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Structure and mechanical properties of a thermotropic liquid crystalline copolyester

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The mechanical properties and structure of a thermotropic liquid crystalline copolyester have been investigated. Shear and tensile moduli of oriented samples were determined over the temperature range −100°C to 190°C. Crystal size and crystal moduli measurements were also undertaken. An analysis of the anisotropic mechanical behaviour is undertaken using a simplified aggregate model. © 1997 Elsevier Science Ltd

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INTRODUCTION

The polymer of interest is a three component copolyester based on the units hydroxybenzoic acid (HBA), isophthalic acid (IA), and hydroquinone (HQ). This polymer, poly(*p*-oxybenzoate-*co*-*p*-phenylene isophthalate) is referred to by the abbreviation HIQ which is derived from the acronyms of the three components. HIQ can be prepared with varying proportions of the three components, bearing in mind that for stoichiometric reasons the relative amounts of IA and HQ must be the same. Samples with different proportions of HBA are designated by the amount (in mol%) of HBA. Thus HIQ-35 has 35% HBA, 32.5% IA and 32.5% HQ. The investigations of the physical properties of HIQ-35 reported here form a natural extension to our earlier studies of other oriented liquid crystal copolymers[1–4]. It also complements our work on the electrical properties of HIQ-40 films[5].

Samples were supplied by Hoechst Celanese of Summit, New Jersey, as highly oriented rods and tapes. HIQ can be processed from the melt to form oriented films, tapes and rods in the same manner as other liquid crystalline copolyesters and can be solution cast to form isotropic films. Tapes were supplied as spun and annealed (4 h at 300°C) in this laboratory. The composition of HIQ is compared with the copolyesters studied previously[1–4] in *Table 1*.

STRUCTURAL STUDIES

Liquid crystalline copolyesters incorporating the isophthalate unit have been investigated only recently[7–9,13–15]. In the case of HIQ systems, liquid crystalline (LC), crystalline (XL), and the amorphous phases can exist, depending on the amount of *p*-oxybenzoate (HBA) present[7,13].

HIQ contains the *meta*-linked isophthalate unit which is conventionally thought of as being disruptive to the formation of straight chains. The effect of the isophthalate group is, however, somewhat more complicated in this system since it is possible to use alternating IA and HQ units to build essentially straight quasi-planar extended chains. This can be clearly seen with reference to *Figure 1*. The chain fragment labelled (a) is made from 100% HBA, while the chain fragment (e) is made of alternating IA and HQ units. Note how the other chain fragments can be considerably more 'sinuous' than the latter structure.

Studies of a copolyester of a similar composition[7,11] to HIQ-35 show a liquid crystal (LC) structure in the quenched phase which changes on annealing to a partly LC, partly crystalline structure[7,11]. Investigations using electron microscopy reveal a complex morphology with a bimodal orientation distribution in quenched material which had not been subject to high extensional flow fields; this changes to a partly crystalline phase with a uniform orientation distribution on annealing[15].

Our investigations show that HIQ-35 is wholly LC in the as-spun state. On annealing, a two phase structure develops with crystallites embedded in an LC matrix. Wide angle X-ray scattering (WAXS) studies show a significant change in the X-ray diffraction pattern on annealing. A set of crystalline peaks is superposed on the typical LC pattern and the diffraction features associated with the LC phase are enhanced. Measurement of the crystalline *d*-values and comparison with the system studied by other workers show that the crystallites appear to be *p*-phenylene-*co*-isophthalate[7]. It has been suggested that these crystallites are a 'zig-zag' structure containing alternate IA/HQ units, but no HBA[7] as shown in *Figure 1e*.

In the present investigation, quantitative X-ray diffraction studies have been directed towards determination of the crystal fraction and crystallite size, quantities of interest in their own right, and also of potential use in mechanical modelling. Estimates of the crystal fraction were made on the basis of changes in density between the as-spun and annealed polymers. The

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Table 1 Compositions (in mol%) of various copolyesters which have been studied in this laboratory

Name	HBA	HNA	TA	IA	PAM	DHN	BP	HQ
HIQ-35	35			32.5				32.5
HIQ-40	40			30.0				30.0
CO3070	30	70						
CO7327	73	27						
CO2,6	60		20			20		
COTBP	60	5	17.5				17.5	
HNATA		60	20		20			
HNATH		60	20					20

Abbreviations: HBA, 4-hydroxybenzoic acid; HNA, 2-hydroxy-6-naphthoic acid; DHN, 2,6-dihydroxynaphthalene; BP, 4,4′-biphenyldiol; IA, isophthalic acid; TA, terephthalic acid; PAM, *p*-amino phenol; HQ, hydroquinone

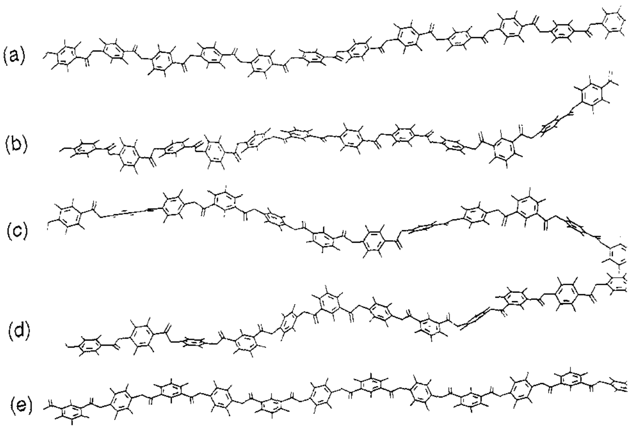

Figure 1 Sections of HIQ chains with varying proportions of HBA: (a) 100% HBA, (b) 66% HBA, (c) 50% HBA, (d) 33% HBA, (e) 0% HBA. These sections were taken from longer sections which were minimized from planar extended starting point. The minimization routine used the Biosym PCFF forcefield

density of crystalline *p*-phenylene-*co*-isophthalate can be found from the unit cell dimensions and contents. Erdemir *et al.*[7] suggest an orthorhombic cell containing four chains with dimensions $a = 1.116\,\mathrm{nm}$, $b = 0.784\,\mathrm{nm}$ and $c = 2.43\,\mathrm{nm}$; whilst Blundell *et al.*[13] suggest an orthorhombic cell containing one chain of dimensions $a = 0.563\,\mathrm{nm}$, $b = 0.395\,\mathrm{nm}$, $c = 2.42\,\mathrm{nm}$; these give densities of $1.49\,\mathrm{cm}^{-3}$ and $1.47\,\mathrm{g\,cm}^{-3}$ respectively for the crystalline phase.

Measured densities vary from $1.394\,\mathrm{g\,cm}^{-3}$ for the as spun polymer to $1.415\,\mathrm{g\,cm}^{-3}$ for the annealed tape. Making the simplistic assumption that the non-crystalline phase does not change in density on annealing, and using a crystalline density of $1.49\,\mathrm{g\,cm}^{-3}$ the measured sample densities would suggest crystal fractions of $X_c = 22\%$ for the tape samples and $X_c = 18\%$ for the rod samples.

Crystallite size measurements were made on the annealed tape samples. The breadths of the {0.1.1}, {1.1.0} and {1.0.0} reflections (of Blundell *et al.*[13]) were used to obtain the lateral crystallite size of about 6 nm × 6 nm. The {0.0.6} and {0.0.10} reflections were used to obtain the *c*-axis crystallite size of about 5.8 nm. The crystallites are thus approximately cubes, with the crystallite size parallel to the draw direction representing 2.5 unit cells or 10 monomers on average.

These observations are difficult to reconcile with the simple view that we are dealing with, as far as is chemically possible, a random copolymer. Accounting for the excluded combinations, the probability of the sequence IA/HQ on a random basis is about 4/9. The probability of five of these sequences together is therefore $(4/9)^5$ or a little under 2%. It may therefore be that the polymer is non-random, or that transesterification occurs on annealing. If we assume that IA and HQ preferentially combine, the probability of extended sequences of IA/HQ would be considerably increased.

Another possibility is that of an isomorphism between the IA/HQ units and the HBA units. The repeat unit IA/HQ has a length of approximately 12 Å. A number of the possible conformations of IA/HQ sequences and those of HBA/HBA sequences have similar repeat unit lengths. Assuming that sequences of IA/HQ and HBA/HBA could co-crystallize could explain the apparent crystal size since there is then no need for long sequences of wholly IA/HQ units.

For the purposes of mechanical analysis, annealed HIQ-35 can be considered to be composed of small crystallites (of linear dimension 6 nm) embedded in a liquid crystal matrix. It is, however, important to note that crystallization in HIQ-35 is probably selective in that IA/HQ units preferentially crystallize. This changes the composition of the LC phase which becomes depleted with respect to isophthalate and hydroquinone.

SHEAR MODULUS MEASUREMENTS

Shear modulus measurements were made on a simple inverted torsion pendulum apparatus of the type described by Heijboer[17] as discussed in a previous publication[4]. Measurements were made on oriented strands of elliptical section, with typical semi-major axes of 0.4 mm, semi-minor axes 0.3 mm and lengths 100 mm. A low-inertia moment arm was needed to obtain sensibly short oscillation periods. This was made from ultra-thin walled cryogenic tube and had a moment of inertia of $4 \times 10^{-6}\,\mathrm{kg\,m}^{-2}$, an order of magnitude lower than previously available. Measurements were made in the temperature range −100°C to 200°C, with an average of three runs on different samples providing the final result.

The shear modulus of the as-spun strand falls from 1.92 GPa at −100°C to 0.17 GPa at 180°C and that of the annealed strand falls from 2.16 GPa at −100°C to 0.33 GPa at 190°C. The frequencies corresponding to these measurements vary from about 2 Hz at low temperatures to 0.5 Hz at high temperatures. *Figure 2* shows the shear modulus of both the as spun and the annealed polymers as a function of temperature. In both

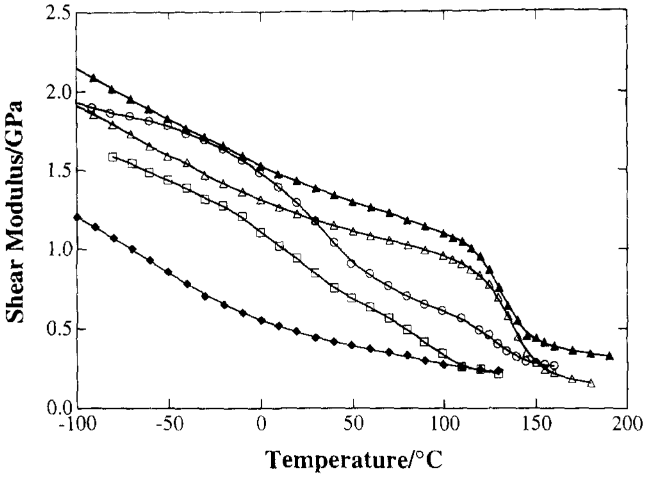

Figure 2 Shear moduli of as-spun and annealed HIQ-35 compared with other liquid crystal copolyesters (see *Table 1*). △, HIQ-35 as spun; ▲, HIQ-35 annealed; ○, HNATA; □, CO 73/27; ◆, COT-BP

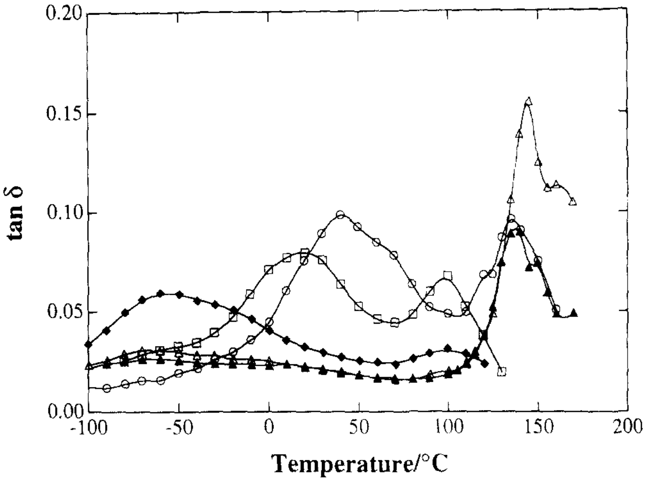

Figure 3 Tan δ (shear) of as-spun and annealed HIQ-35 compared with other liquid crystal copolyesters (see *Table 1*). △, HIQ-35 as spun; ▲, HIQ-35 annealed; ○, HNATA; □, CO 73/27; ◆, COT-BP

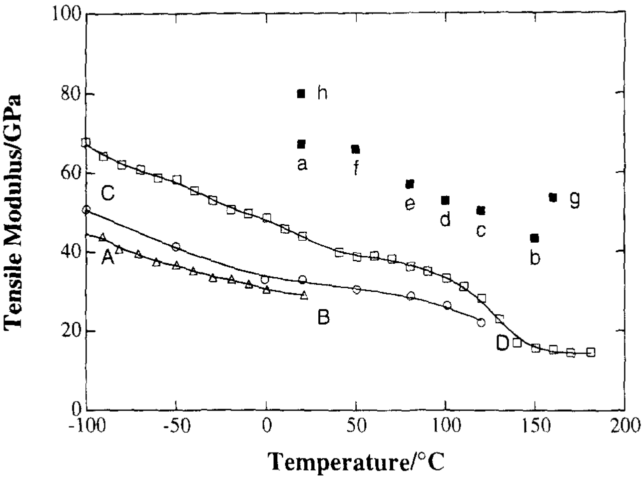

Figure 4 Dynamic tensile modulus (10 Hz) of as-spun HIQ-35. The curve A–B (△) was obtained by following a lengthy conditioning process at 20°C, whereas the curve C–D (○) was obtained following similar conditioning at 100°C. Also shown are measurements on annealed samples (□), and values obtained for the X-ray LC (chain) modulus (■), measured in the order indicated by the letter at each point

cases the modulus declines steadily to about 100°C, and a relaxation process centred at about 130°C causes a more rapid fall between 100°C and 160°C, where the modulus resumes a more gradual decline once more.

The shear loss tangent is plotted as a function of temperature in *Figure 3*. The as spun and annealed polymers both show very weak loss processes centred at about −60°C. In addition there are prominent loss processes at 130°C corresponding to the relaxation noted above.

TENSILE MODULUS MEASUREMENTS

Tensile modulus measurements were made using a forced vibration non-resonance apparatus, details of which were given in a previous publication[4]. Measurements were made at 10 Hz on thin, highly oriented tapes, typically 1 mm × 0.025 mm × 50 mm in dimensions. Two problems were encountered with measurement of the tensile properties of HIQ-35: the first was that the polymer had a substantially non-linear stress–strain relationship which manifested itself as an increase in dynamic modulus with increasing dead-load: and the second was that the polymer deformed irreversibly under the dead-load and this irreversibly increased the modulus.

As spun HIQ-35

In view of the non-linearity mentioned above, the zero load modulus was found by measuring the dynamic modulus as a function of static stress and extrapolating to zero stress using a quadratic fit. In addition, to minimize the effects of irreversible deformation, a 'conditioning' process was undertaken in which samples were first held under a static stress of 100 MPa for a time long compared with the time taken to obtain the dynamic measurements. (The conditioning stress of 100 MPa was the average static stress during dynamic measurements.) Two curves of zero-load tensile modulus vs. temperature are shown in *Figure 4*: the first, labelled A–B, was obtained on a sample which had been conditioned at a temperature of 20°C; the second, labelled C–D, was obtained following conditioning at 100°C.

Annealed HIQ-35

In common with the as-spun polymer, annealed HIQ-35 is non-linear in its stress–strain relationship. It also showed further irreversible deformation under load despite the fact that it was annealed at 300°C under nitrogen for 4 h. Current measurements, shown in *Figure 4*, must therefore be regarded as giving only an indication of the tensile properties of this material.

MEASUREMENT OF CRYSTAL AND LIQUID CRYSTAL MODULI

The meridional diffraction pattern of annealed HIQ-35 is shown in *Figure 5*. X-ray modulus measurements were made following the method of Troughton *et al.*[18]. The shift of the $d = 2.01$ Å peak at a diffraction angle of ~45° was used to determine the chain modulus of the LC component of the polymer, and the shift of the {0.0.10} peak was used to determine the *c*-axis crystal modulus of the crystallites. The LC chain modulus is relatively easy to determine because the LC peaks are intense and the shifts are large. The crystal modulus is, however, much more difficult to determine because the peaks are weaker

Table 2 Comparison of X-ray modulus measurements with macroscopic data for annealed HIQ-35

Temperature (°C)	Chain (LC) modulus[a] (GPa)	Crystal modulus (GPa)	Macroscopic (GPa)
20	67–80	220	40–72[b]
100	53	230	
150	43	210	~25

[a] Dependent on load history
[b] Load and creep dependent

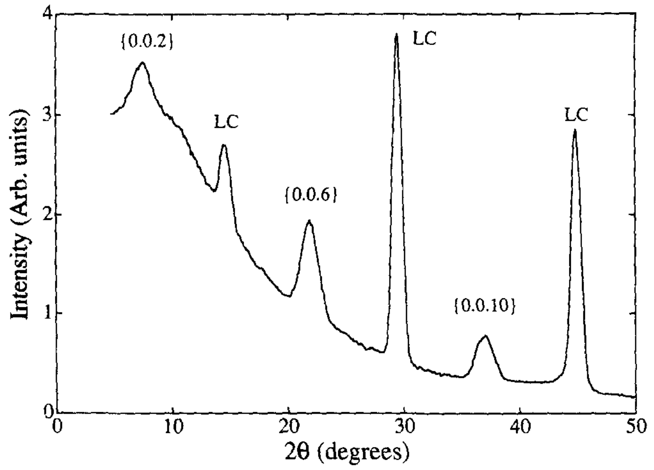

Figure 5 The meridional diffraction pattern of HIQ-35

and the shifts under load are very small. Counting times of 40 s were used for the LC peaks but counting times of 100 s were required to obtain reasonable crystalline peak profiles and the average of several runs was used to obtain reliable value of the moduli. Measurements were made at three temperatures, 20, 100 and 150°C. The results are tabulated in *Table 2*.

Despite the stronger peaks, lack of reproducibility of the LC modulus measurements was a major problem, as can be seen in *Figure 4*. Measurements of the LC chain modulus were made at a variety of temperatures in alphabetical sequence as labelled in the figure. In common with the tensile measurements, the values obtained for the LC chain modulus are clearly dependent upon the previous loading history.

DISCUSSION

As spun HIQ-35: tensile modulus

Considerable difficulty was encountered in obtaining reproducible results for the tensile modulus of as spun HIQ-35. The sample deformed under the influence of stress with a resulting change in macroscopic tensile modulus. Preliminary investigations suggest the deformation to be partly irreversible and partly reversible and also non-linear. It was for this reason that the conditioning process outlined above was adopted to measure the tensile modulus. Tensile moduli for the same sample, measured at 20°C, 100 MPa following a variety of different loading regimes are summarized as

(1) initial results: $E = 33.3$ GPa;
(2) after >2 h at 100 MPa at 20°C: $E = 35.2$ GPa;
(3) after >2 h at 100 MPa at 100°C: $E = 38.4$ GPa.

Even after 30 days was allowed for the sample to relax subsequent to these measurements, the modulus did not change significantly from the value denoted (3). The change is thus taken to be irreversible. It is worth noting that such pronounced irreversible slip behaviour noted here was not observed in the other LCPs studied previously[1–4].

Annealed HIQ-35: X-ray modulus

The values obtained for the *c*-axis crystal modulus of HIQ-35 (*Table 2*) are all about 215 GPa. This value must be regarded as an apparent crystal modulus since it is uncertain whether the macroscopic stress is equal to that on the crystallites. Since the crystal modulus appears to be temperature independent it seems likely that the crystalline and LC phases are connected in series. The crystallites may, however, be weakly mechanically coupled with the stress being transferred through the softer LC phase by shear. This is particularly likely given the crystal aspect ratio of ≈1. Single chain calculations by Karacan[12] suggest a value of about 130 GPa for the modulus of *p*-phenylene-*co*-isophthalate sequences. Since these calculations do not take into account the inter-chain interactions, this would be expected to be less than the true value. The values of 215 GPa and 130 GPa thus probably represent upper and lower bounds for the modulus of the crystalline phase of annealed HIQ-35.

There is a definite relationship between the deformation history of the sample and the measured LC chain modulus. As the experiment progressed, the measured modulus of the sample increased. It seems likely that this is due to irreversible deformation, perhaps due to reorientation of the chain segments. It is noteworthy that this behaviour is associated with the LC phase of the polymer and that it occurs at a molecular level (i.e. evidenced by X-ray measurements).

If the deformation of the LC phase under load is examined in detail it is clear that the stress–strain relationship is linear. Only in measurements above the glass transition is any vestige of the non-linear behaviour characteristic of the macroscopic measurements evident. In the case of deformation of the crystalline phase, there was evidence of a decrease in modulus with increasing load in the measurements at 20°C, however the reverse trend was seen in the 100°C measurements, and further and more careful experimentation is required to draw conclusions from these data.

General comparisons

The shear properties of the different HIQ-35 samples are compared with some other copolyesters in *Figure 2*. In general it can be seen that HIQ-35 has a high shear modulus compared with the other copolyesters. Intuitively, we ascribe this to its more sinuous chain conformations which prevent high chain orientation being achieved and thus leave chain segments in orientations in

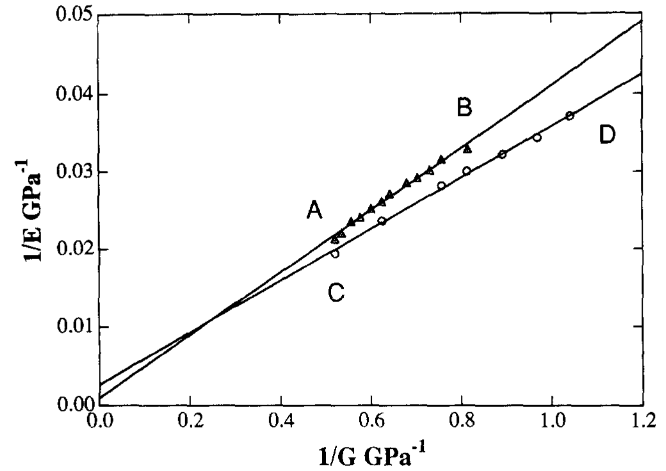

Figure 6 The simple aggregate equation using the data from curves A–B and C–D of *Figure 4* against shear data of *Figure 2*

which covalent bonds resist the shear deformation. This poorer degree of molecular alignment in HIQ is quantitatively confirmed by our aggregate model analysis presented later. It is also seen that annealing increases the shear modulus, presumably as a result of the crystallinity developed on annealing.

Examining the loss spectra of both the as-spun, and annealed polymers (see *Figure 3*), two loss processes are evident. At −60°C there is a very weak process which can be identified with the γ relaxation of the Vectra class of copolyesters. At 130°C, a second and much stronger process can be identified with the α relaxation or glass transition. It is notable that no relaxation process appears to be specifically associated with the isophthalate unit, unlike the Vectra type polymers where there are distinct relaxations associated with both the phenylene and naphthalene units. It is suggested that motion of the isophthalate residues is made so difficult by their *meta*-linked structure as to be made impossible without segmental motion of the main chain.

Examining the shear loss spectra in more detail, we note that the glass transition is at a slightly lower temperature in the annealed material than in the as-spun material. This again is in contrast to the systems studied previously in which annealing has the effect of increasing the glass transition temperature (by 15–20°C). In HIQ, however, the selective crystallization of IA/HQ units has the effect of depleting isophthalate from the LC phase, and since the presence of isophthalate is a key factor in increasing T_g, this accounts for the lower glass transition temperature in the annealed polymer. Returning to the magnitude of the shear modulus, we now see that in annealed HIQ-35 there are competing processes with the LC phase becoming depleted in isophthalate and hence decreasing the shear modulus while crystallization presumably increases the shear modulus. The overall effect is a slight increase in the shear modulus.

HIQ-35 has the lowest tensile modulus of the copolyesters studied so far, this being due to the more sinuous conformations leading to lower orientation in the LC phase. The tensile modulus can be substantially improved by annealing under load, a feature which is common to both the annealed and as-spun polymers. This is presumably due to increased molecular orientation.

Comparing the X-ray and macroscopic moduli of the annealed phase (see *Figure 4*) we see that the macroscopic modulus is significantly lower than that of the LC chains and much lower than the apparent crystallite modulus (*Table 2*). There must therefore be a substantial component of shear between the chains contributing to the macroscopic compliance which is not registered in the X-ray measurements.

Simple aggregate model

The basic assumption of the aggregate model[19,20] is that a polymer can be considered as an aggregate of identical units of structure, each with distinct physical properties, and that the properties of the aggregate thus depend on the intrinsic unit properties and on the unit orientations.

The compliance constants of the unit, represented by a matrix S_{ij} (referred to principal axes) are transformed to a second set of axes O'_x, the principal axes of the aggregate. The compliance constants are then summed (a procedure which implies homogeneous stress and series connectivity) to obtain the compliance of the aggregate. In the case of the compliance parallel to the draw direction (S'_{33}) one obtains (under the assumption of transverse isotropy)

$$S'_{33} = S_{11}\langle\sin^4\theta\rangle + S_{33}\langle\cos^4\theta\rangle + (2S_{13} + S_{44})\langle\sin^2\theta\cos^2\theta\rangle \quad (1)$$

where the primed compliance is that of the aggregate and the unprimed compliances are those of the unit. The shear compliance is similarly obtained from the equation.

$$\begin{aligned} S'_{44} = {} & S_{11}\langle 2\sin^2\theta\cos^2\theta + \sin^2\theta\rangle - S_{12}\langle\sin^2\theta\rangle \\ & - 4S_{13}\langle\sin^2\theta\cos^2\theta\rangle + 2S_{23}\langle\sin^2\theta\cos^2\theta\rangle \\ & + 0.5S_{44}\langle\cos^4\theta + \sin^4\theta - 2\sin^2\theta\cos^2\theta \\ & + \cos^2\theta\rangle \end{aligned} \quad (2)$$

In a highly oriented system, we have previously argued[3] that the above equation reduces to $S'_{44} = S_{44}$ and equation (1) becomes

$$S'_{33} = S_{33} + S'_{44}\langle\sin^2\theta\rangle \quad (3)$$

the simplified aggregate compliance equation. The connection between the macroscopic tensile and shear moduli through the orientation parameter $\langle\sin^2\theta\rangle$ is striking and the equation has given a valuable interpretation of the mechanical properties of a number of highly oriented liquid crystal copolyesters[3,17,18,21]. The aggregate compliance equation as developed above is restricted to single phase systems and therefore is applicable only to as-spun HIQ-35 (which is known to be wholly LC).

Figure 6 shows the zero load tensile compliance plotted against the shear compliance for as-spun HIQ-35. Inspection of the curves shows a linear relationship as predicted by the aggregate compliance equation with parameters as shown in *Table 3*.

We note immediately that the values for $\langle\sin^2\theta\rangle$ are an order of magnitude larger than previously encountered[3,4], quantitatively confirming our claim that the chains in HIQ are more sinuous and less readily oriented.

We also note that the values obtained for S_{33}, the unit compliance, are smaller than previously obtained and

Table 3 Parameters of the aggregate model determined from the lines in *Figure 6*

Conditioning	$\langle\sin^2\theta\rangle$	S_{33} (GPa^{-1})
100 MPa at 20°C	0.040	0.6×10^{-3}
100 MPa at 100°C	0.033	2.6×10^{-3}

Table 4 Compliance constants for a copolyester similar to HIQ-35 at ultrasonic frequencies

Compliance constant	Value (GPa^{-1})
S'_{11}	0.50
S'_{33}	0.048
S'_{12}	−0.23
S'_{13}	−0.022
S'_{23}	−0.032
S'_{44}	0.99

Table 5 Parameters of the modified aggregate model

Conditioning	$\langle\sin^2\theta\rangle$	S_{33} (GPa^{-1})
100 MPa at 20°C	0.043	3.0×10^{-3}
100 MPa at 100°C	0.036	4.3×10^{-3}

correspond to moduli in excess of 380 GPa. Since we do not believe that the units are intrinsically stiffer than those previously considered we have examined the assumptions made in formulating the simplified aggregare compliance equation to explore the possible reasons for this.

Modified aggregate model

Measurements of the compliance constants of a polymer similar in composition to HIQ-35 have been made at ultrasonic frequencies in this laboratory[22]. The samples were injection moulded plaques of generally poor orientation, but with highly oriented outer layers. Typical values of the S_{ij} of the outer layers are listed in *Table 4*.

Although the ultrasonic measurements are at a much higher frequency than the present measurements, they nevertheless allow us to make an estimate of the relative magnitudes of the terms in equations (1) and (2) if we take the value of $\langle\sin^2\theta\rangle$ above as estimates of the $\langle\sin^2\theta\rangle$, and the ultrasonic values quoted above as estimates of the values for the unit compliance constants. We conclude that $2S_{13}\langle\sin^2\theta\rangle$ in equation (1) and $S_{11}\langle\sin^2\theta\cos^2\theta + \sin^2\theta\rangle$ in equation (2) are the next most significant terms. We thus write

$$S'_{33} = S_{33} + (2S_{13} + S_{44})\langle\sin^2\theta\rangle \qquad (4)$$

and, taking $\langle\cos^2\theta\rangle$ as 1

$$S'_{44} = 3S_{11}\langle\sin^2\theta\rangle + S_{44} \qquad (5)$$

If S_{13} and S_{11} are constant as a function of temperature, as would be expected if S_{33} and $v_{13}(= -S_{13}/S_{33})$ are constant, then equation (4) can be rewritten as

$$S'_{33} = (S_{33} - A) + S_{44}\langle\sin^2\theta\rangle \qquad (6)$$

where A is constant.

Further, one might expect S_{11}/S_{44} to be independent of temperature, since both originate from inter-chain interactions and will have similar temperature dependencies. Thus, equation (5) can be rewritten as

$$S'_{44} = S_{44}(1 + B) \qquad (7)$$

where B is another constant (equal to $3(S_{11}/S_{44})\langle\sin^2\theta\rangle$).

Equations (6) and (7) embody a modified linear relationship between S'_{33} $(1/E)$ and S'_{44} $(1/G)$. Calculating the values of the constants A and B from the data of *Table 4*, and refitting the data of *Figure 6*, yields the corrected values of $\langle\sin^2\theta\rangle$ and S_{33} shown in *Table 5*.

It can be seen that the values of $\langle\sin^2\theta\rangle$ have only changed by about 10% but the results for S_{33} are more reasonable than the values initially obtained, implying axial moduli for the units of structure of 300 GPa or less. The failure of the simple model is caused by the large value of $\langle\sin^2\theta\rangle$ resulting from the incorporation of the disruptive isophthalate units.

CONCLUSIONS

Although HIQ-35 has many similarities with the oriented liquid crystal copolyesters studied previously, its behaviour is more complex. As might be expected, the incorporation of *m*-phenylene groups in the main-chain results in a higher shear modulus and a high glass transition temperature (relative to the Vectra type systems). The tensile modulus is lowered, however, due to the lower degree of orientation which is achieved.

Mechanical measurements are complicated by its nonlinear, irreversible behaviour. In addition, samples at room temperature can exist in a mixture of glassy amorphous, glassy nematic or crystalline phases. Quantifying the type, amount and orientation of these phases is difficult.

The aggregate model in its simplest form no longer fully describes the relationship between the shear and tensile moduli of the as-spun samples due to the lower degree of alignment achieved in the spinning process. It is proposed that modification to include the next most important terms in the full analytical equations provides a satisfactory resolution of this issue.

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