Effect of structural variation on the low temperature relaxation of aromatic polyesters

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The mechanical β relaxation in a variety of aromatic polyesters has been examined. Serial changes in the chemical structure have included the introduction of rigid double and triple bonds in the 4-carbon diol, changes in the number of methylene groups in the diol, and comparison of isophthalate and terephthalate polymers. All the polymers exhibit a mechanical β process. The effect of structural variables on peak temperature and intensity indicates that the relaxation is controlled by the structure of the glycol.

INTRODUCTION

The sub-ambient β relaxation of poly(ethylene terephthalate) and other polymers containing phenyl groups in the backbone has been the subject of numerous investigations over the past twenty years. Perhaps the most compelling reason for this sustained interest is the possible relationship between the molecular mobility represented by the β process and the mechanical toughness of these materials at temperatures considerably below the glass transition.

The literature pertaining to the β relaxation of poly(ethylene terephthalate) has recently been reviewed[1]. Despite the variety of techniques and structural variations which have been utilized, no general consensus is available regarding the molecular mechanism of the process. An often-cited mechanism is restricted or hindered rotation about ester and methylene bonds.

Two pieces of evidence seriously question this proposal. Several studies[2 6] have confirmed a contribution to the β process by the crystalline phase, whereas the restraints imposed by the crystalline lattice would be expected to prohibit rotational motion. Rotation also implies a dynamic interconversion of *gauche* and *trans* isomers. However, it is generally felt that the *trans* and *gauche* isomers of the glycol give rise to separate resolvable components of the β relaxation[7–10]. In addition, a polyester with non-interconvertable *cis* and *trans* isomers also exhibits the β process, and each isomer has been identified with a component of the relaxation peak[11].

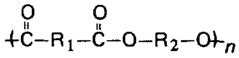
Therefore, it has alternatively been suggested[12] that the β process arises from cooperative wagging and rocking vibrations. These motions extend over several repeat units and involve *trans* or *gauche* isomers. The length of the participating chain segment has not been specified, but clearly can not be too long or the separate contributions of *gauche* and *trans* isomers could not be distinguished.

The chemical structure of the glycol is frequently used as an experimental variable, and indeed has provided the strongest evidence to support the assignment of *trans* and *gauche* components. The chemical structure of the diacid is varied less frequently but could provide an indication of phenyl group participation. Therefore, this study has utilized polyesters of both terephthalic acid, where the colinear ϕ-C bonds may mean that the benzene ring can be replaced by a virtual bond[13], and isophthalic acid, where the benzene ring is substituted non-symmetrically in the 1,3 positions.

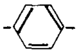
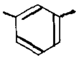
EXPERIMENTAL

Polyethylene terephthalate, poly(tetramethylene terephthalate), poly(tetramethylene isophthalate), poly(hexamethylene terephthalate) and poly(nonamethylene terephthalate) were kindly provided by the Tennessee Eastman Co. The polymers derived from unsaturated glycols were prepared by standard methods (*Table 1*). The acid chloride method was used to prepare the terphthalate and isophthalate polyesters with 2-butyne-1,4-diol. In a typical experiment, 20 mmol of the acid chloride was mixed with 20 mls of methylene chloride in a round-bottom flask which was provided with a stirrer, thermometer, dropping funnel and condenser. The flask was flushed with N_2 and the N_2 was allowed to bubble through the solution as a solution of 20 mmol of 2-butyne-1,4-diol in 4 g of pyridine was added dropwise. Following

Table 1 Aromatic polyesters for torsional braid analysis



$$\left[\overset{O}{\overset{\|}{C}}-R_1-\overset{O}{\overset{\|}{C}}-O-R_2-O\right]_n$$

Code	R_1	R_2	Morphology	T_M(K)
P4MT		$CH_2-CH_2-CH_2CH_2$	Semicrystalline	495
P4C=CT		$CH_2-CT=CH-CH_2$	Semicrystalline	470
P4C≡CT		$CH_2-C\equiv C-CH_2$	Semicrystalline	430
P4MI		$CH_2-CH_2-CH_2-CH_2$	Semicrystalline	410
P4C=CI		$CH_2-CH=CH-CH_2$	Amorphous	–
P4C≡CI		$CH_2-C\equiv C-CH_2$	Amorphous	–

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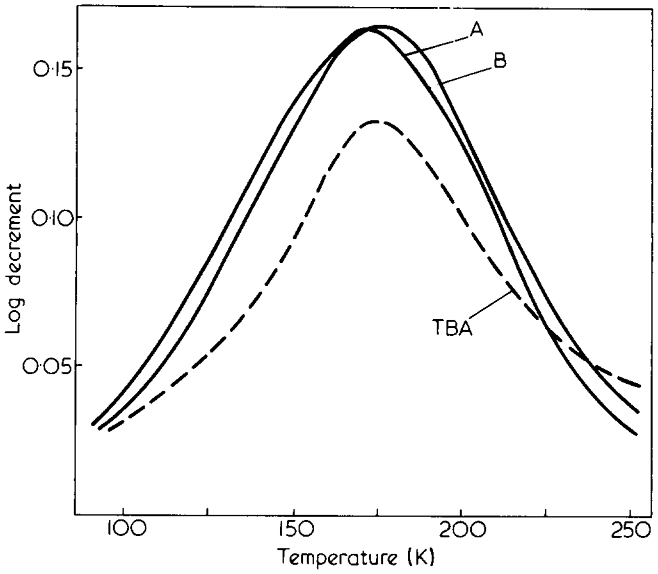

Figure 1 Effect of crystallinity on the β relaxation of P4MT. A, quenched; B, 3 h at 100°C; a torsional braid specimen (TBA) is included for comparison

the addition of the diol in pyridine, the temperature was raised to 60°C for 1 h and then to 150°C for 1–2 h. On cooling, the resultant polymer was alternately washed with water and methanol. Standard transesterification methods were used to prepare polymers from 2-butene-1,4-diol or propane-1,3-diol and dimethyl isophthalate or dimethyl terephthalate[14]. The chemical structure of the polymers was verified by i.r. spectroscopy. Melting points given in *Table 1* were determined by d.s.c. measurements.

Films of the unsaturated polymers were brittle so torsional braid specimens were prepared for dynamic mechanical analysis. The isophthalates were cast on the glass braid support from chloroform and mixtures of chloroform and trifluoroacetic acid were used as solvents for the terephthalates. The latter showed a loss peak due to residual TFA at about 320K. Annealing the specimens at 100°C in vacuum for 3 h eliminated the solvent peak, but caused some of the specimens to crystallize (*Table 4*).

Films of P2MT, P4MT, P4MI, P6MT and P9MT were prepared by compression moulding. Films were moulded at about 10°C above the melting point in a laboratory press between Teflon-coated aluminium sheets. The samples were kept at temperature for 30 sec under a pressure of 4×10^4 p.s.i. then quenched in ice water.

Dynamic mechanical measurements were made with an inverted free oscillating torsional pendulum at a frequency of about 1 Hz over the temperature range 90 to 400K.

RESULTS AND DISCUSSION

Crystallinity

Many of the polyesters are crystallizable. P4MT and P4MI were chosen for an examination of the effect of crystallinity on the β relaxation. When quenched from the melt, both polymers show a β peak at approximately the same temperature (175K) and with the same intensity. A symmetrical peak is observed for P4MT while that of P4MI distinctly shows two components.

Heat treatment has little effect on the β peak of P4MT (*Figure 1*) although X-ray analysis showed that crystallinity has developed. The only change observed is a small but significant shift (10°) to higher temperatures. The crystalline regions are thought to contribute to the β process of polyesters but with less intensity than the amorphous regions. The absence of any significant change in intensity in P4MT with crystallinity is unexpected. The unusual mobility of the crystalline phase may be related to the high energy conformation of the glycol in the α crystalline structure (90°–*trans*–90°)[15]. Whatever the reason, this mobility is probably responsible for the reversibility of the observed crystal-crystal phase transition in P4MT[16].

In contrast to P4MT, the shape of the β peak of P4MI changes significantly upon cyrstallization (*Figure 2*) in a manner similar to that observed for P6MT[8]. The higher temperature component selectively decreases in intensity which suggests that this contribution comes from the crystallizable chain segments. Since P4MI probably crystallizes in an extended conformation, the high temperature component is associated with the *trans* conformation and the lower temperature with the *gauche* conformation.

Loss curves for torsional braid specimens of P4MT and P4MI are included in *Figures 1* and *2*. These specimens have been subjected to the same heat treatment as the annealed films, i.e. 3 h at 100°C. Comparison of the loss curves of the film and braid shows that the absolute values of the logarithmic decrement are lower for the braid specimen, but the general shape of the loss curve and the temperature of the peak are the same.

Glycol stiffness

Chain flexibility was varied by introducing unsaturation into the glycol. Six polyesters were prepared from butane diol, butene diol and butyne diol. The loss curves obtained with torsional braid specimens are shown in *Figures 3* and *4*. Two relaxation regions are observed, the α process or glass transition at higher temperatures and the β process in the range of 175–200K.

Some caution is necessary in comparing the glass transition temperatures because some of the specimens are partly crystalline (*Table 1*). In general the glass transition of polyesters broadens and moves to higher temperatures with increasing crystallinity, and the intensity is reduced. Therefore, the observed glass temperatures of the crystallizable polymers are not directly comparable to those of the amorphous polymers (*Table 1*). However, some trends can be observed. The isophthalates have a lower glass transition

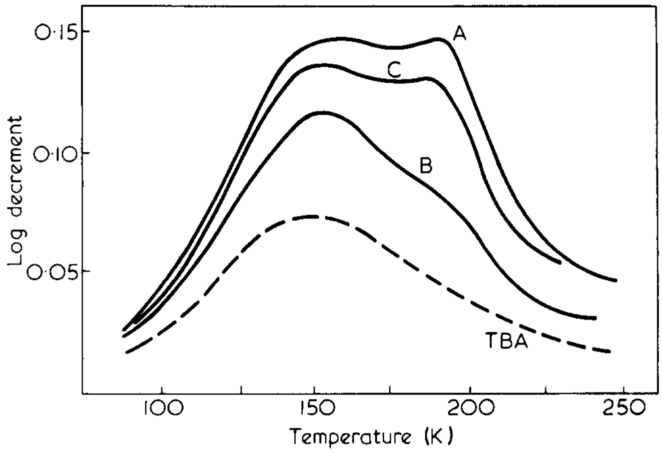

Figure 2 Effect of crystallinity on the β relaxation of P4MI. A, quenched; B, 3 h at 100°C; C, 24 h at 25°C. A torsional braid specimen (TBA) is included for comparison

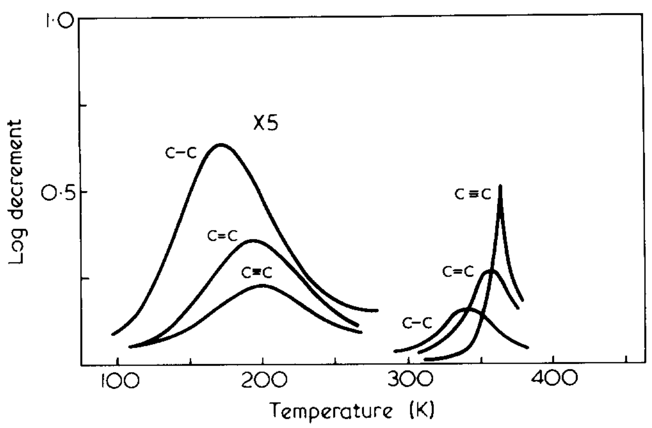

Figure 3 Relaxation curves for the terephthalate series: P4MT, P4C=CT and P4C≡CT

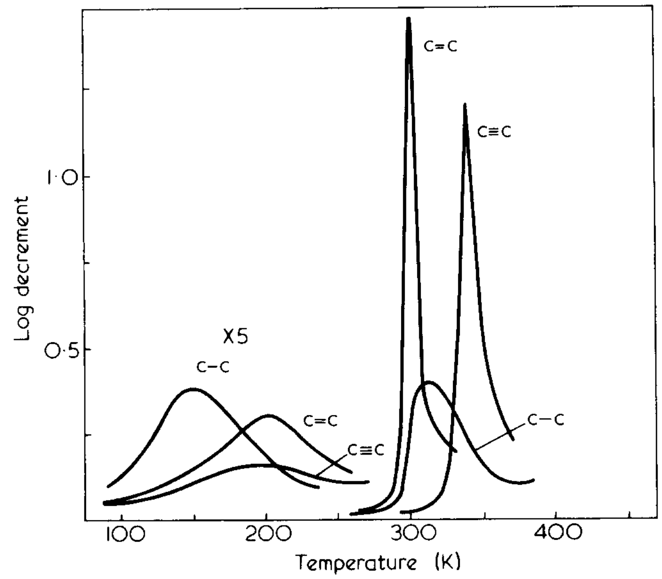

Figure 4 Relaxation curves for the isophthalate series: P4MI, P4C=CI and P4C≡CI

temperature than the corresponding terephthalates. This is attributed to a greater free volume content due to the assymmetrical repeat unit of the isophthalate series. Within a series, the glass temperatures increases in the order of C–C < C=C < C≡C. This trend probably reflects the combination of decreased inherent chain flexibility as unsaturation is introduced and the greater symmetry of the linear triple bond compared to the double bond.

The β relaxation region is approximately the same for the two series of polymers. The β relaxation is observed at approximately the same temperature for the C=C and C≡C specimens (200K), but at a lower temperature for the C–C polymers. The intensity of the β process decreases in the order C–C > C=C > C≡C for both the crystallizable (terephthalate) and non-crystallizable (isophthalate) series. It is clear from these results that the β process depends primarily on the chemical structure of the glycol while the aromatic diacid has much less effect. While this does not exclude participation of the phenyl group, the peak temperature and the intensity appear to depend predominantly on the structure of the glycol.

It is proposed that the temperature of the β process is related to the number of rotatable bonds in the glycol unit. In P4MT and P4MI rotations are possible about all three carbon-carbon bonds of the butane diol, while rotation cannot occur about the double and triple bonds of the butene and butyne diols. The trend in intensity is less easily understood. The observed intensity correlates empirically with the number of conformations available to the glycol unit, however considerations of local packing density may also be important.

Glycol length

The loss curves for a series of poly(methylene terephthalates) are shown in *Figure 5*. The shift to lower temperature with increasing number of methylene groups and the change in asymmetric shape reported previously[7] are observed. For poly(ethylene terephthalate) the peak is steeper on the high temperature side. As the number of methylene groups increases the asymmetry is reversed and for poly(nonamethylene terephthalate) two unambiguous peaks are observed of which the lower temperature one is slightly more intense. There is considerable evidence that the two components of the β process should be identified with *trans* and *gauche* conformations of the glycol. The decrease in relative intensity of the high temperature component with increasing glycol length is attributed to the decreasing probability of obtaining extended conformations as the number of methylene units increases.

The β peaks of the poly(methylene terephthalates) were obtained at a lower frequency than in previous studies and can be easily resolved into two Gaussian components, β_t and β_g. The temperatures of the β_t and β_g components are plotted in *Figure 6*. Included in the plot are the two components of the β process of P4MT and the unresolved β peak of the unsaturated polyesters, the latter plotted as $n = 3$, since one of the bonds is not rotatable. These points fall on the same curve as the poly(methylene terephthalates) and provide additional evidence that the β process is controlled by the chemical structure of the glycol.

CONCLUSIONS

The effect of the chemical structure of glycol and diacid on the β relaxation of aromatic polyesters has been examined. The results lead to the conclusion that the relaxation is predominately controlled by the structure of the glycol. The relaxation can be resolved into two components identi-

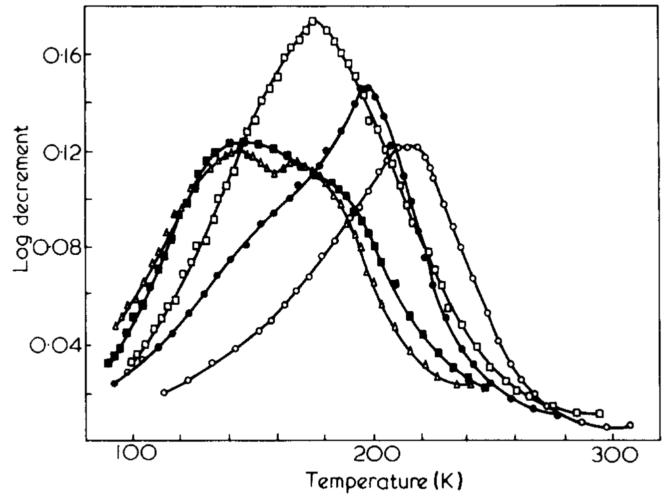

Figure 5 Loss curves at about 1 Hz for a series of poly(methylene terephthalates). ○, P2MT; ●, P3MT; □, P4MT; ■, P6MT; △, P9MT

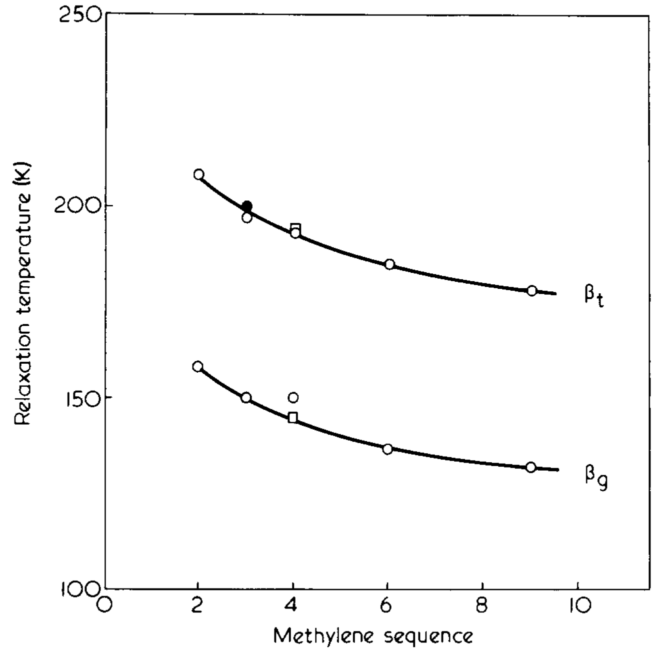

Figure 6 Dependence of the β_t and β_g components on the length of the methylene sequence: ○, poly(methylene terephthalate) series; □, P4MI; ●, polymers from butene diol and butyne diol

fied respectively with *gauche* and *trans* conformations of the glycol. Although generally somewhat weaker, the process is also active in the crystalline phase. These constraints support a β mechanism which is more closely approximated by induced wagging and rocking vibrations than by restricted rotations.

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