# Dynamic mechanical properties of random copolyesters of 4-hydroxybenzoic acid and 2-hydroxy 6-naphthoic acid*

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The dynamic mechanical moduli have been determined in tension and torsion for oriented thermotropic liquid crystalline polymers formed by copolymerization of 4-hydroxybenzoic acid and 2-hydroxy 6-naphthoic acid. The behaviour has been interpreted in terms of an aggregate model of units of structure. On this basis the fall in tensile modulus with increasing temperature can be quantitatively related to two factors, a decrease in the intrinsic chain modulus and a reduction in the shear modulus.

**(Keywords: liquid crystalline copolyesters; dynamic mechanical measurements)**

## INTRODUCTION

Random copolymers of 4-hydroxybenzoic acid (HBA) and 2-hydroxy 6-naphthoic acid (HNA) form thermotropic liquid crystalline melts which can be readily processed into highly oriented fibres or tapes by melt spinning at high windup speeds[1]. Such products exhibit a high tensile modulus and strength at room temperature but both the modulus and the strength fall steadily with increasing temperature. This paper describes a study of the tensile and shear moduli of specimens of two different HBA:HNA ratios. With the aid of data from a companion study[2] of the X-ray determined chain stiffness, this study shows that the fall in macroscopic tensile modulus with increasing temperature arises both from an intrinsic decrease in chain stiffness with temperature and also from a reduction in shear modulus which contributes to the macroscopic tensile modulus due to imperfect chain alignment.

## EXPERIMENTAL

### *Preparation of specimens*

Specimens of two liquid crystalline copolyesters of HBA and HNA with HBA:HNA molar ratios of 73:27 and 30:70 respectively were supplied by Hoechst-Celanese, Summit, New Jersey, USA. In each case two types of specimen were provided: highly oriented monofilaments of about 1 mm diameter and thin tapes 10 $\mu$m thick and 2 mm wide. Specimens designated as 'annealed' were annealed under zero tension in nitrogen at 250°C for 4 h, then similarly annealed at 280°C for 15 h. The thin tapes were designed to give a total stiffness appropriate for dynamic tensile measurements. The monofilaments, on the other hand, were designed to give a torsional rigidity satisfactory for shear modulus measurements in a torsion pendulum apparatus. These measurements will now be described in detail.

### *Dynamic mechanical measurements*

Dynamic shear measurements were made using an inverted torsion pendulum apparatus of the type described by Heijboer[3]. Due to the low shear modulus and the small cross-section of the specimens, a low inertia system had to be constructed. However, the period for some measurements was still as long as 10 s. With low restoring forces and long periods, it was found necessary to encase the whole apparatus in a draught shield.

Tensile measurements were made in an apparatus of our own design[4], shown in *Figure 1*, which incorporates a Solartron 1250 frequency response analyser (FRA) to enable direct determination of the complex modulus. A sinusoidal extension is applied to the specimen by means of a vibrator which is driven from the generator output of the FRA, through an intermediate power amplifier. A yoke around the vibrator forces an elastic spring to undergo the same displacement as the specimen. Forces in the specimen and the spring are monitored by two non-bonded strain gauge displacement transducers whose outputs, after amplification, are measured by the FRA. The ratio of these two signals, which can be measured and displayed as a complex number by the FRA, is proportional to the complex modulus of the specimen. For stiff specimens, however, a correction must be applied to take into account the finite extension of the force transducer connected to the specimen.

In both torsion and tensile measurements the specimen was maintained at constant temperature by passing a stream of temperature-controlled dry nitrogen gas through the specimen enclosure. The frequency of the torsion measurements was about 0.3 Hz but it varied with the specimen and temperature of measurement. Tensile measurements were made at several frequencies from 10 mHz to 10 Hz.

### *Specimen characterization*

Wide angle X-ray diffraction patterns were obtained for all the specimens. These are part of extensive X-ray studies involving determination of average chain moduli and thermal expansion behaviour which will be reported

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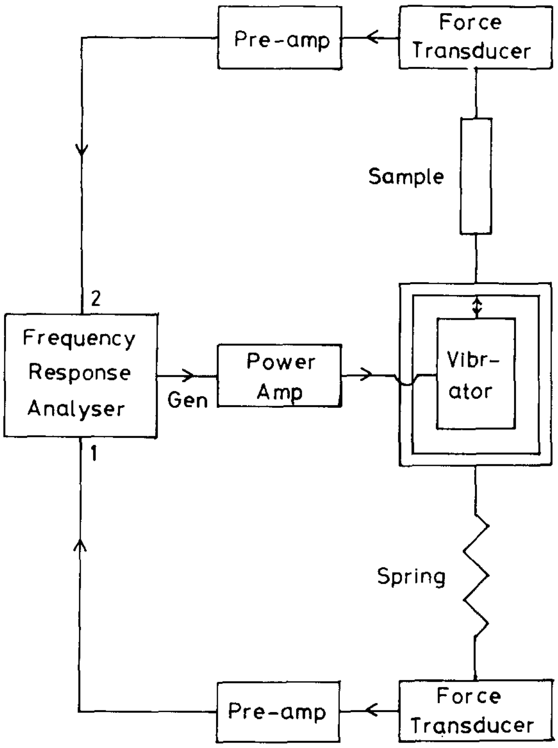

**Figure 1** Schematic dynamic mechanical apparatus (tensile)

elsewhere[2]. All specimens showed high uniaxial orientation, with a general sharpening of the pattern on annealing.

## RESULTS AND DISCUSSION

### *General features*

The dynamic tensile results at 10 Hz are shown in *Figure 2*. It can be seen that for all specimens there is a continuous fall in modulus over the whole temperature range from about 100 GPa at −80°C to about 20 GPa at +120°C. The corresponding $\tan\delta$ plots show two major relaxations at about 100°C and 50°C and a very weak relaxation around −60°C. Following convention, we shall call these the $\alpha$, $\beta$ and $\gamma$ relaxations, in order of decreasing temperature.

The loci of the tensile loss maxima for these transitions are shown in *Figure 3* which also includes dielectric data for unannealed isotropic specimens of similar composition[5]. These data have been included because they show the $\gamma$ process much more clearly and accurately than the mechanical data and also extend the frequency range. The associated activation energies, where even approximately calculable, are summarized in *Table 1*.

It is apparent from the general pattern of the loci in *Figure 3* and the very high activation energy that the $\alpha$ process is akin to a glass transition in a normal polymer. In these materials, however, it presumably corresponds to the material changing from a glassy state to a mobile nematic phase, rather than a rubbery phase. The $\beta$ and $\gamma$ processes would appear to correspond to the usual local mode processes seen below $T_g$ with typically lower activation energies.

The storage modulus curves show only minor differences between the different specimens. The larger changes are due to annealing rather than to changes in chemical composition. The $\tan\delta$ plots, as in previous

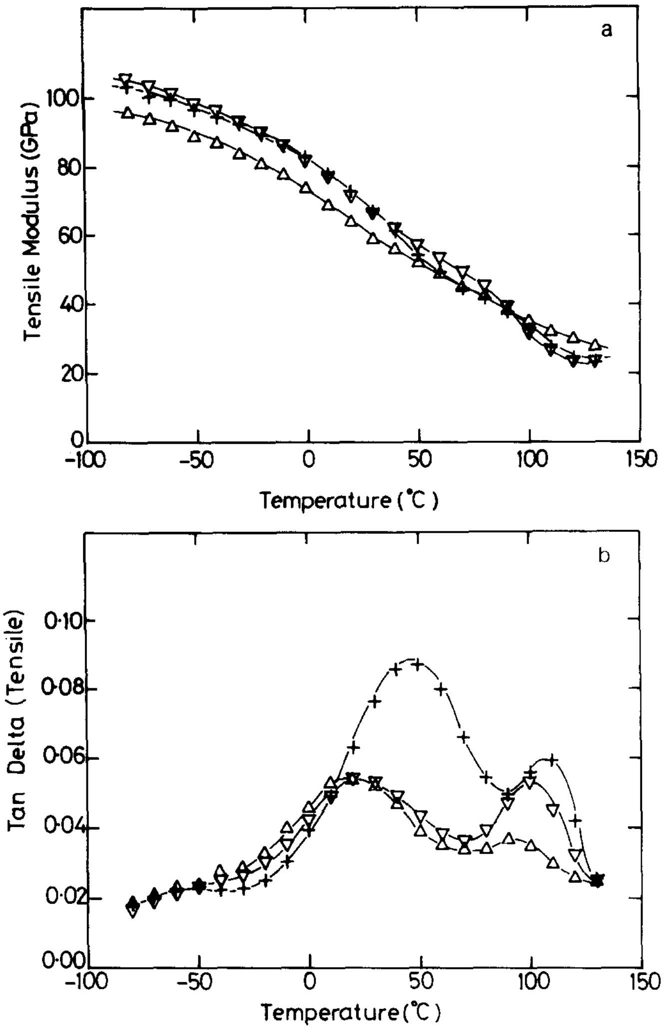

**Figure 2** (a) Dynamic tensile modulus $E$ at 10 Hz; (b) tensile $\tan\delta$. △, Unannealed 73:27 HBA:HNA; ▽, annealed 73:27; +, annealed 30:70

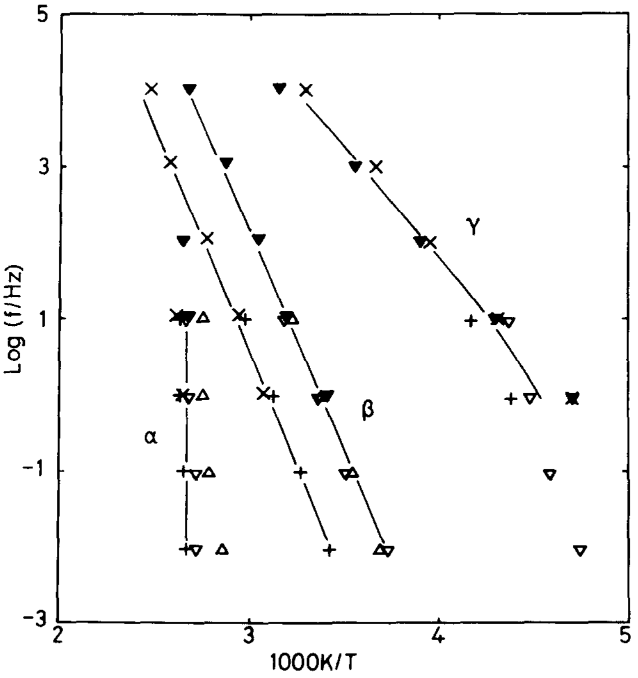

**Figure 3** Loci of loss maxima. Mechanical $\tan\delta$ for oriented specimens, symbols as for *Figure 2*. Dielectric $\varepsilon''$ for isotropic specimens: ▼, 73:27; ×, 30:70

**Table 1** Activation energies from mechanical and dielectric data; U, unannealed; A, annealed

| Specimen | Method | Activation energy (kcal $\text{mol}^{-1}$) $\alpha$ | $\beta$ | $\gamma$ |
|---|---|---|---|---|
| U73/27 | tensile tan $\delta$ | $110 \pm 50$ | $30 \pm 7$ | – |
| A73/27 | tensile tan $\delta$ | $210 \pm 180$ | $26 \pm 7$ | $37 \pm 25$ |
| A30/70 | tensile tan $\delta$ | $370 \pm 520$ | $31 \pm 5$ | – |
| Isotropic<br>73:27 | | | | |
| 30:70 | dielectric $\varepsilon''$ | $\sim 170$ | $25 \pm 5$ | $12 \pm 3$ |

studies[6,7], show that there is a substantial difference in the intensity of the $\beta$ relaxation for different compositions, the greatest intensity corresponds to higher HNA content. This result implies the association of this loss process with motion of the HNA residues.

The dynamic torsion data, shown in *Figure 4*, are remarkably similar in general respects to the tensile results. In this case, however, the tan $\delta$ results for the $\gamma$ process clearly show that there is a higher loss in the 73/27 HBA/HNA specimens. This confirms the association of this process with the HBA residue. This result is consistent with previous studies on these copolyesters[6,7] and confirms previous work where a similar process has been observed in other polymers containing main chain phenyl groups substituted in the *para* position but not where the substitution is in the *meta* position[8].

The reason for the relatively weak tan $\delta$ peak for the mechanical $\gamma$ relaxation is that appreciable rotation of the phenyl groups can occur with little change in chain length and comparatively small accommodation by neighbouring chains. It should be noted, however, that this transition is relatively strong in dielectric studies[5] due to the rotation of the attached carbonyl group which rotates with the phenyl group.

Finally, it should be noted that the shear moduli for these polymers are very low compared with the tensile moduli. Although they are comparable with those for other fibre forming polymers at room temperature, they fall rapidly with increasing temperature.

### *Mechanical modelling*

It is proposed that the observed correlation between the temperature dependence of the tensile and shear moduli can be interpreted to a good approximation in terms of an aggregate model. The aggregate model assumes that the polymer can be regarded as an aggregate of anisotropic elastic units whose elastic properties are those of the fully aligned polymer[9]. For simplicity we will consider the case where both the polymer and the unit possess cylindrical symmetry. The average elastic constants for the aggregate can be obtained in two ways, either by assuming uniform stress throughout the aggregate (which involves averaging the compliance constants and is often termed the Reuss average) or by assuming uniform strain (which involves averaging the stiffness constants and is often termed the Voigt average). It was shown by Bishop and Hill[10] that for a random aggregate the correct value lies between the lower Reuss bound and the upper Voigt bound predicted by these alternative averaging procedures.

We will consider the compliance averaging scheme in the first instance. The macroscopic compliance constants $S_{33}^m$ ($=1/E$) and $S_{44}^m$ ($=1/G$) corresponding to the tensile and shear compliances of the specimen, respectively, are given in terms of the compliance constants of the fully oriented unit ($S_{ij}$) by the following equations[9]:

$$S_{33}^m = S_{11}\langle\sin^4\theta\rangle + S_{33}\langle\cos^4\theta\rangle + (2S_{13}+S_{44})\langle\sin^2\theta\cos^2\theta\rangle \tag{1}$$

and

$$\begin{aligned} S_{44}^m = {} & S_{11}[\langle 2\sin^2\theta\cos^2\theta\rangle + \langle\sin^2\theta\rangle] - S_{12}\langle\sin^2\theta\rangle \\ & - S_{13}\langle 4\sin^2\theta\cos^2\theta\rangle + S_{33}\langle 2\sin^2\theta\cos^2\theta\rangle \\ & + \tfrac{1}{2}S_{44}[\langle\sin^4\theta\rangle + \langle\cos^4\theta\rangle - \langle 2\cos^2\theta\sin^2\theta\rangle + \langle\cos^2\theta\rangle] \end{aligned} \tag{2}$$

where $\langle\sin^4\theta\rangle$, $\langle\cos^4\theta\rangle$, etc., are orientation averages for the aggregate defined in terms of the angle $\theta$ between the symmetry axis of a unit (the chain direction) and that of the specimen (the draw direction of the tapes and the fibre axis in the monofilament).

These equations can be considerably simplified on the basis of two key assumptions. First, all the specimens under consideration possess a high degree of molecular alignment. We can therefore assume that $\langle\cos^4\theta\rangle$ and $\langle\cos^2\theta\rangle \approx 1$, $\langle\cos^2\theta\sin^2\theta\rangle = \langle\sin^2\theta\rangle$ and $\langle\sin^4\theta\rangle \ll \langle\sin^2\theta\rangle \approx 0$. Secondly, the units will be highly anisotropic such that $S_{44}$ is about two orders of

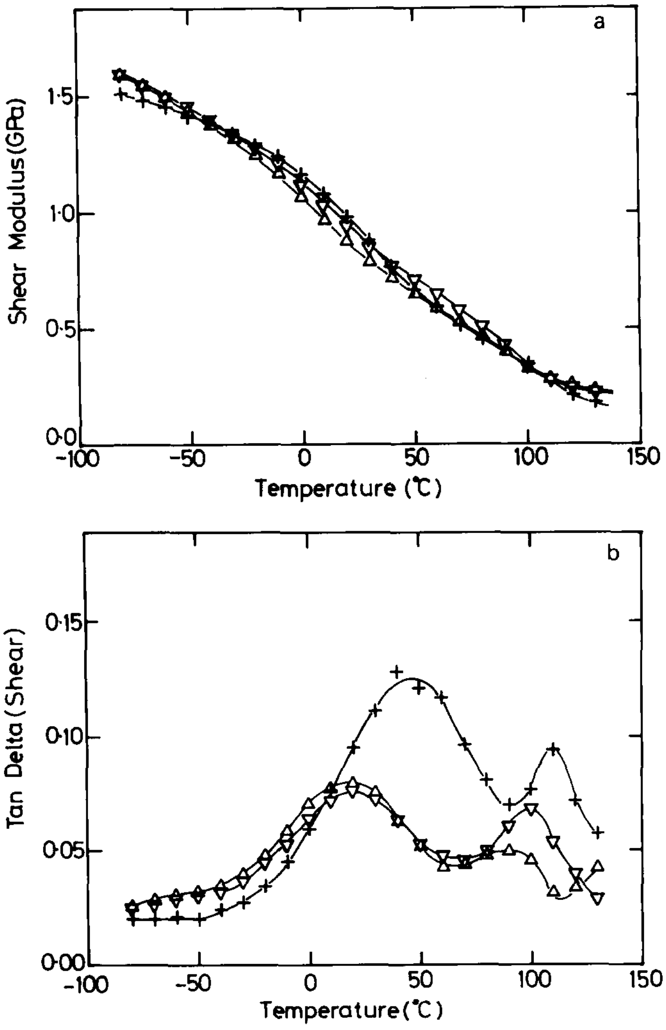

**Figure 4** (a) Dynamic shear modulus $G$ at $\sim 0.3$ Hz; (b) shear tan $\delta$. Symbols as for *Figure 2*

magnitude greater than $S_{33}$ or $S_{13}$, and is about one order of magnitude greater than $S_{11}$ and $S_{12}$.

Equation (1) then reduces to

$$S^m_{33} = S_{33} + S_{44}\langle \sin^2\theta \rangle \tag{3}$$

Because $S_{44} \gg S_{33}$ it can make an important contribution to $S^m_{33}$ in spite of the small magnitude of $\langle \sin^2\theta \rangle$.

Equation (2) reduces very simply to

$$S^m_{44} = S_{44} \tag{4}$$

Equation (4) shows that, on the compliance averaging procedure, $S_{44}$ for the unit can be obtained directly from the measured shear modulus $G$ because $S^m_{44} = 1/G$. Hence $S_{44} = 1/G$. If it is further assumed that $S_{33}$ for the unit can be obtained from the apparent chain modulus $E_c$, deduced from the shift in the meridional X-ray pattern under stress, we can put $S_{33} = 1/E_c$.

Substituting these values for $S_{44}$ and $S_{33}$ into equation (3) the tensile modulus of the specimen $E(=1/S^m_{33})$ is related to $E_c$ and $G$ by

$$\frac{1}{E} - \frac{1}{E_c} = \frac{1}{G}\langle \sin^2\theta \rangle \tag{5}$$

The three measured quantities $E$, $E_c$ and $G$ are then related by equation (5) to the orientation average $\langle \sin^2\theta \rangle$ describing the overall molecular orientation in the specimen.

In the simplest test of equation (5) it is assumed that the chain modulus $E_c$ is independent of temperature. The relationship between $E$ and $G$ is examined where the variation in these quantities is due to temperature only. This requires that the dynamic tensile and shear moduli for the highly aligned specimens (assumed equivalent) be estimated at the same frequency over the range of temperatures measured. The dynamic tensile modulus at each temperature was therefore corrected to the frequency of the shear measurement by interpolation of dynamic data at different frequencies.

The results of this comparison, which are plotted in *Figure 5*, show that there is a general correlation between $1/E$ and $1/G$. A value for $\langle \sin^2\theta \rangle$ of about 0.007 is required to fit the data. This corresponds to an average misalignment of about five degrees, which is reasonable for a highly oriented specimen.

Despite the general correlation shown by *Figure 5*, it is obvious that there is a systematic curvature for all specimens and that the 'best fit' line does not pass through $1/E_c$ at $1/G = 0$ ($1/E_c$ is the low temperature X-ray value obtained at −80°C). It is possible that this is caused by a defect in the modelling because the properties of the specimen are not adequately represented by the lower bound of the aggregate model obtained by averaging compliances. It is, of course, possible to obtain an upper bound by averaging the stiffnesses of the units to predict $C^m_{33}$ and $C^m_{44}$. Unfortunately, these coefficients cannot readily be derived from the measured tensile and shear moduli. The predictions of the upper bound model cannot therefore be so readily checked. In support of the 'lower bound' approach it should be noted that previous investigators have found that this model gives more reasonable predictions where the behaviour is dominated by shear[11], i.e. the shear compliance of the aggregate units is high. This is certainly true for these systems because the shear compliance is at least 50 times the tensile compliance over the whole temperature range. We therefore favour the lower bound model as being more nearly correct and more amenable to experimental verification.

We believe that the curvature in *Figure 5*, which is drawn assuming a constant $E_c$, arises primarily from the temperature dependence of $E_c$, which is indeed observed. Unfortunately, data for $E_c$ are only available at three temperatures[2], namely −80, 20 and 120°C. Using these data, however, we obtained the results shown in *Figure 6*.

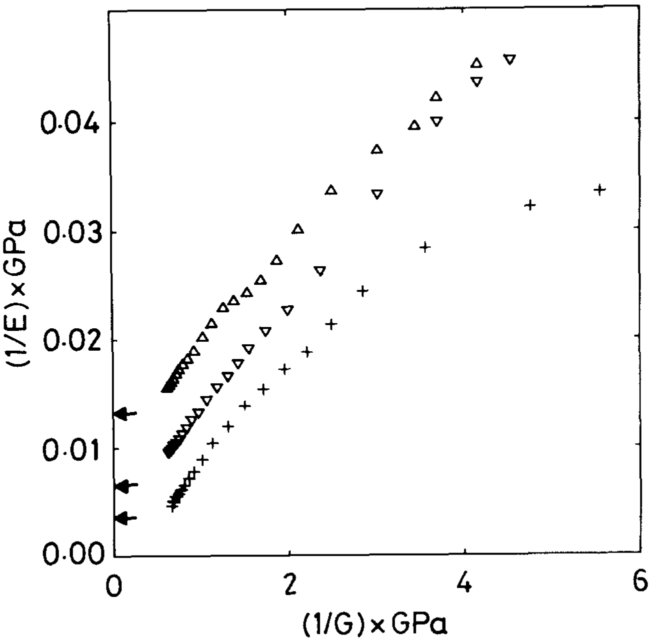

**Figure 5** $1/E$ *versus* $1/G$. Symbols as for *Figure 2*. For clarity, the annealed 73:27 data have been shifted up by 0.005 GPa$^{-1}$ and the annealed 30:70 data have been shifted down by a similar amount. The arrows indicate the value of $1/E_c$ obtained from X-ray data at −80°C (also shifted where required)

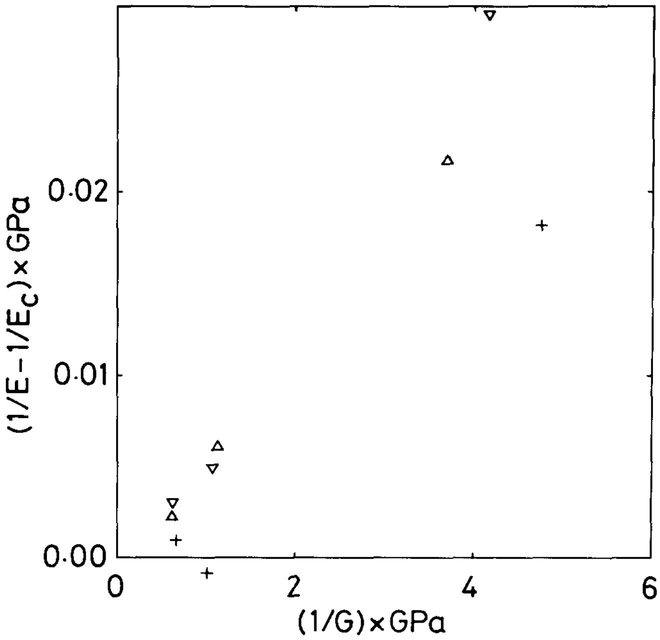

**Figure 6** $1/E - 1/E_c$ *versus* $1/G$ using $E_c$ from X-ray data. Symbols as for *Figure 2*

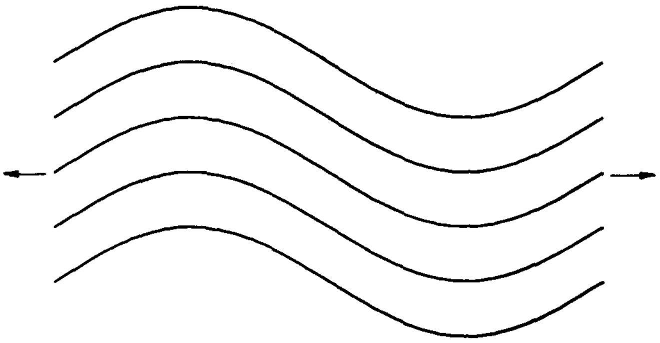

**Figure 7** Schematic arrangement of sinuous chains

It is seen that the data might be fitted by a straight line through the origin but in view of the limited number of points this cannot be regarded as conclusive. Special consideration must be given to the room temperature data point for the 30/70 specimen because at this temperature $E_c$ is found to be less than the measured extensional modulus. We believe that this is due to the extremely low effective frequency of the measurement of $E_c$ and the location of the $\beta$ process for this specimen. Referring to *Figure 4* it can be seen that for this specimen, measurements at 0.3 Hz (torsion/tension) and $10^{-4}$ Hz (X-ray) are on 'opposite sides' of the $\beta$ peak, hence leading to a lower modulus for $E_c$. This is not true for the 73/27 specimens where all measurements fall on the same side of the $\beta$ process and the differences in frequency are therefore not so important. It is interesting to note that this explanation, in itself, is an argument for the frequency dependence of $E_c$ and hence its temperature dependence.

At first sight, it is difficult to see how the true chain modulus in an approximately linear polymer can be so temperature dependent that it virtually halves on going from −80°C to 120°C. Certainly, the bond stiffnesses are not temperature dependent to any great extent.

We believe that this temperature dependence arises from the sinuous nature of the chains and their tendency to pack with the local chain directions parallel as shown in *Figure 7*. A single chain in this 'bent' configuration would have a very low apparent tensile modulus but inter-chain interactions can considerably stiffen the assembly. This can be seen if *Figure 7* is interpreted as a fibre-reinforced composite. A single 'bent' fibre, or a bundle of isolated fibres would give a very low tensile modulus but the same bundle of fibres in a matrix would be much stiffer because straightening the fibres would involve shear in the matrix.

At low temperatures, therefore, we see a high chain modulus due to effective inter-chain interactions. As the temperature is raised, rotational mobility ensues and chains move further apart. This leads to weakened inter-chain interactions and a lower tensile modulus.

## CONCLUSIONS

Three relaxation transitions are seen in these measurements. The highest temperature transition, the $\alpha$ process, is akin to a 'glass transition'. The high temperature phase is a liquid crystal rather than a rubbery phase. The lower temperature $\beta$ and $\gamma$ processes are local mode processes associated with the naphthalene and phenylene moieties, respectively.

These transitions cause a large drop in macroscopic tensile modulus which, in terms of an aggregate model, arises from two effects:

1. The 'chain modulus' is intrinsically temperature dependent.
2. Imperfect orientation results in the fall in the shear modulus of the units. This substantially reduces the macroscopic tensile modulus.

In a sense, both of these effects are manifestations of the weakening inter-chain interactions as the temperature is raised.

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