Liquid crystalline polymorphism in a new class of semiflexible polyesters containing a 2-phenyl-benzoxazole group

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The synthesis and phase behaviour of a new class of semiflexible polyesters based on aliphatic dicarboxylic acids (from octanedioic to tetradecanedioic acid) and 2-(4-hydroxy-phenyl)-6-hydroxy benzoxazole are described. All the polymers synthesized are mesogenic and show a nematic or a smectic A phase (or both) depending on the length of the flexible spacer, the smectic mesomorphism being favoured for longer spacers. For the smectogenic polymers, the observed layer periodicity is equal to about half the length of the monomeric unit. A possible explanation is the occurrence of a regularly intercalated packing of the chains, with lateral matching of aliphatic and aromatic molecular sections.

(Keywords: semiflexible polyesters; liquid crystalline; polymorphism; smectogenic; benzoxazole)

INTRODUCTION

Semiflexible polyesters based on aliphatic dicarboxylic acids and linear diphenols may exhibit liquid crystalline behaviour; many of these systems have been investigated and reported in the literature[1]. Nematic phases with marked odd–even effects on the isotropization temperatures and enthalpies are frequently observed for such systems, although some examples of smectogenic behaviour are also documented. Furthermore, while liquid crystalline polymorphism is quite frequent in low molar mass compounds, including dimeric and trimeric analogues of semiflexible polyesters[2,3], it is rather unusual in the field of truly polymeric semiflexible mesogens.

The study of polyesters based on non-linear diphenols is more recent. The investigation of these systems is of interest because the structural features of such diphenols (the C–OH terminal bonds are neither colinear nor parallel and are not constitutionally equivalent) should confer a more wavy shape to the polymer chains and also introduce constitutional disorder, with possible effects on the transition temperatures and on the crystallinity of the polymers. The non-linearity of the mesogen, on the other hand, should not intrinsically prevent the resulting polymers from being mesogenic, as recently reported for some semiflexible and fully aromatic[5–7] polymer systems. However, it has been suggested that the non-linearity of the mesogen should favour the formation of nematic phases rather than smectic ones[4].

We are currently investigating the phase behaviour of polymer systems based on a non-linear mesogen containing the 2-phenyl-benzoxazole group. In a previous paper[7] we described the phase behaviour of a fully aromatic polyester obtained by reaction of terephthalic acid and 2-(4-acetyloxy-phenyl)-6-acetyloxy-benzoxazole, which shows definite thermotropic liquid crystalline behaviour. The present paper discusses the phase behaviour of semiflexible polyesters having the formula
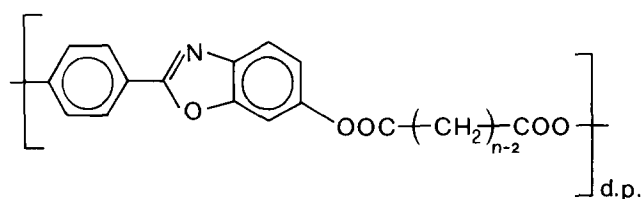
PnBZA

which are based on aliphatic dicarboxylic acids and diphenol 2-(4-hydroxy-phenyl)-6-hydroxy-benzoxazole. As shown below, all PnBZA polymers investigated are mesogenic and show smectic or nematic phases depending on the length of the flexible spacer; moreover, some of these polymers show liquid crystalline polymorphism with a smectic to nematic phase transition.

EXPERIMENTAL

Polymers PnBZA ($8 \leqslant n \leqslant 14$) were prepared by interfacial polymerization starting from chlorides of the aliphatic dicarboxylic acids and diphenol 2-(4-hydroxy-phenyl)-6-hydroxy-benzoxazole. Acylic chlorides were prepared by reaction of the corresponding diacid with thionyl chloride and were vacuum distilled. The diphenol was prepared by saponification of 2-(4-acetyloxy-phenyl)-6-acetyloxy-benzoxazole which, in turn, was prepared according to ref. 7. A detailed description of the synthesis of P11BZA is given. A solution formed by dissolving 0.995 g

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Table 1 Elemental analysis and intrinsic viscosity of P*n*BZA polymers

	%C		%H		%N		[η]
n	calc.	found	calc.	found	calc.	found	(dl g⁻¹)
8	69.03	68.86	5.24	5.35	3.83	3.84	1.48
9	69.64	69.53	5.58	5.65	3.69	3.66	2.62
10	70.21	70.02	5.89	6.00	3.56	3.49	1.71
11	70.75	70.52	6.18	6.28	3.44	3.39	1.64
12	71.24	70.98	6.46	6.48	3.32	3.18	1.04
14	72.14	71.93	6.95	6.82	3.12	3.02	1.33

(3.93 mmol) undecanedioyl chloride in 37 ml anhydrous chloroform was rapidly added to a vigorously stirred (Waring commercial blender) solution containing 0.902 g (3.97 mmol) of the diphenol, 0.562 g (1.66 mmol) of tetrabutylammonium hydrogen sulfate as interfacial agent, and 0.664 g of KOH in 50 ml of water. The mixture was stirred vigorously for 6 min, then 200 ml n-hexane was added to precipitate the polymer, which was recovered by filtration. The precipitate was washed with chloroform/n-hexane solution (50:50), ethanol and water, then it was dried at 80°C in an oven.

The results of quantitative elemental analysis of polymers P*n*BZA are reported in *Table 1*, which also shows the results of intrinsic viscosity measurements performed in chloroform solutions at $26.19 \pm 0.01°C$ (Ubbelohde viscosimeter). I.r. and ^1H n.m.r. data are consistent with the polymer formulas. I.r. data for P11BZA: $3064 \, cm^{-1}$ (w; aromatic C–H), $2924 \, cm^{-1}$, $2851 \, cm^{-1}$ (vs; aliphatic C–H), $1760 \, cm^{-1}$ (vs; C=O), $1623 \, cm^{-1}$ (vs), $1608 \, cm^{-1}$ (vs), $1497 \, cm^{-1}$ (vs), $1477 \, cm^{-1}$ (vs), $1121 \, cm^{-1}$ (vs; C–O). I.r. spectra were recorded using a Bruker IFS 66 FT spectrometer on films obtained by casting from chloroform solutions. N.m.r. data were recorded using a Bruker AC-270 MHz spectrometer. The phase behaviour of the polymers was examined by d.s.c. using a Perkin–Elmer DSC 7 apparatus. Samples were examined under dry nitrogen atmosphere at a scanning rate of $10°C \, min^{-1}$. Unless otherwise stated, the transition temperatures and enthalpies reported in this paper pertain to polymer samples previously crystallized from the melt at a cooling rate of $10°C \, min^{-1}$.

Optical observations were performed using a Leitz polarizing microscope equipped with a Linkam micro-furnace. X-ray diffraction data were recorded photographically by a flat film camera (CuKα radiation) equipped with a microfurnace to allow temperature control. For measurements at high temperature, samples were sealed in Lindemann capillaries under argon atmosphere. The diffracted intensity along the meridional and equatorial lines for fibres of P11BZA polymer was collected by the counter method (Enraf Nonius CAD 4 automatic diffractometer). The integrated intensity was determined through an ω scan of 1° at a scan speed of $0.3° \, min^{-1}$ in points spaced every $2\Theta = 0.29°$. The room temperature spectrum of *Figure 3* was recorded on a cylindrical camera (57.3 mm radius) utilizing CrKα radiation.

RESULTS AND DISCUSSION

Relevant thermodynamic data of polymers P*n*BZA are reported in *Table 2*. We shall begin by discussing the phase behaviour of P11BZA which, in addition to the

nematic, shows enantiotropic smectic mesomorphism homologous to that found for polymers with $n = 10, 12, 14$.

Three endothermic signals are present in the d.s.c. thermogram obtained on heating a melt-crystallized sample of P11BZA (*Figure 1a*). The first, centred at 153°C, corresponds to the melting of the crystal phase. The rather low enthalpic change observed may be enhanced by annealing (*Figure 1b*). The phase which forms after melting is a liquid crystal phase. Its X-ray diffraction pattern, recorded photographically at 170°C from a fibrous sample and reported in *Figure 2*, consists of a principal halo and a low-angle strong reflection. This pattern is typical of simple smectic phases (A or C); the observed mutually perpendicular polarization of the principal halo and of the inner ring should also be sufficient not to favour a smectic C phase, unless with quite a small tilt angle. The calculated end-to-end length of the monomeric unit in the most extended conformation, taking literature values for bond lengths and angles[8,9] is 25.5 Å. The observed smectic periodicity, on the other hand, is about half this value, $d = 12.0$ Å at 170°C, while other lower angle reflections are not observed in the X-ray diffraction pattern, at least for Bragg distances not greater than 62 Å. If we note that the length of the rigid group is 11.4 Å (distance between the two terminal oxygen atoms) and that of the flexible spacer in the all *trans* conformation is 12.6 Å (distance between the two terminal carbonyl carbon atoms), we may conclude that the relevant difference observed between the smectic periodicity and the length of the monomeric unit cannot reasonably account for conformational disorder of the flexible spacer.

On the other hand, the observed periodicity in a layered structure in which the chain axes are normal to the layer surfaces may be obtained, in the most simple hypothesis, if laterally adjacent chains are shifted by $L/2$ in the direction of the chain axis, L being the length of the monomeric unit. In the resulting regularly intercalated structure, layers with a thickness of $L/2$ are found in which aromatic moieties are laterally packed with aliphatic moieties, and *vice versa*. As far as we know, no smectic phase having such a structure has been reported to data for a polymeric substance.

A satisfactory explanation of the occurrence of such a peculiar smectic A packing is not a straightforward matter. In fact, strongly preferred interactions among

Table 2 Thermodynamic data of P*n*BZA polymers[a]

|	K→LC	Sm→N		N→I		Sm→I	
n	T (°C)	T (°C)	ΔH (J g⁻¹)	T (°C)	ΔH (J g⁻¹)	T (°C)	ΔH (J g⁻¹)
8	200.4		–	250.3	12.8		–
9[b]	171.8		–	193.7	6.05		–
10	192.2	181.0	4.3	215.1	12.9		–
11[c]	153.0	172.4		182.9			–
12	164.5		–		–	191.3	27.6
14	152.7		–		–	183.3	29.8

[a] $\sigma(T)/T \leqslant 0.01$, $\sigma(\Delta H)/\Delta H \leqslant 0.1$. K = solid; LC = liquid crystal; Sm = smectic; N = nematic; I = isotropic liquid
[b] P9BZA exhibits solid-state polymorphism, which is discussed in the text
[c] The d.s.c. endothermic signals corresponding to Sm→N and N→I transitions are not well resolved, so evaluation of the enthalpic changes was not possible. The total enthalpic change from Sm to I is 22.7 J g⁻¹
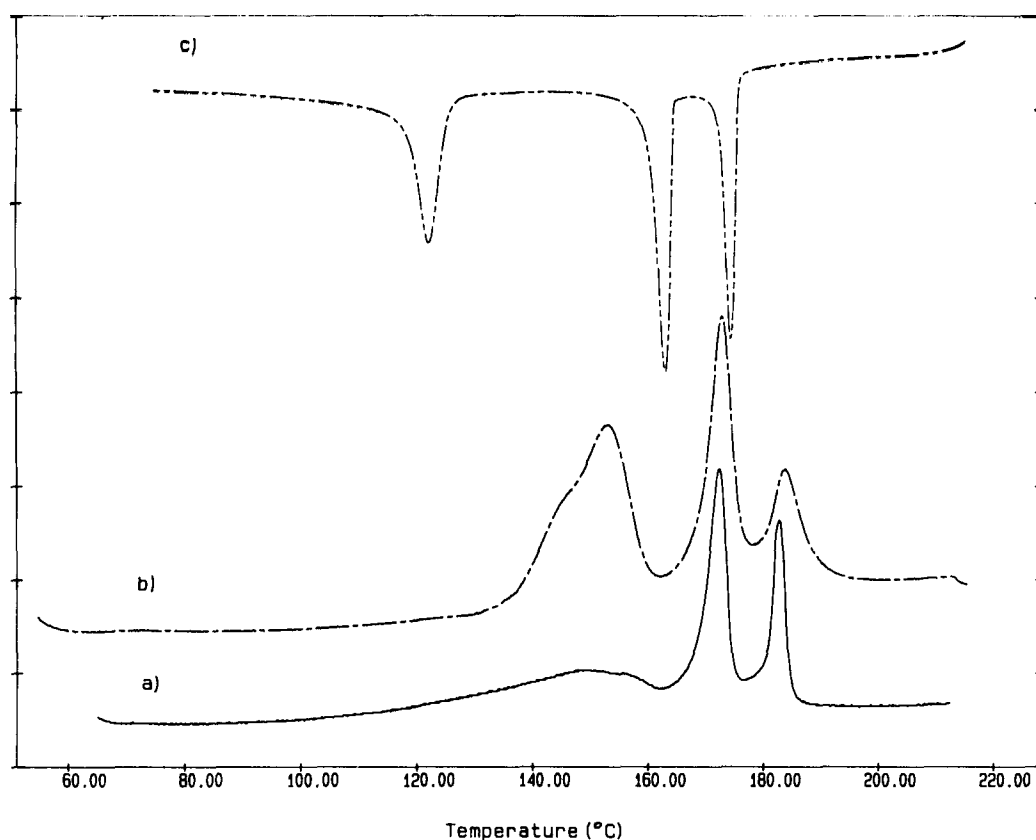
Figure 1 D.s.c. thermograms of P11BZA. (a) Heating cycle of a sample previously crystallized from the melt at a cooling rate of $10°C\,min^{-1}$; (b) heating cycle of a sample after annealing at 130°C for 30 min; (c) cooling cycle from the isotropic liquid
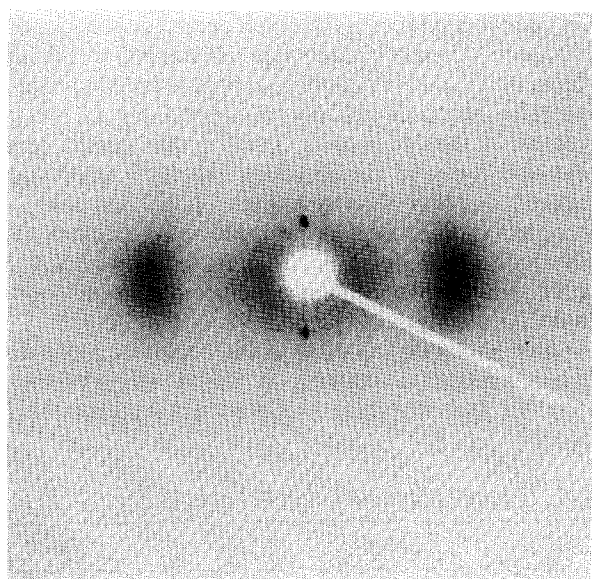
Figure 2 X-ray diffraction pattern of a fibre of P11BZA recorded at 170°C
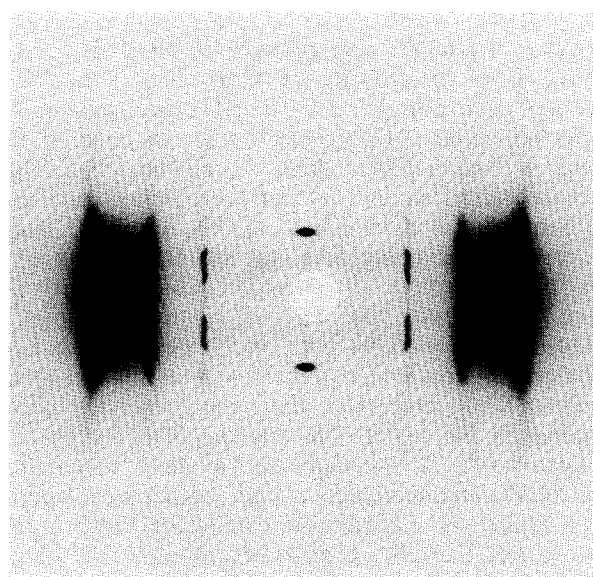
Figure 3 X-ray diffraction photograph of a fibre of P11BZA previously annealed at 130°C for 30 min. Room temperature

aromatic and aliphatic groups are likely to be excluded in our system. On the other hand, we may suppose that the increased chain waviness, due to the non-linearity of the mesogen, produces different cross sections in different parts of the chains, and the requirement for dense packing may play a role.

The smectic periodicity is also maintained, almost unchanged, in the crystal phase ($d = 12.2$ Å at 25°C). As a preliminary analysis of the crystalline diffraction pattern (*Figure 3*) this periodicity, taking into account the

spacings of the layer lines, might account for the sixth diffraction order of the identity period, which would therefore contain three monomeric units in extended conformation ($c = 73.2$ Å). The meridional line (i.e. the line containing the 00l reflections) is perpendicular to the layer lines in the fibre spectrum (*Figure 3*), thus indicating that the c^* axis is, to a good approximation, perpendicular to the (a^*b^*) reciprocal plane. The pattern of the reflections observed along the meridional line for a crystalline fibre of P11BZA is reported in *Figure 4*.
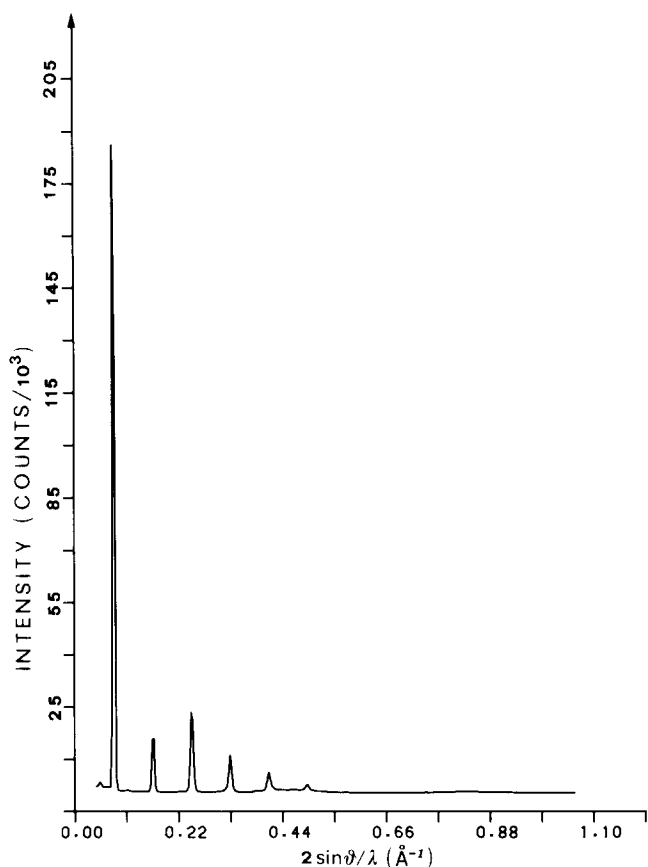
Figure 4 X-ray diffraction profile along the meridional line for a crystalline fibre of P11BZA, previously annealed at 130°C for 30 min. Room temperature

the crystal and smectic phases of P11BZA is planned for the future. The above considerations do, however, agree with a picture in which the periodicity of the smectic phase is preserved as a crystallographic repetition in the crystal. The transition from the crystal phase to the smectic phase should involve mainly the loss of lateral positional order of the chains, but the axial register and, at least partially, the conformation of the chains are retained. Similar behaviour is probably shown by other polymers of the series which exhibit smectic mesomorphism (see *Table 3*). Crystal phases with a layered structure have been observed by de Abajo et al.[4]

Reflections 0 0 l with l odd are not observed. Furthermore, among the 00l reflections with l even, 006 and its successive diffraction orders up to the sixth (i.e. up to the 0036 reflection) have distinctly higher intensities. It should be remembered that the structural periodicity corresponding to the most intense 006 meridional reflection is equal to half the length of the monomeric unit.

The diffracted intensity along the meridian for a smectic fibre of P11BZA (obtained by extrusion of the polymer in the liquid crystal phase followed by rapid cooling in air) is reported in *Figure 5* for comparison. Well defined diffraction orders of the most intense reflection at $d = 12.2$ Å are observed up to the fifth order, having Bragg spacings almost identical to those observed for the crystal phase. The equatorial pattern of the same fibre, on the other hand, is typical of liquid-like phases (*Figure 6*), as it contains only a halo centred at $\sin \Theta/\lambda = 0.243$ Å^{-1}, which corresponds to a mean lateral separation of about 4 Å between adjacent chains. The pattern of *Figure 5* is rather unusual for simple smectic phases, such as the A type, in which diffraction orders of the layer periodicity higher than the second are rarely observed; this suggests a high regularity in the succession of the layers, with rather small displacements of the atoms, along c, from their ideal positions (the minimum observed Bragg spacing is 1.20 Å, which corresponds to a faint tenth diffraction order). This might be partially related to the polymeric nature of the smectic phase, which imposes a high translational correlation between adjacent layers, and also with the fact that the diffraction pattern was recorded at ambient temperature.

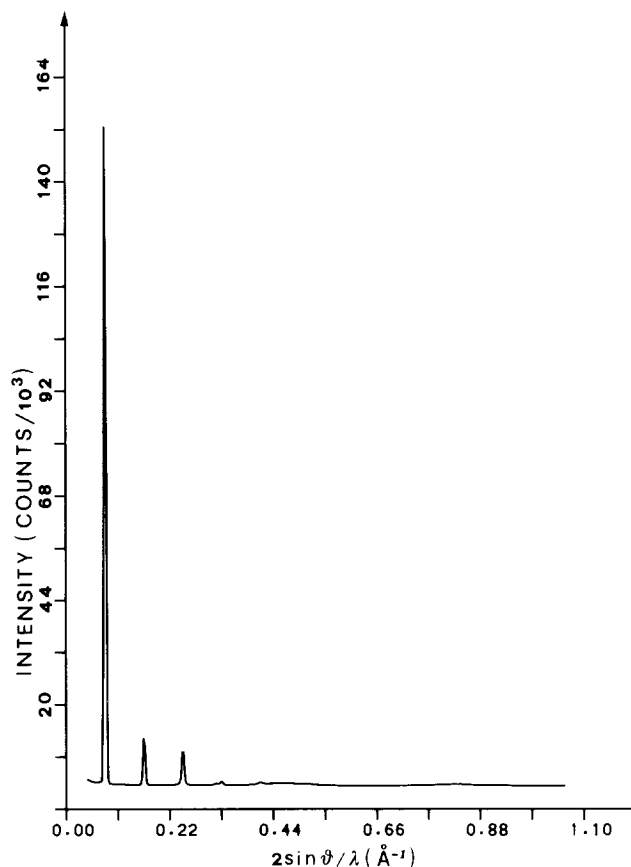A more detailed analysis of the structural features of

Figure 5 X-ray diffraction profile along the meridional line for a fibrous smectic sample of P11BZA obtained by extrusion of the polymer in the liquid crystal phase followed by rapid cooling in air. Room temperature
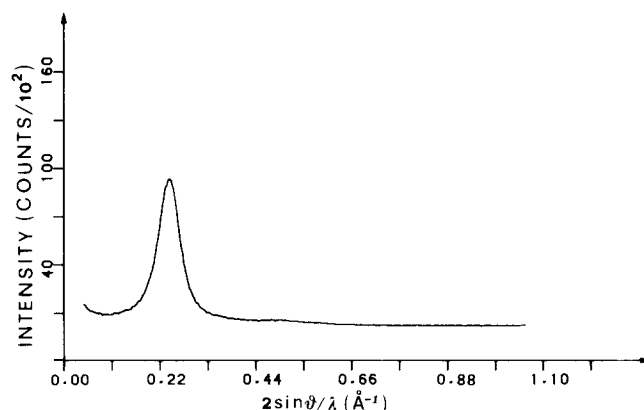

Figure 6 X-ray diffraction profile along the equatorial line for a fibrous smectic sample of P11BZA (same sample as in *Figure 5*). Room temperature

Table 3 Spacing of the most intense meridional reflection for P*n*BZA polymers[a]

n	K, *d* (Å)	Sm, *d* (Å)
9	10.9	–
10	11.3	11.3
11	12.2	12.0
12	12.6	12.3
14	–	13.4

[a] K = crystal; Sm = smectic A. $\sigma(d)/d \leqslant 0.02$. The spacings of the crystal phases were measured at ambient temperature on crystalline fibres obtained by annealing near the melting temperature semicrystalline or non-crystalline fibres previously extruded in the liquid crystal phase and cooled in air. For the smectic phase the spacings were measured at the following temperatures: 170°C for P11BZA and P12BZA; 164°C for P14BZA. For P10BZA the spacing was measured at ambient temperature on a fibrous smectic sample obtained by rapidly cooling the liquid crystal phase
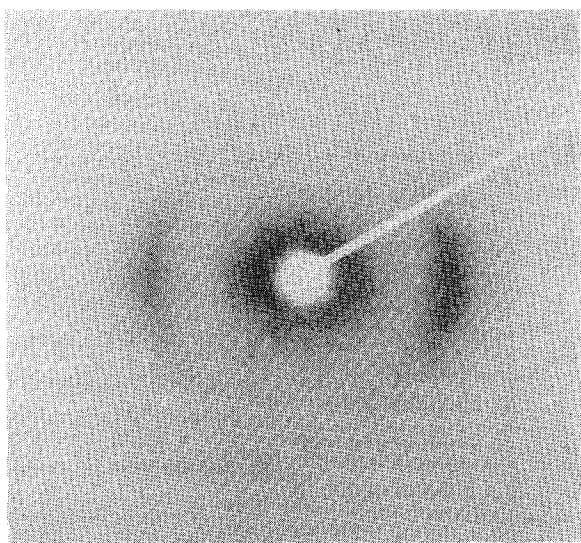
Figure 7 X-ray diffraction photograph of a fibre of P11BZA recorded at 177°C

in some semiflexible poly(ester–imide)s based on a non-linear mesogenic group. In that case, however, the observed layer periodicities are substantially comparable with the length of the monomeric units, thus indicating a conventional smectic-type arrangement of the chains. Moreover, those polymers all melt to give a nematic phase rather than a smectic one.

The smectic phase of P11BZA transforms at 172.4°C into a second liquid crystal phase, whose X-ray diffraction pattern, reported in *Figure 7*, contains only a wide-angle halo and is unmistakably typical of a nematic phase. The nematic phase finally isotropizes at 182.9°C. Polymer P11BZA therefore exhibits a definite liquid crystalline polymorphism with two liquid crystal phases stable between the crystal phase and the isotropic liquid. The smectic A to nematic phase transition has a first-order character.

Turning attention to the other polymers, it can be seen from *Table 2* that once odd–even effects and the overall mesophase stability are taken into account, the stability of the smectic phase is depressed by decreasing the length of the flexible spacer. So in P10BZA the smectic phase, which is monotropic, may only be observed by cooling the nematic phase or may be metastably obtained at ambient temperature by rapidly cooling the nematic

phase, while P9BZA and P8BZA are solely nematogenic. For the latter two polymers, it is interesting to note that the crystal phase shows different features. In particular, for P8BZA the line containing the meridional reflections is not perpendicular to the equator, but a four-spot pattern is observed which, under the hypothesis of a layered crystal structure, would suggest a tilt of the chain axes with respect to the layer normal. P9BZA, on the other hand, exhibits a complex solid-state polymorphism, which will be briefly discussed.

Two different solid phases are present in the as-prepared, solution crystallized material. One of them, termed α, melts at 171.8°C to the nematic phase and is identical to the phase which is obtained by slow crystallization of the melt ($\leqslant 10°C \, min^{-1}$); the other, termed β, melts at 182°C and may only be observed in solution-crystallized samples. The crystal nature of the β phase is suggested by its X-ray diffraction pattern, which contains several wide-angle reflections, and also by the possibility of increasing its melting enthalpy upon annealing. If the liquid crystal phase is cooled rapidly (as for example when the polymer is extruded in the liquid crystal phase with subsequent rapid cooling in air) a new solid phase is obtained, termed γ. However, while great differences in the X-ray diffraction patterns of α and γ solid phases are observed (*Figure 8*), the melting temperatures are virtually coincident and the d.s.c. curves (*Figures 9a* and *b*), lack any evidence of recrystallization or interconversion phenomena between the two phases.

By increasing the length of the flexible spacer, the smectic phase becomes more stable than the nematic one. So, P12BZA and P14BZA are only smectogenic. Actually, for P12BZA, a shoulder in the isotropization peak is observed in the d.s.c. curve on heating, which might suggest a close superposition of the smectic A–nematic and nematic–isotropic phase transitions. However, no analogous evidence is detectable in the d.s.c. thermogram on cooling. The observed strengthening of the smectogenic character with increasing length of the flexible spacer, which is a trend often[1] although not invariably observed in semiflexible polymers (e.g. an opposite trend is shown by dimeric model compounds of semiflexible polyesters based on 4,4′-dihydroxy-α-methyl-stilbene and aliphatic dicarboxylic acids[2]) might, in this case, be related to the unusual structure of the smectic A phase formed. In particular, if an axial register in which a lateral packing of aromatic with aliphatic sections of the chains is formed, we may expect that the length of the rigid group (including the terminal oxycarbonyl groups), which is 13.05 Å, and that of the flexible spacer (including the terminal carbonyl groups) are as close as possible. The calculated length of the spacer (*trans* planar conformation, distance between the terminal carbonyl carbon atoms) is 10.1, 11.3, 12.6, 13.8 and 16.3 Å for P9BZA, P10BZA, P11BZA, P12BZA and P14BZA, respectively. It may not be entirely meaningless that the stability of the smectic phase has its maximum for *n* = 12 (*T*(smectic–isotropic) = 191.3°C). However, increasing the length of the flexible spacer also has the effect of lowering the isotropization temperature of polymers having the same parity of carbon atoms in the spacer (*Table 2*). This effect, together with the odd–even fluctuations of the isotropization temperature, is expected as it is typical of semiflexible mesogenic polymers based on aliphatic dicarboxylic acids and diphenols[1].
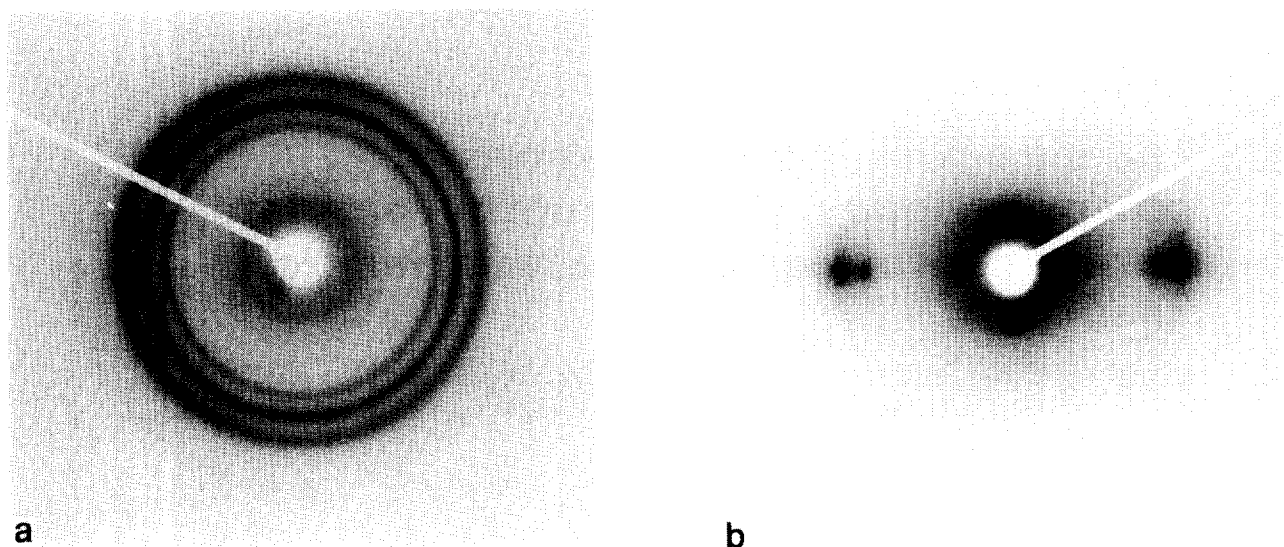
Figure 8 P9BZA polymer. (a) X-ray diffraction pattern of a sample cooled from the nematic phase at a rate of 10°C min^{-1}. Room temperature. (b) X-ray diffraction pattern of a fibre obtained by extrusion of the polymer in the nematic phase followed by cooling in air. Room temperature
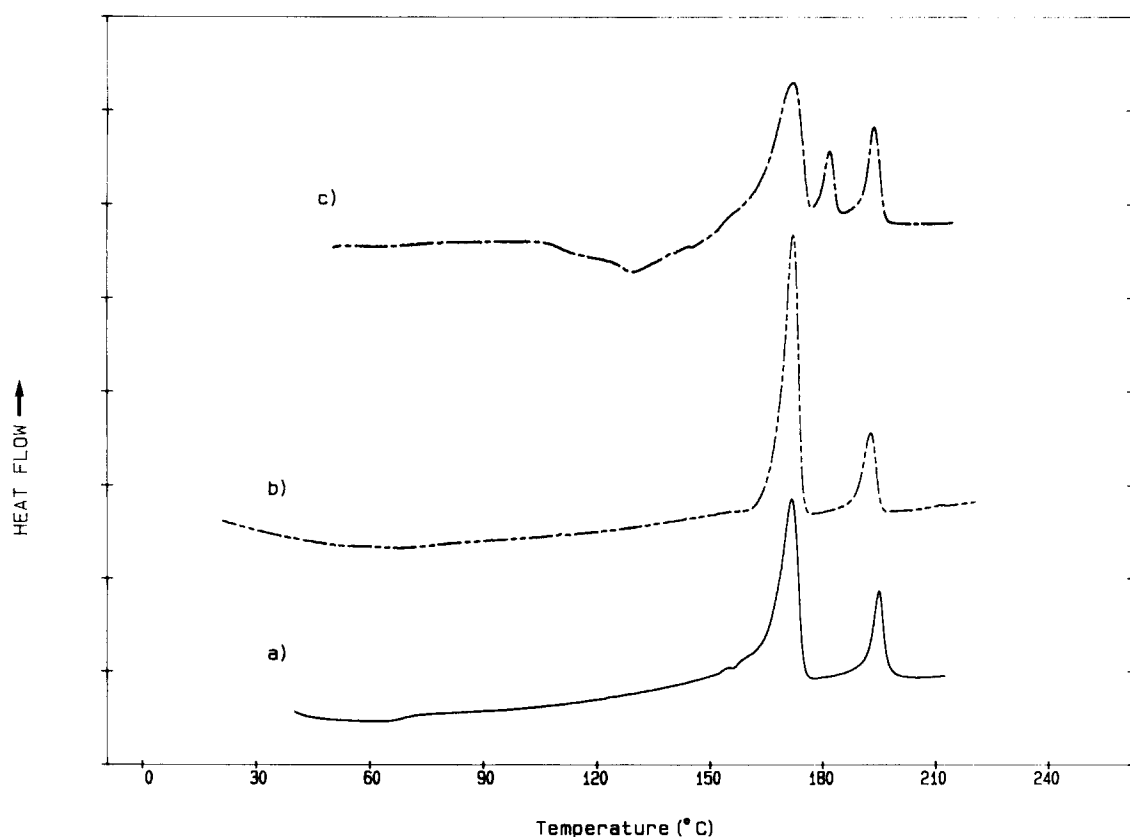
Figure 9 D.s.c. thermograms of P9BZA. (a) Heating cycle of a sample as described for *Figure 8a*; (b) heating cycle of a sample as described for *Figure 8b*; (c) heating cycle of an as-prepared sample

ACKNOWLEDGEMENTS

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