Thermotropic polyesters: fibres and mouldings from poly(chloro-1,4-phenylene terephthalate-*co*-4,4'-oxybisbenzoate)s

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Fibres melt-spun from nematic mesophases of poly(chloro-1,4-phenylene terephthalate-co-4,4'oxybisbenzoate)s (50/50 and 60/40) contain ordered crystalline regions and are highly oriented. Although heat treatments of the 'as-made' fibres do not affect their orientation or crystallinity, they result in increased tensile strength and extension at break. These improvements in tensile properties are ascribed to a rise of the molecular weight due to a solid-phase post-polycondensation. Mouldings produced from the 50/50 copolymer exhibit distinct anisotropy with a complex distribution of molecular orientation. Their tensile modulus in the flow direction is satisfactory at room temperature (\sim 13 GPa), but at elevated temperatures there is a pronounced drop in stiffness due to a loss process associated with the glass transition.

(Keywords: aromatic polyesters; thermotropic; nematic; liquid crystalline; fibres; mouldings)

INTRODUCTION

The early work on thermotropic liquid-crystalline polymers has been summarized in several reviews¹⁻³. Such polymers based upon rigid-rod units in the main chain are potentially useful for fibres, films and mouldings. Fibres made by melt-spinning them are highly oriented, but their mechanical properties are initially inferior to those of fibres obtainable from nematic solutions of rigid main-chain aromatic polyamides. Extended heat treatment improves their tensile strength and extension at break, but major industrial exploitation awaits improved competitiveness with established highstrength high-modulus aramid fibres³. The fibre-forming process^{4,5} and fibre structure⁶⁻⁸ are being widely studied.

In contrast to fibres, mouldings produced from these thermotropic polymers offer a combination of properties not readily achieved with other materials. They combine high tensile strength and modulus with low melt viscosity and very low mould shrinkage^{1-3,9}. Here research is concentrating upon an understanding of the complex morphology^{9,10} and orientation distribution^{11,12} in the mouldings.

Much of the recent work concentrates on shaped articles produced from copolyesters containing both 1,4-phenylene and 2,6-naphthylene groups in the main chain^{5,7,9-12}, because such materials have been made available from industrial sources, notably from Celanese Corporation. Characterization of shaped articles made from other polymers, such as those containing angular moieties in the chain, has received less attention, although many such materials have been shown to be nematogenic¹³⁻¹⁸ and fibre-forming^{8,13,14}.

Poly(chloro-1,4-phenylene terephthalate-co-4,4'-

oxybisbenzoate)s (I-co-II)



4,4'-Oxybisbenzoate (II)

consisting of rod-like sequences of variable length interrupted by ether oxygen elements, are nematogenic throughout the whole composition range¹⁸. Copolymers containing between 25 and 75 mol% of units (I) (i.e. compositions from 25/75 to 75/25) display a nematic temperature interval in excess of 100°C (see table 1 of ref. 19) and should therefore be readily melt-processable. This paper is concerned with characterization of both 'asmade' and heat-treated fibres from 50/50 and 60/40 copolymers and with the properties of mouldings from the 50/50 copolymer.

EXPERIMENTAL

Polymers

Polymer preparation and characterization have been described in a previous paper¹⁸. All polymers were prepared using 2% excess of chlorohydroquinone diacetate. Their intrinsic viscosities (determined in *p*-chlorophenol at 45°C) ranged from 1.21 to 1.36 dl g⁻¹.

Fibre preparation

Dried polymers (16 h at 120°C under vacuum) were melt-spun from a nematic mesophase using a hydraulically operated rod-spinning machine with a maximum polymer capacity of approximately 70 g. A

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spinneret with five holes, each of diameter 0.23 mm, was employed. The length of the spinline was approximately 1.2 m. The winding speeds were between 200 and 520 m min^{-1} . The drawdown ratios λ were calculated from the cross-sectional area attenuation as follows:

$$\lambda = (\pi/4) \times 10^6 \times (D_{\rm h}^2 \rho/T) \tag{1}$$

where D_h (m) is the spinneret hole diameter and T is the measured linear density of the fibre expressed in tex units (1 tex = 10⁻⁶ kg m⁻¹); it is determined by the ratio of the mass throughput per spinneret hole and the winding speed. The fibre density ρ was approximately 1460 kg m⁻³, irrespective of the spinning conditions. The drawdown ratios were between 36 and 98. The linear densities of the fibres lay between 0.62 and 1.67 tex; this corresponds to fibre diameters ranging from 23 to 38 μ m.

In the initial trials the spinning temperature was set at 295°C (i.e. about 10°C above the end of the melting endotherm determined by $d.s.c.^{18}$). However, the resulting fibres showed short-range (<1 mm) diameter irregularities, and consequently had poor tensile properties. This problem was alleviated by increasing the spinning temperature to 315°C. Under the conditions employed the decrease of intrinsic viscosity during spinning did not exceed 0.25 dl g⁻¹.

The 'as-made' fibres were wound onto a glass tube (diameter 34 mm) and heat-treated under nitrogen in a specially designed glass apparatus. A fluidized sand bath (Tecam SBL-2) was used as the heating medium.

Fibre characterization

Prior to testing, fibres were conditioned for at least 24 h at $20\pm 2^{\circ}$ C (relative humidity $65\pm 2^{\circ}$). The linear density of the fibre was obtained from the weight of 10 m of the yarn. The tensile properties were measured with an Instron Tensile Tester Model 1122 equipped with a 2511-101 measuring cell, using a test length of 20 mm and a nominal strain rate of 0.05 min⁻¹. The results (average of 15 measurements) were expressed in terms of specific stress, using units of newtons per tex (N tex⁻¹).

Wide-angle X-ray diffraction patterns were taken with a flat-plate camera. The optical birefringence was measured using a Pluta polarizing interference microscope equipped with a Wollaston compensator¹⁹; 1-chloronaphthalene was a suitable immersion medium. The transition temperatures were determined on a Du Pont 990/910 Differential Scanning Calorimeter using fibres cut to approximately 3 mm lengths; the heating rate was 20° C min⁻¹. The effect of temperature on the dimensional stability was evaluated using the Mettler TA 3000 system; the TMA 40 module was employed in the extensional mode (10 mm test length). The selected load gave a tensile stress of approximately 15 MPa; the heating rate was 10° C min⁻¹. A correction for the thermal expansion of the clamps was applied to the resulting data.

Mouldings

Mouldings were produced using a laboratory injection moulding apparatus from Mining and Chemical Products, Wembley, London, with barrel capacity of approximately 30 g. Cold moulds were used to obtain the test pieces for tensile tests (dimensions similar to those given in example M-III in ASTM 638M-81) and for flexural tests (dimensions $3.0 \times 12.7 \times 126.8$ mm). The tensile properties were measured with an Instron 1186 at an extension rate of 0.5 mm min⁻¹. The flexural properties were determined with an Instron 8033 using a three-point loading with a 48 mm span and a crosshead speed of 2 mm min⁻¹.

The effect of temperature on the dimensional changes was evaluated using the Mettler 3000 system with a TMA 40 module in the penetration mode and a flat probe (diameter 1 mm); the load of 0.01 N gave a pressure of approximately 13 MPa. The heating rate was 5°C min⁻¹.

The dynamic mechanical analysis was carried out with a Du Pont 982 DMA module at a heating rate of 2° C min⁻¹.

RESULTS AND DISCUSSION

'As-made' fibres

The main emphasis was placed on investigation of fibres from 50/50 copolymers, produced by melt-spinning from a nematic mesophase at temperatures ranging from 295 to 315°C with drawdown ratios between 36 and 98. The optical birefringence, which is a measure of overall orientation, remained constant (0.40 ± 0.01) fibre irrespective of the spinning conditions. Clearly, even the lowest drawdown employed is higher than that required to reach the maximum level of orientation. This is consistent with the behaviour reported⁴ for other polymers melt-spun from a nematic mesophase, where a drawdown of less than 3 was sufficient to achieve nearly complete orientation. The wide-angle X-ray diffraction patterns were also unaffected by the spinning conditions. Their features, summarized in Table 1, are consistent with the presence of crystalline regions with a high degree of orientation. Further details of the X-ray studies will be presented elsewhere²⁰, but here it is worth noting that the crystalline regions are due to a regular packing of chloro-1,4-phenylene 4,4'-oxybisbenzoate units.

The d.s.c. curves of the 'as-made' fibres were similar to those obtained for unoriented quenched polymers of similar intrinsic viscosities¹⁸. They showed a glass transition region with an onset at 97°C spreading over a temperature interval of approximately 20°C. The crystalnematic transition showed up as a double endotherm. The main endotherm with peak temperature $T_m'' = 279$ °C was partially overlapped by a small endotherm with an onset temperature of approximately 210°C and a peak temperature $T_m' = 250$ °C. The enthalpy of fusion found for the 'as-made' fibres was approximately 19 J g⁻¹, i.e. about twice the value for the quenched unoriented copolymer¹⁸.

Thermomechanical analysis (t.m.a.) of an 'as-made' fibre (sample 3 in Table 2) revealed remarkable

 Table 1
 Features of wide-angle X-ray diffraction patterns of 'as-made' and heat-treated fibres

Location	d spacing (nm)	Note
Equator	0.488)	Strong; azimuthal
-	0.434 0.272	half-height width $\sim 8^{\circ}$ Weak
Meridian	0.418	Weak streak
1.2 nm layer line	0.332	Strong

Table 2 'As-made' fibres produced at 315° C: spinning conditions andfibre properties

Fibre sample number	1	2	3	4	5
Composition, A/B	50/50	50/50	50/50	50/50	60/40
Winding speed $(m \min^{-1})$	210	350	220	520	400
Drawdown ratio	36	37	43	98	42
Intrinsic viscosity $(dl g^{-1})$	1.07	1.21	1.28	1.15	1.10
Linear density (tex)	1.67	1.62	1.42	0.62	1.44
Tenacity (N tex ⁻¹)	0.39	0.45	0.45	0.41	0.43
Extension at break (%)	2.2	2.0	1.9	2.0	1.7
Initial specific modulus					
$(N \text{ tex}^{-1})$	19	24	26	20	27
Linear density (dl g^{-1}) Linear density (tex) Tenacity (N tex ⁻¹) Extension at break (%) Initial specific modulus (N tex ⁻¹)	1.07 1.67 0.39 2.2 19	1.21 1.62 0.45 2.0 24	1.28 1.42 0.45 1.9 26	1.15 0.62 0.41 2.0 20	1. 1. 0. 1. 27

dimensional stability in the axial direction. Up to the glass transition temperature there was a small expansion, which was then followed by a small contraction. However, the net shrinkage at 210° C was only about 0.03 %.

As already mentioned, only the spinning at 315°C resulted in fibres that were sufficiently regular for a meaningful evaluation of tensile properties. These 'asmade' fibres (Table 2) had tenacities of about 0.4 N tex^{-1} , i.e. similar to those of 'conventional fibres' produced from linear flexible-chain polymers by melt-spinning followed by drawing. However, the extensions at break (around 2%) are substantially lower than those for fully drawn 'conventional fibres' (typically above 10%), and the initial specific moduli are significantly higher $(23 \pm 3 \text{ N tex}^{-1} \text{ against } 5-10 \text{ N tex}^{-1})$. For the fibres spun from the nematic phase, the ratio of the tenacity s_b and the strain at break $(e_b/100)$ (mean value $21 \pm 2 \text{ N tex}^{-1}$) is close to the value of the initial specific modulus. This means that for these fibres stress is nearly a linear function of strain up to the break point. Consequently, a reasonable estimate of the specific work rupture W_b $(MJ kg^{-1})$ can be obtained as:

$$W_{\rm b} = \frac{1}{2} s_{\rm b} (e_{\rm b} / 100) \tag{2}$$

The mean value of this quantity for the 'as-made' fibres obtained from the 50/50 copolymers is 4.3 ± 0.2 kJ kg⁻¹.

The intrinsic viscosities of the 50/50 fibres produced from different batches of polymer at drawdown ratios around 40 varied from 1.07 to 1.28 dl g⁻¹ (*Table 2*). Within this narrow range, an increase in the intrinsic viscosity results in a small increase in tenacity and a small decrease in extension at break. Comparison of samples 1 and 2 with sample 4 indicates that, at a given intrinsic viscosity, increased drawdown does not significantly affect the tensile properties.

In addition to the fibres produced from the 50/50 copolymers, a limited investigation of a fibre from a 60/40 copolymer was carried out (sample 5 in *Table 2*). The optical birefringence of this fibre was 0.37, i.e. lower than that of the 50/50 fibres. This is almost certainly due to a lower intrinsic birefringence of the 60/40 copolymer rather than to lower orientation. The wide-angle X-ray diffraction pattern of the 60/40 fibre was similar to those of the 50/50 fibres. The decrease in the content of angular 4,4'-oxybisbenzoate units resulted in a marginal increase of the initial modulus, but the tenacity was close to the values obtained for the corresponding 50/50 fibres.

The results are consistent with a view that the 'as-made' fibres spun from a nematic mesophase consist of

copolymer chains with a high degree of alignment along the fibre axis. Locally, the chloro-1,4-phenylene 4,4'oxybisbenzoate units are brought into register to form crystalline regions.

Heat-treated fibres

Heat treatment of many fibres produced from nematogenic copolymers results in increased molecular weight^{1-3,5,13} and, in some cases, in distinct structural changes⁸. Consequently, the tensile properties of heattreated fibres are improved in comparison with those of 'as-made' fibres. The nature of the changes occurring during the heat treatment of these materials was investigated.

Heat treatments of the 50/50 'as-made' fibres were carried out without difficulty at temperatures ranging from 210 to 240°C for periods of up to 4 h; however, at 250°C, some filament-to-filament fusion occurred due to partial melting. Heat treatment of the 60/40 fibres was carried out at 230°C for up to 20 h. As expected, the heat treatments resulted in an increase of intrinsic viscosity (*Tables 3* and 4) due to the solid phase postpolycondensation.

Measurements of the optical birefringence and density and quantitative analysis of the X-ray diffraction patterns²⁰ did not reveal any structural changes resulting from the heat treatments of 50/50 or 60/40 fibres.

Previous work¹⁸ has shown that even a brief annealing of the unoriented copolymer resulted in the appearance of an additional endotherm approximately 20°C above the annealing temperature. Consequently, it was of interest to conduct a d.s.c. investigation of the heat-treated 50/50 fibres. The heat treatments did not influence the glass transition temperature. The upper endotherm observed in the 'as-made' fibres was not affected by the heat treatments carried out at 210 and 230°C; its peak temperature T_m^m remained at 279–280°C in spite of the

Table 3 Effect of heat-treatment temperature (T_a) on properties^{*a*} of the 50/50 fibre (duration of heat treatment was 4 h)

T _a (°C)	$\begin{bmatrix} \eta \\ (dl g^{-1}) \end{bmatrix}$	ΔH (J g ⁻¹)	$(N \text{ tex}^{-1})$	е _ь (%)	$\frac{M}{(N \text{ tex}^{-1})}$	W _b (kJ kg ⁻¹)
b	1.28	19	0.45	1.9	26	4.36
210	1.40	23	0.59	2.1	29	6.04
230	1.76	29	0.59	2.3	25	6.86
240	1.80	-	0.60	2.4	23	7.37

 ${}^{a}[\eta] = \text{intrinsic viscosity}; \Delta H = \text{enthalpy of fusion}; s_b = \text{tenacity}; e_b = \text{extension at break}; M = \text{initial specific modulus}; W_b = \text{estimated specific work of rupture}$

^b As-made' fibre (sample 3 in Table 2)

Table 4 Effect of the duration of the heat treatment at 230° C on properties of the 60/40 fibre (for symbols see *Table 3*)

t _a (h)	$\begin{bmatrix} \eta \\ (dl g^{-1}) \end{bmatrix}$	$(N \text{ tex}^{-1})$	е _в (%)	$\frac{M}{(N \text{ tex}^{-1})}$	W _b (kJ kg ⁻¹)
a	1.10	0.43	1.7	27	3.69
1	1.19	0.50	2.4	23	5.99
2	1.33	0.62	2.6	24	8.09
4	1.44	0.62	2.7	24	8.31
8	1.66	0.73	2.8	25	10.09
20	2.09	0.83	2.6	33	10.61

"'As-made' fibre (sample 5 in Table 2)

Table 5 The effect of heat-treatment temperature (T_a) and duration (t_a) on the endotherm peak temperature T'_m (°C) in 50/50 fibres

		t_{a} (h)	
T _a (°C)	1	2	4
210	241	_	244
230	255	259	263
250	277	-	

increase in polymer molecular weight¹⁸. On the other hand, the lower endotherm became progressively larger and sharper with heat treatment, and its peak temperature T'_m increased with increasing temperature and duration of the heat treatment (*Table 5*). After 1 h at 250°C this peak rose to 277°C and almost completely overlapped the upper endotherm, which then showed only as a shoulder. Sauer *et al.*²¹ recently described similar changes in the melting behaviour of an unoriented heat-treated thermotropic copolyester of an unspecified composition supplied by Bayer AG.

The occurrence of double melting endotherms in linear flexible-chain polymers is well documented²²⁻²⁵. Various interpretations of this phenomenon have been proposed, but it is now recognized that in the absence of polymorphism the double melting peak arises from recrystallization taking place during the heating. The heat-treatment-sensitive endotherm with peak temperature T''_m is related to the melting of the crystalline regions formed during the heat treatment whilst the endotherm with peak temperature T''_m is a result of the final melting of the material, which is subjected to repeated melting and recrystallization during the scan²²⁻²⁵. The melting behaviour of these highly oriented nematogenic copolymers can reasonably be interpreted in the same way.

Accurate evaluation of the enthalpy of fusion was hindered by the difficulties in establishing the exact baseline position. Nevertheless, it is clear that the overall enthalpy of fusion increases after the heat treatment (see *Table 3*). If the presence of the double melting endotherms is indicative of recrystallization taking place during the scan, it is doubtful whether the increase in the enthalpy of fusion can be ascribed to increased crystallinity of the heat-treated fibres²³⁻²⁵. This doubt is reinforced by the absence of evidence from the X-ray analysis of any changes in crystallinity caused by heat treatments.

Heat treatments of both 50/50 and 60/40 fibres resulted in somewhat enhanced tensile properties (see *Tables 3* and 4). Whilst for the 50/50 fibres the changes in the initial specific modulus were probably insignificant, for the 60/40 composition there seems to be a significant initial drop in the modulus, which is then followed by a small gradual increase. For both compositions the heat treatments result in a simultaneous increase of both tenacity and extension at break; hence there is an increase in the specific work of rupture W_b estimated by the relationship (2).

In the absence of clear evidence of improvements in the physical structure, the changes in the tensile properties are ascribed to increases of the molecular weight. A recent computer simulation of the behaviour of a parallel array of fully extended polyethylene chains of finite length predicts that, with increasing chain length, both tenacity and extension at break should increase, whilst the initial modulus can be considered to be essentially constant²⁶. However, no simple relationship between the tenacity and the molecular weight could be established from these simulations.

We found that the relationship between the tenacity s_b (N tex⁻¹) and the intrinsic viscosity $[\eta]$ (dl g⁻¹) of the copolyester fibres can be expressed in the following form:

$$s_{\rm b} = A - B/[\eta] \tag{3}$$

as shown in Figure 1. For the 50/50 fibres $A = 0.92 \text{ N tex}^{-1}$ and $B = 0.57 \text{ N tex}^{-1} \text{ dl g}^{-1}$; the correlation coefficient for 12 fibres (four 'as-made' and eight heat-treated) is 0.92, and hence its value is highly significant (better than the 0.1% confidence level). For the 60/40 fibres $A = 1.27 \text{ N tex}^{-1}$ and $B = 0.92 \text{ N tex}^{-1} \text{ dl g}^{-1}$; the correlation coefficient for six fibres is 0.99, and hence its value is again highly significant. The 60/40 copolymer, with a lower content of angular units, is capable of yielding fibres with better mechanical properties at a given level of viscosity (Figure 1).

The Mark-Houwink exponent of the copolymers investigated is probably close to 1 (see ref. 18). Hence, the tenacity of the fibres is apparently a linear function of the reciprocal of the number-average molecular weight, in accordance with the relationship found by Vincent²⁷ for the brittle strength of several isotropic polymers.

It is concluded that, although the heat treatment of the fibres affects their melting behaviour, the resulting structural changes are small and cannot be detected by birefringence measurements or by analysis of the wideangle X-ray diffraction patterns. The rise of the molecular weight occurring during the heat treatment is clearly the dominant factor controlling the tensile properties of the fibres. A reduced level of angular units in the copolymer results in better tensile properties at a given level of intrinsic viscosity.



Figure 1 Tenacity s_b as a function of the reciprocal of the intrinsic viscosity: \bigcirc , 'as-made' 50/50 fibres; \bigcirc , heat-treated 50/50 fibres; \square , 'as-made' 60/40 fibre; \blacksquare , heat-treated 60/40 fibres

Table 6 Mechanical properties of moulding from 50/50 copolymer $([\eta] = 1.25 \text{ dl g}^{-1})$

	Tensile	Flexural
Number of tests	10	6
Strength (GPa) Specific strength (N tex ⁻¹)	$\begin{array}{c} 0.13 \pm 0.01 \\ 0.09 \pm 0.01 \end{array}$	0.18 ± 0.02
Extension at break (%)	1.6 ± 0.3	4.0 ± 0.8
Modulus (GPa) Specific modulus (N tex ⁻¹)	13.4 ± 1.8 9.2 ± 1.2	$\begin{array}{c} 8.7 \pm 1.1 \\ -\end{array}$

Mouldings

Preliminary results obtained from mouldings produced from the 50/50 copolymer without any optimization of the processing conditions showed that the mechanical properties (Table 6) are similar to those obtained for other nematogenic polymers 1-3. This is true particularly for the flexural properties. In order to facilitate comparison with the fibres, Table 6 also gives the tensile properties of mouldings expressed in terms of specific stress. The specific modulus of the mouldings is approximately 40%of the value obtained for the fibres, so the average molecular orientation in the flow direction is undoubtedly quite high. However, examination of the broken test pieces by scanning electron microscopy showed a distinct skin-core effect. Such effects have been observed previously with other nematogenic polymers and have been shown to be due to differences in chain orientation with distance from the mould surface⁹⁻¹².

The pronounced orientation of the mouldings is also manifest in the anisotropy of the thermal expansion measured by t.m.a. The total expansion up to 210°C in the flow direction was only about 0.2%, which is in accordance with the outstanding dimensional stability of oriented fibres in the axial direction already noted. The corresponding expansion in the lateral direction (i.e. perpendicular to the moulding thickness) was much larger and rather variable (2.4-3%). This variability is most likely to be caused by the distribution of orientation in the moulding. Although at this stage this effect was not investigated systematically, it appears that t.m.a. could be employed for the assessment of the distribution of orientation in mouldings; it is certainly much less laborious than other techniques used for this purpose so far^{11,12}.

The t.m.a. measurements also showed that, below the glass transition temperature, the linear expansion coefficient in the lateral direction β_{\perp} was between 0.8×10^{-4} and 1.3×10^{-4} K⁻¹, which is close to a typical value for isotropic linear flexible-chain polymers²⁸. As expected, β_{\perp} increases in the glass transition region. However, above the glass transition region it does not level off and instead shows a continuous rise.

At ambient temperature, the mechanical properties of nematogenic polymers, at least in the flow direction, are generally satisfactory. However, at elevated temperatures there is an unacceptable drop in mechanical performance; this is due to the mechanical loss process^{2,29}. Dynamic mechanical analysis (d.m.a.) showed that the copolymer investigated is no exception (see *Figure 2*). Owing to the complex distribution of the molecular orientation in the moulding and the complex deformation mode employed in the instrument, it is difficult to relate the measured

storage modulus directly to the moduli obtained by other tests. However, as expected, it is closer to the value obtained from the flexural tests than to that obtained by tensile deformation. Nevertheless, the changes in the recorded modulus occurring with increasing temperature are sufficient to indicate the changes to be expected in the mechanical performance at elevated temperatures.

The d.m.a. showed that the α loss process, associated with the glass transition, occurs at around 120°C. A similar loss process was observed in other nematogenic polymers^{2,21,29}. In addition, there is a β loss process at around 40°C; this process was observed previously²⁹ in nematogenic polymers containing 2,6-naphthyl groups, where it was ascribed to a coordinated rotation of these naphthyl groups and neighbouring carbonyl groups about the main polymer axis. However, since β loss was also found²¹ in nematogenic polymers that do not contain 2,6-naphthyl moieties it is obvious that its occurrence is a more general phenomenon. Although at this stage we are not able to provide a molecular interpretation of the β loss process in the copolymer investigated, its existence results in a noticeable decrease of the storage modulus from ambient temperature upwards. Owing to the combined effect of β and α loss processes, the storage modulus at 160°C drops to about 30% of its initial value.

It is apparent that the mouldings produced from the 50/50 copolymer are in all respects similar to mouldings obtained from other nematogenic copolyesters: they exhibit distinct anisotropy together with a complex distribution of molecular orientation. Their mechanical performance in the flow direction is satisfactory at ambient temperature, but there is a pronounced loss of stiffness at elevated temperatures. This is obviously a key problem in the practical utilization of thermotropic nematogenic polymers.

CONCLUSIONS

Fibres melt-spun from nematic mesophases of 50/50 and 60/40 poly(chloro-1,4-phenylene terephthalate-*co*-4,4'- oxybisbenzoate)s consist of chains with a high degree of orientation with respect to the fibre axis. Locally, the chloro-1,4-phenylene 4,4'-oxybisbenzoate units are brought to register to form crystalline regions.

Heat treatments of the 'as-made' fibres affect their melting behaviour, but the resulting structural changes



Figure 2 Dynamic mechanical analysis of a 50/50 moulding

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are small and cannot be detected by birefringence or Xray measurements. Increased tensile strength of the heattreated fibres is ascribed to the rise of the molecular weight caused by solid-phase post-polycondensation. A reduced level of angular units in the copolymer is advantageous since it results in improved tensile properties at a given intrinsic viscosity.

Mouldings produced from a 50/50 copolymer are highly anisotropic with good strength and stiffness in the flow direction. A mechanical loss process, occurring around 120° C and associated with the glass transition, results in a decreased stiffness at elevated temperatures.

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