Liquid Crystals
Publication details, including instructions for authors and subscription information:
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To cite this Article Motamedi, Farshad , Jonas, Ulrich , Greiner, Andreas and Schmidt, Hans-Werner(1993) 'Preparation and characterization of fibres from a thermotropic liquid crystal polyester with non-coplanar biphenylene units', Liquid Crystals, 14: 4, 959 — 970

To link to this Article: DOI: 10.1080/02678299308027803

URL: http://dx.doi.org/10.1080/02678299308027803

LIQUID CRYSTALS, 1993, VOL. 14, NO. 4, 959–970

Preparation and characterization of fibres from a thermotropic liquid crystal polyester with non-coplanar biphenylene units

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Fibres were prepared from the nematic melt of poly(2,2′-dimethyl-4,4′-biphenylene phenylterephthalate). The phenyl substitution in the terephthalic acid moiety in combination with the non-coplanar biphenyl moiety prevent crystallization of this thermotropic polyester. Oriented fibres were prepared by two different methods. Similarly to other thermotropic liquid crystal polymer fibres, chain orientation can be achieved by an elongational flow in a down draw process. This polyester also allows tensile deformation of the spun fibres around the glass transition temperature. In both routes similar degrees of orientation and mechanical properties were obtained. Tensile moduli in the order of 40–45 GPa and tensile strengths up to 550–650 MPa were obtained. The orientation function values were determined to be in the order of 0·8–0·9. A comparison with other unsubstituted thermotropic liquid crystal polyesters at the same level of orientation revealed that the moduli are the same, although the substituents increase the chain diameter. This result may be attributed to an increase of the apparent shear modulus due to an interlocking mechanism of the rigid lateral substituents.

1. Introduction

Thermotropic aromatic LC polyesters have been extensively investigated and developed as injection moldable, high performance, engineering resins and materials for high strength, high modulus fibres and films. The motivation in this area is based on a unique mixture of intrinsic material properties, such as low melt viscosity, very little mold shrinkage, low thermal expansion coefficient and excellent mechanical properties, combined with easy and cost-efficient processing techniques [1]. Thermotropic polyesters can be converted into high strength, high modulus fibres using conventional melt-spinning equipment. The macroscopic orientation of the domains of the thermotropic melt is easily achieved in a shear flow and/or elongational flow field, and the chain orientation develops very rapidly with increasing draw down ratios. The structures of melt spun fibres of wholly aromatic polyesters have been reported to contain very little crystallinity. A heat treatment step of the fibres, typically 10–20°C below the melting temperature, has in most cases no effect on fibre modulus, but substantially improves the fibre tenacity [2–5]. In particular, with respect to the spinning process, thermotropic LC polymers have clear advantages over the earlier developed lyotropic LC polymers, such as the aromatic polyamides and heterocyclic polybenzoxazoles and polybenzthiazoles, which often have to be processed from corrosive and aggressive solvents [5–7].

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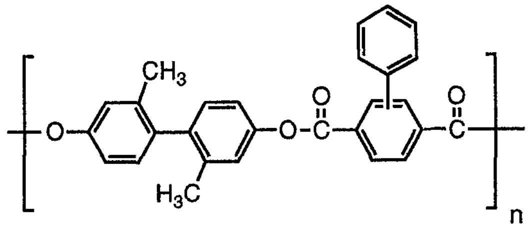


1a - 1c

	1a	**1b**	**1c**
[η]	1.84 dl/g	2.40 dl/g	5.90 dl/g

Figure 1. Structure of thermotropic liquid crystalline poly(2,2′-dimethyl-4,4′-biphenylene phenylterephthalate), **1a**–**1c**.

In this paper, we report on the preparation and characterization of fibres from a thermotropic liquid crystalline polyester poly(2,2′-dimethyl-4,4′-biphenylene phenylterephthalate), PDBPT [8–10]. This substituted *para*-linked aromatic polyester has a broad nematic phase. The rigid phenyl substitution in the terephthalic acid moiety in combination with the non-coplanar 2,2′-dimethyl-substituted biphenyl moiety reduces the interchain interactions and prevents crystallization. In particular the non-coplanar units induce a strong twist of the polymer backbone. As a consequence of the lack of crystallization, the nematic structure can be transferred into a nematic glass below the glass transition temperature [8, 9]. Similar to other thermotropic LCP fibres, chain orientation can be achieved through a down drawing process. This polyester also allows conventional tensile deformation of the as-spun fibres around the glass transition temperature. The solid-state structure and properties of the differently prepared fibres are reported. The results are compared to a variety of structurally similar thermotropic LCPs.

2. Experimental

2.1. *Materials*

Poly(2,2′-dimethyl-4-4′-biphenylene phenylterephthalate) PDBPT was synthesized by melt polycondensation of 4,4′-dihydroxy-2,2′-dimethylbiphenyl and phenylterephthalic acid chloride according to a previously published procedure [10]. Different batches with intrinsic viscosities of 1·84 dl g^{-1} **1a**, 2·40 dl g^{-1} **1b** and 5·90 dl g^{-1} **1c** were used for this study. The intrinsic viscosity was determined with a Cannon Ubbelhode type (No. 25) viscometer at 30°C.

2.2. *Melt spinning*

Fibres were spun from the nematic melt at various temperatures. Polymers with intrinsic viscosities 1·8, 2·4 and 5·9 dl g^{-1} were melt spun at 200, 275 and 280°C, respectively, using an Instron Rheometer (model 3211). Fibre wind-up equipment was employed in the melt spinning process in order to induce various drawdown ratios in the fibres. The diameters of the as-spun fibres were typically 320, 410 and 473 μm for the polymers with respectively increasing intrinsic viscosities. Heat drawing of the as-spun fibres of intrinsic viscosity 2·4 dl g^{-1}, as well as mechanical testing of all fibres, was performed with an Instron tensile tester (Model 1122) equipped with a constant temperature chamber.

2.3. *Solution processing*

Solution spinning was performed with a 5 and a 25 per cent (w/w) solution of the polymer with the intrinsic viscosity of 2·4 dl g^{-1}, in 3-phenoxytoluene and a 7 per cent (w/w) polymer solution in chloroform. Solutions were prepared at room temperature and subsequently wet spun into acetone using laboratory extrusion equipment. The as-spun fibre was dried in a vacuum oven at room temperature. Typically, the dried fibres were of about 275 μm diameter.

2.4. *Tensile drawing and mechanical testing*

Fibres of length 20 mm were heat drawn at a rate of 5 mm min^{-1} at various temperatures. Tensile properties were tested at room temperature. The gauge length was 20 mm and the rate of elongation was 20 mm min^{-1}. In all cases, the draw ratio was calculated as the ratio of the final fibre denier to the initial denier. As will become clear later, the usual method of recoiling at temperatures above T_m used for the accurate measurement of draw ratio was found to be unsuitable for this polyester.

2.5. *Characterization*

Thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out with a Mettler TA 3000 system at a rate of 20° min^{-1} and 10° min^{-1}, respectively. X-ray diffraction studies were performed using a Philips flat film X-ray diffractometer (Model PW 1729). Scanning electron microscopy (SEM) was carried out with a Cambridge S90 instrument.

3. Results and discussion

Several concepts of structural modification have been described in the literature to control and modify the thermal and solubility properties of *para*-linked aromatic polyesters. An effective approach to lower the melting temperature and to enhance the solubility, without initially reducing the chain stiffness, is the incorporation of 2,2′-disubstituted biphenylene units [10–14]. The phenyl rings are forced by the substituents into a non-coplanar conformation, which reduces substantially the interchain interactions. The combination of non-coplanar biphenyl units with mono-substituted phenylene units further changes the interchain interactions. As a result thermotropic *para*-linked aromatic polyesters with low transition temperatures, non-crystalline, amorphous structure and good solubility in common organic solvents are obtainable. Poly(2,2′-dimethyl-4,4′-biphenylene phenylterephthalate), PDBPT, represents an example of such a type of thermotropic polyester. The DSC investigations (see figure 2) revealed only a glass transition around 135–140°C and no indication of an additional endothermic transition up to 300°C. The actual value of the glass transition temperature is, as expected, dependent on the molecular weight. The glass transition temperatures for the polyesters used in this study were at 135°C (**1a**), 137°C (**1b**) and 141°C (**1c**). At temperatures about 20–30° above the glass transition, the sample is still relatively viscous. A low viscous nematic melt is generally observed about 60–80° above the glass transition. DMTA measurements on fibres with different degrees of orientation and thermal history did not reveal any indication of partial crystallinity.

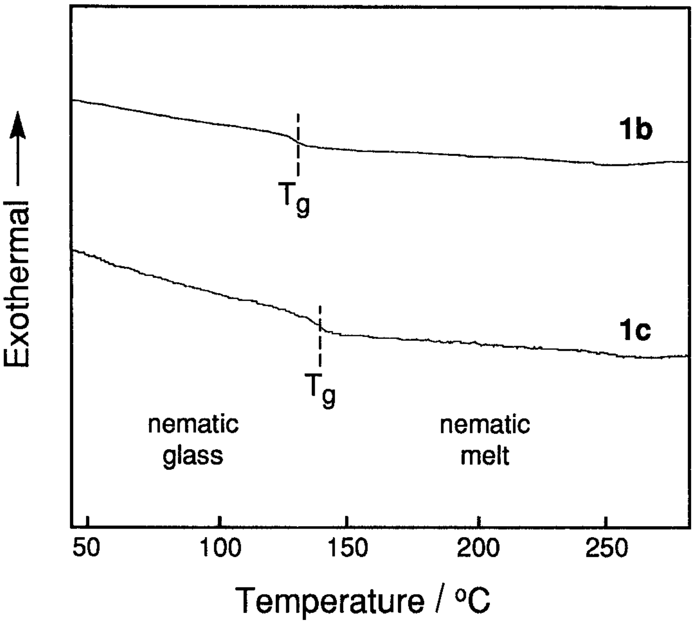


Figure 2. DSC curves (2nd heating) of poly(2,2′-dimethyl-4,4′-biphenylene phenylterephthalate) **1b** and **1c**. (Heating rate 10° min^{-1}; samples cooled at 10° min^{-1}.)

Table 1. Mechanical properties of as-spun fibres of poly(2,2′-dimethyl-4,4′-biphenylene phenylterephthalate) **1a–1c** from the nematic melt.

Polymer no.	Spin temperature/ °C	Denier/ g m^{-1}†	Modulus/ GPa	Strength/ MPa	Elongation/ %
1a	200	1045	11·6	190	2·0
1b	240	1835	15·2	100	0·9
1b	257	1845	14·4	120	1·0
1b‡	279	1670	18·8	150	0·9
1c	280	2220	4·9	130	2·7

† Density was measured as 1·40 g cm^{-3}.
‡ Fibre used for heat draw experiments.

The storage modulus upon heating above T_g falls to zero. As a consequence of the absence of crystallinity, the nematic structure can be transferred into a nematic glass below the glass transition temperature.

Fibres of PDBPT were prepared by conventional melt spinning and wet spinning techniques. The melt spinning experiments gave by far the best results. Solution spinning was found to be an unsuitable processing route for this polymer. Solution spinning was performed with 5 and 25 per cent w/w solutions of the polymer **1b** in 3-phenoxytoluene and a 7 per cent w/w polymer solution in chloroform. Solutions were prepared at room temperature and wet spun into a variety of low boiling solvents. The fibres produced showed a white and porous morphology. Mechanical properties were quite low at a modulus of 1·3 GPa, tensile strength of 20 MPa and elongation at break of 2·5 per cent.

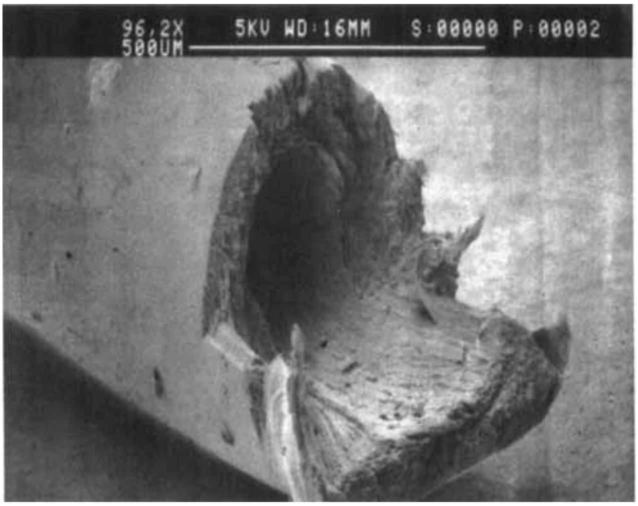


Figure 3. SEM photograph of a fractured melt spun, as-spun fibre of **1b**.

In contrast, melt-spun fibres were off white in colour, relatively uniform and had better mechanical properties. Table 1 summarizes different spin temperatures and the mechanical properties of the as-spun fibres where no down draw was applied. The mechanical properties were in the range of 12–19 GPa for the modulus and 100–190 MPa for the tensile strength. The variations in mechanical properties for the as-spun fibres with intrinsic viscosity are probably more representative of the degree of orientation induced by shear flow or small amounts of elongational flow, than an influence of molecular weight. Figure 3 shows a SEM photograph of a fractured as-spun fibre of **1b**. A typical skin-core morphology is observed.

The degree of orientation and consequently the mechanical properties could be improved by tensile deformation. In order to find the optimal drawing conditions, experiments at various temperatures around the glass transition temperature were performed. Figure 4 shows the heat drawing behaviour of PDBPT fibres **1b** (as-spun: modulus 18·8 GPa, strength 150 MPa) at various temperatures. From this plot, 150°C was chosen as the optimum draw temperature. The draw behaviour, even at 150°C seems to be non-affine, with considerable chain slippage within the structure. However, tensile deformation significantly enhanced the chain alignment and consequently the modulus and tensile strength of the fibres. Table 2 summarizes the mechanical properties of the heat drawn fibres at various draw ratios. The tensile modulus could be improved up to 46 GPa and the tensile strength up to 550 MPa. We should point out again that the heat drawing process does not produce affine drawing of the macromolecules, as is usually encountered in the drawing of flexible chain polymers such as polyethylene. The structure of PDBPT is able to accommodate high degrees of orientation at moderate draw ratios due to the extended chain structure of the *para*-linked polyester backbone. At the same time, the polymer structure allows chain orientation through heat drawing in the presence of the bulky stiff phenyl substituents, which act both to separate the chains, allowing slippage, and also to create the opportunity for an interlocking mechanism.

The common way to develop chain orientation in thermotropic liquid crystalline polymers is based on the macroscopic orientation of the liquid crystalline domains in

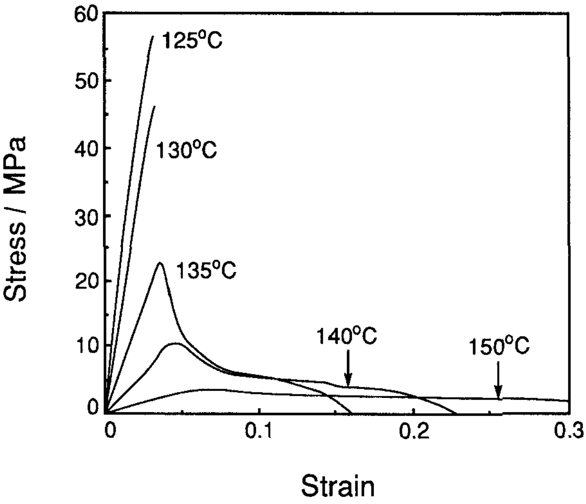


Figure 4. Drawing behaviour of melt-spun fibres of **1b** at various temperatures around the glass transition temperature.

Table 2. Mechanical properties of heat drawn fibres of poly(2,2′-dimethyl-4,4′-biphenylene phenylterephthalate) **1b**.

Draw temperature/ °C	Draw ratio	Denier/ g m^{-1}†	Modulus/ GPa	Strength/ MPa	Elongation/ %
150	8	225	28	270	1·1
150	59	31	30	390	1·5
150	78	24	46	550	1·5

† Density was measured as 1·40 g cm^{-3}.

capillary shear flow and an applied elongational flow field through down draw. Figures 5 and 6 show the development of modulus and tensile strength of the melt-spun PDBPT fibres of **1b** and **1c** with various draw down ratios. The modulus is seen to increase quite rapidly to reach values of 35–40 GPa around draw down ratios of 10–15. Further drawing did not improve the modulus dramatically. The tensile strength seems to increase more slowly. Maximum values in the order of 0·6–0·7 GPa were obtained. Figure 7 shows a SEM photograph of a draw down PDBPT fibre fractured during tensile testing.

A similar development of mechanical properties for different draw down ratios was published for thermotropic copolyesters based on 6-hydroxy-2-naphthoic acid (HNA) and 4-hydroxybenzoic acid (HBA) (Vectra) fibres [2, 3]. In the case of the unannealed HBA/HNA copolymer with a molar co-monomer ratio of 75/25, the modulus of fibres with draw down ratios above 20 is reported to be around 60 GPa. In such semi-crystalline LC polyesters, heat treatment, typically 10–20°C below the melting temperature, has in most cases no effect on fibre modulus, but improves substantially the fibre tenacity. Traditionally this improvement is believed to occur due to an increase in crystallinity and crystal size. However, recently in the case of the

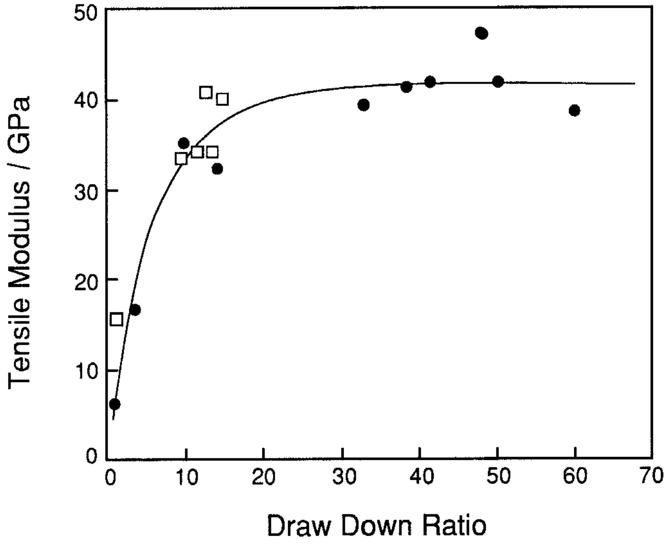


Figure 5. Tensile modulus versus draw down ratio of melt spun fibres of **1b** (□) and **1c** (●).

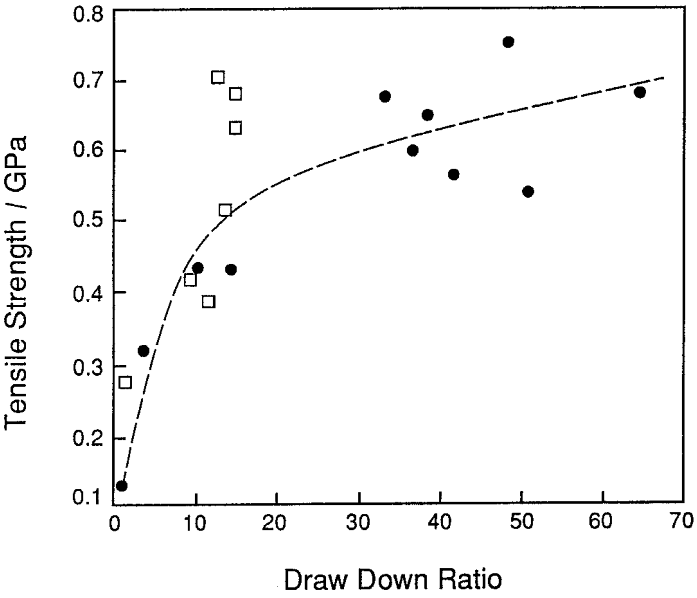


Figure 6. Tensile strength versus draw down ratio of melt spun fibres of **1b** (□) and **1c** (●).

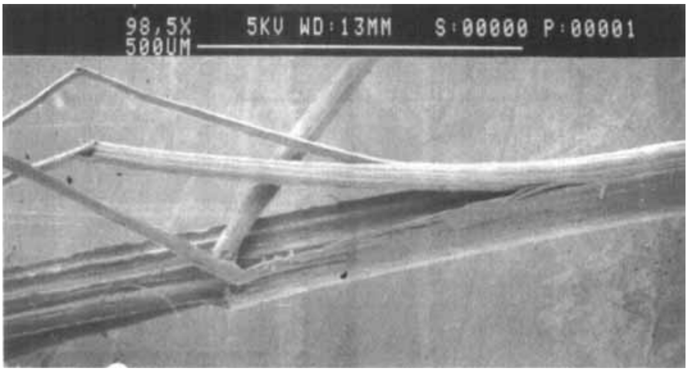
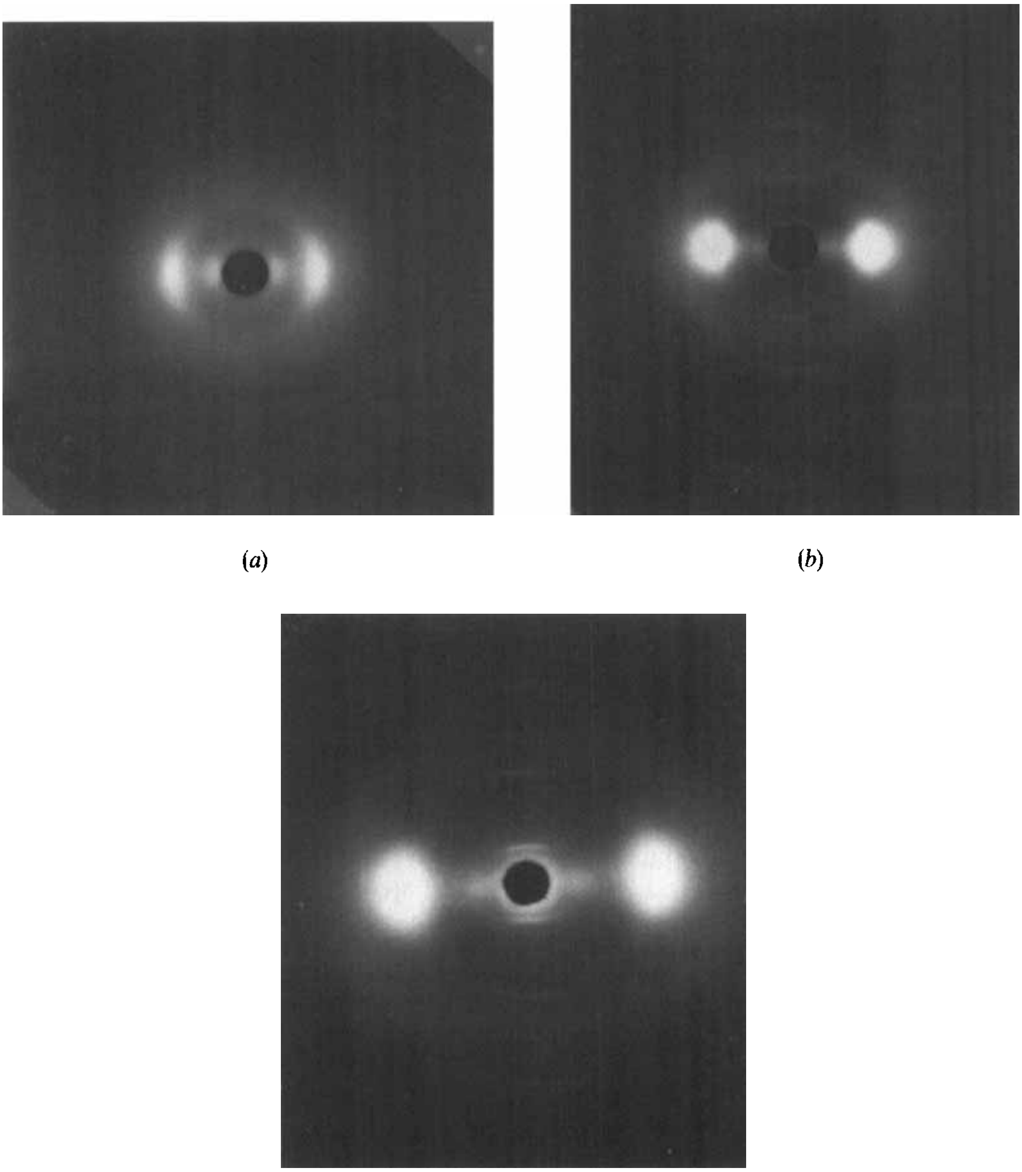


Figure 7. SEM photograph of a drawn fibre of **1b**, fractured during tensile testing.

thermotropic aromatic polyesters, this has been attributed to a solid-state polymerization and an attendant increase in molecular weight [14]. For the PDBPT fibres, annealing at 150°C under vacuum for 18 h only increased the modulus and tensile strength values around 10 per cent. Annealing at higher temperatures is not possible because the fibres soften and deform due to the lack of crystallinity. This observation reaffirms the belief that the incorporation of lateral substituents, in combination with non-coplanar units, distorts the interchain interaction sufficiently and prevents crystallization. Melt spun drawn PDBPT fibres were seen to retain up to 25 per cent of their room temperature modulus and tensile strength at 150°C and around 5 per cent of modulus and over 10 per cent of tensile strength at 170°C.

Different types of phenyl substituted thermotropic polyesters and copolyesters, are reported in the patent literature. As-spun fibres of thermotropic polyesters based on phenylterephthalic acid have moduli in the range of 38–43 GPa and tensile strengths in the range of 0·37–0·56 GPa[15, 16]. These values are identical to those achieved with PDBPT. If the phenyl substituent is next to the oxygen of the ester linkage, as in phenylhydroquinone [17, 18] or 3-phenyl-4-hydroxybenzoic acid [19], the properties for the as-spun fibres are slightly higher. Tensile moduli in the range of 45–50 GPa and tensile strength values about 0·5–0·7 are reported.

The degree of orientation for the different fibres was investigated by wide angle X-ray diffraction. Figure 8 compares diffraction patterns of an as-spun fibre, a fibre prepared with down draw fire ($\lambda = 15$) and a heat drawn fibre ($\lambda = 20$) of PDBPT **1b**. As expected, the as-spun fibre (see figure 8 (*a*)) shows a small degree of pre-orientation, which typically is induced by shear flow and some elongational flow of the nematic melt. The patterns of the down drawn and heat drawn fibres in figures 8 (*b*) and (*c*) are similar and show a substantially increased orientation. Each pattern contains two sets of equatorial reflections and up to four sets of meridional reflections. Bragg maxima on the equator represent *d*-spacings of 11·8 Å and 5·2 Å and there seems to be significant two dimensional order of the chains. The meridional reflections represent *d*-spacings of 14·7 Å, 5·3 Å, 3·2 Å and 2·0 Å, respectively. The X-ray patterns resemble those for the HBA/HNA fibres. The equatorial *d*-spacings calculated for the PDBPT fibres are quite close to the orthorhombic unit cell dimensions of $a = 9{\cdot}2$ Å and $b = 5{\cdot}2$ Å for the as-spun fibres of copoly(HBA/HNA) with a 75/25 molar co-monomer ratio [15, 20, 21]. Under the assumption that PDBPT has a similar structure to copoly(HBA/HNA), unit cell dimensions from X-ray analysis would be $a = 11{\cdot}8$ Å and $b = 5{\cdot}2$ Å. The larger a axis of



(*a*) (*b*)

(*c*)

Figure 8. Wide angle X-ray diffraction patterns of melt-spun poly(2,2′-dimethyl-4,4′biphenylene phenylterephthalate) fibres **1b** (chain axis is vertical). (*a*) As-spun, (*b*) as-spun with draw down ratio of ~15, (*c*) heat drawn fibre (draw ratio: ~20).

PDBPT fibres can be explained as being due to the pendent phenyl side group and methyl substituents.

Films from PDBPT were also prepared by pressing the melt at 250°C. X-ray diffraction of the films show order along the shear direction. This manifests itself in modulus and tensile strength values of, respectively, 3 GPa and 50 MPa along the flow direction and 1 GPa and 20 MPa perpendicular to this direction. Figure 9 shows a

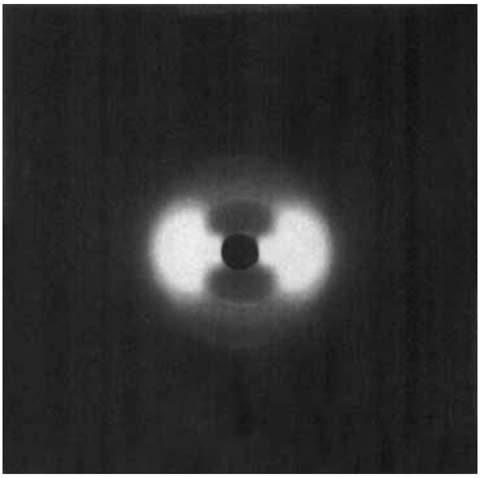


Figure 9. Wide angle X-ray diffraction patterns of a film of poly(2,2′-dimethyl-4,4′-biphenylene phenylterephthalate **1c** melt pressed at 250°C (chain axis is vertical).

diffraction pattern on the melt pressed film of PDBPT **1c** at 250°C. The pattern is similar to the fibre pattern, and considerable order along the shear direction is visible.

Further quantitative evidence of the degree of ordering can be obtained by calculating the Herman's orientation function f using the equation $f=[\langle(3\cos^2\theta-1)\rangle/2]$ [22]. The angular half widths of the equatorial reflections from figures 8 (*a*)–(*c*) were found to be 22·4°, 16·5° and 14·8° respectively, corresponding to orientation function values of 0·77 (as-spun), 0·88 (down drawn) and 0·90 (heat drawn).

Although substituents generally reduce the mechanical properties due to an increase in the effective area occupied by the chain, it can be assumed that in the case of stiff lateral substituents, the shear moduli may increase compared to those for the non-substituted cases. An increase in shear modulus would be due to a type of interlocking mechanism of the rigid lateral substituents caused by the non-coplanar and twisted structure of the polymer chain and the steric hindrance of the substituents. The shear modulus can be calculated using the equation developed by Troughton *et al.* [23]:

$$1/E-1/E_c=\langle\sin^2\theta\rangle/G, \qquad (1)$$

where E is a tensile modulus at a particular orientation condition, E_c is the chain modulus, G is the effective shear modulus and θ is the angle between the chain direction and the fibre axis.

An interesting comparison can be made between the apparent shear moduli of PDBPT and HBA/HNA copolyesters. The values are compared at an orientation function $f=0{\cdot}9$, which is the highest value obtained for the PDBPT fibres. This corresponds to $\theta=15°$. For HBA/HNA fibres at an orientation function of 0·9, a modulus of 42 GPa and a chain modulus E_c of 200 GPa has been reported [2, 3]. Using equation (1), an apparent shear modulus G of 3·4 GPa can be calculated. It should be pointed out here that the commercially available HBA/HNA fibres have been reported to possess an orientation function f greater than 0·98, resulting in a modulus of 90 GPa [3]. The chain modulus E_c for PDBPT can be calculated by multiplying the HBA/HNA chain modulus of 200 GPa by the ratio of the cross-section area occupied per chain of HBA/HNA to that of PDBPT, i.e. $E_{\mathrm{cPDBPT}} = 200 \times (23{\cdot}92/30{\cdot}68) = 156\,\mathrm{GPa}$. This assumes that the reduction in modulus is solely due to the dilution effect of the substituents. For $f = 0{\cdot}9$, $E = 45\,\mathrm{GPa}$, and thus the apparent shear modulus $G = 4{\cdot}2\,\mathrm{GPa}$. This represents a value significantly greater than that of the HBA/HNA system and proves the hypothesis that rigid bulky substituents increase the apparent shear modulus by a type of interlocking mechanism.

4. Conclusions

PDBPT, like most other thermotropic liquid crystalline polymers, is readily oriented under moderate shear flow and elongational flow conditions and the processed fibres comprise a highly ordered structure. The phenyl substitution in the terephthalic acid moiety, in combination with the non-coplanar biphenyl moiety, prevent crystallization of this thermotropic polyester. No evidence of crystallinity was observed before or after fibre spinning. Highly oriented fibres were prepared by chain orientation through an elongational flow in a down draw process and by tensile deformation of the as-spun fibres around the glass transition temperature. In both routes, similar degrees of orientation and mechanical properties were observed. Tensile moduli in the order of 40–45 GPa and tensile strengths up to 550–650 MPa were obtained. Incorporation of rigid substituents is seen to increase the apparent shear modulus G via a type of interlocking mechanism. The apparent shear modulus was calculated to be 4·2 GPa.

The authors are grateful to Professor Paul Smith for many stimulating discussions and helpful suggestions. The authors are indebted to Dr Kyo Jin Ihn for useful comments on the X-ray analysis of the fibres. This work was partially supported by a grant from the Hoechst-Celanese Corporation (Summit, New Jersey).

References

[1] See, for example, (a) WEISS, R. A., and OBER, C. K. (editors), 1990, *Liquid-Crystalline Polymers* (ACS Symposium Series 435, Washington, DC). (b) CIFERRI, A. (editor), 1991, *Liquid Crystallinity in Polymers* (VCH Publishers). (c) SEYMOUR, R. B., and KIRSHENBAUM, G. S. (editor), 1986, *High Performance Polymers* (Elsevier). (d) KWOLEK, S. L., MORGAN, P. W., and SCHAEFGEN, J. R., *Encyclopedia of Polymer Science and Engineering*, Vol. 9, edited by H. F. Mark, N. M. Bikales, C. G. Overberger and G. Menges (Wiley), p. 1.

[2] CHUNG, T. S., CALUNDANN, G. W., and EAST, A. J., 1989, *Handbook of Polymer Science and Technology*, Vol. 2, edited by N. P. Cheremisinoff (Marcel Dekker, Inc.).

[3] YOON, H. N., CHARBONNEAU, L. F., and CALUNDANN, G. W., 1992, *Adv. Mater.*, **4**, 206.

[4] HONGU, T., and PHILLIPS, G. O., 1990, *New Fibres* (Ellis Horwood Limited).

[5] YANG, H. H., 1989, *Aromatic High-Strength Fibres* (Wiley).

[6] JAFFE, M., and SIDNEY JONES, R., 1985, *Handbook of Fibre Science and Technology:* Volume III, *High Technology Fibres Part A*, edited by M. Lewin and J. Preston (Marcel Dekker), p. 349.

[7] ADAMS, W. W., EBY, R. K., and MCLEMORE, D. E. (editors), 1989, *The Materials Science and Engineering of Rigid-Rod Polymers* (Materials Research Society).

[8] SCHMIDT, H.-W., 1989, *Makromolek. Chem. Makromolek. Symp.*, **26**, 47.

[9] GREINER, A., ROCHEFORT, W. E., GREINER, K., HEFFNER, G. W., PEARSON, D. S., and SCHMIDT, H.-W., 1991, *Integration of Fundamental Polymer Science and Technology-5*, edited by P. J. Lemstra and L. A. Kleintjens (Elsevier Applied Science), p. 258.

[10] SCHMIDT, H.-W., and GUO, D., 1988, *Makromolek. Chem.*, **189**, 2029.

[11] SINTA, R., GAUDIANA, R. A., MINNS, R. A., and ROGERS, H. G., 1987, *Macromolecules*, **20**, 2374.

[12] SINTA, R., MINNS, R. A., GAUDIANA, R. A., and ROGERS, H. G., 1987, *J. Polym. Sci.* C, **25**, 11.

[13] HOHLWEG, M., and SCHMIDT, H.-W., 1989, *Makromolek. Chem.*, **190**, 1619.

[14] Yoon, H. N., 1990, *Colloid. Polym. Sci.*, **268,** 230.
[15] Harris, J. F., 1981, U.S. Patent 4 294 955.
[16] Harris, J. F., 1983, U.S. Patent 4 391 966.
[17] Payet, C. R., 1979, U.S. Patent 4 159 365.
[18] Prevorsek, D. C., 1982, *Polymer Liquid Crystals*, edited by A. Ciferri, W. R. Krigbaum and R. B. Meyer (Academic Press), p. 329.
[19] Calundann, G. W., 1981, U.S. Patent 41 279 803.
[20] Sun, Z., Cheng, H. M., and Blackwell, J., 1991, *Macromolecules*, **24,** 4162.
[21] Gutierrez, G. A., Chivers, R. A., Blackwell, J., Stamatoff, J. B., and Yoon, H., 1983, *Polymer*, **24,** 937.
[22] White, J. L., and Cakmak, M., 1987, *Encyclopedia of Polymer Science and Engineering*, Vol. 10, edited by H. F. Mark, N. M. Bikales, C. G. Overberger and G. Menges (Wiley). p. 595.
[23] Troughton, M. J., Davies, G. R., and Ward, I. M., 1989, *Polymer*, **30,** 58.