U - 1)/(2\epsilon_U + 1) = Pd_s/M. \quad (10)$$

Thus, ϵ_2 may be calculated from ϵ_U and the ratio of the crystal and specimen densities d_2/d_s . The latter ratio was assumed to be equal to the room temperature value and the individual values of d_2 and d_s were those used in computing the degree of crystallinity. At temperatures $< T_g$ the value of ϵ_U was taken as the value of ϵ_U from equation (2a) and the parameters of Table 2. At $T > T_g$, ϵ_U was calculated from the value of ϵ_U at T_g and a thermal expansion correction using the Clausius–Mosotti equation. The measured values of $\Delta V/\Delta T$ of 5.0×10^{-4} , 8.5×10^{-4} , 3.8×10^{-4} and $5.9 \times 10^{-4} \text{ cm}^3 \text{ } ^\circ\text{C}^{-1}$ were used for 6–6, 6B–6, 5–7 and 6–10 polyesters, respectively. The 6–6/6B–6 copolymers were assumed to have the same thermal expansions as 6–6 homopolymer.

With reasonable estimates of ϵ_2 available, equations (7) and (8) were used to calculate lower and upper bounds to ϵ_1 from the ϵ_R values constructed from the parameters of Tables 2 and 3 and equation (2b). A sample result is shown in Table 5. The amorphous phase dielectric constant is well specified using these bounding equations. Equations (5) and (6) are also bounds themselves, although much less effective than equations (7) and (8). Equation (5) constitutes a mixture rule that is often invoked. Table 5 shows that for the γ process the values of ϵ_R and ϵ_2 are so close that the bounds or mixture rules used do not effect the derived ϵ_1 . However, for the $\gamma + \beta$ processes the lamellar mixture upper and lower bounds (equations (7) and (8)) give similar values for ϵ_1 but the ‘parallel’ and ‘series’ capacitor formulae (equations (5) and (6)) or mixture rules give very poor results.

With the amorphous phase dielectric constants determined on a rational and reliable basis, the Kirkwood–Onsager equation (equation (4)) can be applied to the calculation of the correlation factor, g . The unrelaxed value for the amorphous phase was determined from the specimen ϵ_U in a manner similar to that for ϵ_2 discussed previously, but the amorphous to sample density ratio, d_1/d_s , was used. A dipole moment of 1.72D was used for the ester group. The correlation factors thus calculated are plotted in Figure 13 for the 6–6, 5–7 and 6–10 homopolymers and in Figure 14 for the copolymer series. The data used for the solid 5–7 and 6–10 polymers is from Part 4 of this series³⁰ and from Table 4 for all of the melts.

It is important to establish what the appropriate physical interpretation of the correlation factor is likely to be. The correlation factor can be written as

$$g = 1 + \sum_j \langle \cos \gamma_{ij} \rangle \text{ where } \langle \cos \gamma_{ij} \rangle \text{ is the average of the}$$

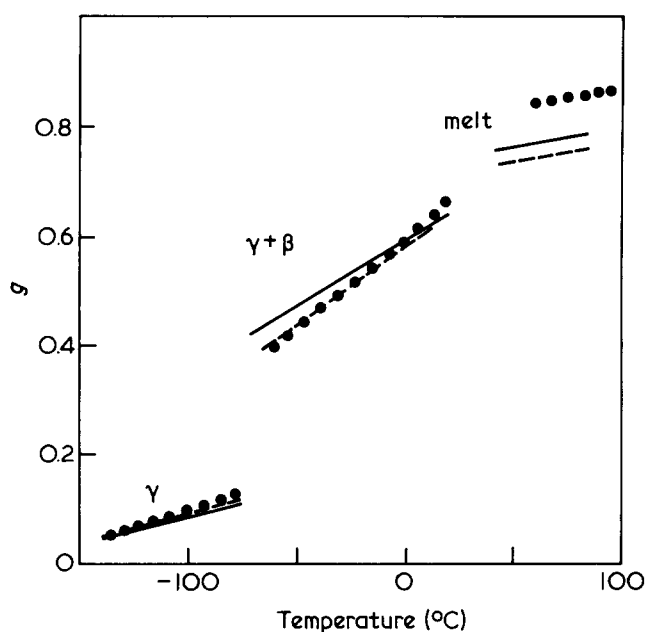


Figure 13 Amorphous fraction dipole correlation factor, g , versus temperature for solids and melts of 6-6 (—), 5-7 (---) and 6-10 (●●●) homopolymers. Correlation factor is calculated from amorphous-phase dielectric constant using the Kirkwood-Onsager equation. Amorphous dielectric constant is calculated from specimen values using lamellar composite bounding equations

projection of a dipole j on that of a typical central one, i . The intramolecular contribution to the sum in polymer chains has been treated in detail³³. In the polymers here the dipoles are sufficiently separated by intervening groups that the direct intramolecular contribution to the correlation may be small. This is confirmed by Figure 13 where there is little difference between the g factors of the 6-6 and 5-7 homopolymers, while intramolecular correlation effects would be expected to be different. The planar zig-zag conformation (favoured with lowering of temperature) would increase the correlation factor in the 5-7 polymer but decrease it in the 6-6 (and 6-10). That a small degree of intermolecular dipole-dipole correlation may be noticeable is suggested by the melt results where none of the correlation factors in the melt are exactly 1 (Figure 13) but the 6-10 polymer which is more dipole dilute is closer to unity.

An overall interpretation of the solid $\gamma + \beta$ process results that is probably the most appropriate is the following. Consider a dipole that is sufficiently uncoupled from other dipoles that its orientational states have no direct dependence on the orientational states of the others. However, if the orientational states available to it are separated in energy then the correlation factor will be < 1 and temperature dependent. For example, site theories^{31,32} for two sites separated by energy, U , reduce the general formulation to

$$g = 2(1 - \cos \theta) e^{-U/kT} / (1 + e^{-U/kT})^2 \quad (11)$$

where θ is the angle through which the dipole re-orient. All of the solid specimens show a correlation factor significantly less than one and increasing with temperature. This is probably best viewed as resulting from the crystal phase inducing restrictions on amorphous chain re-orientation by removing available states or introducing significant energy differences between orientational states. With this in mind, further

discussion of the copolymer series results is desirable (Figure 14). The correlation factor for the $\gamma + \beta$ process in 6B-6 noncrystalline homopolymer is also significantly less than one. However, its g curve is well above those for the crystalline specimens and has a significantly less steep slope. Although it may well be that there is noticeable intramolecular correlation induced by the shorter and structurally distinct 6B units, it is also apparent that the onset of crystallization in the 60-40 polymer has a distinct effect on reducing the correlation factor. Therefore, both the comparison of solid samples with melts and the copolymer behaviour leads to the important conclusion that the presence of the crystal phase does inhibit amorphous chain re-orientation in an equilibrium sense.

Turning to the γ process it is evident that the correlation factors for the aliphatic 6-6, 5-7 and 6-10 homopolymers are virtually identical. In the interpretation that the γ process involves certain conformational sequences able to re-orient in the glass (for example, $\cdots TGTG'T \cdots \cdots TGTGT \cdots$ transitions¹²) the correlation factor is simply the fraction of amorphous dipoles in such a sequence but modulated by the possibility of the angular re-orientation being less than 180° and the presence of site energy differences. From the data it is not possible to resolve the temperature dependence of the γ process g values in Figure 13 into a site energy difference and a fraction of dipoles participating. However, it would appear that the fraction would have to be of the order of 15-20%. (In various dipole decorated polyethylenes this fraction is between 10 and 20%³.) This is perhaps consistent with the idea of only selected conformational sequences participating. However, in the context of the specific suggestion of $TGTGT$ re-orientations, this fraction seems higher than reasonable estimates of the number of such sequences found using equilibrium conformational statistics. In Figure 14 the progression of g towards lower values from the 6-6 homopolymer to the 6B-6 homopolymer is simply a manifestation on the difference in relaxation strength (i.e., availability of

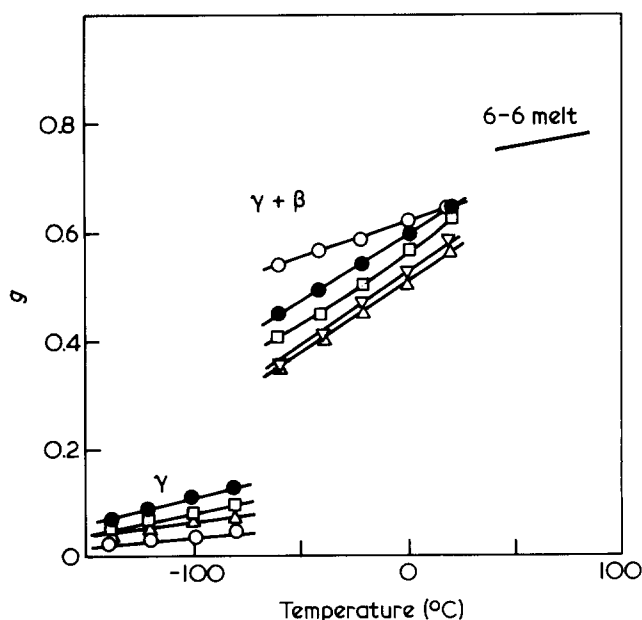


Figure 14 Amorphous fraction dipole correlation factor, g , versus temperature for copolymer series (see also caption to Figure 13). (○, 6B-6; △, 60-40; □, 80-20; ▽, 90-10; ●, 6-6)

suitable conformational sequences) postulated to occur between the 6-6 and 6B-6 units as discussed previously for the γ process.

Relation to other polymers

It has been demonstrated that for the β relaxation the presence of the crystal phase has a profound influence on the relaxation broadness and contributes to inhibiting the strength of the amorphous relaxation also (reduced g factor). While these effects are highly significant it is also apparent that in polymers such as LPE and POM they must be still more significant. It is appropriate to speculate that this is due to the ability of a crystalline α process to induce further amorphous phase immobilization beyond that present in crystalline polymers without an α process (or where it is ineffective in doing so). The underlying mechanism of the α process in polyethylene involves a translation of a CH_2 unit by $C/2$ along the c -axis (accompanied by 180° rotation)¹³ thus providing a means for crystal chain translation. It is reasonable to suppose that the availability of these translations at the crystallization temperature results in pulling amorphous chains more taut after crystallization than if they were not available⁹; i.e., isothermal thickening during crystallization is probably assisted by the α process and this isothermal thickening could well be accompanied by amorphous chain tightening and immobilization of a degree beyond that obtained without the presence of an α process. In branched polyethylene there is indeed an α crystal process and also a prominent β process, but in that case the crystal translations are limited to short ones by the exclusion of short chain (C_4) branches from the crystals and isothermal thickening and/or further amorphous chain tightening is, therefore, limited. In polyamides, aromatic polyesters and the aliphatic polyesters there is no α process to assist this further tightening and they all show broad but still prominent β relaxations.

ACKNOWLEDGEMENTS

The authors are indebted to the National Science Foundation, Division of Materials Research, Polymers Program (DMR 80 18326) for financial support of this

work. They are also grateful to Dr A. Hasan for making the measurements of the dielectric constant of 6-10 polyester in the melt.

REFERENCES

- 1 McCrum, N. G., Read, B. E. and Williams, G. 'Anelastic and Dielectric Effects in Polymer Solids' John Wiley and Sons, Inc., New York, 1967
- 2 Hoffman, J. D., Williams, G. and Passaglia, E. *J. Polym. Sci.*, C 1966, **14**, 173
- 3 Ashcraft, C. R. and Boyd, R. H. *J. Polym. Sci., Polym. Phys. Ed.* 1976, **14**, 2153
- 4 Boyd, R. H. and Biliyar, K. *Am. Chem. Soc., Polym. Prepr.* 1973, **14**, 329
- 5 Eby, R. K. *J. Acoust. Soc. Am.* 1964, **36**, 1485
- 6 Boyd, R. H. and Yemni, T. *Polymer Eng. Sci.* 1979, **19**, 1023
- 7 Illers, K. H. *Kolloid, Z. Z. Polym.* 1973, **251**, 394
- 8 Gray, R. W. and McCrum, N. G. *J. Polymer Sci., A-2* 1969, **7**, 1329
- 9 Boyd, R. H. *Polymer Eng. Sci.* 1979, **19**, 1010
- 10 Stehling, F. C. and Mandelkern, L. *Macromolecules* 1970, **3**, 242
- 11 Schatzki, T. F. *Amer. Chem. Soc. Meeting, Prepr.* 1965, **6**, 646
- 12 Boyd, R. H. and Breitling, S. M. *Macromolecules* 1974, **7**, 855
- 13 Mansfield, M. and Boyd, R. H. *J. Polym. Sci., Polym. Phys. Ed.* 1978, **16**, 1227
- 14 Beatty, C. L. and F. E. Karasz *J. Macromol. Sci.—Rev. Macromol. Chem.* 1979, **C17**, 37
- 15 Carothers, W. H. and Hill, J. W. *J. Am. Chem. Soc.* 1932, **54**, 1559
- 16 Fuller, C. S. and Frosch, C. J. *J. Am. Chem. Soc.* 1939, **61**, 2575
- 17 Fuller, C. S. *Chem. Rev.* 1940, **26**, 143
- 18 Ito, M., Nakatani, S., Gokin, A. and Tanaka, K. *J. Polym. Sci., Polym. Phys. Ed.* 1977, **15**, 605
- 19 Ito, M., Kubo, M., Tsuruta, A. and Tanaka, K. *J. Polym. Sci., Polym. Phys. Ed.* 1978, **16**, 1435
- 20 Pochan, J. M. and Hinman, D. F. *J. Polym. Sci., Polym. Phys. Ed.* 1975, **13**, 1365
- 21 Aylwin, P. A. *Ph.D. Dissertation* University of Utah, 1981
- 22 Boyd, R. H. and Aylwin, P. A. *Polymer* 1984, **25**, 323
- 23 Havriliak, S. and Negami, S. *Polymer* 1967, **8**, 161
- 24 Cole, K. S. and Cole, R. H. *J. Chem. Phys.* 1941, **9**, 341
- 25 Davidson, D. W. and Cole, R. H. *J. Chem. Phys.* 1950, **18**, 1417
- 26 Yoshihara, M. and Work, R. N. *J. Chem. Phys.* 1980, **72**, 5909
- 27 Kirkwood, J. G. *J. Chem. Phys.* 1939, **7**, 911
- 28 Maxwell, J. C. 'Treatise on Electricity and Magnetism' 3rd ed'. Clarendon Press, Oxford, 1904, Vol. I, p. 440
- 29 Boyd, R. H. *J. Polym. Sci., Polym. Phys. Edn.* in press
- 30 Boyd, R. H. and Hasan, A. A. *Polymer* 1984, **25**, 347
- 31 Hoffman, J. D. and Pfeiffer, H. G. *J. Chem. Phys.* 1954, **22**, 132
- 32 Frohlich, H. 'Theory of Dielectrics' 2nd ed., Oxford University Press, London, 1958
- 33 Flory, P. J. 'Statistical Mechanics of Chain Molecules' Interscience, New York, 1969