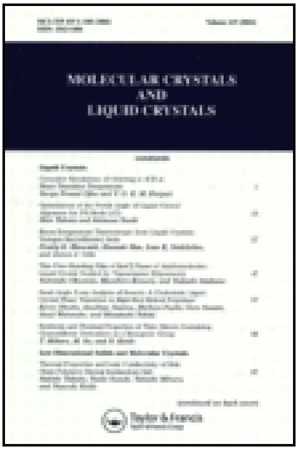

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An X-Ray Study of Thermotropic Liquid Crystalline Poly(Ester-β-Sulphide)s

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AN X-RAY STUDY OF THERMOTROPIC LIQUID CRYSTALLINE POLY(ESTER-β-SULPHIDE)S†

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Abstract Samples of liquid crystalline poly(ester-β-sulphide)s containing twin bis(p-oxybenzoate) units were studied by X-ray diffraction analysis as a function of temperature. The occurrence was observed of nematic (or cholesteric) and smectic phases, whose thermal stability and character strongly depended on the chemical structure of the repeating unit of the polymer.

INTRODUCTION

Poly(ester-β-sulphide)s are a new class of thermotropic liquid crystalline polymers which display complex mesomorphic behavior affected by fine details of chemical structure.[1-4] We have started a systematic study of poly(ester-β-sulphide)s derived from twin diacrylates consisting of two p-oxybenzoate diads interconnected by a polymethylene segment and coupled by α,ω-polymethylene dithiols.[2,4]

In this paper we report on the liquid crystal behavior, with reference to the X-ray scattering, of the mesophases of samples of two series of poly(ester-β-sulphide)s of general structure:

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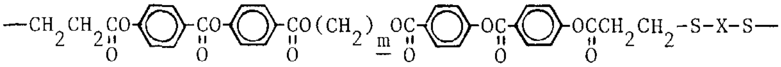

Series I (C9Sn) $\underline{m}=9$ $X: (CH_2)_{\underline{n}}$ $\underline{n} = 3, 5$, or 10

Series II (CmS6*) $\underline{m}=6, 7$, or 9 $\underline{X}: (CH_2)_2\overset{*}{C}H(CH_3)(CH_2)_3$

Details on the synthesis and structural and thermal characterizations of the polymers will be described elsewhere. X-ray studies of polymers are of great value in identifying different mesophases and may provide information on the effect of chemical and stereochemical structure on specific features of thermotropic polyesters.[5]

EXPERIMENTAL

The poly(ester-β-sulphide)s were prepared by a Michael-type polyaddition reaction[1-4] of α,ω-alkylene bis|4-(4-acryloyloxybenzoyloxy)benzoate|s[6] with α,ω-alkylene bisthiols (C9S$\underline{n}$) or (R)-3-methyl-1,6-hexanedithiol (C$\underline{m}$S6*) at room temperature in the presence of triethylamine. The physicochemical characteristics of the studied polymers are summarized in Table I. The phase transition temperatures were determined by polarizing microscopy and differential calorimetry (rate 10 °/min). The X-ray powder diffraction traces were recorded in a transmission geometry with a conventional diffractometer using the Ni filtered CuKα radiation ($\lambda = 1.54$ Å).

RESULTS AND DISCUSSION

Series I C9Sn The two polymers C9S5 having different molecular weights ($|\eta| = 0.06$ dl/g, $\bar{M}_w = 3400$ and $|\eta| = 0.24$ dl/g, $\bar{M}_w = 10800$, respectively) show at room temperature very similar diffraction patterns. A typical example is reported in Fig.1 for sample C9S5-a ($|\eta| = 0.06$dl/g). In the low angle region there exist two relatively sharp peaks with Bragg distances of ∿24 and ∿20 Å. On heating up to the melting temperature, several crystalline peaks emerge from the amorphous halo in the wide angle region, while an intense peak is present at low angles corresponding to a spacing of 25.8 Å (Fig.1b). These results indicate the presence of a new lamellar crystalline phase, a maximum degree of crystallinity ($X_c \simeq 35\%$) being

TABLE I Physicochemical characteristics of thermotropic liquid crystalline poly(ester-β-sulphide)s

Polymer	$\lvert\eta\rvert$ (dl/g)	Tm^a (K)	Ti^a (K)	ΔSi (cal/mol·K)
C9S3	0.32	390	401	0.3
C9S5-a	0.06	353	385	0.2
C9S5-b	0.24	384	407	0.5
C9S10	0.41	389	395	0.8
C6S6*	0.35	390	421	3.9
C7S6*	0.24	363	371	3.6
C9S6*	0.26	342	408	0.1

[a] See text for other mesophase-mesophase transitions

reached at 70°C. Above this temperature, all the peaks start to collapse and above 90°C the diffraction spectra of C9S5-a are consistent with the existence of a nematic phase (Fig.2a), in agreement with microscopy observations. On cooling of the isotropic melt, a monotropic disordered smectic phase is established at 72°C (Fig.2b). The interlayer distance d = 23.3 Å remains unaltered in all the smectic range and the average intermolecular distance is D ≃ 4.4 Å. A new mainly amorphous phase is obtained starting from 45°C, with broad small angle signals corresponding to ∿43 and 23 Å repeating lengths.

The C9S5-b ($\lvert\eta\rvert$ = 0.24 dl/g) presents a similar behavior on cooling of the isotropic melt (Fig.3). A monotropic smectic phase occurs in the range 105-80°C, with an interlayer distance d = 23.9 Å which is unaffected by temperature and D ≃ 4.5 Å. It appears therefore that the nature of the metastable smectic phase is the same in the two samples having rather different molecular weights. However, the longitudinal coherence length evaluated from the small angle peak widths, after correction for the experimental resolution[7] is found to be of the order of 100 Å and 200 Å, for the two polymers respectively. The increase of molecular weight of the polymer enhances the degree of correlation among the anisotropic units along the macromolecular chain axis giving rise to a better organized smectic mesophase[8]. A systematic investigation of the effects of the molecular weight on the liquid crystal properties

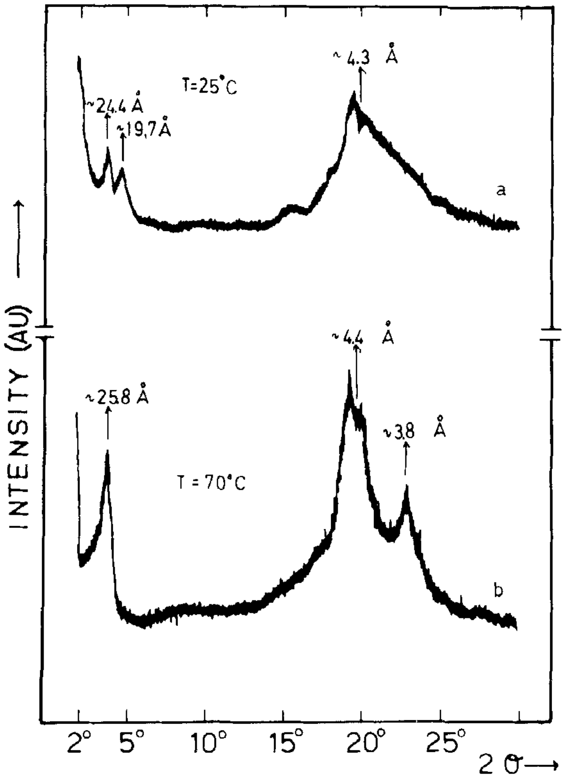

FIGURE 1. X-ray diffraction patterns of polymer C9S5-a: semicrystalline at 25°C (a) and 70°C (b).

of poly(ester-β-sulphide)s is now in progress.

The X-ray profiles of polymer C9S3 at different temperatures are reported in Fig.4. On cooling the isotropic melt, the enantiotropic nematic phase (Fig.4c) is stable down to 110°C, while the onset of a monotropic smectic phase is observed below that temperature. Two sharp peaks appear in the low angle region corresponding to Bragg distances of ∿44 and ∿22 Å, superimposed to poorly resolved broad halos (Fig.4d). On further cooling, the angular position of the two peaks remains practically unaffected, but their intensity increases,

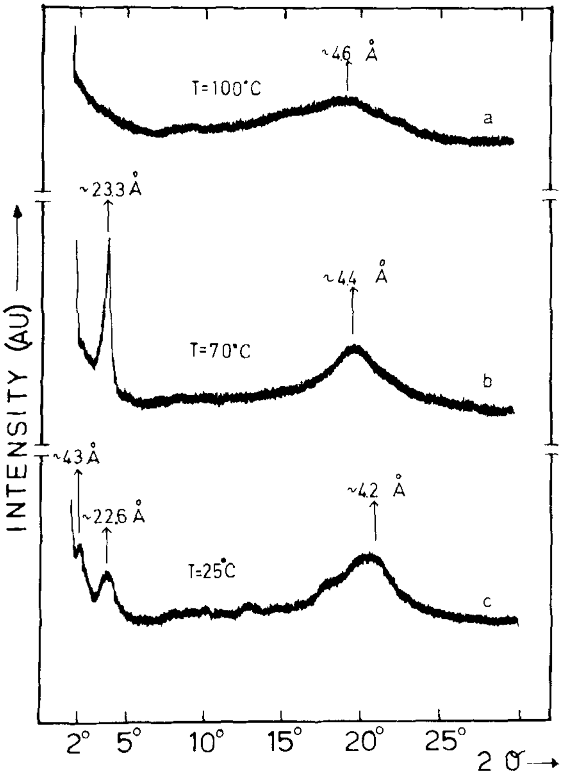

FIGURE 2. X-ray diffraction patterns of polymer C9S5-a: nematic (a); (monotropic) smectic (b); melt-crystallized (c).

according to an increased concentration of these layered domains[9] Such a structure is maintained frozen-in at room temperature (Fig.4e).

Optical microscopy and thermal analyses strongly suggest the occurrence of a monotropic smectic phase for polymer C9S10 too. However, X-ray experiments did not provide unambiguous results for this sample, because it was not possible to supercool sufficiently the crystallization relative to the onset of the metastable phase. The existence of an enantiotropic nematic phase was only detected.

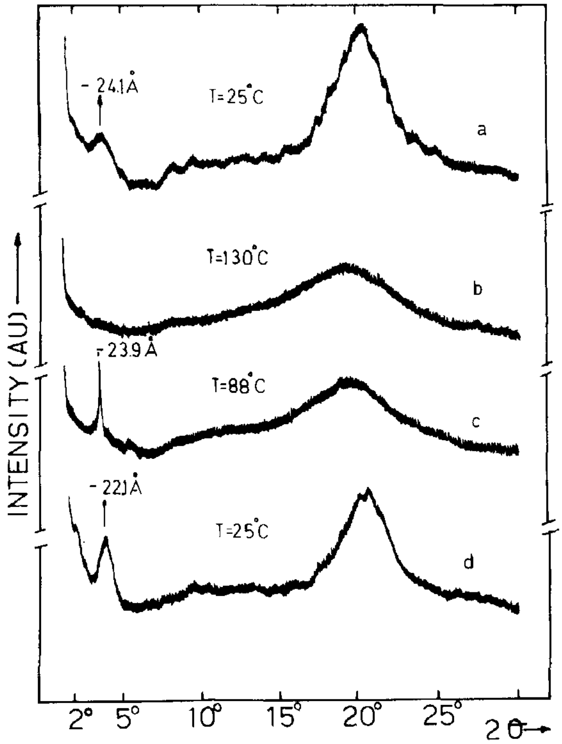

FIGURE 3. X-ray diffraction patterns of polymer C9S5-b: virgin semicrystalline (a); nematic (b); (monotropic) smectic (c); melt-crystallized (d).

Series II CmS6* The three investigated polymers of this class show at room temperature X-ray curves characterized by a small angle diffuse scattering with a weak shoulder at $2\theta \simeq 2°$ and signals of low intensity corresponding to periodicity lengths in the range 20-25 Å, depending on the chemical structure (Fig.5). The degree of crystallinity is low in all cases ($X_c < 30\%$). On heating, the small angle scattering decreases and the signals become progressively more intense, consistent with the annealing of structural defects above the glass transition temperature.

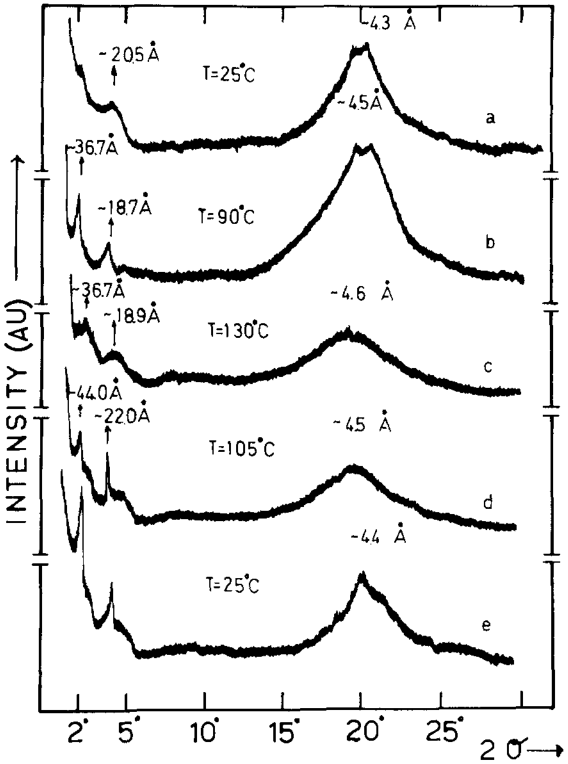

FIGURE 4. X-ray diffraction patterns of polymer C9S3: semicrystalline at 25°C (a) and 90°C (b); nematic (c); (monotropic) smectic (d); melt-crystallized (e).

Above 69°C, polymer C9S6• presents X-ray profiles typical of a disordered smectic phase ($D \simeq 4.5$ Å) (Fig.5b). The sharp signal at $2\theta \simeq 3.7^\circ$ corresponds to a Bragg interlayer distance of 23.9 Å. Two other broad and weak signals suggest the occurrence of periodicities of $\sim$18.5 and $\sim$40.5 Å, both of which characterized by a low degree of positional correlation. While it may be not fortuitous that the two combined lengths correspond to the overall length of the repeating unit in its

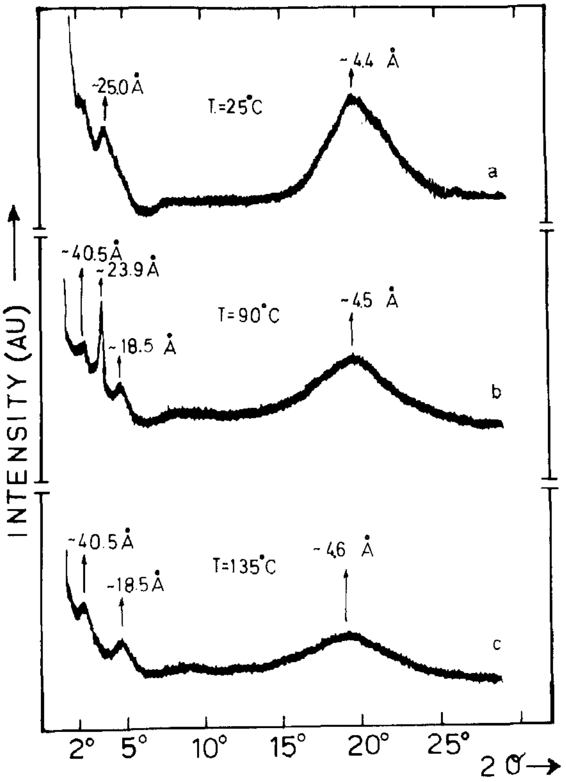

FIGURE 5. X-ray diffraction patterns of polymer C9S6* : virgin semicrystalline (a); smectic (b); cholesteric (c).

fully extended conformation (L ≃ 59 Å), the former length should be correlated with a bis(p-oxybenzoate)-containing moiety and the latter length with the rest of the repeating unit in the most extended conformation. Above 103°C, the smectic order is disrupted and the X-ray patterns maintain the same two broad inner reflections at 2Θ ≃ 4.8 and 2.2° (Fig.5c). This suggests the existence of a cholesteric phase which may have a somewhat layered structure, analogous to what has also been observed for some cholesteric side-chain polymers.[10] On the contrary, polymers C6S6* and C7S6* possess only a cholesteric phase, with quite similar diffraction profiles in the small angle region (Fig.6). It is interesting to note that, while the reflection corresponding to 18.5 Å remains unaffected by varying the chemical structure, the second signal corresponds to a Bragg length[11] of ∿36.7 and ∿38.0 Å, in the two polymers respectively. Such differences in the three chiral polymers are coherent with the incremental variations of the number m of methylene

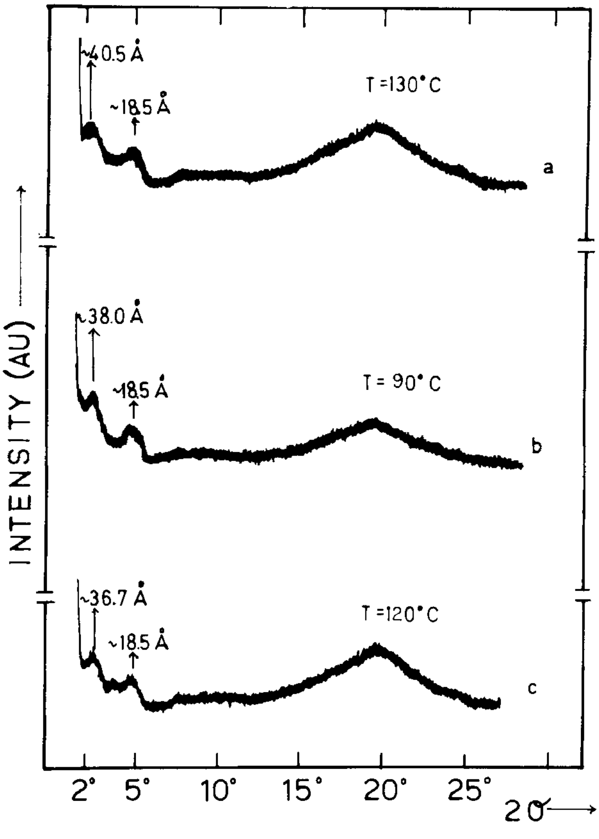

FIGURE 6. X-ray diffraction patterns of the cholesteric phase of polymers: C9S6* (a); C7S6* (b); C6S6* (c).

units in the alkylene segment in the extended conformation parallel to the long molecular axis.

CONCLUSIONS

The nature of the mesophases of some thermotropic poly(ester-β-sulphide)s has been elucidated by X-ray analysis as a function of temperature. A structural model of their smectic and cholesteric phases should accommodate the existence of periodicities of various lengths associated with different fragments of the repeating unit. It is anticipated that, while subtle changes in the polymethylene segment result in pronounced differences of mesomorphic behavior, variations of the length of the dithiyl segment may produce regular and predictable alternations of the liquid crystal properties of the polymers.

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