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An aggregate model for random liquid crystalline copolyesters*

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Several aromatic liquid crystalline copolyesters with different compositions have been examined in an attempt to reach a molecular understanding of their mechanical properties. This has been aided by use of a simplified aggregate model and by theoretical calculations. Replacement of hydroxynaphthoic acid residues by straighter intrinsically stiffer biphenyl residues enhances the chain modulus. At the same time the macroscopic shear modulus drops, presumably because the straighter chains can move relative to one another more easily. The tensile compliance of the sample depends on both these properties with the contribution from shear decreasing with increasing orientation. Improved molecular orientation caused by straightening of chains or fibrils probably explains the stress dependence of the extensional moduli of these materials.

(Keywords: liquid crystalline copolyesters; aggregate model; mechanical properties; stress dependence; molecular orientation)

INTRODUCTION

There is considerable interest in the family of main chain thermotropic liquid crystalline copolyesters formed from various *para* di-substituted aromatics for two main reasons. First, the use of ester linkages, which are more flexible than amide linkages, and the incorporation of different aromatic residues, which decreases the structural regularity of the chains, are of benefit to processing. At the same time, the aromatic portions retain their intrinsic stiffness and thus offer the prospect of good macroscopic mechanical properties. The molecular chains of the different members of this family may be regarded as randomly arranged aromatic residues joined by ester linkages. The disposition of the ester linkages and the specific aromatic residues present in the chains depend on the compounds from which the chains are synthesized.

In several earlier papers[1,2] we have investigated the X-ray modulus (or more specifically the chain modulus using an X-ray technique) and other mechanical properties of copolyesters synthesized from 4-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA). This work drew attention to the importance of the intrinsic moduli of the monomers and the shear modulus of the samples. Moreover, an aggregate model was used to relate the X-ray and macroscopic moduli, although the success was limited by the data available for the X-ray modulus. The present paper extends this analysis to two further members of the family, COTBP and CO2, 6. The X-ray modulus is examined much more extensively and these results are combined with measurements of macroscopic mechanical properties reported earlier[3] using a simplified aggregate model to produce a more detailed analysis of these materials than that presented for the HBA/HNA systems.

The copolyesters considered in this paper were synthesized from a range of compounds which include terephthalic acid (TPA), 2,6-dihydroxynaphthalene (DHN) and 4,4′-biphenyldiol (BP) in addition to HBA and HNA. Details of composition are given in *Table 1*. The different phenyl and naphthyl residues in the samples are distinguished by subscripts 1, 2 and 3 indicating that they are bounded by one ether oxygen atom and one carbonyl carbon atom, or two carbonyl carbon atoms or two ether oxygen atoms, respectively. All biphenyl residues are bounded by two ether oxygen atoms. Although attention here is focused on CO2, 6 and COTBP details of the HBA/HNA systems are also given in *Table 1* for comparison.

EXPERIMENTAL

Samples

Samples of two different copolyesters, CO2, 6 and COTBP, were supplied by Hoechst-Celanese (Summit, New Jersey, USA) in the form of highly oriented monofilaments of about 1 mm diameter, and tapes 20 μm thick and 5 mm wide. Both tapes and rods were produced by spinning from the melt with an extensional flow field sufficient to induce high orientation. Both sets of samples were freely annealed in nitrogen; CO2, 6 for 2 h at 230°C followed by 16 h at 270°C, and COTBP for 4 h at 300°C only. The high orientation of these samples was confirmed at a microstructural level by wide angle X-ray scattering (WAXS) photography and at the more macroscopic fibrillar level by microscopy. Densities of the extruded rod samples were lower and had a wider spread than did those of corresponding tape samples because of the presence of voids. Typical values for rods considered suitable for investigation were about 1.28 g cm^{-3} whilst those for the tapes were 1.395 g cm^{-3} in the case of COTBP and 1.388 g cm^{-3} for CO2, 6. Small ellipsoidal defects were also a common feature of the CO2, 6 tapes. Both sets of tapes were dimensionally

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Table 1 Composition of copolyesters

	Molar percentage of					Phenyl content[a]				Naphthyl content			
Polymer	HBA	HNA	TPA	DHN	BP	Total	P_1[b]	P_2	P_3	Total	N_1	N_2	N_3
CO73/27	73	27	—	—	—	73	73	—	—	27	27	—	—
CO30/70	30	70	—	—	—	30	30	—	—	70	70	—	—
COTBP	60	5	17.5	—	17.5	77.5	60	17.5	—	5	5	—	—
CO2, 6	60	—	20	20	—	80	60	20	—	20	—	—	20

[a] From HBA and TPA only

[b] Subscripts indicate bonding of aromatic ring to: 1, one ether oxygen and one carbonyl carbon; 2, two carbonyl carbon atoms; 3, two ether oxygen atoms

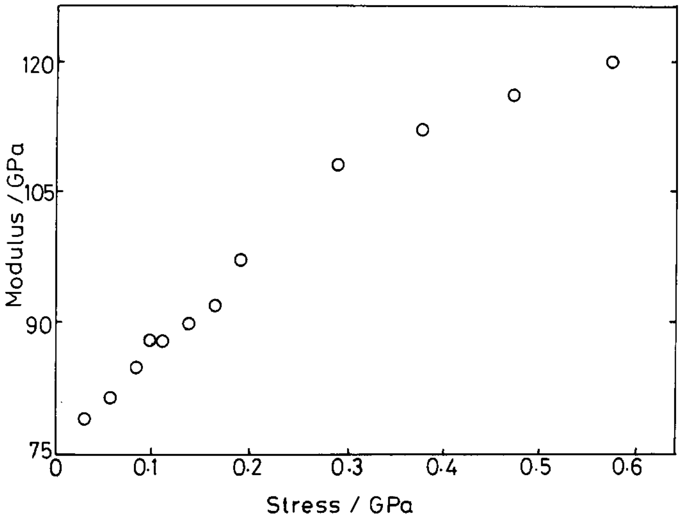

Figure 1 Tensile modulus of copolyester COTBP as a function of temperature

stable at temperatures up to 200°C, well in excess of the experimental temperatures employed.

Macroscopic mechanical properties

The results of dynamic measurements of the tensile modulus, E_s, of oriented tapes and the shear modulus, G_s, of oriented rods have been reported in an earlier paper[3]. Measurements of the tensile modulus of the tapes over the complete temperature range were made at frequencies of 0.1, 1 and 10 Hz under a static stress of 100 MPa. The shear moduli, on the other hand, were determined at approximately zero tensile stress and frequencies between 0.2 Hz and 0.5 Hz, depending on the temperature, on the lower density rod samples.

For the modelling purposes described here it is necessary that the data relate as closely as possible to identical measuring conditions. Therefore simple frequency and density corrections were applied to the results of tensile modulus to render them compatible with those of the shear modulus. As well as being dependent on temperature and frequency the moduli are also dependent on the static tensile stress used during measurement. *Figure 1* shows how the tensile modulus of COTBP varies with static tensile stress at a frequency of 10 Hz and a temperature of 20°C. A similar increase in modulus with stress has been reported in other thermotropic copolyesters by Nakamae *et al.*[4]. The stress correction factor required to convert the modulus measured under conditions of 100 MPa static loading to that expected for zero stress loading can be found from *Figure 1*. Using a graph such as *Figure 1*, extrapolation by eye gives the modulus for zero stress loading to an accuracy of about 1%. Thus a stress correction factor which relates the modulus at zero stress to that at a stress of 100 MPa can be obtained. The stress dependence of the modulus, and hence the stress correction factor, was obtained at 50°C intervals between −100°C and 150°C and corrections at intermediate temperatures obtained by interpolation. This correction to zero static stress, rendering tensile measurements compatible with shear measurements, was more significant than either the frequency or the density corrections, especially at high temperatures (about T_g).

X-ray modulus

There is considerable uncertainty concerning the existence of crystallinity in this family of copolyesters centred around the interpretation of the X-ray diffraction patterns[5–9]. Whether or not crystallinity is present, Chivers and Blackwell[5] have shown that diffraction from oriented randomly substituted chains contributes to the aperiodic meridional reflections. The sharpness of these reflections gives an indication of the coherence length of the diffracting units, a value of 10 monomers being typical for similar copolyester systems[10,11]. Consequently, measurements of the shift in 2θ space with stress for the meridional reflections are related to the average molecular strain over a segmental length of about 10 monomers and not confined to strain within any crystalline regions.

Measurements of average X-ray modulus, E_x, for these tapes were made at an equivalent frequency of $\sim 4 \times 10^{-3}$ Hz by recording the shift in 2θ space of the aperiodic meridional reflection at about 43° for copper $K\alpha$ radiation (0.21 nm) as a function of stress applied in the axial direction. The technique and apparatus are more fully described elsewhere[1]. Measurements were made at temperatures between −100°C and 160°C, although for CO2, 6 sample failure at relatively low axial stresses for temperatures greater than 60°C restricted the range of investigation. As is usual in such measurements, the assumption of homogeneous stress is used to obtain the molecular stress. Experimental errors, dominated by those arising from dimensional inhomogeneities and the slope of the diffraction peak shift against stress plot, put an upper limit of 10% to the uncertainty in the results.

Figure 2 shows the temperature dependence of the X-ray modulus of COTBP and CO2, 6 whilst values at three temperatures are tabulated in *Table 2*. Also included, for comparative purposes, are data for the HBA/HNA copolyesters CO73/27 and CO30/70 published earlier[1]. The highest modulus is shown consistently throughout the investigated temperature range by COTBP. All materials show a variation in the X-ray

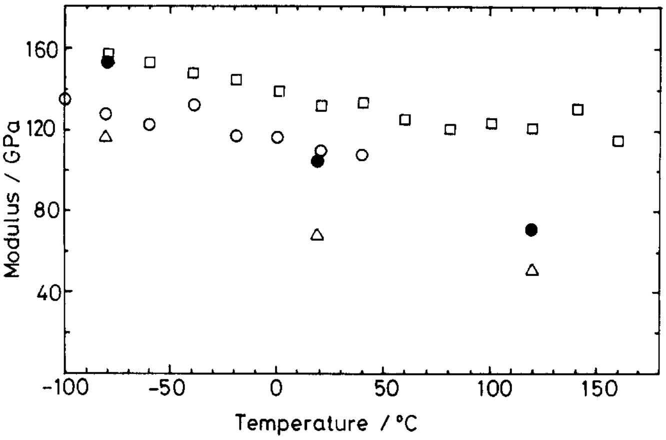

Figure 2 X-ray modulus of some aromatic copolyesters as a function of temperature. □, COTBP; ○, CO2, 6; ●, CO73/27; △, CO30/70

Table 2 Comparison of apparent crystal modulus of annealed liquid crystalline copolyesters

	Apparent crystal modulus (GPa)		
Polymer	−80°C	20°C	120°C
COTBP	156	132	123
CO2, 6	128	110	—
CO73/27	153	105	72
CO30/70	116	68	53

modulus with temperature. For COTBP this temperature sensitivity is considerably reduced above about 80°C. It is more difficult to make similar conclusions for the other materials because CO2, 6 is too brittle above about 60°C to allow data to be collected and previous data on the copolyesters CO73/27 and CO30/70 were limited to three fixed temperatures. Overall, the temperature dependence of the X-ray modulus is similar in form but less pronounced than that of the macroscopic tensile modulus.

For modelling purposes, only a density correction is applied to the X-ray modulus results to render them compatible with those of the macroscopic mechanical properties. A stress correction is not necessary because the X-ray modulus is independent of stress within experimental error. The frequency correction is unknown because of the limited range of measurements but the comparatively small temperature dependence of the results suggests that any correction would be small.

THEORETICAL

Early studies[1] on random liquid crystalline copolyesters have suggested that the sinuosity of the chains is of critical importance in determining the extensional modulus of the chain. Because of this complication it is more useful to consider the intrinsic moduli of the constituent monomers and values for these are presented here. Each monomer is composed of an aromatic residue joined to an ester linkage. The method of calculation is a primary bond analysis after Treloar[12] using force constants quoted by Tashiro *et al.*[13] and is described in more detail elsewhere[1].

Values for the intrinsic moduli of the constituent monomers are given in *Table 3*. The disposition of the ester linkage has no effect on the intrinsic modulus of the monomer and therefore it is only necessary to consider the effect of the different aromatic (namely phenyl, naphthyl and biphenyl) residues. The cases of phenyl and naphthyl residues have been considered earlier[1] and values of 155 and 126 GPa, respectively, were obtained for the moduli of these monomers. The biphenyl monomer has a modulus of 163 GPa which is a higher value than those of the other monomers as might be expected with the introduction of the direct phenyl linkage. An effective cross-section per monomer of 21.72 Å^2, obtained from the structure of the poly(p-hydroxybenzoic acid) unit cell[14], has been used to calculate the moduli. *Table 3* also lists values for the modulus for two other values of cross-sectional area obtained from density and X-ray diffraction measurements on HBA/HNA systems[5]. These suggest an average interchain separation on a hexagonal lattice of 4.5 and 5.2 Å, respectively. Clearly, the results in *Table 3* suggest that chains constructed predominantly from HBA and BP residues would be stiffer than those in which the BP residues are replaced by HNA residues. As well as this simple direct relationship between the chain modulus and composition it is important to recognise that more indirect relationships might also exist. In particular, modifications to the chain composition might alter the ability of the chains to pack, thereby changing the effective cross-section and consequently the chain modulus. It is also possible that the intermolecular interactions, which have been ignored here, are sensitive to composition. It is thus important to recognise that incorporation of stiffer units in the copolymer chains might not necessarily enhance the chain modulus.

AGGREGATE MODELLING

Simplified model

The basic assumption of this model is that the aggregate is constructed of anisotropic units which have distinct physical and mechanical properties. The properties of the aggregate are obtained by summing the contributions from the constituent units and thus depend on the intrinsic properties of the units and certain parameters which express the orientation of the units within the aggregate. In the case of the mechanical properties the coupling between the units and hence the summation procedure is also important. The two limiting values for the mechanical properties are obtained for the conditions of homogeneous strain, corresponding to parallel connectivity and providing the upper bound to the modulus of the aggregate, and homogeneous stress, corresponding to series connectivity and giving the lower bound. The different elastic constants of the aggregate

Table 3 Theoretical calculations of intrinsic moduli of some monomers for different cross-sections

	Modulus (GPa)		
		Hexagonal packing with $a=$	
Aromatic residue	Area = 21.72 Å	4.5 Å	5.2 Å
Phenyl	155	191	143
Naphthyl	126	156	117
Biphenyl	163	201	151

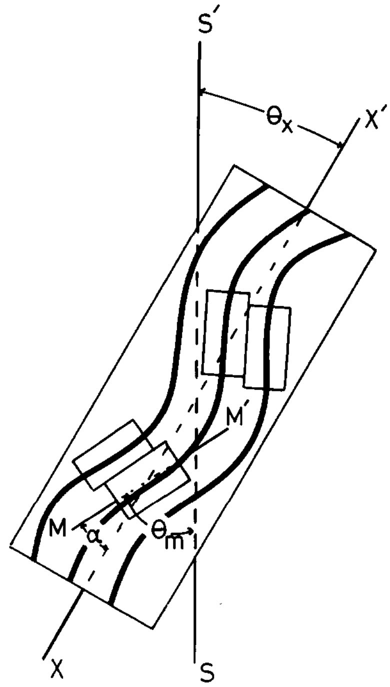

Figure 3 Schematic representation of the orientation of different aggregate units to the fibre symmetry axis of the sample

have been explicitly given in terms of the properties and orientation of the units for both conditions by Ward[15]. Generally, however, the model proves more successful when homogeneous stress is assumed to prevail.

Under certain conditions the more rigorous equations of the aggregate model can be simplified considerably. More specifically, for a highly oriented system in which homogeneous stress applies, the model predicts a simple relationship between the aggregate extensional (E_a) and shear (G_a) moduli.

$$\frac{1}{E_a}=\frac{1}{E_u}+\frac{1}{G_a}\langle\sin^2\theta\rangle \qquad (1)$$

Here E_u is the intrinsic extensional modulus of the aggregate unit and θ the inclination of the fibre symmetry axis of a unit to the fibre symmetry axis of the aggregate. The brackets $\langle\ \rangle$ indicate that the average is taken over all the units. In deriving this simplified relationship it can be shown that to a very good approximation, the shear modulus is the same at all levels within the aggregate, i.e. the aggregate shear modulus is the same as the intrinsic value for the unit. This follows from consideration of the full equation for the shear modulus of a highly oriented aggregate.

Equation (1) has been used successfully to relate the temperature dependences of the tensile and shear moduli when the aggregate is identified with the macroscopic material[2]. It is important to note, however, that the aggregate properties do not have to be identified with those of the sample. The model may apply equally well at a submacroscopic level and thus be able to explain the temperature dependence of the X-ray modulus, which, as discussed above, relates to the structure at the level of about 10 monomers. In *Figure 3* the director XX′ represents the fibre symmetry axis of an X-ray domain which is assumed to be composed of units MM′. The fibre symmetry axis of the sample is represented by SS′. It is possible to treat, in turn, both the X-ray domain and the sample as aggregates of smaller units with the level at which the model is tested depending on which mechanical measurements are identified as aggregated properties. Thus a plot of $1/E_s$ against $1/G_s$ identifies the sample as the aggregate and information from this plot relates to the units which constitute the sample. A plot of $1/E_x$ against $1/G_s$, on the other hand, identifies the X-ray domains with the aggregate because the measured shear modulus can be equated to that of the X-ray domains for the reason given above. The parameters obtained from this plot relate to the units which constitute the X-ray domains. It might be expected that the units constituting both aggregates are the same (i.e. units MM′ in *Figure 3*) and that the different aggregate properties arise because of different unit orientations. This possibility was investigated using the experimental data for the different polymers.

Both the above plots implicitly assume that the modulus of the aggregate unit is independent of temperature. Furthermore, no specific interpretation of the nature of the unit is necessary for testing the model. It is possible to be more specific in the interpretation of the nature of the unit by identifying the X-ray modulus with that of the unit and plot $(1/E_s-1/E_x)$ against $1/G_s$, in which case E_x, the unit modulus, can be temperature dependent. Such a plot tests the possibility that the sample can be regarded as an aggregate of X-ray domains and should be a straight line through the origin with a slope related to the orientation of the X-ray domains within the sample.

Application to copolyesters

In examining the behaviour of the copolyesters the following considerations will be addressed:

(1) Sample as an aggregate of units, each with a temperature-independent modulus. This unit will be interpreted at the level of the monomer residues;
(2) X-ray domains as an aggregate of units, identical to those considered in (1);
(3) Sample as an aggregate of X-ray domains.

These three different ways of interpreting the aggregate model are tested here using appropriate plots of the measurements of X-ray modulus, described above, and measurements of the macroscopic tensile and shear moduli reported in a previous paper and corrected as outlined above to allow comparison. The assumption that $\langle\sin^2\theta\rangle$ is independent of temperature, implicit in the use of equation (1), is considered justifiable because results have been corrected to the case of zero stress.

Figure 4 illustrates plots of $1/E_s$ against $1/G_s$ and $1/E_x$ against $1/G_s$ for COTBP. These plots, respectively, consider the sample and the X-ray domains as the aggregate. Both plots are linear intercepting the *y* compliance axis at a common point within experimental error and corresponding to E_u about 185 GPa. Similar plots for CO2, 6 are shown in *Figure 5*. Again the graphs are linear although they do not intercept the *y* compliance axis at the same point. *Figure 6* shows the aggregate plots for COTBP and CO2, 6 when the aggregate unit is identified with the X-ray domains and the aggregate with the sample. Both follow straight line fits but only that for COTBP passes through the origin. All the straight lines in *Figures 4–6* are weighted least squares fits to the data. The aggregate model appears satisfactory for both materials since all plots are linear but certain discrepancies arise in the case of CO2, 6 which can be appreciated more readily when the different values for the model parameters obtained from the different plots are compared. To enable such a comparison these are listed in *Table 4*.

In the case of COTBP it is possible to regard the sample as either an aggregate of units of modulus 199 GPa with a value for $\langle\sin^2\theta\rangle$ of 0.0049 or as an aggregate of X-ray domains with $\langle\sin^2\theta\rangle=0.0041$ (and with a temperature-dependent modulus). Alternatively the mechanical properties of the X-ray domains can be explained by an aggregate model of units of modulus 173 GPa with a value of $\langle\sin^2\theta\rangle=0.0008$. The agreement, albeit just within experimental error, of the moduli of the units constituting the sample and those constituting the X-ray domains, as is shown by the common intercept in *Figure 4*, suggests that the units are indistinguishable. The possibility that they may be identified with the monomers is discussed later. The different tensile properties of the domain (X-ray modulus) and the sample (macroscopic modulus) are explained by the different orientations of the units relative to the principal axis of the aggregate concerned. The higher orientation of the units within the X-ray domains is

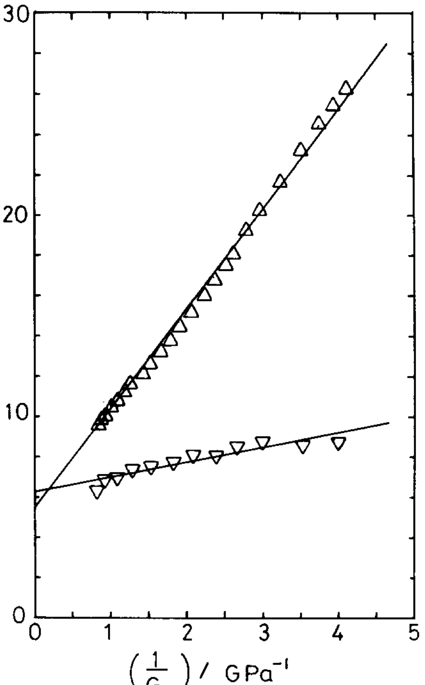

Figure 4 Application of the aggregate model to COTBP. Aggregate identified with the sample (△) and X-ray domain (▽)

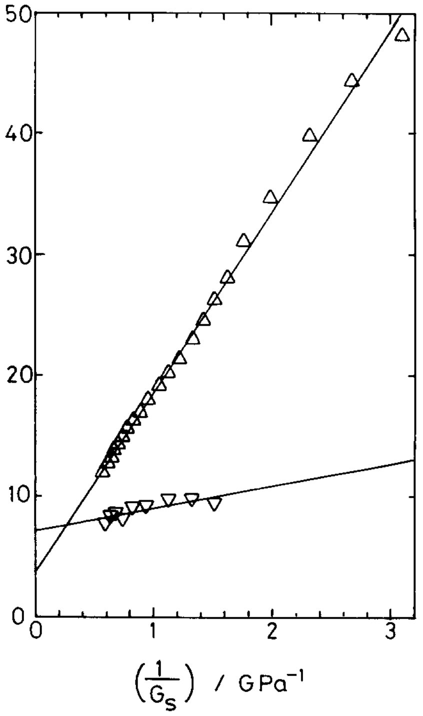

Figure 5 Application of the aggregate model to CO2, 6. Aggregate identified with the sample (△) and X-ray domain (▽)

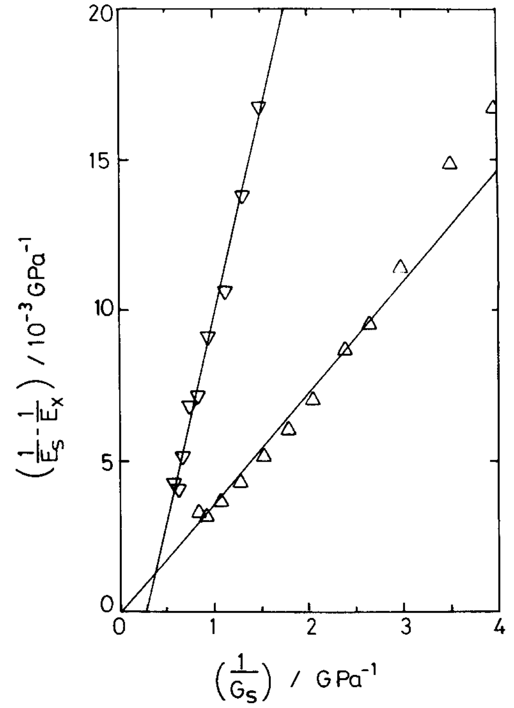

Figure 6 Application of the aggregate model to copolyesters with the sample and X-ray domain identified with the aggregate and unit, respectively. △, COTBP; ▽, CO2, 6

Table 4 Summary of aggregate parameters

	COTBP			CO2, 6		
Plot	Aggregate unit	Modulus (GPa)	$\langle\sin^2\theta\rangle$	Aggregate unit	Modulus (GPa)	$\langle\sin^2\theta\rangle$
$1/E_s$ vs. $1/G_s$	Indeterminate	199 (12%)	0.0049 (4)	Indeterminate	310 (12%)	0.0153 (13)
$1/E_x$ vs. $1/G_s$	Indeterminate	173 (5%)	0.00075 (14)	Indeterminate	150 (5%)	0.0020 (5)
$(1/E_s-1/E_x)$ vs. $1/G_s$	X-ray domain	Temperature dependent	0.0041 (5)	X-ray domain	Temperature dependent	0.0134 (17)

shown by the lower slope in *Figure 4* (lower $\langle \sin^2 \theta \rangle$ in *Table 4*).

Returning to *Figure 3*, the relationship between the sample and the different units may be considered in more detail. Depending on the scale of observation the sample can be considered to be composed of units XX′ or MM′ the orientation and mechanical properties of which dictate the properties of the samples along the fibre symmetry direction SS′. If the units XX′ and MM′ subtend angles θ_x and θ_m, respectively, with SS′, and MM′ is inclined at an angle α to XX′, for no preferred orientation of the units MM′ both about XX′ and SS′ the orientation average for XX′ about SS′ can be calculated from the Legendre addition theorem.

$$\langle P_2(\cos \theta_m) \rangle = \langle P_2(\cos \theta_x) \rangle \langle P_2(\cos \alpha) \rangle \qquad (2)$$

which for small θ reduces to

$$\langle \sin^2 \theta_x \rangle = \langle \sin^2 \theta_m \rangle - \langle \sin^2 \alpha \rangle \qquad (3)$$

The value calculated in this way is 0.0042 for COTBP which agrees well with the value of 0.0041 calculated from the slope in *Figure 6* and given in *Table 4*. It should be noted that this is an alternative, rather than independent, way of finding the value of $\langle \sin^2 \theta_x \rangle$.

A similar interpretation applied to CO2, 6 encounters mixed fortune. The slopes of the different graphs in *Figures 5* and *6* indicate considerable resemblance to COTBP. Orientation of the units within the X-ray domain is greater than that of the units relative to the sample axis and there is good agreement between the domain orientation calculated using equation (2) (0.0133) and that found from the slope in *Figure 6* (0.0134). Differences in the behaviour of CO2, 6 and COTBP however, are evident in that the intercepts for the former, specifically that in *Figure 6* and that for the sample aggregate in *Figure 5*, are not consistent with the expectations of this model. It should be noted, however, that a systematic error or contribution of about $3 \times 10^{-3}\,\mathrm{GPa}^{-1}$ affecting only $1/E_s$ can remove these discrepancies. Perhaps the most obvious source of this is through the presence of a crystalline component in CO2, 6 causing a lower than expected sample tensile compliance. This view might be supported by the fact that the macroscopic tensile modulus of CO2, 6 (ref. 3) is significantly greater than that of HBA/HNA copolyesters[2] of comparable phenyl and naphthyl contents for temperatures greater than that of the β relaxation. This discrepancy however, might also arise because measurements were not made under identical stress conditions. Other systematic errors can arise because of simplification of the aggregate model; contributions from the transverse compliance term s_{11} may not be insignificant and the approximation that the shear modulus is the same at all levels within the sample may not hold. It is also possible that there are systematic errors in the measurements of the moduli, and more specifically that the density correction used to relate the different shear and tensile moduli is not as simple as that used.

DISCUSSION

A molecular understanding of the different relaxation processes in these copolyesters has been established through investigations of the mechanical and dielectric properties[3]. Generally there are three distinct relaxations, the γ, β and α, which are, respectively, associated with rotation/libration of the phenyl units (−100°C to −50°C), rotation/libration of the naphthyl units (20–50°C), and the glass transition (about 100°C). The glass transition is believed to arise from cooperative rotation/libration of longer molecular sequences. Altering the disposition of the ester linkages, and hence changing the type of bond linked to the aromatic units, has been shown to have a negligible affect on the mechanical relaxation spectra of these copolyesters. The introduction of BP into the chains produces a small relaxation at about −20°C, associated with rotation of the corresponding units, which is still close to the corresponding relaxation for the phenyl groups alone. Thus it is still convenient to think specifically of three relaxations in this family of copolyesters.

An important feature of these materials is that the shear losses are considerably greater than the tensile losses implying that rotational motions predominate with little change in chain length. This is not surprising for comparatively straight rigid molecules in which the onset of rotational or librational motions does not alter significantly the molecular length. Measurements of X-ray modulus which only record changes in chain length over a distance of about 10 monomers would be particularly insensitive to these relaxations. Measurements of macroscopic tensile modulus would be more sensitive since these incorporate a contribution from intermolecular shear which would be affected by the relaxations. It is this shear term which explains the differences, both in temperature sensitivity and absolute value, of tensile moduli measured macroscopically and using the X-ray technique.

This explanation is given further support by the success of the simplified aggregate model which clearly identifies this shear contribution to the macroscopic tensile modulus, and thus explains the close correlation between the temperature dependences of the tensile and shear moduli. The aggregate model also shows that these materials can be interpreted either as an aggregate of molecular sequences with a temperature-dependent modulus or as an aggregate of smaller units with a temperature-independent modulus. This temperature independence suggests that the smaller units might be identified with sections of molecule whose conformation is unaffected by temperature. Consideration of the relaxation processes suggests that this occurs at the level of the individual monomers. Theoretical calculations of the moduli of the monomeric residues support their identification with the smaller aggregate units and suggest that the X-ray modulus of an aggregate of biphenyl residues would be higher than that of an equivalently oriented aggregate of naphthyl residues.

At first sight theoretical calculations might also appear to provide a means of determining E_x and indeed this approach has been applied to the HBA/HNA system, but certain limitations were discovered. Calculations were generally found to be too low, especially when compared with the results of X-ray measurements. This discrepancy was attributed to the omission of an important contribution from intermolecular interaction in the calculations. This can be explained with reference to the shear between comonomers in adjacent chains as they tend to straighten.

Table 1 shows that the main difference between the two copolyesters examined here is the replacement of the majority of naphthyl residues in CO2, 6 by biphenyl residues to produce COTBP. The higher X-ray modulus of the latter can be explained simply by the incorporation of the stiffer biphenyl residues in the chain. The lower temperature dependence of the X-ray modulus arises because straighter chains are produced by the incorporation of the biphenyl residues as is indicated by the lower value of $\langle \sin^2 \alpha \rangle$ shown by COTBP.

Finally the aggregate model also suggests that the stress dependence of the macroscopic tensile modulus can be explained by a stress sensitive value for $\langle \sin^2 \theta \rangle$. Reference to equation (1) shows that if $\langle \sin^2 \theta \rangle$ decreases as the stress increases, or in other words the orientation of the aggregate units improves, the contribution to the tensile compliance from the shear term falls and consequently the tensile modulus will rise with applied stress. This is what is observed in practice and the improvement in orientation may be attributed to the straightening of molecular chains or to the straightening of the sinuous fibrils known to be present in these materials. Several models to explain the stress dependence of the modulus have recently been proposed[16,17], but all analysis here has been performed at zero stress and it is not necessary to consider this additional complication at this stage.

CONCLUSIONS

A range of aromatic copolyesters incorporating hydroxybenzoic acid, hydroxynaphthoic acid, terephthalic acid, dihydroxynaphthalene and biphenyldiol have been examined and a deeper molecular understanding of the mechanical properties has been obtained. Incorporation of the stiffer biphenyl residues into the molecular chains enhances the chain modulus. The temperature dependence of the chain modulus is controlled by the β and γ relaxation processes associated with rotation of the naphthyl and phenyl residues, respectively. Elimination of the naphthyl content results in a chain modulus which is temperature independent above the γ relaxation and beyond the α relaxation. The implication is that activation of the α relaxation has no significant effect on the chain length but this relaxation does affect the macroscopic tensile properties by encouraging shear of chains relative to one another. Hence the macroscopic tensile modulus falls in this temperature region. Use of a simplified aggregate model has shown that these materials can be interpreted as an array of highly oriented rods with their mechanical tensile properties heavily dependent on the shear characteristics. Different possible interpretations of these rods have also been discussed.

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