Experimental and theoretical longitudinal chain moduli of copolymers of hydroxybenzoic acid with 2-hydroxy-6-naphthoic acid

M. J. Troughton, A. P. Unwin, G. R. Davies and I. M. Ward*

Department of Physics, University of Leeds, Leeds, LS2 9JT, UK

The changes with stress of the meridional X-ray scattering patterns from liquid crystalline copolymers of hydroxybenzoic acid with hydroxynaphthoic acid have been used to measure the average chain moduli. The values obtained have been compared with theoretical estimates of the chain moduli and in general found to be greater than the latter at low temperatures. It is concluded that, although an isolated chain has a comparatively low modulus, in the polymer environment the need to overcome intermolecular shear forces results in an enhancement of the modulus. The importance of the shear modulus in determining sample properties is discussed and the conformational implications for the copolymer molecules are examined.

(Keywords: chain modulus; liquid crystal copolymers)

INTRODUCTION

In recent years interest in rigid chain liquid crystalline copolymers has grown considerably. Of particular interest has been the copolyester prepared from hydroxybenzoic acid and 2-hydroxy-6-naphthoic acid. This material can be produced with a high degree of chain extension and orientation to display excellent thermal and mechanical properties.

One unusual feature shown by these copolymers is a well defined X-ray diffraction pattern. Efforts to interpret this have concentrated on the aperiodic meridional reflections and there is now general agreement[1-5] that these peaks arise as a result of diffraction from oriented randomly substituted copolymer chains, and not necessarily from areas of crystallographic order. Chivers and Blackwell[6] have shown that the equatorial X-ray scattering pattern can be explained by a model consisting of a nematic array of chains of random conformation and, although there may be regions of crystalline material as suggested by Blundell[7], Windle et al.[8] and Butzbach et al.[9], recent work by Blackwell et al.[10] suggests that even the off-axis diffraction spots require a comparatively small amount of three-dimensional order.

The presence of strong meridional peaks in the X-ray diffraction patterns of these copolymers is potentially very useful because these peaks provide a means of measuring molecular strain. Such measurements, supported by theoretical calculations, are valuable not only because they relate to the molecular structure but also because this information forms an integral part of our understanding of the macroscopic mechanical properties. The extension of these techniques to the copolymers considered here encounters several difficulties. First, in semicrystalline polymers such as polyethylene, measurements of the X-ray strain using the

meridional crystal reflections[11] yield a value for the chain modulus in the crystalline regions, whereas similar measurements in these copolymers are not specific to crystalline regions but instead record an average over all the chains. Second, the obvious lack of precise order, both conformationally and crystallographically, in the copolymers means that more recent techniques[12-14] for calculating the theoretical chain modulus cannot be usefully employed. Thus, although it has certain limitations, the early approach described by Treloar[15] is most appropriate.

The work reported here therefore uses the primary force approach described by Treloar to calculate the chain moduli of copolymers of hydroxybenzoic acid (HBA) with 2-hydroxy-6-naphthoic acid (HNA). The effects on theoretical chain modulus of changes in conformation of the monomers comprising the chain is examined and the results are discussed in relation to the experimentally obtained values from copolymers of different relative HBA/HNA concentrations.

EXPERIMENTAL

Materials

The two different copolyesters investigated in this work were prepared from 4-hydroxybenzoic acid, (HBA), and 2-hydroxy-6-naphthoic acid, (HNA), and were supplied by the Celanese Research Company. Samples with HBA/HNA monomer ratios of either 73/27 or 30/70 were produced, the spun tapes showing a high degree of molecular orientation. Annealing was performed at constant length in nitrogen at 250°C for 4 h and then at 280°C for 15 h.

X-ray measurements

X-ray measurements of apparent chain modulus were made using copper K_α radiation from a Siemens X-ray

---

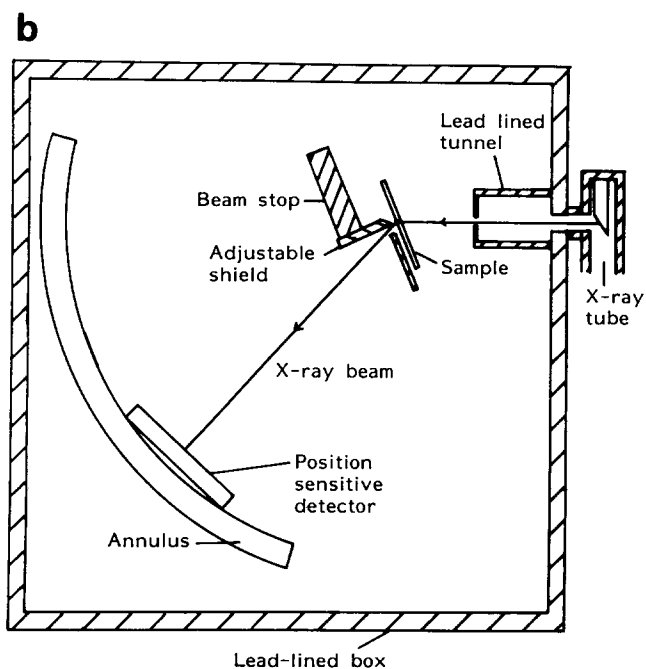* To whom correspondence should be addressed
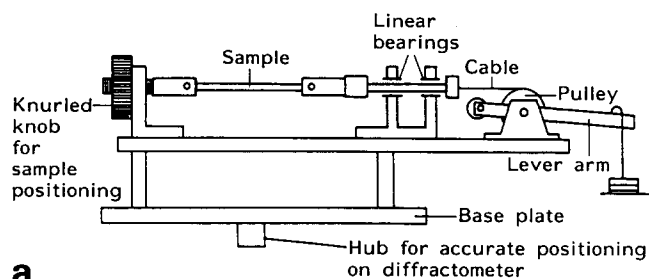
Figure 1 (a) Side elevation of horizontal extensometer. (b) Schematic representation of the diffractometer and detector assembly

tube, a transmission method being employed to investigate the response to stress of the meridional reflection at $2\theta = 43°$. The sample under investigation was mounted on an extensometer and could be accurately located at the centre of a standard Philips X-ray diffractometer table. The extensometer was designed so that large loads could be applied to the sample. Lateral movement was avoided so that the X-ray beam always illuminated the same area of the sample. In the arrangement used here (*Figure 1a*) the sample was gripped between two clamps mounted on a system of low friction linear bearings. One clamp was fixed and a load could be applied to the other via a lever arm and pulley system. The sample was housed in a polystyrene enclosure/oven which was fed by a stream of temperature regulated nitrogen. A position sensitive detector, with its active area lying on the chord of a circle whose centre coincided with that of the diffractometer table, sampled the diffracted X-ray beam. A schematic diagram of the diffractometer and detector assembly is shown in *Figure 1b*. The position sensitive detector was interfaced to a Norland inotech 5300 multichannel analyser, so that the multichannel analyser recorded the diffracted X-ray intensity along the chord, and consequently enabled the 2θ profile of the peak to be recorded.

Measurements were performed at temperatures of $-80, 20$ and $120°C$, on tapes mounted horizontally in the extensometer so that the sample draw direction was parallel to the loading direction. For high temperature measurements, the polystyrene oven was replaced by one of polyurethane. A period of 20 min was allowed for samples to reach thermal equilibrium, and temperature control was estimated to $1°C$ in the absence of significant thermal gradients across the oven, an assumption considered reasonable because of the small size of the ovens. At low temperatures the formation of ice on the outside of the oven was prevented by continuously blowing a stream of warm air across the critical surfaces.

Because of the low intensity of the reflection examined, significant care had to be taken to reduce contributions from air scattering. This was achieved by the appropriate positioning of lead shielding. When a suitable diffraction profile had been obtained the spectra for a series of different stresses were recorded. With the lever arm and pulley arrangement the actual load experienced by the sample was stepped up by a factor of 9.37 from the applied load. The loading programme involved a series of increasing loads followed by a series of decreasing intermediate loads. Between each of these loads a reference spectrum was obtained from the sample subjected to a small constraining load. Such a cyclic loading programme allowed drifts in the X-ray beam to be identified. This could be important because the data collection time for each load was 200 s, so that a full programme took approximately 3 h to complete.

Because of the asymmetry of the X-ray reflection (*Figure 2*) the merit in identifying the peak position by our standard method of Gaussian curve fitting was called into question, particularly in view of the fact that typical shifts were less than 1 channel. Therefore a new method of calculating the peak shift was used. This involved forming an average template for reference from all the recorded spectra. This was done simply by averaging the intensity recorded at each channel number for the whole series of spectra. For each peak profile the sum of the squares of the deviations of the experimental peak from the average template was computed. The procedure was repeated for shifts of the peak by 1 channel either side of its original position, resulting in a set of three values for the sum of the squares of the deviations against peak position for each of the peaks. A parabolic fit to these results (*Figure 3*) yielded the value of channel shift, and hence $\Delta 2\theta$, which gave the minimum least squares deviation from the template. Finally, a plot of channel shift against applied load was constructed and the gradient of the resultant straight line was calculated using an unweighted least squares fitting program. *Figure 4* shows typical plots at different temperatures for the annealed 73/27 HBA/HNA sample. The small amount of scatter in these plots supports the use of this technique in detecting peak shifts of less than one channel. The apparent chain modulus was then calculated from the gradient of the peak shift *versus* applied load graph and the sample cross-sectional area.

Results

Table 1 summarizes the results for the annealed samples with two different monomer ratios. Measurements were also made on an unannealed sample with a HBA/HNA monomer ratio of 73/27. Quoted results are the averages of five separate measurements on three different samples from the same batch of material, and all have errors of approximately 10%. The errors in

Figure 2 The meridional peak (at 43°) of annealed 73/27 HBA/HNA copolymer with the best fit theoretical curve

Figure 3 Determination of peak shift using the average profile method

individual results arose from the uncertainty in the cross-sectional area and the error in the gradient of the straight line fitted to the peak shift *versus* load graph. These errors were calculated to be 4% except at low temperatures where a value of 7% was found.

The results in *Table 1* show that the chain modulus determined in this manner varies considerably with temperature and that, at all temperatures considered, the samples with the higher HBA content show the larger apparent chain modulus. The effect of annealing on the 73/27 sample can also be seen, with a slightly higher apparent chain modulus being shown by the annealed sample.

THEORETICAL CALCULATION OF CHAIN MODULUS

Because of the random nature of the copolymers and the lack of any obvious crystallographic structure it is not possible to consider any single basic unit in the analysis of the mechanical properties of the chain. Furthermore, in constructing the molecules the specific conformations adopted by the individual monomers are unknown, although potential energy calculations would indicate preferential conformations. In the approach adopted
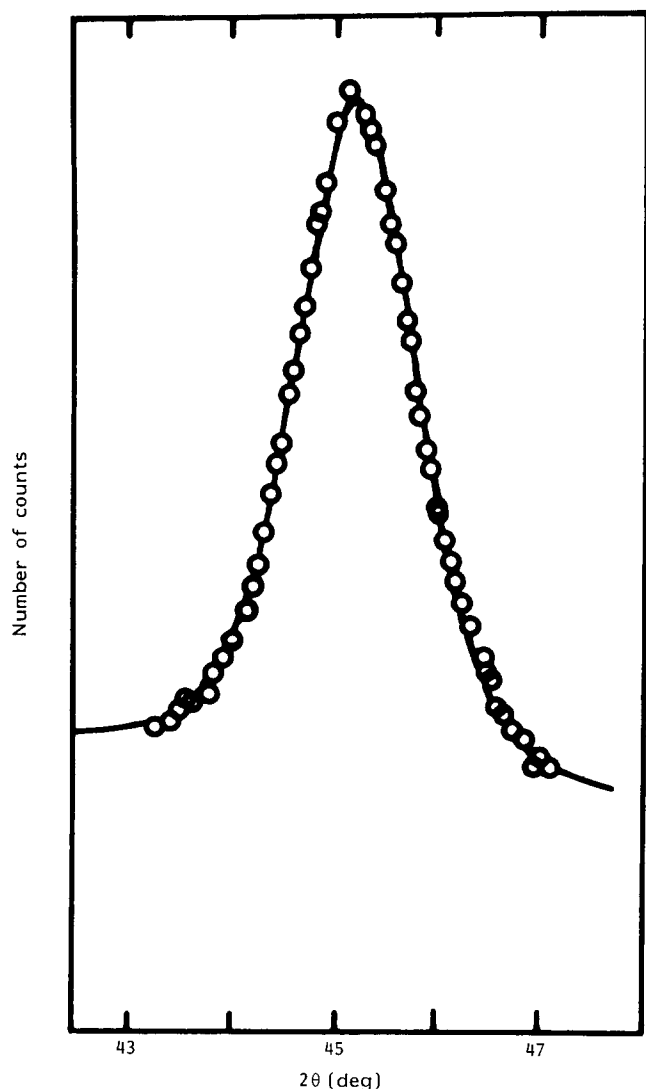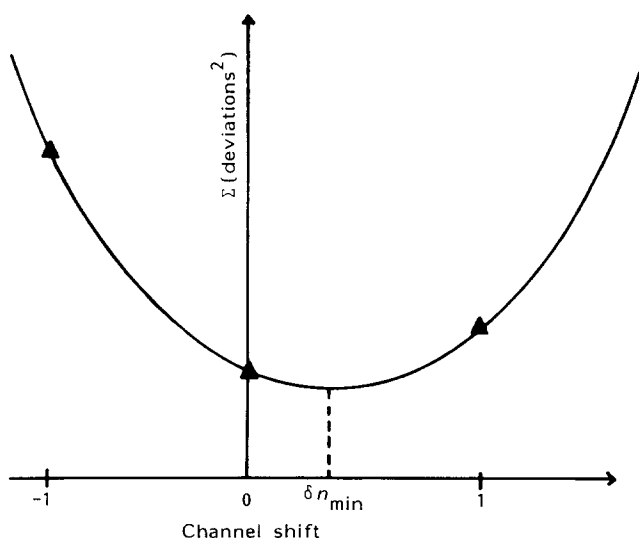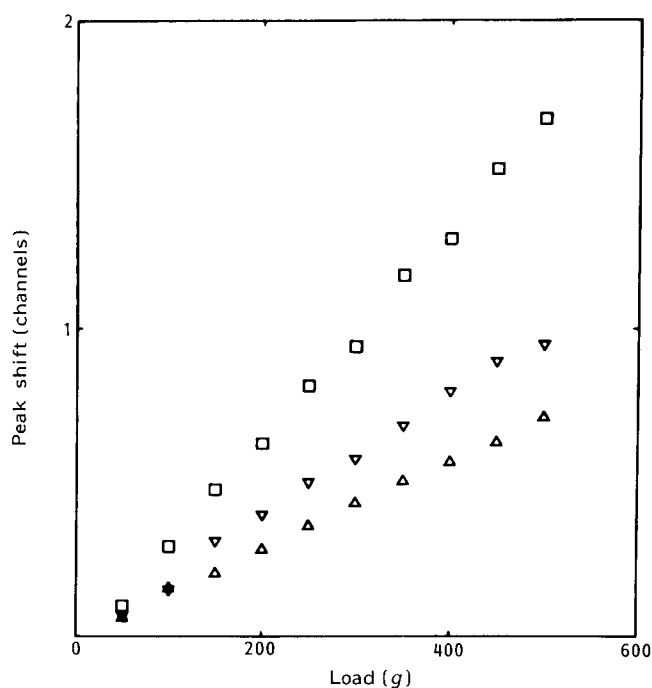

Figure 4 Plot of channel shift against applied load for an annealed 73/27 HBA/HNA sample at: $\triangle$, $-80°C$; ∇, $20°C$; $\square$, $120°C$. A shift of 1 channel corresponds to a strain of $\approx 0.11\%$

Table 1 Measurement of molecular modulus on HBA/HNA copolymers of differing monomer ratios

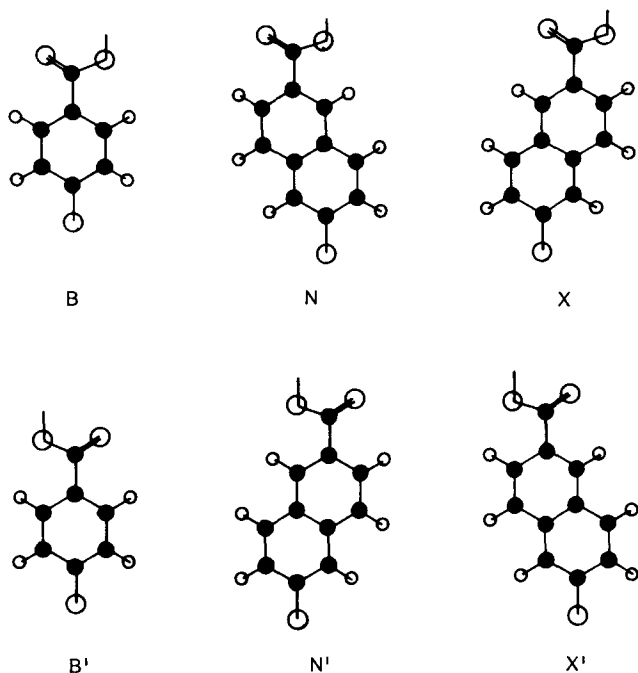| Treatment	HBA/HNA ratio	Temperature (°C)	Modulus (GPa)	
			X-ray	Macro at 1 Hz
Unannealed	73/27	−80	121 ± 12	96 ± 3
		20	97 ± 9	64 ± 2
		120	65 ± 3	28 ± 3
Annealed	73/27	−80	153 ± 14	105 ± 6
		20	105 ± 9	71 ± 5
		120	72 ± 10	23 ± 4
Annealed	30/70	−80	116 ± 8	105 ± 4
		20	68 ± 5	76 ± 3
		120	53 ± 4	28 ± 4

Figure 5 Conformations used to construct the molecules

here, we consider first that the molecular chain is planar, and then subsequently discuss deviations from a planar structure. To reduce the calculations to manageable proportions it is considered that the chains are constructed from six possible different units, the mechanical analysis being performed on the resulting constructed chains, whose length can be arbitrarily decided. The six possible (1 HBA and its reflection and 2 HNA and their reflections) conformations of the two monomers used to form the planar chains are shown in *Figure 5*. The distinction between any conformation, e.g. B and its reflection, B', only becomes apparent when sequence lengths are constructed. Thus, there is a considerable difference between the homopolymer sequences BBBBB and BB'BB'B, but no physical difference between the sequences BBBBB and B'B'B'B'B'. The coordinates for each atom in the monomers are obtained from Blackwell *et al.*[2]. The molecules are built keeping the aromatic ring to ester oxygen bonds and aromatic ring to carbonyl carbon bonds parallel. *Figure 6* shows a 60/40 HBA/HNA chain with monomers in the BB'XXB conformations. The fully extended chain would contain monomers of B and X (or B' and X') conformations only. In the analysis which follows, since it is assumed that the molecular backbones are planar, only contributions to molecular extension from bond stretching and angle opening need to be considered.

The basic approach described by Treloar[15] has been used to calculate the chain modulus. It is simplest to consider the three contributions to molecular extension separately. These arise from:

1 Bond stretching excluding the aromatic rings;
2 Bond angle opening excluding the aromatic rings; and
3 The deformation of the benzene and naphthalene rings.

Figure 6 shows a typical sequence length which might be considered. The full line represents the line of action of the applied force. If θ_i is the inclination of the ith bond to the direction of the applied force, the contribution to chain

extension per unit force from bond stretching is given by $\sum \cos^2 \theta_i / k_i$, where k_i is the stretching force constant for the ith bond.

The contribution to chain extension arising from bond opening is obtained by considering the torques operating on each apex. These are dependent on the position of the line of action of the applied force since the torque on each apex is proportional to its distance from this line. The position of the line of action for the applied force is obtained by noting that for equilibrium to be maintained there must be no net torque acting on the sequence length. Initially the line of action is chosen arbitrarily and the net torque on the sequence calculated by summing the contributions at each apex. An iterative program is then used to find the position which results in zero torque. That position is then chosen to evaluate the changes in inclination of each bond in the sequence and the contribution to the chain extension per unit force is calculated from $\sum -l_i \sin \theta_i \, \delta\theta_i$, where $\delta\theta_i$ denotes the change in inclination of the ith bond of length l_i to the line of action. The only unknown, $\delta\theta_1$, can be found by requiring that both ends of the sequence lie on the line of action of the applied force after deformation.

The third contribution to the molecular extension involves the deformation of the benzene and naphthalene rings. The deformation of the benzene ring has been considered by Treloar[16] and for the case of symmetric application of the forces it is given by

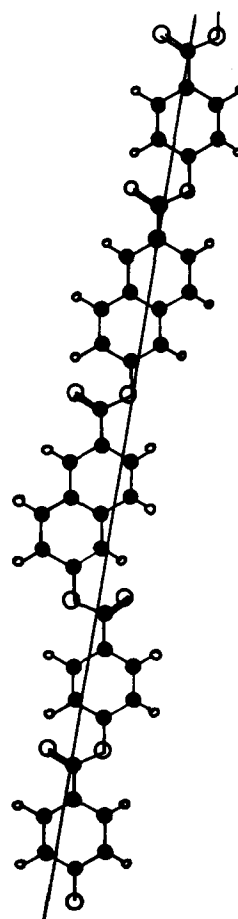$$\frac{\delta L}{F} = \frac{l^2}{4k_\alpha} + \frac{3}{4k_l} \qquad (1)$$

Figure 6 Example of constructed sequence, conformation BB'XXB

Table 2 Force constants used in calculation of chain moduli

Bond stretching

Bond	Force constant (N Å^{-1} × 10^{-8})
O–C(=O)	6.18
C(=O)–C(b)	4.50
C(b)–C(b)	6.43
C(b)–O	5.09

Angle opening

Angle	Force constant (N Å rad^{-1} × 10^{-8})
O–C(=O)–C(b)	0.8
C(b)–C(b)–C(=O)	0.934
C(b)–C(b)–C(b)	0.934
C(b)–C(b)–O	0.934
C(b)–O–C(=O)	1.3

Table 3 Chain moduli for different sequences of HBA/HNA copolymers

Sequence	HBA (%)	Modulus (GPa)
BBBBB	100	155
XXXXX	0	197
NNNNN	0	126
BBBBX	80	150
BBBXX	60	148
BBXXX	40	158
BXXXX	20	175
BBBBN	80	107
BBBNN	60	88
BBNNN	40	91
BNNNN	20	108
BNBNN	40	108
BNBBN	60	108
BNBN	50	113
BB'	100	105
NN'	0	77
BB'XXB	60	94

where l is the length of the aromatic carbon carbon bond and k_α and k_l are the angle opening and bond stretching force constants respectively. This equation is also used here although the forces acting on the ring are not necessarily symmetric. An approximation to the extension per unit force of the naphthalene ring can be obtained by considering it to behave as two benzene rings coupled together appropriately. For a fixed applied force the extension due to angle opening is assumed to be 3/2 times that for the benzene ring alone. The extension from bond stretching is obtained by considering the fraction of the applied force acting along each section of the ring and performing the summation $\sum \cos^2(\theta/k_i)$. This leads to a contribution of $4/3k_l$ from bond stretching. The total extension per unit force is then given by

$$\frac{\delta L}{F} = \frac{3l^2}{8k_\alpha} + \frac{4}{3k_l} \qquad (2)$$

The force constants used in the present calculations are listed in *Table 2*[13].

Results

Table 3 displays some of the results obtained for different sequences of HBA/HNA copolymers. Clearly

there is a wide range of values for the different copolymers which does not depend solely on the relative proportions of the constituent monomers. Looking first at the intrinsic properties of each monomer, it can be seen that the HBA monomer has a chain modulus of 155 GPa whereas the chain modulus of the HNA monomer depends on its conformation. In the X (or X') conformation it has a modulus of 197 GPa whereas in the N (or N') conformation the modulus is 126 GPa. It might be expected that copolymers of HBA and HNA would show chain moduli which reflected these moduli depending on the relative proportions of each conformation. The relationship, however, is not so simple.

Figure 7 shows the effect of systematically replacing the last B monomer in a sequence of five B monomers by one of the other five conformations. The uppermost curve, marked X, predicts the behaviour of the fully extended copolymer for different concentrations of the intrinsically stiffer HNA, i.e. sequences BBBBX, BBBXX, BBXXX etc. Initially there is a small drop in the modulus. This arises
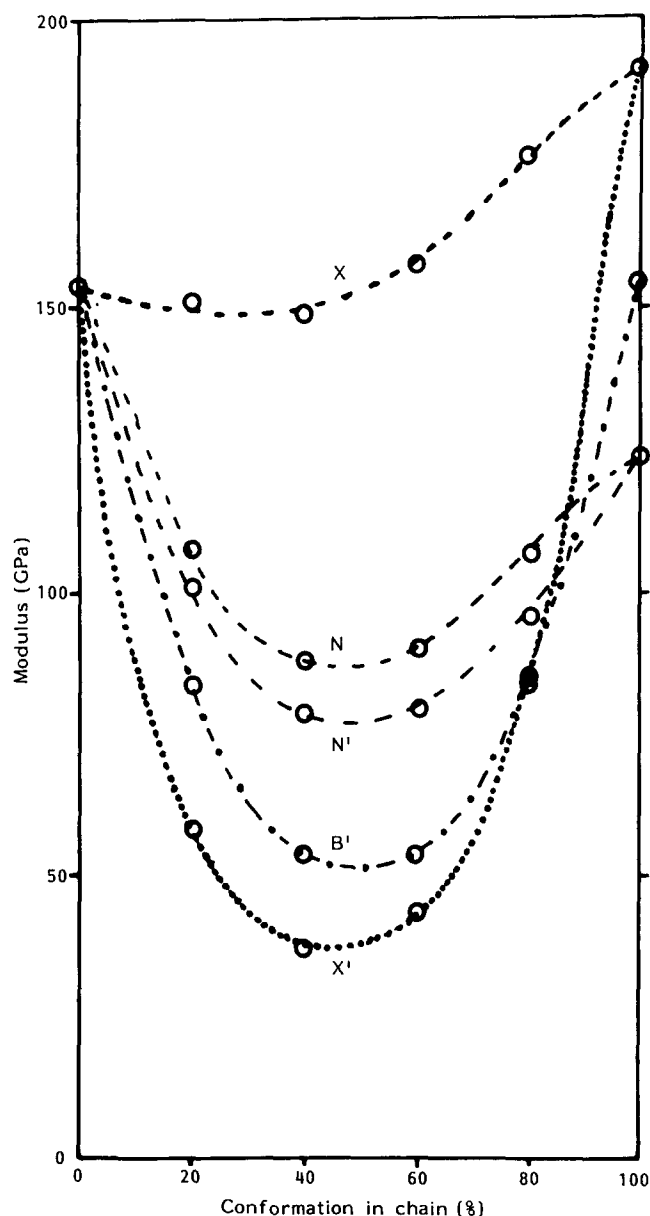

Figure 7 Modulus of five monomer sequence lengths as a function of the concentration of each monomer. In each case the rest of the sequence contains monomers of conformation B
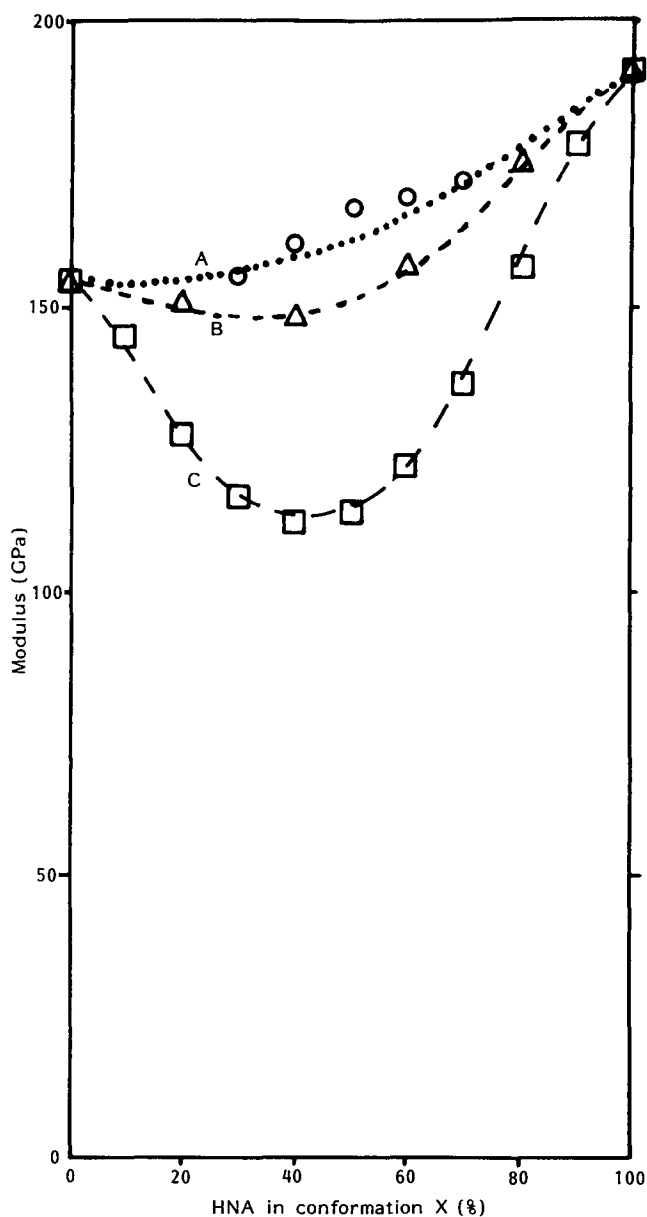
Figure 8 Modulus of different sequences as a function of concentration of X monomer. In each case the rest of the sequence contains monomers of conformation B. Curves A–C are explained in the text

because of the slightly different positions and inclinations of the monomer end-to-end vectors (relative to the line of action of the applied force) in the copolymer from those in the homopolymers of single conformation. A consequence of this is the generation of larger torques at the comparatively weak carbonyl carbon and ester oxygen atoms, and thus an increased contribution to the molecular extension from bond opening. As the concentration of HNA increases, however, the greater intrinsic stiffness of the HNA becomes more dominant and the modulus of the copolymer starts to rise.

For a sequence in which the monomers are not all in the B or X conformation there is a marked difference in behaviour. As can be seen from *Figure 7*, the replacement of a B monomer in a sequence of five B monomers by a B', X', N or N' conformation results in chain moduli varying between 108 GPa and 58 GPa. *Figure 7* shows the effect of continuing this substitution. It should be noted, however, that these results are for block copolymers and

that the effect of breaking up these blocks is significant. Thus, for example, a sequence BB'BB'B has a modulus of 89 GPa compared with a value of 53 GPa for a BBBB'B' sequence.

Figure 8 illustrates the influence of blockiness by showing how a range of values for the chain modulus can be obtained by only altering the sequential ordering of the different monomers in copolymers with the same HBA/HNA ratio. Curve B is obtained by starting with a sequence of five HBA units in the B conformation and successively replacing the final unit with an HNA monomer in the X conformation in the manner described above. Curve C is obtained by following the same procedure on a sequence of 10 units. Immediately it is seen that there is a large difference in the values of the chain modulus for chains of the same relative HBA/HNA concentrations. This difference is attributed to the existence of larger blocks of conformationally regular homopolymer with a resulting greater deviation from the line of action of the applied force of the main chain atoms, with corresponding greater torques on the bond angles at the ester oxygen and the carbonyl carbon.

It is clear from these considerations that the highest chain moduli are obtained by restricting the deviation of the main chain atoms from the line of action. In other words, for a given copolymer composition the maximum modulus is obtained by keeping the sinuosity of the chain to a minimum, but this requires non-random positioning of the monomers along the chain. Curve A in *Figure 8* shows the effect of increasing the relative concentration of HNA in the copolymer while attempting to comply with this restriction. A clear consequence of this is the conclusion that an increase in the relative concentration of HNA in the X conformation produces initially a small drop in the chain modulus, followed by a significant increase.

Further calculations were undertaken for long sequences (≈ 100 units) constructed by randomly positioning the different possible conformations along the chain. Not only was the chain modulus very low (< 10 GPa) but also there was an additional problem concerning the packing requirements of such chains to give a satisfactory macroscopic density. These chains are very sinuous and can deviate by more than 6 Å from the line of action, which compares with an interchain distance of between 4.5 and 5.2 Å from density and X-ray measurements[6].

We are therefore drawn to the conclusion that the sinuosity of the chain is restricted. One possibility is to increase the probability that an HBA monomer unit has the opposite conformation to the previous one in the chain, and similarly for HNA. Furthermore, if X and X' conformations are considered to be absent, the chain will mainly be composed of dimers BB' and NN' and longer sequences such as BNN'B'. The moduli for BB' and NN' dimers are 107 and 77 GPa, respectively, while those for chains containing these conformations tend to be about 80 GPa.

In the theoretical analysis described here, it has been assumed that both the monomers and the constructed molecules are planar. It is known that the monomers themselves are not planar because of the tilt of the benzene and naphthalene rings, but this is not expected to affect the modulus results because the main chain atoms used in the calculation are unaffected by this. A further

problem arises from the probability that the constructed molecules will contain twists due to a distribution of orientations of the monomers about the chain direction. Of course each monomer reflection, discussed above, is the special case of rotation of the monomer by 180°, so clearly twists in the chain will affect the sinuosity and hence the calculations of modulus. Nevertheless, this problem does not affect the intrinsic mechanical moduli of the monomers nor the general conclusions of this work.

DISCUSSION

It is useful first to summarize the main conclusions of the theoretical analysis. The results above show that the chain moduli of copolymer blocks depend critically on the conformation and positional ordering of the different monomers within the chain and not just the HBA/HNA ratio. Highest values are obtained by restricting the deviation of the main chain atoms from the line of action of the applied force (or restricting the sinuosity of the chains). Complying with this restriction, the trend in the chain modulus with increasing HNA content depends on whether the HNA units are in their fully extended conformation (X or X') or not. If this is the case the modulus is expected to rise; otherwise a fall is predicted. Totally random chains have very low moduli and present packing difficulties. Thus although there may be random positioning of the monomers along the chain, there cannot be a random distribution of all possible conformations. These packing difficulties can be avoided by increasing the probability of having BB' and NN' dimers in the chain, but the moduli of chains containing these conformations are only ≈ 80 GPa.

The chain modulus obtained from theoretical calculations should be independent of temperature provided there are no conformational changes. For these copolymers rotation of the oxybenzoic and oxynaphthoic acid residues can occur without affecting the chain backbone atoms, and the onset of these relaxations should not affect the chain modulus. It is only the onset of conformational changes following increased chain mobility at temperatures above the glass relaxation which would alter the chain modulus. Dynamic mechanical measurements[17], supported by interpretation of nuclear magnetic resonance (n.m.r.) data[18], suggest that increased chain mobility sufficient to allow conformational changes only occurs at temperatures above 100°C. In theory therefore, the chain modulus should be independent of temperature below 100°C. This has to be reconciled, however, with the observed temperature dependence of the X-ray measurements of apparent chain modulus at temperatures below the glass transition, T_g.

We feel we should reiterate that the interpretation of the X-ray measurements of molecular strain in HBA/HNA copolymers differs in one important respect from that of similar measurements in crystalline polymers. In HBA/HNA copolymers the meridional X-ray diffraction peak does not arise solely from crystalline material. It is the result of scattering from individual random sequences of chains of persistence length ≈ 10 units[3,4], and consequently all the chains, not just those found in the crystalline regions (if there are any), contribute. Any shift in the position of this diffraction peak is therefore the result of strains in all the chains irradiated by the beam, so that the modulus obtained from the experimental

technique can be correctly regarded as the average chain modulus (averaged over all the chains).

This can be contrasted with polyethylene, which is a semicrystalline polymer. In polyethylene the X-ray strain is specifically associated with the crystalline regions, and the change in the apparent crystal modulus with temperature can be linked primarily to changes in the stress on the crystalline regions, due to changes in the compliance of the amorphous regions with temperature. The fall in apparent crystal modulus with increasing temperature does not require the intrinsic chain modulus to be temperature dependent (which would require the intramolecular force constants to vary with temperature) but can be quantitatively explained by increasing stress concentration on the crystals, as the amorphous regions become more compliant[11].

Because the X-ray measurements are not specific to any regions within the HBA/HNA copolymers it is unproductive to attempt to explain the temperature dependence of the average chain modulus using Takayanagi models or their equivalent which assume the distinction between crystalline and amorphous regions. At the same time it is desirable to avoid introducing a temperature dependent intrinsic chain modulus at temperatures below T_g, although it is recognized that there will be some variation with temperature due to the atomic thermal vibrations[19].

An alternative approach is suggested by comparison between the low temperature experimental results and the theoretical calculations of the chain modulus of different sequences. It is generally seen that these experimental values are greater than the theoretical values for any but the most regular sequences, yet the existence of such sequences is not supported by an analysis of the X-ray diffraction patterns. Theoretical calculations of the chain modulus of randomly substituted copolymer chains subject to packing constraints yield values considerably less than the low temperature measurements. If the intrinsic chain modulus is assumed to be low there is no longer the problem of having to account for a drop in average chain modulus as the temperature is increased, but instead it is necessary to explain the rise in apparent chain modulus as the temperature is decreased.

A low intrinsic modulus may seem surprising for aromatic chains but is explained by the importance of angle opening at large distances from the line of action of the applied force. In simple terms it can be considered to arise through the rotation of the constituent HBA and HNA units towards the direction of the applied force, resulting in a change in the projection of these units along the line of action. It is an average value of this change which is provided by the X-ray measurements. For a single isolated chain such deformation changes would be unhindered and a low chain modulus would be obtained. In a polymer environment, with many other extended irregular chains, the same deformation process would not proceed without overcoming the shear forces between adjacent units in different chains. It follows that the apparent chain modulus recorded by the X-ray measurements would rise as the shear modulus increased.

Consideration of the possible chain loading mechanisms also shows the importance of shear in the role of stress transfer within the sample. This would suggest the adoption of either an aggregate or a fibre composite model to predict the behaviour of the

macroscopic mechanical properties. As will be shown in a subsequent paper[17], the aggregate model is particularly successful in this respect. The aggregate model can be applied at a microscopic level, with the intrinsic mechanical properties of the monomers providing the necessary model parameters for the units of the structure.

It has been shown elsewhere[17] that for these highly oriented tapes the aggregate model can be simplified to give the following relationship between the macroscopic extensional compliance S_{33} and the intrinsic unit extensional and shear compliances s_{33} and s_{44} respectively:

$$S_{33} = s_{33} + s_{44} \langle \sin^2 \theta \rangle \qquad (3)$$

where θ is the inclination of a unit to the principal extensional axis and the angle brackets indicate that the average over all the units is used. In testing the model, the level at which it is applied (molecular or submolecular) determines which orientation and compliance values are used. However, for a system in which the orientation is incomplete (i.e. $\langle \sin^2 \theta \rangle > 0$) and the shear modulus is low it can be seen that there is a large contribution to the macroscopic compliance from the shear term in equation (3). Moreover, it is this shear term which accounts for the difference between the apparent chain modulus and the macroscopic modulus (*Table 1*). The X-ray strain does not record this shear contribution and thus the apparent chain modulus will be greater than the macroscopic value, as can be seen in *Table 1*. The exception is shown by the two values for the annealed 30/70 HBA/HNA sample at 20°C. This is explained more fully elsewhere[17] and arises because the frequency dependence of the relaxations results in the measurements being either side of a relaxation process and therefore not directly comparable.

At low temperatures, although the intrinsic chain modulus of the copolymer molecules is low due to the sinuosity of the chains, it is the mechanical properties of the monomers which are important in determining the macroscopic properties. The absence of HNA in its intrinsically stiffer fully extended conformation, X, accounts for the failure to observe an improvement in either the average apparent chain modulus or the macroscopic modulus as the concentration of HNA is increased. Instead the conformation adopted by the HNA monomer is intrinsically less stiff than that of the HBA monomer and there is thus a decrease in the X-ray and macroscopic moduli as the HNA content is increased. This is consistent with X-ray results[4], which indicate that the HNA monomer adopts either the N or the N' conformation.

At high temperatures, when the shear modulus is very low it might be expected that the average chain modulus recorded by the X-ray measurements would tend to approach the intrinsic chain modulus. It is interesting to note that the apparent chain modulus at 120°C is ≈ 70 GPa, which agrees quite well with the theoretical calculations of the modulus of chains of random substitution meeting packing requirements.

CONCLUSIONS

The meridional X-ray scattering pattern from liquid crystalline copolymers of hydroxybenzoic acid with hydroxynaphthoic acid have been used to examine molecular strain within stressed samples. This X-ray pattern is the average Fourier transform of chain lengths of ≈ 10 units and X-ray measurements therefore give the average chain modulus throughout the whole sample. Comparison of these results with theoretical calculations of the chain moduli of model sequences of copolymer reveals several interesting conclusions. First, although the chain modulus of an isolated chain is comparatively low, constraints imposed on the deformation of individual chains by lateral packing result in an enhancement of the average chain modulus. This enhancement arises from the additional shear forces which must be overcome as molecules deform. Second, the temperature dependence of the apparent chain modulus below T_g arises not from changes in the intrinsic chain modulus but from the temperature dependence of this shear modulus. Above T_g, changes in the intrinsic chain modulus, following the onset of conformational changes, would also contribute to the temperature dependence of the apparent chain modulus.

It has also been proposed that the mechanical behaviour of these copolymers may be interpreted in terms of an aggregate model and this allows us to explain the difference between the macroscopic modulus and the apparent chain modulus. The macroscopic modulus contains an important contribution from the shear compliance which is not recorded by the apparent chain modulus and thus values of the apparent chain modulus are greater than those for the macroscopic modulus.

Finally, measurements of the mechanical properties of HBA/HNA copolymers, together with theoretical calculations of chain moduli, have provided supporting evidence that the HNA monomers do not adopt the fully extended conformation, X, but instead adopt the N (or N') conformation. This result is in agreement with X-ray measurements of the repeat distance. The decrease in modulus with increase in HNA content is probably due to the presence of HNA predominantly in the less stiff N or N' conformation.

REFERENCES

1   Gutierrez, G. A., Chivers, R. A., Blackwell, J., Stamatoff, J. B. and Yoon, H. *Polymer* 1983, **24**, 937
2   Blackwell, J., Gutierrez, G. A. and Chivers, R. A. *Macromolecules* 1984, **17**, 1219
3   Chivers, R. A., Blackwell, J. and Gutierrez, G. A. *Polymer* 1984, **25**, 435
4   Mitchell, G. R. and Windle, A. H. *Colloid. Polym. Sci.* 1985, **263**, 250
5   Davies, G. R. and Jakeways, R. *Polym. Commun.* 1985, **26**, 9
6   Chivers, R. A. and Blackwell, J. *Polymer* 1985, **26**, 997
7   Blundell, D. J. *Polymer* 1982, **23**, 359
8   Windle, A. H., Viney, C., Golombok, R., Donald, A. M. and Mitchell, G. R. *Faraday Discuss. Chem. Soc.* 1985, **79**, 55
9   Butzbach, G. D., Wendorff, J. H. and Zimmerman, H. J. *Makromol. Chem. Rapid. Commun.* 1985, **6**, 821
10 Blackwell, J. Personal communication
11 Clements, J., Jakeways, R. and Ward, I. M. *Polymer* 1978, **19**, 639
12 Tashiro, K., Kobayashi, M. and Tadokoro, H. *Macromolecules* 1977, **11**, 908
13 Tashiro. K., Kobayashi, M. and Tadokoro, H. *Macromolecules* 1977, **10**, 413
14 Tashiro, K., Kobayashi, M. and Tadokoro, H. *Macromolecules* 1977, **10**, 731
15 Treloar, L. R. G. *Polymer* 1960, **1**, 95
16 Treloar, L. R. G. *Polymer* 1960, **1**, 279
17 Troughton, M. J., Davies, G. R. and Ward, I. M. in preparation
18 Clements, J., Humphreys, J. and Ward, I. M. *J. Polym. Sci., Polym. Phys. Edn* 1986, **24**, 2293
19 Li, T., Tashiro, K., Kobayashi, M. and Tadokoro, H. *Macromolecules* 1987, **20**, 347