Similarity of dynamic mechanical transitions of thermotropic polyesters in extension and torsion*

K. F. Wissbrun† and H. N. Yoon
Hoechst Celanese Research Division, Morris Avenue, Summit, NJ 07901, USA
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The frequency dependence of the dynamic mechanical transitions of several thermotropic polyesters were measured in tension on highly oriented fibres and in torsion on moulded bars. The transition temperatures were not affected by the differences in the mode of deformation and in the degree of orientation of the test specimens. It is concluded that the molecular motions responsible for the transitions, and the environment in which they occur, are independent of the macroscopic orientation. They are determined, rather, by the local state of orientation, which is highly ordered in both test specimens. The results are also consistent with other data, which suggest that the macroscopic tensile modulus of liquid-crystal polymers, over a range of time and of temperature, is strongly influenced by variation of the shear modulus.

(Keywords: dynamic mechanical; moduli; transitions; thermotropic polymers; orientation)

INTRODUCTION

The dynamic mechanical spectra of aromatic copolyester liquid-crystal polymers were determined in order to correlate their chemical structure and mechanical behaviour[1]. Three transitions were identified in the temperature range from −100°C to the melting point. The source of the very weak lowest-temperature transition, labelled γ, was identified as the *p*-phenylene linkage. The stronger β-transition was attributed to motion of the 2,6-naphthalene moiety. The highest-temperature α-transition was believed to involve motion distributed over a number of chain segments, analogous to the glass transition of amorphous polymers. These assignments have been verified by subsequent work using dielectric and nuclear magnetic resonance (n.m.r.) measurements in addition to mechanical spectroscopy[2,3].

A more detailed study of some compositions has been undertaken for correlation with studies of creep behaviour[4], and part of that work is the subject of this paper. Specifically, the topic is a comparison of the frequency dependence of the transition temperatures as measured in tension on highly oriented fibres to that measured in torsion on relatively unoriented injection-moulded specimens. A conclusion of this study is that the molecular motions and the local environments in which these motions occur are the same, independent of the macroscopic orientation and of the type of deformation imposed.

A corollary of this conclusion is that the temperature dependence of the shear modulus is largely, if not exclusively, responsible for the observed temperature dependence of the tensile modulus. This corollary is based on consideration of the orientation dependence of compliances in terms of the aggregate model[5] for the anisotropic mechanical properties of oriented crystalline polymers. A similar conclusion had been reached independently[4,6,7] by direct comparison of shear and tensile moduli as functions of temperature, again on the basis of the aggregate model. The mechanical properties of poly(*p*-phenylene terephthalamide) fibres spun from a lyotropic liquid crystal are also described by such a model[8,9]. Analogously, the time dependence of the shear modulus accounts for the flexural creep of thermotropic polyesters[4], and this is also explicable in terms of the aggregate model.

EXPERIMENTAL PROCEDURES

Two polymers were used in this work. One was a copolyester of 4-hydroxybenzoic acid (HBA) and 6-hydroxy-2-naphthoic acid (HNA), in a molar ratio of 73/27 HBA/HNA. The other was a poly(ester amide) composed of 60 mol% HNA and 20 mol% each of *p*-aminophenol (AP) and terephthalic acid (TA). Polymers were prepared from the acetates of the monomers by melt polymerization, as described by Calundann and Jaffe[10].

The complex torsional moduli were measured by forced torsional oscillation on a Rheometrics Mechanical Spectrometer. The specimens were cut from injection-moulded bars or plaques, and had dimensions of length ~4 cm, width 1.27 cm and thickness 0.31 cm. The oscillation amplitude was 0.005 rad, corresponding to a maximum strain of less than 0.05%, at which the moduli are independent of strain. Data were taken at frequencies of 0.0159, 0.159 and 1.59 Hz at intervals of 5 or 10°C, with a soak time of 5 min after changing temperature for thermal equilibration.

The injection-moulded specimens had the layered structure previously observed with thermotropic polymers[11,12]. The Herman's orientation function was measured at various distances from the centre of a bar by wide-angle X-ray diffraction[13]. The values are in the

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† To whom correspondence should be addressed

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range of 0.8 to 0.9, corresponding to orientation angles of ~15–21°. These results, together with the anisotropic moduli determined on the plaques[7], are consistent with other data reported on injection-moulded samples[12].

Fibre samples were prepared by melt spinning. The anisotropic polymer melts were extruded into ambient air through a die with diameter of 254 μm and drawn down in the melt to about 11.4 μm diameter (5 denier per filament). The extrusion temperatures were 315°C for the 73/27 HBA/HNA polymer and 340°C for the 60/20/20 HNA/AP/TA polymer. The fibres were then subjected to a heat treatment step to improve their tensile strengths. In the heat treatment the fibres were subjected to temperatures about 10°C below their melting temperatures in a chemically inert environment for about 12 h. As a result of the heat treatment, the tensile strength of the fibres increased from about 11 gpd (1.35 GPa) to about 30 gpd (3.7 GPa). However, the fibre tensile modulus did not increase significantly with the heat treatment, remaining at about 80 GPa. This is consistent with a result of a wide-angle X-ray diffraction (WAXD) study of the fibres, showing no discernible change in chain orientation with the heat treatment. The WAXD patterns of the fibres showed that the heat treatment converted the pseudo-hexagonal oriented nematic structure of as-spun fibres to a well defined orthorhombic arrangement of polymer chains.

The dynamic tensile modulus and loss tangent of the fibres were measured by forced tensile oscillation using an automated Rheovibron. Aligned fibre bundle specimens of 40 fibres per bundle were used for the measurement. The specimens were subjected to an initial tension of 0.03 GPa and an oscillatory strain of 1.5×10^{-4} was used to measure the dynamic moduli. The moduli were determined at three different frequencies, 3.3, 11 and 110 Hz, over the temperature range of −100 to 250°C.

RESULTS

The tension and torsion moduli and loss tangents for the two polymers are compared graphically in *Figures 1* and *2*. The β- and γ-transitions identified by Yoon[1] are clearly visible; the low-temperature γ-transition is seen as a shoulder on the tan δ curve. In order to plot the data on a common scale the torsion modulus and the tension tan δ have been multiplied by a factor of 10. There is an obvious visual similarity of the curves for both polymers except at high temperatures, where the tensile moduli of the heat-treated fibre are less temperature-dependent, and the loss tangents are correspondingly smaller. The retention of modulus above the α-transition, in contrast to the usual behaviour of amorphous polymers, is attributed to a packing order that does not give rise to the identifiable X-ray reflections associated with full three-dimensional crystallinity[14], but that accounts for the d.s.c. endotherm near the temperature at which the material becomes fluid.

The difference in the high-temperature behaviour is attributed to the different thermal histories of the specimens used for the torsion and tension measurements. This interpretation was supported by comparison of the torsional moduli of a bar as-moulded with those of one that had been annealed in stages, for 2 h at 220°C, for 2 h at 250° and then for 20 h at 270°C. This comparison is shown in *Figure 3*. The heat treatment has little effect at and below the α-transition temperature of ~110°C. Above the transition, however, the heat-treated sample has a modulus that is higher and less temperature-dependent, and a correspondingly lower tan δ, than the untreated control.

The reversible nature of the heat treatment effect is shown in *Figure 4*. Here the comparison is between a heat-treated fibre before and after a ~5 s 'melting' at a temperature near 500°C. The decreased modulus and increased tan δ at high temperatures is evident. The reversible effect of the heat treatment is attributed to differences in the perfection of the packing of the chains alluded to above.

The visual similarity of the transition temperatures measured in tension and torsion is qualitative in nature, and does not show identical peak temperatures. A quantitative assessment requires consideration of the dependence of the transition temperatures upon the frequencies at which they were measured. The frequency

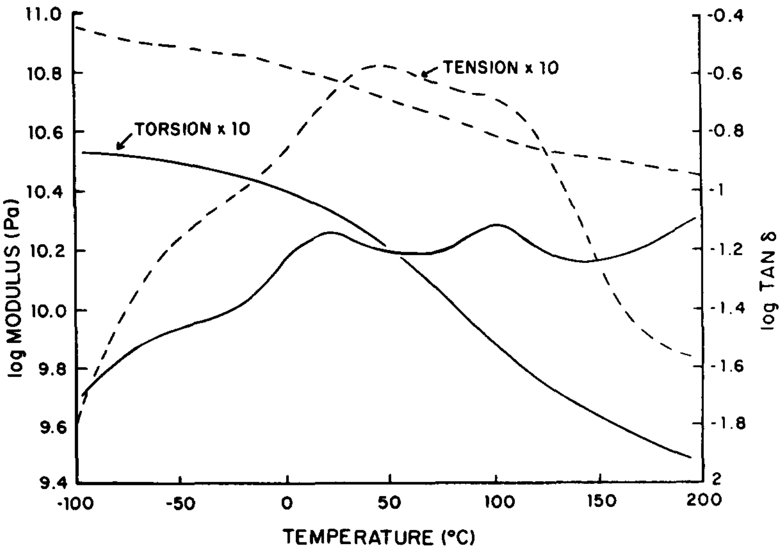

Figure 1 Comparison of tensile modulus and tan δ (– – – –) of heat-treated fibre with torsional modulus and tan δ (——) of moulded bar of 73/27 HBA/HNA. Torsion modulus and tension tan δ have been multiplied by 10

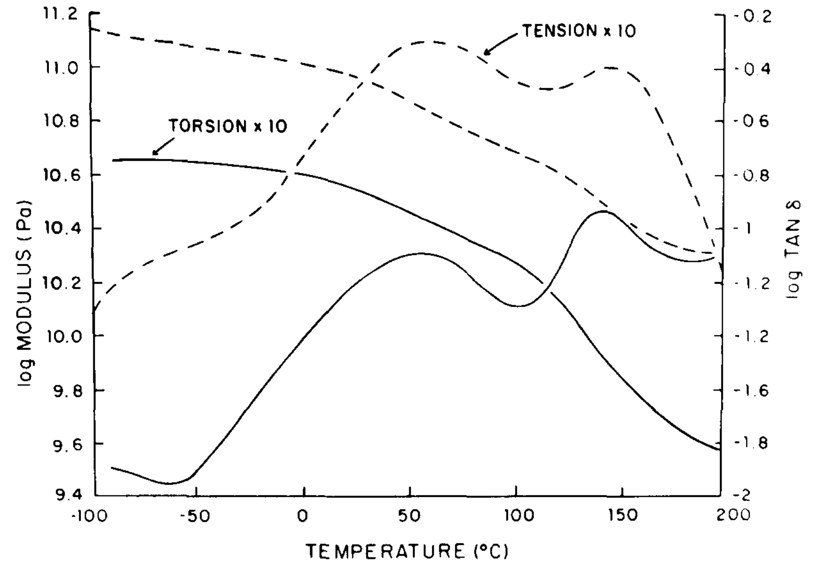

Figure 2 Comparison of tensile modulus and tan δ (– – – –) of heat-treated fibre with torsional modulus and tan δ (——) of moulded bar of 60/20/20 HNA/AP/TA. Torsion modulus and tension tan δ have been multiplied by 10

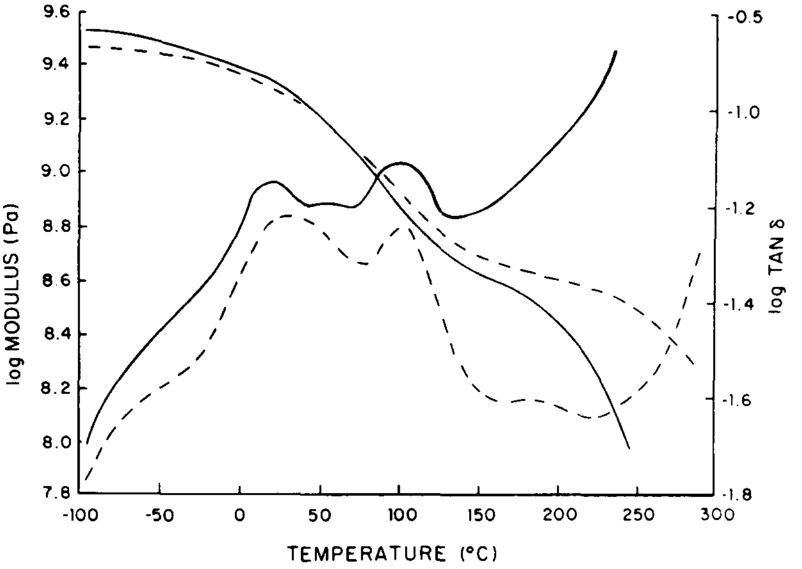

Figure 3 Effect of heat treatment on torsional moduli of HBA/HNA moulded bar: as-moulded (——) and annealed 24 h at 220–270°C (– – – –)

dependence is shown in *Figure 5*. The three points at 3.3, 11 and 110 Hz were obtained in tension on fibres, the points from 0.017 to 1.7 Hz in torsion on bars. The γ-transition was not observed clearly at the lower frequencies and is therefore omitted. An α′-transition was tentatively identified as a weak transition or splitting of the α-transition at the two lowest frequencies and is shown.

Figure 5 shows clearly that the transition temperatures measured in two different deformation modes, on samples with very different states of macroscopic orientation, lie on the same line. *Figure 6* is an Arrhenius plot, on an expanded temperature scale, for the β-transition, which is the one that has the largest range of temperature variation, and the largest departure from linearity. The activation energies derived from Arrhenius plots for the three transitions are given in *Table 1*. The results of Troughton *et al.*[15], derived from tensile and dielectric measurements on a similar 73/27 HBA/HNA copolymer, are shown for comparison. The results seem to be in reasonable agreement, considering their rather large error estimates.

Table 1 Activation energies of transitions (kcal mol^{-1} °C^{-1})

	This work	Troughton *et al.*	
Transition	Tension/torsion	Tension	Dielectric
α	~100–150	210±180	~170
β	30±3	26±7	25±5
γ	10±2	37±25	12±3

DISCUSSION

Effect of orientation on transition temperatures

The observation from *Figure 5* that the transition temperatures are the same, when measured at the same

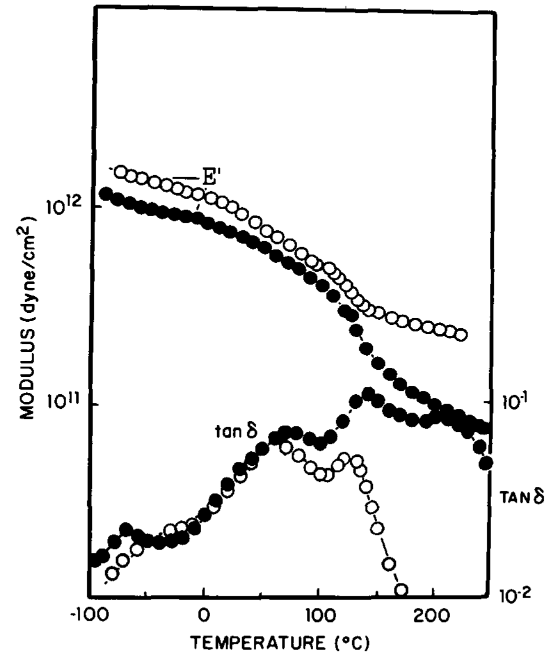

Figure 4 Effect of 'melting' heat-treated fibre. Comparison of heat-treated fibre before (○) and after (●) 5 s exposure to ~ 500°C

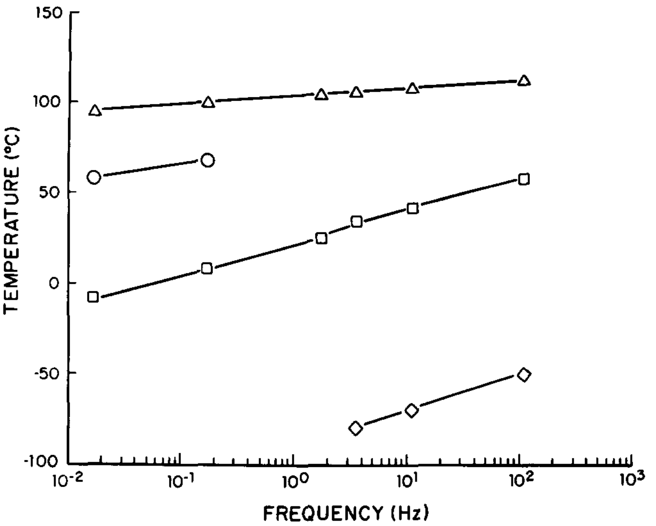

Figure 5 Frequency dependence of transition temperatures. Lower three frequencies measured in torsion of moulded bars; higher frequencies in tension of oriented fibres. Transitions: △, α; ○, α′; □, β; ◇, γ

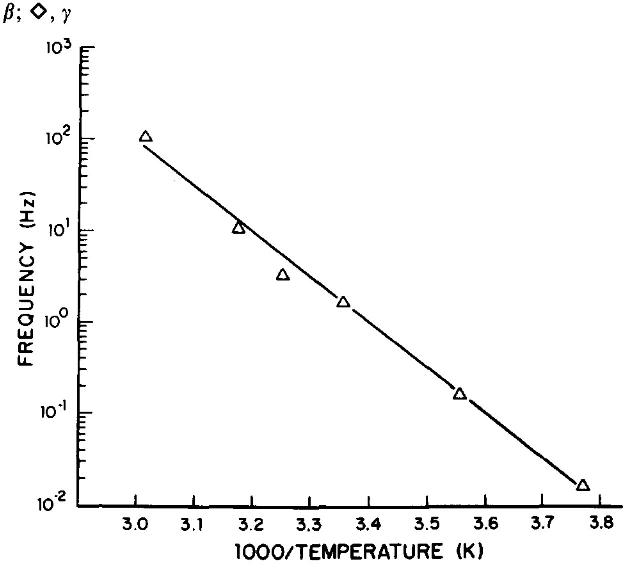

Figure 6 Arrhenius plot of β-transition temperature

frequency, for the relatively poorly oriented moulded samples and the highly oriented fibres, differs from literature observations on conventional flexible polymers. This literature is summarized and reviewed by Murayama[16]. For poly(ethylene terephthalate) (PET), for example[17,18], the shape and location of the α-transition is strongly affected by drawing. The interpretation is complicated by the fact that drawing increases not only orientation but also crystallinity. However, comparison with data on unoriented samples that were crystallized thermally shows that only 20°C of the shift of the transition from 80°C to 132°C is accounted for by increased crystallinity. The remainder is due to orientation and/or other changes of morphology induced by drawing. The α-transition of nylon-6,6 is similarly affected by orientation[19,20].

In both PET and nylon, stretching changes the morphology in a complex manner. It may increase the degree of crystallinity, affect the size of the crystals and their spatial arrangement, and establish orientation directions for the crystallites and for the amorphous material connecting them. The changes of the dynamic mechanical transitions apparently reflect these changes of morphology.

The microscopic structure of liquid-crystal polymers is far less sensitive to differences in macroscopic orientation. There is a high degree of local order, of parallel arrangement of chains, even in the absence of macroscopic orientation[21,22]. The effect of stretching, then, is primarily to establish an orientation direction. It does not affect appreciably the degree of order, except perhaps insofar as it removes disclinations, which represent a small fraction of the total volume of material. The dynamic mechanical transitions have been shown to result from the motions of individual moieties (or small groups of moieties) along the polymer chain[1–3]. The independence of the transition temperatures on macroscopic orientation is interpreted as evidence that these motions and the environment in which they occur are not affected by the orientation. This interpretation is consistent with the morphological evidence.

Relation of shear and tensile moduli

The magnitudes of the moduli and loss tangents of the moulded specimens and the oriented fibres are very different. That is not surprising if one thinks naively about the difference in microscopic response to an imposed stress. For a perfectly oriented array of linear chains the tensile modulus should be determined by the intramolecular force constants for bending and stretching the bonds along the chain, perhaps with some modification because of interactions with the surrounding chains. The response to a shear stress, on the other hand, would be to cause relative motion or slippage of neighbouring chains. The shear modulus should depend, then, primarily on the intermolecular forces. This sort of argument may account for the observed difference in the magnitudes of the shear and tensile moduli. However, it leaves the observed similarity of the temperature dependences of the moduli and transitions totally unexplained.

The origin of the connection between the moduli was realized[3,6,8,9] to be the combination of imperfect orientation and of a very large difference in magnitude of shear and chain moduli. From a microscopic viewpoint, if a stress is applied at even a small angle to the chain direction, relative slippage of chains is preferred to stretching of chains. Macroscopically this is expressed by the aggregate model[5]. For uniaxially oriented materials with a high degree of orientation, the expression for the tensile modulus is:

$$E^{-1} = E_c^{-1} + G^{-1} \langle \sin^2\theta \rangle$$

where E is the measured tensile modulus, E_c the chain modulus, G the shear modulus and $\langle \sin^2\theta \rangle$ the mean square of the sine of the angle between chains, which expresses the imperfection of orientation. If $G \ll E_c$, the measured modulus E will be sensitive to variations of G.

The intramolecular force constants should be relatively insensitive to changes of temperature, especially for rod-like extended chains. The intermolecular interactions, arising from dispersion forces, are strongly dependent upon intermolecular distance and should therefore change relatively strongly as thermal expansion occurs with increasing temperature. These expectations are confirmed by experiment. Over the temperature range -80 to 120°C the chain modulus of HBA/HNA copolymers varies by about a factor of 2 (ref. 23). Aromatic polyamides show a similarly small variation of chain modulus[24]. The shear modulus is considerably more temperature-sensitive, with $\sim(6 \pm 1)$-fold variation over this temperature range[6,7]. Therefore, the variation of tensile modulus with temperature should mirror that of the shear modulus, as is indeed observed.

The qualitative argument from this work is that the equivalence of the shear and tensile transition temperatures indicates that the magnitude of the observed tensile modulus is strongly influenced by the shear modulus. Quantitative measurements of the temperature dependence of the moduli[6,7,23], analysed in light of the aggregate model, are consistent with this interpretation. The only serious inconsistency noted is that the shear moduli of Troughton *et al.*[6] are lower than those measured here by a factor of ~ 2.5 over the entire temperature range reported. The reason for this discrepancy is not known at this time.

Another application of the aggregate model for the description of the mechanical properties of these polymers is to the time dependence of the modulus[4]. The flexural creep modulus varies with time and temperature in the same manner as does the shear modulus. The assumption that the chain modulus is independent of time and that all of the observed time dependence of the flexural modulus is due to the change of the shear modulus appears to account satisfactorily for the results. The details of this work will be published elsewhere[25].

The significant role played by the relative deformation between neighbouring chains in these polymers can also be seen in the tensile strength of highly oriented fibres and its dependence on molecular weight[26]. Typically, the strength of fibres exhibits a strong dependence on the number-average molecular weight, ranging from a few tenths of a gigapascal to about 4 GPa. A model was developed based on the idea that the fibre fracture originates at the chain ends because of inability to support the shear load concentration, and was found to describe accurately the molecular-weight dependence of the tensile strength.

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