

Synthesis and mesomorphic properties of a new thermotropic liquid-crystalline 'backbone' copolyester

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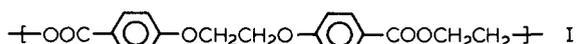
Details of the thermal behaviour of the following liquid-crystalline 'backbone' copolyester are reported: $-\left[OC-C_6H_4-O\right]_{10,6} + \left[OOC-C_6H_4OCH_2CH_2O-C_6H_4-COOCH_2CH_2\right]_{10,4}$. Between 218° and 337°C, observations using a polarizing microscope indicate the formation of a birefringent melt that exhibits a Schlieren texture. From the observation of disclinations of strength $\pm 1/2$, the mesophase can be identified as a nematic phase. The isobaric phase diagram of mixtures of copolyester and *N,N'*-di-(*p*-methoxy benzylidene)- α,α' -bi-*p*-toluidine and X-ray diffraction patterns provide definite proof as to the nematic structure of the birefringent melt. Addition of a chiral compound to the copolyester in the nematic state causes the formation of the typical textures of cholesterics. The temperature dependence of the order parameter has been determined from *FTi.r.* polarized spectra. At high temperature *S* is found to be 0.3. Such a result confirms the recent theory of Ronca and Yoon: the isotropic-nematic transition of semiflexible polymers does not entail a very high degree of order in the resultant nematic phase.

(Keywords: liquid crystalline polymers; optical textures; isobaric phase diagram; oriented mesophase; infra-red dichroism; order parameter)

INTRODUCTION

The use of *p*-oxybenzoyl as a structural element in thermotropic liquid crystals is well known¹⁻³. Jackson and Kuhfuss⁴ described the preparation and properties of *p*-hydroxybenzoic acid copolyesters obtained by the reaction of *p*-acetoxybenzoic acid with poly(ethylene terephthalate). Since it was thought that the unusual anisotropic properties of these copolyesters might be due to the liquid-crystalline nature of the polymer melts, other copolyesters were prepared by acidolysis reaction from poly(ethylene terephthalate) and a variety of dicarboxylic acids and acetylated difunctional phenols⁵. At the same time, the synthesis and structure of wholly aromatic copolyesters, viz. condensation copolymers of *p*-hydroxybenzoic acid, 2,6-dihydroxynaphthalene and terephthalic acid, were described^{6,7}. For proportions of *p*-hydroxybenzoic acid between 30 and 70 mol%, the melts are liquid crystalline. This order is retained during spinning, leading to highly oriented high-strength fibres.

In this work we report the synthesis and mesogenic behaviour of a copolyester obtained by the reaction of *p*-acetoxybenzoic acid with polyester I:



Some of our results were presented at the IUPAC International Symposium on Interrelations Between Processing Structure and Properties of Polymeric Materials, Athens (13-18 September 1982).

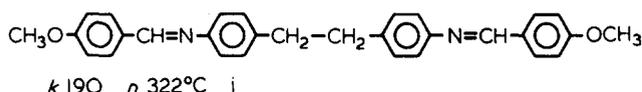
EXPERIMENTAL

Materials

Polyester I was prepared by conventional polycondensation. Ethylene glycol and 4,4'-dicarbomethoxy-1,2-diphenoxy ethane (UENO-FINE) were obtained from commercial sources. *p*-Acetoxybenzoic acid was synthesized by acetylating the corresponding hydroxybenzoic acid and was purified by crystallization.

The copolyester was prepared in the Centre de Recherches des Carrieres, Rhône-Poulenc, Saint-Fons, France, by the procedure described in ref. 4. A mixture of polyester I (40 mol%) and *p*-acetoxybenzoic acid (60 mol%) was placed in a flask equipped with a stainless-steel stirrer, an attachment for applying a vacuum and a short head with an inlet and an outlet for nitrogen. After the reaction flask was evacuated and purged with nitrogen, it was heated to 270°-280°C. As soon as the temperature reached 240°-250°C, the mixture began evolving acetic acid. After approximately 40 min, the pressure was reduced to 0.5 mm and stirring continued for about 5 h at 275°C to aid in the removal of acetic acid. After cooling the resulting copolyester was white-yellow. Quantitative elemental analysis gives the following result: Calc.: C, 67.32%; O, 28.35%; H, 4.33%; Found: C, 67.35%; O, 28.27%; H, 4.38%.

The reference compound used to identify the mesophase was *N,N'*-di-(*p*-methoxy benzylidene) α,α' -bi-*p*-toluidine (Eastman Organic Chemicals):



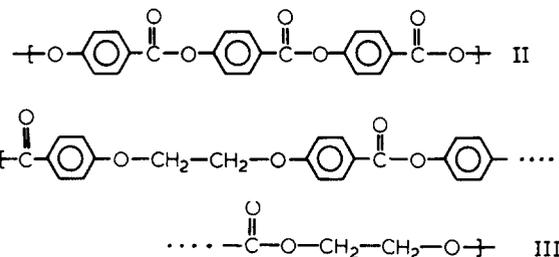
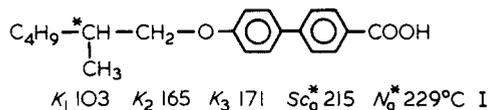
freshly cleaved mica surfaces. The homogeneous alignment of the samples was routinely checked under a polarizing microscope.

RESULTS AND DISCUSSION

The copolyester is insoluble in virtually all common solvents at room temperature. Solubility was obtained with dichloroacetic acid, although decomposition occurs.

Since the copolyester was obtained by a reaction similar to that used in preparing liquid-crystalline polyesters from polyethylene terephthalate⁴, it is expected to contain segments II and III in addition to polyester I segments:

The conversion of polymeric mesophase to the cholesteric form was performed by the addition of 4'-(2-methylhexyloxy)biphenyl-4-carboxylic acid:



The copolyester ¹³C n.m.r. spectra obtained at 25°C in dichloroacetic acid solution and in bulk under conditions of dipolar decoupling, magic angle spinning and cross polarization are shown in Figures 1 and 2. Owing to the

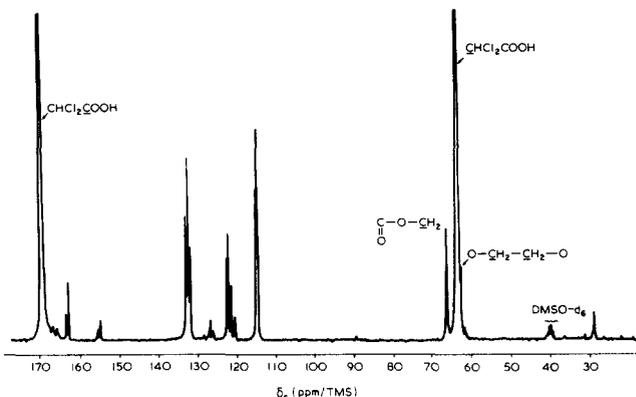


Figure 1 62.9 MHz ¹³C n.m.r. spectrum of copolyester in dichloroacetic acid solution at 25°C. DMSO-d₆ was used as an external lock

The preparative procedure was described in ref. 8.

Methods

High-resolution ¹³C n.m.r. spectra were measured on a CHCl₂COOH solution of the copolyester at 62.9 MHz with a Bruker WP-250 spectrometer.

Cross-polarization, magic-angle-spinning ¹³C n.m.r. spectra were collected at 12.07 MHz on a home-built spectrometer as has been described⁹.

D.s.c. measurements were made by means of a Du Pont Model 990. The samples were kept under a dry nitrogen flow.

The texture of polymeric mesophase was observed between slips with a polarizing microscope equipped with a programmable heating stage (Mettler FP 5).

Binary mixtures were prepared by the contact procedure¹⁰ and phase diagrams were constructed by polarizing light microscopy of these mixtures. Well defined compositions were examined for the phase diagrams to ensure a degree of accuracy for the composition coordinate.

For the X-ray measurements, the samples were contained in 1 mm diameter Lindemann glass tubes. Low-angle diffraction patterns were recorded on flat films. For experiments requiring wide-angle diffraction data, X-ray study was done in a standard cylindrical camera. In both cases Ni-filtered CuK α radiation was used.

The polarized infra-red spectra were recorded for aligned nematic specimens using a Nicolet 7199 Fourier transform infra-red spectrometer. The polarization of the infra-red beam was obtained by the use of a Perkin-Elmer gold wire grid polarizer, the high efficiency of which makes polarization correction unnecessary. Well aligned specimens of nematic copolyester were obtained by using

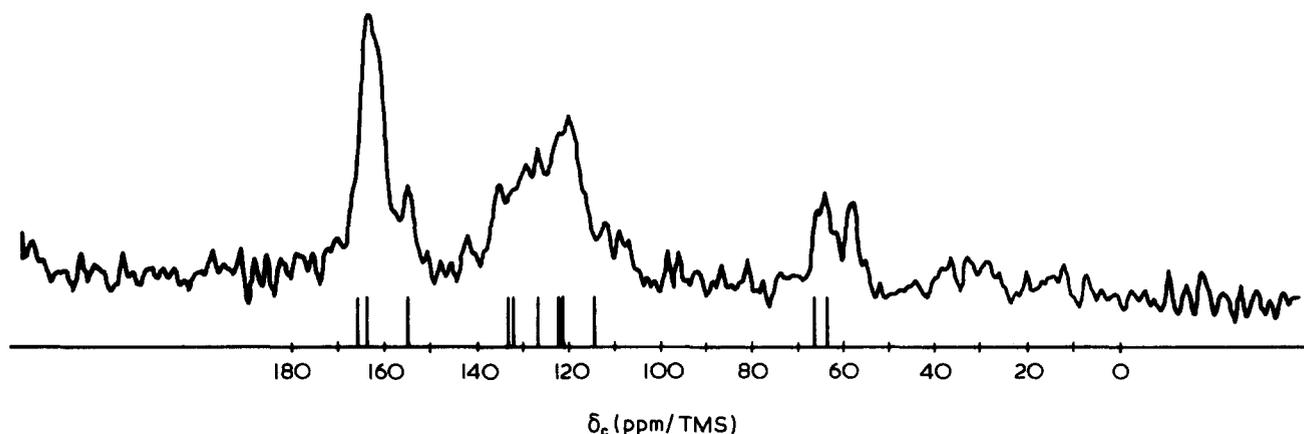
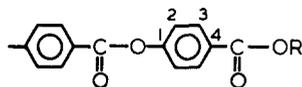
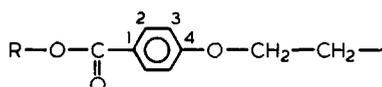


Figure 2 12.07 MHz magic-angle cross-polarization ¹³C n.m.r. spectrum of copolyester in bulk at 25°C. CP contact time: 1 ms. The stick spectrum was calculated from Figure 1

presence of dichloroacetic acid, the carboxyl region is not easy to analyse in the vicinity of 170 ppm. According to experimental ^{13}C chemical shift determinations of *p*-oxybenzoyl tetramer and polymer¹¹, and calculations based on empirical parameters in substituted benzenes¹², the aromatic C1, C2, C3 and C4 carbons of the

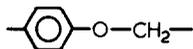


unit, where $\text{R} = \text{---} \text{C}_6\text{H}_4 \text{---}$ (i.e. segment II), are expected to present resonances at about 155, 122, 137 and 127 ppm, respectively. The similar unit, in which $\text{R} = \text{---CH}_2\text{---CH}_2\text{---}$ (i.e. segment III), will lead to smaller peaks in the vicinity of the preceding ones. In the same way, peaks corresponding to the C1, C2, C3 and C4 carbons of the

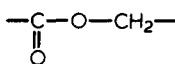


sequence must be located at about 122, 132, 115 and 163 ppm, respectively, each of these signals being doubled due to the two different substituents $\text{R} = \text{---} \text{C}_6\text{H}_4 \text{---}$ (i.e. segment III) and $\text{R} = \text{---CH}_2\text{---CH}_2\text{---}$ (i.e. segment I). The experimental solution ^{13}C spectrum (Figure 1), which shows two peaks at about 163, 155, 127 and 115 ppm and four peaks at about 132 and 122 ppm, is consistent with the presence of these four structural units and, hence, confirms that the preparation described leads to a copolymer containing segments I, II and III.

In the solution ^{13}C spectrum, the methylene carbons of the



group resonate at 63.2 ppm, as in polyethylene oxide, and those of the



group have chemical shifts of 66.7 ppm.

In the carboxyl and aromatic regions, solution and bulk ^{13}C spectra are quite similar (Figures 1 and 2). However, it must be noticed that, in the solid state, the methylene carbons undergo an upfield shift. Such a result may be interpreted in terms of different conformer populations, and likely more *trans* conformations in bulk as observed for polyethylene terephthalate¹³. In the solution spectrum one small signal is observed in the methyl region. Since this peak does not appear in the solid spectrum, it may be assigned to some degradation of copolyester in the presence of dichloroacetic acid.

In Figure 3 a typical d.s.c. curve of copolyester is shown. In the temperature range 40°–400°C, four transitions occur when going from low to high temperature: the glass transition at about 60°C, a cold crystallization exotherm, the melting peak at 218°C and the mesophase–isotropic liquid transition at about 337°C. As observed by Grebovicz and Wunderlich¹⁴ for low-molecular-weight liquid crystals, the low-temperature behaviour has been found to be dependent upon the cooling rate. The slower

the cooling rate, the smaller are the glass transition and the cold crystallization exotherm.

Polymer observations using a polarizing microscope indicate at 218°C the formation of a birefringent melt which exhibits a Schlieren texture. When observed between crossed polarizers, the Schlieren texture shows dark brushes which joint at certain points. In some cases, four extinction bands are seen to radiate from the centre (Figure 4). Such points indicate disclinations of strength ± 1 in the structure¹⁵. However, there are also disclinations of strength $\pm \frac{1}{2}$ which appear as points at which only two dark brushes meet (Figure 5). From the observation of the latter defects the mesophase can be unambiguously identified as a nematic phase. Indeed, in contrast to the nematic Schlieren textures in which disclinations with $S = \pm \frac{1}{2}, \pm 1$ are possible, the smectic textures have points with only four Schlieren¹⁵. Conventional liquid crystals have a well defined 'clearing point', but, in the copolyester, the transition occupies a range of temperatures within which there is an equilibrium two-phase microstructure. Coexistence of mesomorphic and isotropic phases has been seen in other copolyesters¹⁶. It may be due to the polydispersity of the samples.

The isobaric phase diagram of mixtures of copolyester and *N,N'*-di-(*p*-methoxy benzylidene)- α,α' -bi-*p*-toluidine is shown in Figure 6. The polymeric mesophase is

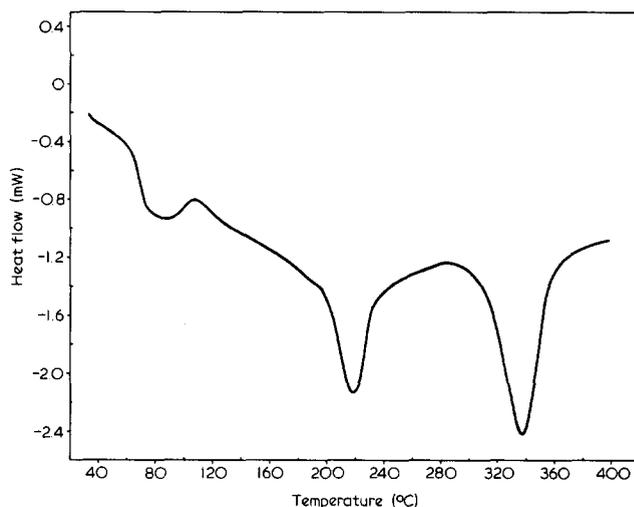


Figure 3 D.s.c. heating trace of the as-received copolyester (5.4 mg). Heating rate 20 K min⁻¹ in dry nitrogen

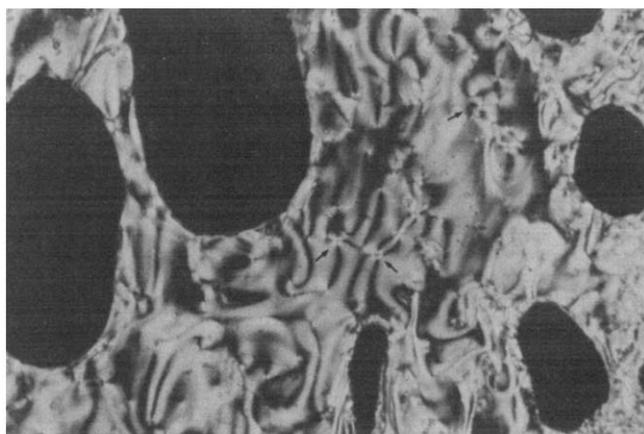


Figure 4 Schlieren texture of copolyester. Recognizable singularities $S = -1$ and $S = +1$ (crossed polarizers, 280°C, $\times 150$)

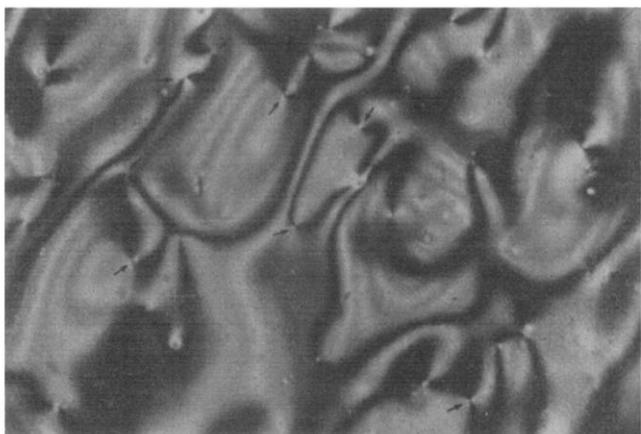


Figure 5 Schieren texture of copolyester with singularities $S = +1/2$ and $S = -1/2$ (crossed polarizers, 260°C, $\times 200$)

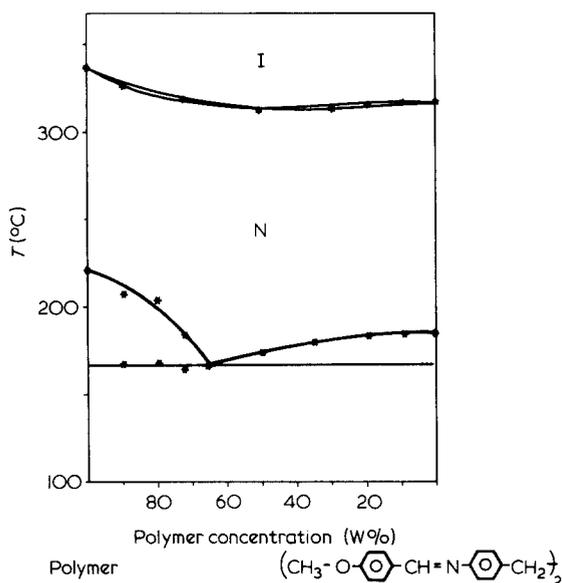


Figure 6 Isobaric binary phase diagram for the system copolyester/*N,N*-di-(*p*-methoxy benzylidene)-*x,x'*-bi-*p*-toluidine

isomorphous with the nematic phase of the reference compound. The nematic-isotropic transition line deviates slightly from linear due to difficulties in packing dissimilar molecules. This deviation is expressed by a flattened minimum. The mixtures show an eutectic at a composition of approximately 65% copolyester by weight. Similar binary phase diagrams have been encountered for other mixtures of a nematic polymer and a small molecule nematogen^{9,17-20}.

The nematic phase of the copolyester can be transformed to the cholesteric one by dissolving an optically active compound in it. Figures 7 and 8 show that the copolyester is totally miscible with 4'-(2-methylhexyloxy) biphenyl-4-carboxylic acid. This chiral compound on addition to the copolyester mesophase causes the formation of the typical planar texture of cholesterics. As shown in Figure 9 oily streaks are formed and Moiré fringes appear.

The 'as-received' polymer is fibrous in form and, hence, suitable for X-ray studies on oriented material. The X-ray diffraction patterns obtained from the original unannealed samples show few reflections blurred in broad and diffuse crescents, which indicates that the crystalline phase

is present in a small amount, with predominant scattering from the amorphous phase. Annealing above T_g , for example at 140°C, causes a steep rise in crystallinity. However, it can be seen from Figure 10a that a certain amount of amorphous phase always remains. Indeed, along the equator two pronounced crescents and two diffuse spots are observed at $q = 0.35-0.83 \text{ \AA}^{-1}$ and $1.2-1.7 \text{ \AA}^{-1}$, respectively ($q = 4\pi \sin \theta / \lambda$ where 2θ is the scattering angle and λ the radiation wavelength). The crystalline phase is evident from the 'fibre' pattern where off-meridional reflections (indexed as hkn reflections) can be observed up to the fourth layer line ($n = 4$). From the position of these reflections the unit cell parameter c is found to be 18.4 Å. Therefore, the two spots along the meridian line which correspond to a spacing of 9.1 Å may be indexed as (002) reflection. In addition to these sharp maxima, arced diffractions can also be seen in the meridian at $d = 3.05$ and 2.04 Å. For the copolyester under investigation the parameter c cannot be assigned unambiguously to the length of any residue I, II or III in the most extended *trans* conformation. However, it should be noted that all the observed reflections are consistent with a hexagonal cell with dimensions $a = 25.7 \text{ \AA}$ and $c = 18.4 \text{ \AA}$ so that the molecular packing may be similar to that observed for the *p*-hydroxybenzoic acid polymer²¹. Such a similarity suggests the presence of either long sequences of *p*-hydroxybenzoic acid units in the structure of the copolyester or small amounts of *p*-hydroxybenzoic acid homopolymer. From optical and electron microscopy and X-ray analysis, Zachariades *et al.*²² have drawn the same conclusion as to the structure of the copolyester of poly(ethylene terephthalate) and 80 mol% of *p*-acetoxybenzoic acid.

The structure described so far does not change with increasing temperature up to a temperature close to the melting point. At about 215°C the nematic mesophase was quite evident: most of the Bragg peaks disappeared and the diffuse crescents broadened. However, trace amounts of crystalline material still persisted in the melt. On further heating to 228°C, the copolyester was entirely melted. Figure 10b shows that the anisotropy was still clearly visible although the sample tends to misorient. The outer pronounced crescents, related to the lateral in-

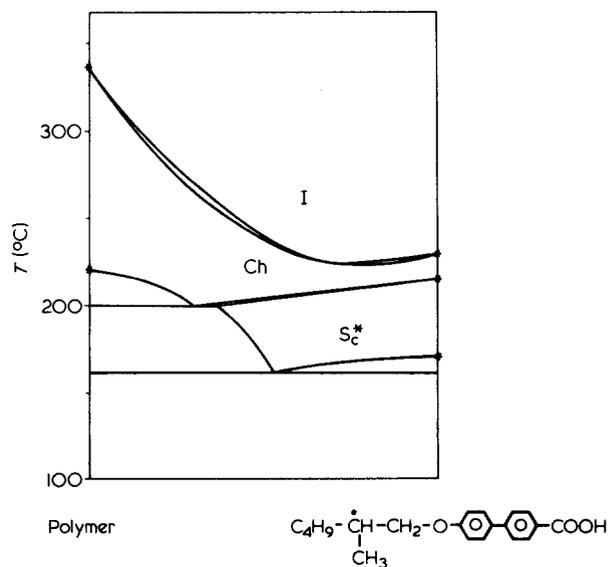
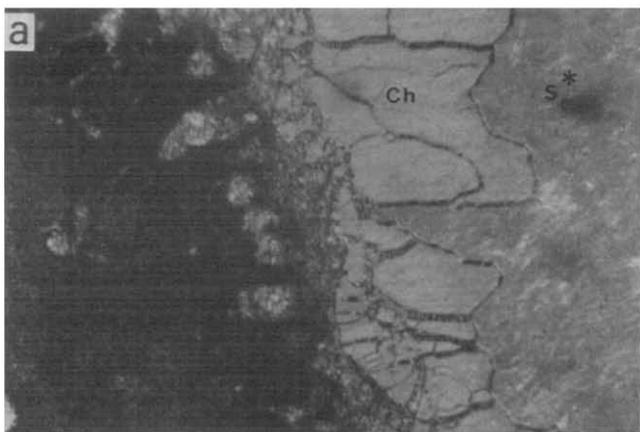
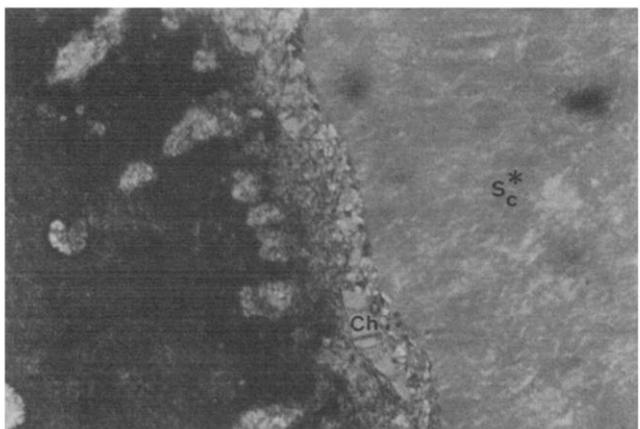


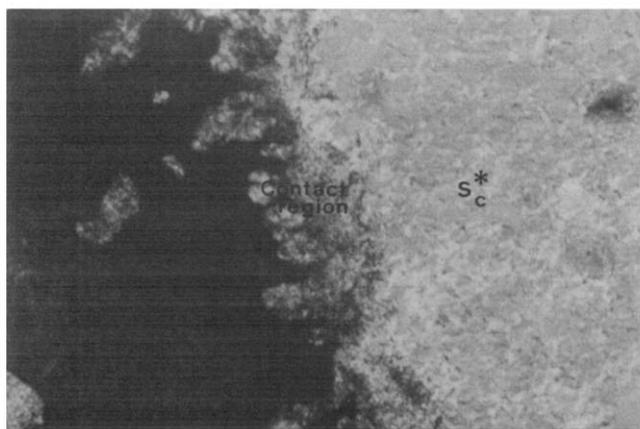
Figure 7 Isobaric binary phase diagram for the system copolyester/4'-(2-methylhexyloxy) biphenyl-4-carboxylic acid



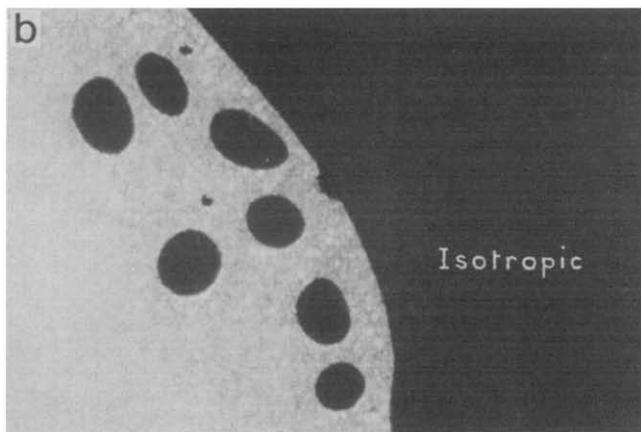
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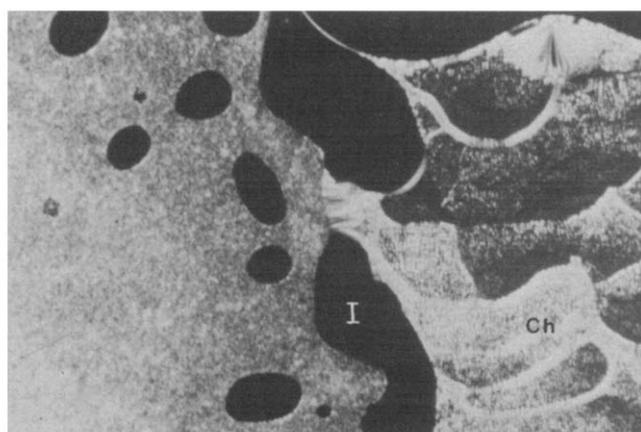
206 °C



178 °C



230 °C



227 °C

Figure 8 Contact preparation between copolyester (left) and 4'-(2-methylhexyloxy)biphenyl-4-carboxylic acid. (a) Growth of the cholesteric phase in the contact region. (b) Growth of the isotropic phase (crossed polarizers, $\times 150$)

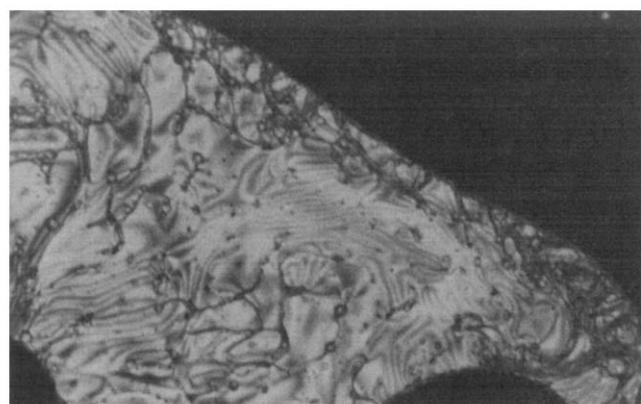


Figure 9 Typical planar texture obtained at 250 °C by the addition of 4'-(2-methylhexyloxy)biphenyl-4-carboxylic acid to copolyester (crossed polarizers, $\times 200$)

interactions of neighbouring entities, have intensity maxima located around $q=1.35 \text{ \AA}^{-1}$ which gives an average lateral distance of 5.2 Å between adjacent chains which are parallel to the director.

A final remark will concern the 'glassy liquid crystal'. It is well known that polymeric liquid crystals supercool quite rapidly and X-ray diffraction or optical microscopy have been used to demonstrate the existence of the quenched nematic liquid crystal. However, no quantitative arguments have been presented up to now to demonstrate whether the resultant glass retains the liquid-crystal alignment or not. Using the dichroic ratio of the bands in the i.r. spectra we have determined the order parameter of aligned specimens either in the nematic state or quenched from the nematic state.

The degree of orientational order in liquid crystals is generally defined by the degree of order, S , measured relative to the long axis of the molecule:

$$S = \frac{3\langle \cos^2\theta \rangle - 1}{2} \quad (1)$$

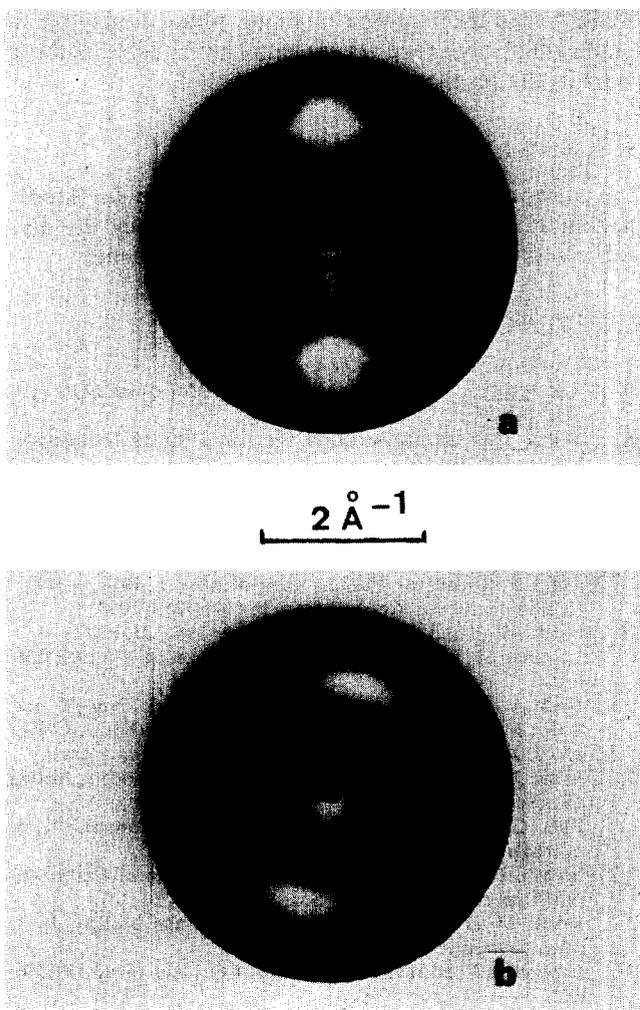


Figure 10 X-ray diffraction patterns of the copolyester (flat camera). (a) At 140°C the crystalline solid coexists with small amount of amorphous phase. (b) At 228°C, the nematic phase (the fibre axis is horizontal)

where θ is the angle between the direction of the long axis of the molecule and the optical axis of the uniformly oriented liquid crystal.

If a system has uniaxial symmetry, such as a nematic, the dichroic ratio, R , is given by²³:

$$R = \frac{\epsilon_{\parallel}}{\epsilon_{\perp}} = \frac{4 \cos^2 \alpha \langle \cos^2 \theta \rangle + 2 \sin^2 \alpha \langle \sin^2 \theta \rangle}{2 \cos^2 \alpha \langle \sin^2 \theta \rangle + \sin^2 \alpha \langle 1 + \cos^2 \theta \rangle} \quad (2)$$

where ϵ_{\parallel} and ϵ_{\perp} are the absorption coefficients measured with the infra-red radiation polarized \parallel and \perp to the optical axis, respectively. α is the angle between the long axis of the molecule and the direction of the vibrational transition moment.

When the vibrational transition moment is directed along the long axis of the molecule we can write:

$$R = \frac{1+2S}{1-S} \quad \text{and} \quad S = \frac{R-1}{R+2}$$

This is practically the case for the two bands at 1605 cm^{-1} and 1508 cm^{-1} . Associated with the vibrations of the aromatic ring 8a and 19a, they are strong, narrow and spectrally isolated from all the other i.r. bands and thus ideally suited to the study of the molecular orientational order (Figure 11).

Figure 12 shows the temperature dependence of S for

the copolyester under investigation. The transition of the nematic mesophase to a glass with nematic order upon quenching is confirmed quantitatively. Furthermore, our results demonstrate that, in spite of the thermal shock, the macroscopic alignment remains throughout the whole process.

It is apparent from Figure 12 that S decreases steadily from 0.55 to 0.45 as the temperature is raised from 250°C ($\sim 32^\circ\text{C}$ above the melting point) up to 285°C. Without making any claims to great accuracy, it is nevertheless possible to attempt an evaluation of the degree of orientational order from the X-ray diagrams²⁴. If β is the mean angle of inclination of the molecules to the axis of texture, the degree of order S is given by:

$$S = 1 - \frac{3}{2} \sin^2 \beta$$

The value of S thus calculated is about 0.5 at 260°C, which is in relatively good agreement with infra-red data. These S values are rather low compared with the values of 0.88–0.72 deduced from n.m.r. measurements for the nematic polyester:

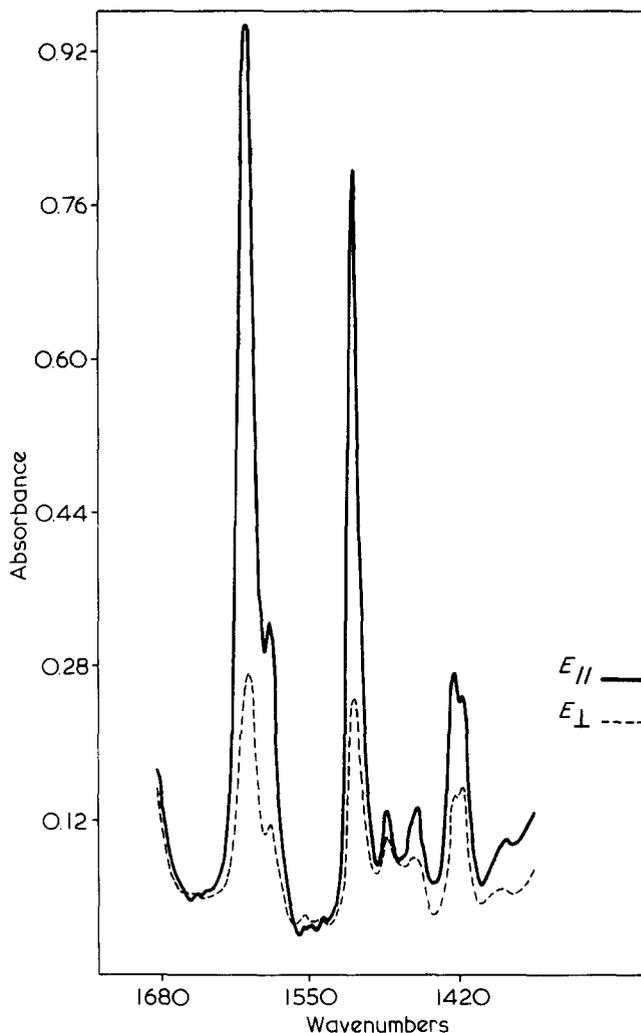
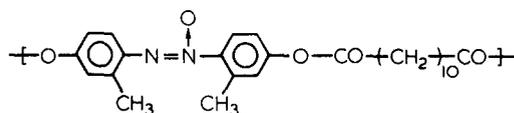


Figure 11 FTIR polarized spectra of oriented thin copolyester film at 285°C. E_{\parallel} and E_{\perp} refer to the electric vector of radiation polarized parallel and perpendicular to the optic axis, respectively

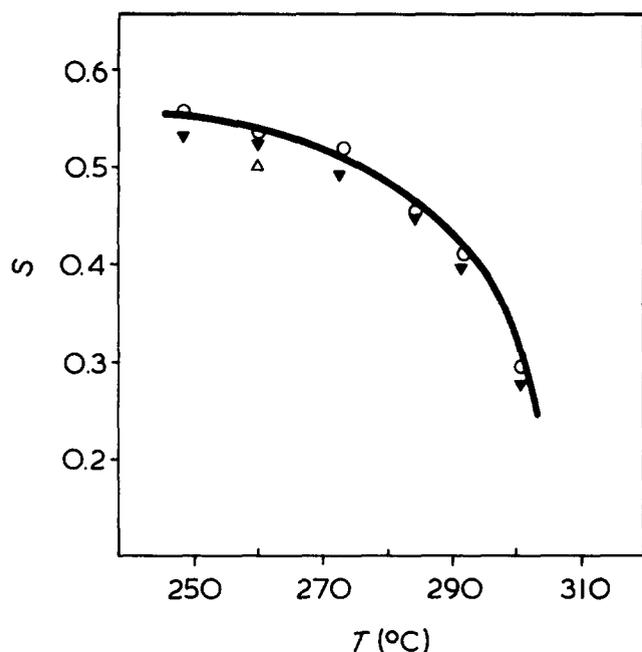
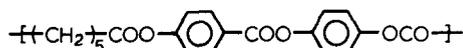


Figure 12 Temperature dependence of orientational order parameter S . Infra-red data: (○) oriented specimens in the nematic state; (▲) oriented samples quenched from the nematic state to room temperature. X-ray data: (△) oriented specimen in the nematic state at 260°C

the molecular weight of which is 7000 (ref. 25). However, they are in good agreement with the value of 0.54 reported by Liebert *et al.*²⁶ for the copolyester:



of reasonably high molecular weight. As pointed out by these authors, the order parameter seems to depend markedly on the sample molecular weight. S appears to decrease from 0.64 to 0.54 as the inherent viscosity of the copolyester increases from 0.29 (A) to 0.54 dl g⁻¹ (B). In fact, Hardouin *et al.*²⁷ have shown that the apparent viscosity plays an important role in the tendency for macromolecular chains to align when placed in a magnetic field. Complete orientation is obtained only for the less viscous samples. Thus, the anisotropy of the magnetic susceptibility $\Delta\chi$ of the polyester A (apparent viscosity 1100 cP) approaches a nearly constant saturation value of 1.1×10^{-7} emu cgs g⁻¹, which corresponds to the diamagnetic anisotropy usually exhibited by conventional liquid crystals in the nematic phase²⁸ while a weaker anisotropy is found for the polyester B (apparent viscosity 2620 cP).

As usually observed for many types of small-molecule liquid crystals²⁸, the S value decreases sharply as the clearing point is approached (Figure 12). The order parameter at 300°C is found to be ~0.3. This result thus confirms the recent theory of Ronca and Yoon²⁹, which

predicts that the isotropic-nematic phase transition of semiflexible polymers does not entail a very high degree of order in the resultant nematic phase.

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REFERENCES

- 1 Vorländer, D. Z. *Phys. Chem.* 1923, **105**, 211
- 2 Van Meter, J. P. and Klaudermann, B. H. *Mol. Cryst. Liq. Cryst.* 1973, **22**, 285
- 3 Steinsträsser, R. *Angew. Chem. Int. Edn.* 1972, **11**, 633; *Angew. Chem.* 1972, **84**, 636
- 4 Jackson, W. J. Jr and Kuhfuss, H. F. *J. Polym. Sci. Polym. Chem. Edn.* 1976, **14**, 2043
- 5 McFarlane, F. E., Nicely, V. A. and Davis, T. G. in 'Contemporary Topics in Polymer Science', Vol. 2, (Eds. E. M. Pearce and J. R. Schaefgen), Plenum Press, New York, 1977, p. 109
- 6 Calundann, G. W. (Celanese), US Pat. 4067852, 1978
- 7 Blackwell, J. and Gutierrez, G. *Polymer* 1982, **23**, 671
- 8 Leclercq, M., Billard, J. and Jacques, J. *C.R. Acad. Sci.* 1968, **266**, 654
- 9 Bosio, L., Fayolle, B., Friedrich, C., Laupretre, F., Noel, C. and Virlet, J. in 'Liquid Crystals and Ordered Fluids', (Eds. A. Griffin and J. Johnson), Plenum Press, New York, Vol. 4, in press
- 10 Kofler, L. and Kofler, A. in 'Thermomikromethoden', Verlag Chemie, Weinheim, 1954
- 11 Fyfe, C. A., Lyerla, J. R., Volksen, W. and Yannoni, C. S. *Macromolecules* 1979, **12**, 757
- 12 Wehrli, F. W. and Wirthlin, T. 'Interpretation of Carbon-13 NMR spectra', Heyden and Son, London, 1976
- 13 Sefcik, M. D., Schaefer, J., Stejskal, E. O. and McKay, R. A. *Macromolecules* 1980, **13**, 1132
- 14 Grebovitz, J. and Wunderlich, B. *Mol. Cryst. Liq. Cryst.* 1981, **76**, 287
- 15 Demus, D. and Richter, L. 'Textures of Liquid Crystals', Verlag Chemie, Weinheim, 1974
- 16 Viney, C. and Windle, A. H. *J. Mat. Sci.* 1982, **17**, 2661
- 17 Millaud, B., Thierry, A. and Skoulios, A. *Mol. Cryst. Liq. Cryst. Lett.* 1978, **41**, 263
- 18 Noel, C. and Billard, J. *Mol. Cryst. Liq. Cryst. Lett.* 1978, **41**, 269
- 19 Fayolle, B., Noel, C. and Billard, J. *J. Physique (Lett.)* 1979, **40**, 485
- 20 Griffin, A. C. and Havens, S. J. *J. Polym. Sci. Polym. Lett. Edn.* 1980, **18**, 259
- 21 Economy, J., Storm, R. S., Matkovich, V. I., Cottis, S. G. and Nowak, B. E. *J. Polym. Sci. Polym. Chem. Edn.* 1976, **14**, 2207
- 22 Zachariades, A. E., Economy, J. and Logan, J. A. *J. Appl. Polym. Sci.* 1982, **27**, 2009
- 23 Neff, V. D. in 'Liquid crystals and plastic crystals', (Eds. G. W. Gray and P. A. Winsor), Ellis Horwood, Chichester, 1974, Vol. 2, p. 231
- 24 Chistyakov, I. G. and Chaikowsky, W. M. *Mol. Cryst. Liq. Cryst.* 1969, **7**, 269
- 25 Volino, F., Martins, A. F., Blumstein, R. B. and Blumstein, A. *C.R. Acad. Sci.* 1981, **292**, 829; *J. Physique (Lett.)* 1981, **42**, L-305
- 26 Liebert, L., Strzelecki, L., Van Luyen, D. and Levelut, A. M. *Eur. Polym. J.* 1981, **17**, 71
- 27 Hardouin, F., Achard, M. F., Gasparoux, H., Liebert, L. and Strzelecki, L. *J. Polym. Sci., Polym. Phys. Edn.* 1981, **20**, 975
- 28 Kelker, H. and Hatz, R. 'Handbook of Liquid Crystals', Chap. 3, Verlag Chemie, Weinheim, 1980
- 29 Ronca, G. and Yoon, D. Y. *J. Chem. Phys.* 1982, **76**, 3295