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Liquid-Crystalline Schiff's Base Polymers

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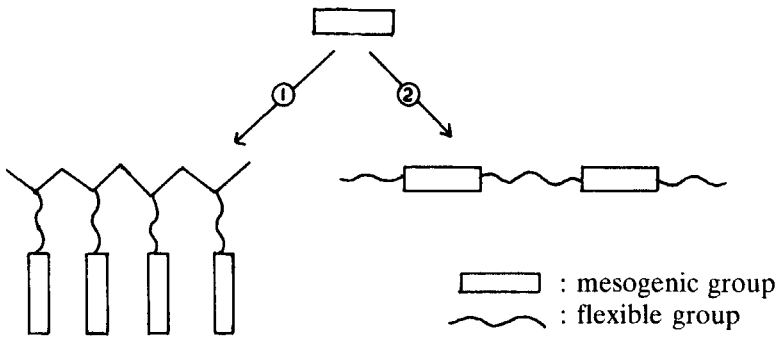
Liquid-crystal polymers are reported which are prepared from di-(*p*-formylphenyl) α-ω-alkanedicarboxylates and *p*-phenylenediamine. Neither component forms a mesophase but the polymers are typical main-chain liquid crystal polymers. The synthesis of a series of such polymers is described, and the properties of the products are discussed.

INTRODUCTION

Liquid crystal polymers, which have been the subject of much scientific and technological research,[1,2] are divided in two categories: "side-chain" and "main-chain." In the former case, the mesogenic group is attached to the chain *via* a flexible spacer, and the molecular conformation may not be altered by the formation of the mesophase. Thus, the polymeric and mesogenic effects are essentially uncoupled. On the other hand, if the polymers have the mesogenic unit and the flexible spacer in the main chain, the polymer molecule must adopt a conformation and packing which is compatible with the structure of the particular mesophase; hence, in this case, the polymeric and mesogenic properties are closely coupled. Modification of the repeating units may affect the molecular packing and cause the prop-

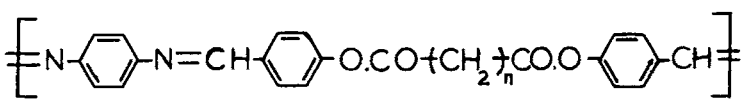
erties of the mesophase to depart from those of the low molecular-weight mesogen. Conversely, the formation of a mesophase can affect the conformation of this type of polymer. From the above arguments, polymers having the mesogenic units and flexible spacers in the main chain are clearly of great interest.



Main-chain liquid crystal polymers can be constructed either by incorporating a mesogenic group, *i.e.*, a group which has a tendency to form liquid crystal phases in the polymer backbone, or by incorporating groups which are not mesogenic in low molecular weight compounds but which nevertheless result in a polymer system showing liquid crystal properties due to the introduction of a degree of order during the development of macromolecular structure through polymerization.

We have previously described the synthesis and properties of some liquid crystal polyesters incorporating mesogenic units derived from *p,p'*-dihydroxytolan,[3] *p,p'*-bis(hydroxyphenoxy)benzene,[4] and *p,p'*-*bis*(hydroxyphenoxy)biphenyl.[5] The present investigation is concerned with the synthesis of main-chain polymers with non-mesogenic groups, in order to carry out a further study of the mesophases exhibited by these polymers with the objective of exploring the order introduced by the development of macromolecular structure.

Poly(Schiff's base)s (I) have been synthesized by condensation of di-(*p*-formylphenyl) α,ω-alkanedicarboxylates (II) with 4-phenylenediamine. The general repeating unit in these polymers can be represented as:



I

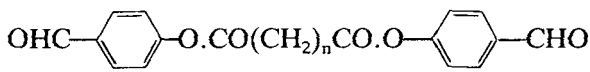
where n = 3,4,7, and 8. This polymer is designated SBn, where n is the number of methylene units in the acid residue.

EXPERIMENTAL

Preparation of monomers

Acyl chloride $ClOC(CH_2)_nCOCl$. Acyl chlorides were prepared by boiling a mixture of the acids $HO_2C(CH_2)_nCO_2H$, where n = 3,4,7 or 8, with an excess of thionyl chloride under reflux and removing surplus reagent *in vacuo*. The acyl chlorides were distilled under vacuum before use.

Di-(p-formylphenyl) α,ω-*aklanedicarboxylates*



II

The acyl chloride $ClOC(CH_2)_nCOCl$ (0.01 mole) was dissolved in dry pyridine (5 cm^3), and a solution of 4-hydroxybenzaldehyde (2.6 g, 0.021 mole) (Aldrich Chemicals) in pyridine (3 cm^3) was added. The solution was stirred at room temperature overnight, then diluted with ether (30 cm^3). The ether solution was washed twice with cold water, then with 10% HCl, twice with saturated $NaHCO_3$ solution, finally with cold water, and then dried with anhydrous $MgSO_4$. Ether was removed *in vacuo* and the residue was crystallized twice to give white crystals in 50–75% yield. Melting points and analytical data are presented in Table I.

Polymerizations

In a 50 cm^3 round-bottom, three-neck flask, equipped with a mechanical stirrer, reflux condenser and gas-inlet tube, a mixture of 4-phenylenediamine (0.54 g, 5 mmole, Aldrich Chemicals, crystallized

TABLE I

Data for Monomers II

n	M.p. (°C)	Found (Calcd.) % C	H
3	89	67.0 (67.1)	5.1 (4.7)
4	88	68.0 (67.8)	5.45 (5.1)
7	73	69.7 (69.7)	6.4 (6.1)
8	70	69.0 (69.1)	5.1 (4.7)

twice from ether-benzene), di-(*p*-formylphenyl) alkanedicarboxylate (5 mmole), ethanol (15 cm^3) and ethanoic acid (1 drop), was refluxed under a nitrogen atmosphere for 4 hr. The pale yellow precipitate which formed was removed by filtration, washed with methanol and propanone, and dried in a vacuum oven at 60°C.

Polymer characterization

Inherent viscosities were determined at 30°C using a solution of polymer (0.5 g) in concentrated H_2SO_4 (100 cm^3). A viscomatic MS-type 5300 Fica viscometer was used. In the absence of calibration, and in view of possible protonation by the solvent, the results have only indicative value.

Differential scanning calorimetry (DSC) analysis was performed with a Perkin Elmer DSC-2 Calorimeter. All samples were examined at a heating/cooling rate of 20°C/min under dry nitrogen flow. The maximum in the DSC endothermic peak was taken as the transition temperature. Indium of 99.99% purity was used for temperature calibration.

X-ray diffraction patterns were obtained using a Philips D1009 diffractometer. Ni-filtered CuK_α-radiation was used. After the diffraction spectra were recorded for the virgin sample at room temperature, the sample tube was heated in a silicone oil bath to a few degrees above the first phase-transition temperature, and then cooled quickly to room temperature by immersing in an ice-bath.

The optical observations were made using a Leitz Polarizing microscope equipped with a Mettler FP2 heating stage and photographic camera. Polymer texture was studied using a sample mounted between a slide and cover slip, using slight pressure at the phase-transition temperature. Nitrogen gas was passed over the sample during the course of the observations.

RESULTS AND DISCUSSION

All the polymers are insoluble in virtually all common organic solvents including DMF and DMSO. Solubility is obtained with concentrated H_2SO_4, although decomposition occurs. ^1H NMR spectra could not be obtained as the polymers are insoluble in all the common NMR solvents at room temperature, but quantitative elemental analysis gave satisfactory results. The following data were obtained. SB3 gave: N% 6.9, Calcd. 6.8; SB4: N% 6.9, Calcd. 6.6; SB7: N% 6.1, Calcd. 6.0; and SB8: N% 6.00, Calcd. 5.8.

Thermal analysis

Transition temperatures and glass-transition temperatures corresponding to maxima of endotherms in the DSC heating curves, together with the inherent viscosities of the polymers, are collected in Table II. The polymers are insoluble in the reaction medium and precipitate immediately upon formation before reaching a high molecular weight, as is reflected by their inherent viscosities (η_{inh}) (column 2, Table II).

The phase-transition temperature accompanying the transition of a polymer to the liquid crystal state is designated T_{K-N}, and that to the isotropic phase T_{N-I}, and these data are quoted in columns 4 and 5 of Table II, respectively. These DSC transitions were confirmed by the appearance of liquid crystal and isotropic states in hot-stage microscopy. The $\Delta T = T_{N-I} - T_{K-N}$ values in column 6 indicate the temperature range over which the liquid crystal phase exists. This is quite broad, amounting to 65° for SB4 and *ca.* 130°C for SB3. These polymers are thermally quite stable, and can be investigated as the melts without risk of decomposition (Figure 1).

All the polymers exhibit well-defined endotherms (crystal to liquid crystal and liquid crystal to isotropic phases) in addition to the glass transition, as demonstrated by the DSC thermograms in Figure 1. As can be seen from Figure 2, both T_{N-I} and T_{K-N} vary with the number of methylene units (n) in the spacer group, in the familiar zig-zag fashion. Further, the phase-transition temperatures are higher for polymers having an even number of methylene units than for those with an odd number. The same general trend has been reported for almost all main-chain liquid crystal polymers.[6]

TABLE II

Properties of the poly-Schiff's bases SBn

Polymer designation	η_{inh} dl/g^{-1}[a]	T_G[b]	T_{K-N}	T_{N-I}	$\Delta T = T_{N-I} - T_{K-N}$
				°C	
SB3	0.23	85	175	303	128
SB4	0.18	80	255	320[c]	65
SB7	0.20	75	160	244	84
SB8	0.27	55	170	270	100

[a]The relative viscosity (η_r) so obtained was converted to inherent viscosity (η_{inh}) by the standard relationship, $\eta_{inh} = \ln\eta_r/C$.

[b]Obtained by DSC.

[c]With decomposition.

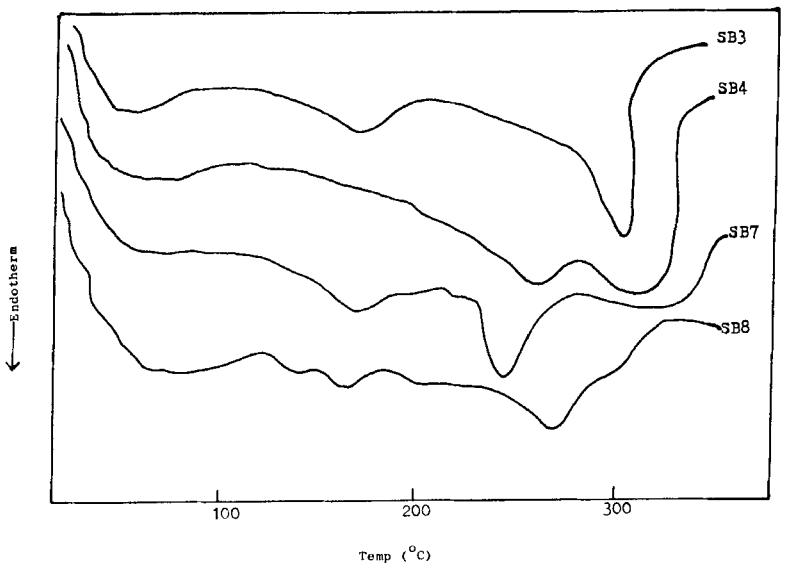


FIGURE 1 DSC thermograms of untreated samples of SBn polymers.

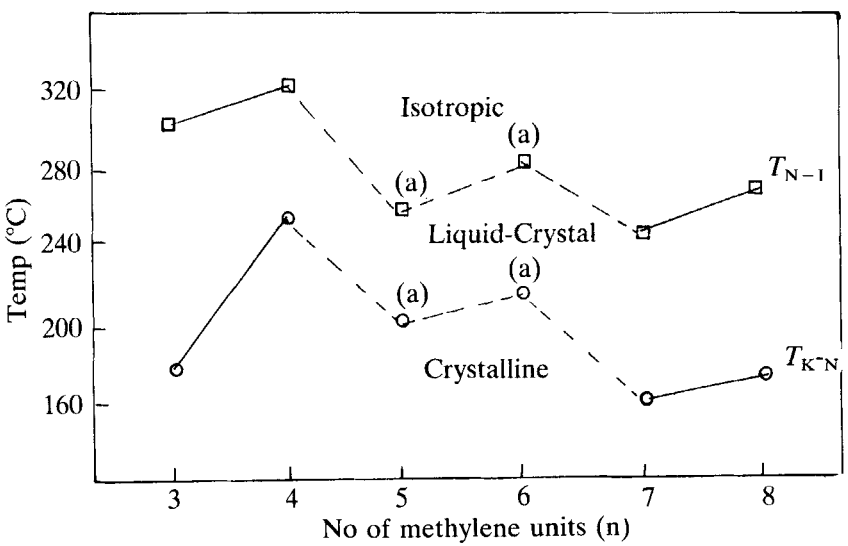


FIGURE 2 Dependence of T_{K-N} and T_{N-I} on the length of the flexible spacer (n) in the polymers SBn.

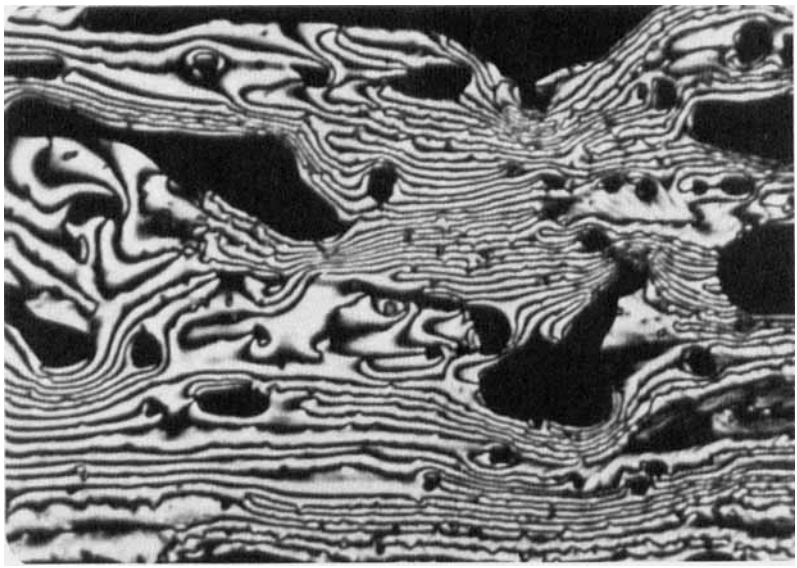


FIGURE 3 Nematic Schlieren texture of the quenched melt of SB7 (between crossed polars). See Color Plate X.

Optical observations

The textures, as studied in the polarizing microscope, present basically the same appearance for all four polymers. Figure 3 illustrates the texture of the SB7 polymer, which exhibits a typical *Schlieren* texture, corresponding to a nematic phase. As the temperature increases, the number of brushes and black lines decreases, and black regions of the isotropic phase appear (Figure 4). On cooling to room temperature, the Schlieren texture forms again.

SB4, illustrated in Figure 5, has a Schlieren-like texture. It should be noted that the texture is observed in both bright-field microscopy and between crossed polars; it appears to be unchanged almost until reaching the isotropic phase.

X-Ray diffraction

X-ray diffraction patterns have been analyzed mainly according to the method devised by de Vries,[7] based on low molecular weight liquid crystals. For an unoriented sample, the smectic phase shows a very sharp inner ring (which is related to the layer spacing existing in the liquid crystal system) from which the length of the repeating unit can be deduced. The outer ring is ascribed to the lateral inter-

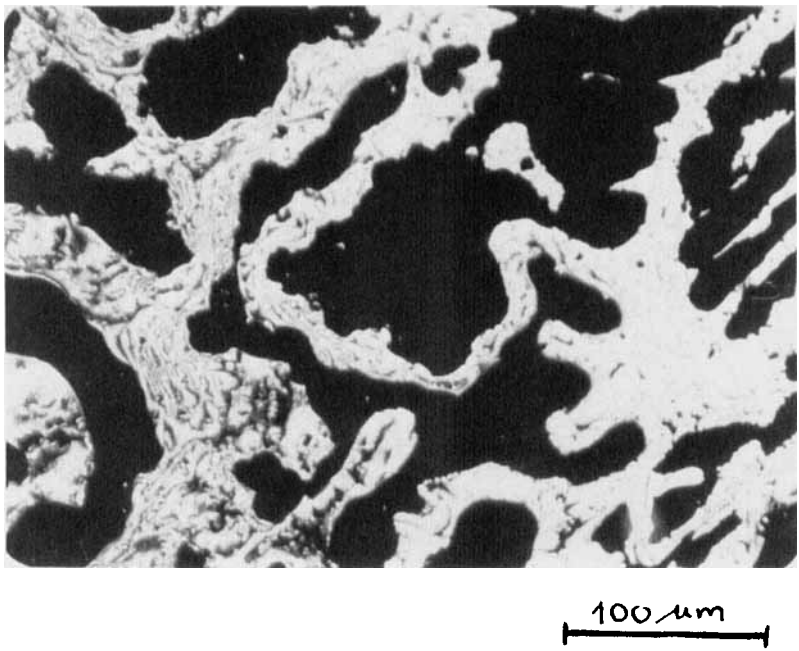


FIGURE 4 The isotropic state and some birefringent nematic regions of SB7 at 217°C. See Color Plate XI.

action of neighboring chains (and provides information on the average inter-chain distance). In contrast, the nematic phase is expected to show only a weak, diffuse inner ring and a strong (diffuse-halo) outer ring. However, some liquid crystal polymers do not fit into the de Vries classification.[8]

The lattice distances obtained for the original polymer powder and for quenched samples, along with a visual indication of their intensities, are listed in Table III. The original samples showed only a few diffraction rings (Figure 6A), typical of semi-crystalline polymers. However, the X-ray diffraction patterns of the polymer samples which were quenched from the liquid crystal melt exhibited a broad and weak inner ring and a strong (diffuse-halo) outer ring, with an observable maximum at about 4.8 Å (Figure 6B).

CONCLUSION

The result of this study—based on DSC, polarizing microscopy and X-ray diffraction patterns—shows that these polymers exhibit thermotropic mesomorphic properties which can be identified as nematic.

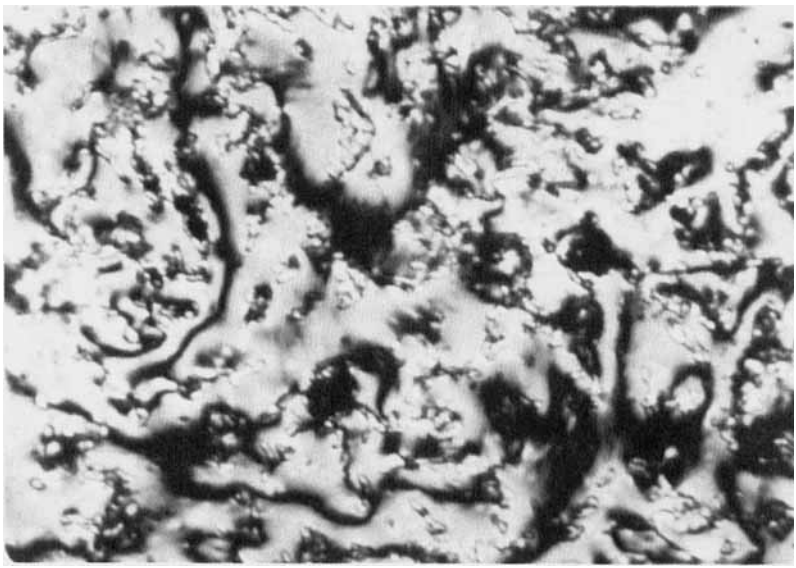


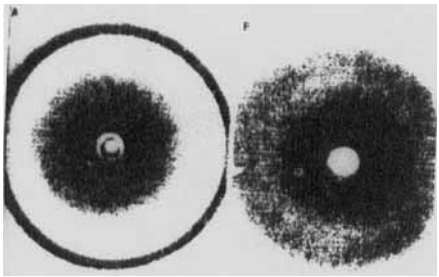
FIGURE 5 Texture of SB3 in the biphasic region. **See Color Plate XII.**

TABLE III

The X-ray diffraction spacings (d)[a] of the SBn polymers

Polymer designation	Crystalline state at room temperature d Å	Sample quenched from the liquid crystal state d Å
SB3	4.5 (m) 4.8 (s) 5.2 (v) 14.7 (m)	4.98 (halo) 13.8 (vw)
SB4	4.6 (m) 4.9 (s) 16.1 (m)	4.88 (halo) 14.04 (vw)
SB7	4.4 (w) 4.8 (s) 18.8 (m)	4.78 (halo) 5.2 (vw)
SB8	4.5 (w) 5.0 (s) 18.2 (m)	4.78 (halo) 15.3 (vw)

[a]The positions of the reflections were converted into inter-planar spacings by means of the de Vries modification of the Bragg equation, $2d\sin\theta = 1.117\lambda$.
Symbols: s = strong, m = medium, w = weak, vw = very weak.



(A) (B)

FIGURE 6 X-Ray diffraction pattern of SB7: (A) in the crystalline state at room temperature; (B) the quenched melt from the liquid crystal state.

Although neither monomer component displays mesomorphic properties (non-mesogenic), we are clearly dealing with a system in which the appearance of a nematic mesophase is associated with the development of polymeric structures. That is, on polymerization of non-mesogenic units, a mesogenic polymer is formed, the observed increase in order being a direct consequence of the polymerization process.

References

1. A. C. Griffin and J. F. Johnson (eds.), *Liquid Crystals and Ordered Fluids*, Plenum, New York (1984).
2. A. Ciferri, W. R. Krigbaum and R. B. Meyer (eds.), *Polymer Liquid Crystals*, Academic, New York (1982).
3. A. H. Al-Dujaili, A. D. Jenkins and D. R. M. Walton, *J. Polym. Sci., Polymer Chem. Ed.*, **22**, 3129 (1984).
4. A. H. Al-Dujaili, A. D. Jenkins and D. R. M. Walton, *Makromol. Chem., Rapid Commun.*, **5**, 33 (1984).
5. A. H. Al-Dujaili, A. D. Jenkins and D. R. M. Walton, in course of publication.
6. C. K. Ober, J. I. Jin and R. W. Lenz in *Liquid Crystal Polymers I* (M. Gordon and N. A. Platé, eds.), Springer-Verlag, Berlin (1984).
7. De Vries, *Pramana, Suppl. No. 1*, 93 (1975).
8. S. B. Clough and A. Blumstein, in *Mesomorphic Order in Polymers and Polymerization in Liquid Crystal Media* (A. Blumstein, ed.) *ACS Symp.*, **74** (1978).