

Synthesis and properties of some polyesters with mesogenic groups and flexible spacers in the main chain

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Polymers containing, in the main chain, various mesogenic moieties separated by flexible spacers have been prepared by condensation of the corresponding diphenol or diol with an aliphatic diacid chloride. The polymers have been characterized by X-ray, d.s.c. and polarizing microscopy. The diacids used were sebacic (SEB), succinic (SUC) and 3-methyladipic (MAA). The biphenols were 4-hydroxy-*N*-benzylidene-4'-hydroxyaniline(1), 4,4'-biphenol(2), 4,4'-bis(2-hydroxyethoxy)-biphenyl(5) and 3,3'-dimethyl-4,4'-di(2-hydroxyethoxy)-stilbene(7). The polymers SEB-1 and SEB-2 were classified as giving thermotropic lamellar mesophases; SEB-5, SEB-7 and SUC-5 as potentially nematic; MAA-2 and SUC-2 gave crystalline polymers.

Keywords Condensation; polyester; synthesis; properties; characterization; mesogenic group

INTRODUCTION

Polymers in which rigid, anisotropic moieties (the mesogenic moieties) are incorporated into the backbone of the polymer chain are known to give rise to liquid crystalline behaviour. Solutions of such polymers have been found to display properties of a nematic liquid crystal at concentrations which depend on the axial ratio of the mesogenic moieties¹ and on the attractive forces between them. Thermotropic phase transitions, however, are located at or above the thermal decomposition temperature of the polymer. Thus polymers with mesogenic elements in the backbone are rather difficult to obtain in their thermotropic liquid crystalline state and even more difficult to study in this state².

Fortunately, one can substantially lower the crystal-to-liquid crystal transition temperatures of such polymers by separating the rigid mesogenic moieties with regularly spaced sequences of methylene or oxymethylene groups. This has been shown in 1975 by Roviello and Sirigu^{3,4} on the example of polymeric Schiff base derivatives of *p,p'*-dihydroxy- α,α' -dimethylbenzalazine and, subsequently, by us^{5,6} in the example of polyester derivatives of *p,p'*-dihydroxybiphenyl and dihydroxystilbene.

In this paper, we would like to report in more detail about the synthesis and properties of such polymeric liquid crystals.

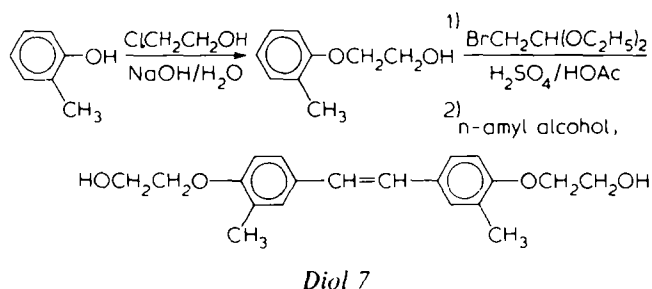
All polymers were obtained by condensation of a bisphenol or diol containing the mesogenic unit with an aliphatic diacid or diacid chloride. In the description of properties each polymer is given a notation consisting of a sequence of letters followed by a number. The letters refer to the diacid and the number refers to the bisphenol as given in Table 1. For example, poly(*p,p'*-benzylidene aminophenylsebacate) prepared by condensation of sebacic acid (SEB) with bisphenol 1 is represented by the notation SEB-1.

EXPERIMENTAL

(1) Preparation of monomers

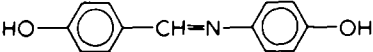
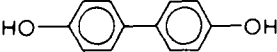
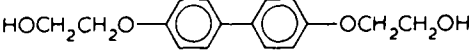
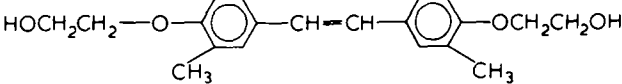
Sebacyl, succinyl and 3-methyladipic acid chlorides were obtained either commercially and purified by distillation under reduced pressure or prepared by reaction of the corresponding diacids with thionyl chloride, according to the standard procedure⁷. They were distilled immediately before use. Bisphenols 2 and 3 were obtained commercially and purified by recrystallization from aqueous ethanol. Bisphenol 1 was prepared by condensation of 4-hydroxybenzaldehyde with 4-aminophenol. The condensation was carried out in methanol. Bisphenol 1 was recrystallized from a mixture of acetone and hexane.

Diol 5 was obtained by the condensation of 4,4'-biphenol with 2-chloroethanol under alkaline conditions according to the procedure of Reynolds and Van der Berghe⁸. M.p. of the diol obtained was 209–211°C. Yield: 80%. Diol 7 was obtained as shown in the scheme below:



The first step is a condensation of *o*-cresol with 2-chloroethanol similar to the one involved in the preparation of Diol 5. The crude product was distilled under reduced pressure to give a clear, colourless liquid. (100°C/5 mm). Yield: 42%.

Table 1 Diacids and bisphenols used as monomers

	Diacids	Abbreviation
$\text{HOOC}-(\text{CH}_2)_8-\text{COOH}$	Sebacic acid	SEB
$\text{HOOC}-\text{CH}_2\text{CH}_2-\text{COOH}$	Succinic acid	SUC
$\text{HOOC}-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2\text{CH}_2-\text{COOH}$	3-Methyl adipic acid (racemic form)	MAA
Bisphenols		
	4-hydroxy-N-benzylidene-4'-hydroxyaniline	1
	4,4'-biphenol	2
	4,4'-bis(2-hydroxyethoxy)-biphenyl	5
	3,3'-dimethyl-4,4'-di(2-hydroxyethoxy)-stilbene	7

The second step was carried out according to the procedure of Young *et al.*^{9,10}. It is an electrophilic substitution in the aromatic ring, followed by thermal rearrangement in amyl alcohol. The crude product was washed several times with methanol and dried to give the diol 7 in 46% yield. M.p.: 215°–216°C. Elemental analysis:

calculated:	$\frac{\text{C}}{73.15\%}$	$\frac{\text{H}}{7.37\%}$
experimental:	73.25%	7.54%

(2) Preparation of model compounds

The model compounds were prepared by condensing the corresponding diol or bisphenol with decanoylchloride in 1,2 dichloroethane in the presence of a slight excess of pyridine. The crude products were purified by recrystallization.

(3) Preparation of polymers

The polymers were prepared by condensation of the appropriate diacid chloride and of the diphenol or diol. In some cases high temperature transesterification was used. Some typical polycondensation procedures are as follows:

Poly (*p,p'*-benzylideneaminophenylsebacate) (SEB-1)

A solution of 6.43 g (30.2 mmol) of bisphenol-1, 2.41 g of sodium hydroxide and 0.6 g of benzyltriethyl ammonium chloride in 100 ml water was placed in a blender. Sebacyl chloride 7.21 g; (30.2 mmol) in 80 ml chloroform was added to it rapidly with vigorous stirring. The resulting viscous slurry was stirred for about 15 min and poured into 250 ml methanol. The cream coloured precipitate was filtered, washed with water, dried and extracted with methanol in a soxhlet extractor. It was finally dried *in vacuo* at 70°C.

Poly (*p,p'*-diphenylsebacate) (SEB-2)

The interfacial polymerization of SEB-2 is similar to SEB-1. An example of preparation of SEB-2 by melt

polymerization is given below:

In a 100 ml 3-necked round-bottomed flask were placed 1.810 g (6.70 mmol) of 4,4'-bisphenol diacetate, 1.354 g (6.70 mmol) of sebacic acid and 2 mg of magnesium metal. Through one neck a capillary tube reaching the bottom of the flask was introduced as inlet for nitrogen. A distillhead leading to a condenser was placed in the second neck and the third was stoppered. The flask was purged with a slow, steady stream of nitrogen for 30 min and the flask was heated to 260°C. The reactants melted and acetic acid started to distill almost immediately. The temperature was kept at 260°C for 45 min and then raised to 275°C. The nitrogen was cut off and the pressure was gradually reduced to about 2 mm. The molten liquid started to solidify. This process was complete after about 15 min. Heating was continued in vacuum for 75 min after which the polymer was allowed to cool to room temperature in vacuum (~2 h). The mass of polymer obtained was powdered, extracted with methanol in a soxhlet extractor and dried in vacuum at 70°C. Yield of polymer: 1.94 g (84%).

	(C%)	(H%)
Elemental analysis: calculated:	74.98	6.96
experimental:	75.01	7.16

Poly(bisethyleneoxy-*p,p'*-diphenylsebacate) (SEB-5)

Preparation by solution polymerization: *p,p'*-biphenoxydiethanol (9.065 g; 33 mmol) was suspended in 90 ml dry, distilled 1,2-dichloroethane. Eight ml (99.3 mmol) of dry pyridine was added to it and the slurry cooled to 0°C in an ice bath. A solution of 7.942 g (33.2 mmol) of sebacyl chloride in 80 ml dichloroethane was added dropwise to the above slurry at 0°C over 45 min. Stirring was continued for 30 min at 0°C and then the mixture was refluxed for 12 h. The warm homogeneous solution was poured into 800 ml methanol which precipitated the polymer. The crude polymer was collected, extracted with methanol (soxhlet) and dried *in vacuo* at 60°C. Yield: 13.64 g (89%).

		(C%)	(H%)
Elemental analysis:	calculated:	70.89	7.32
	experimental:	70.66	7.55

(4) Physical properties of polymers

The viscosity measurements were performed in mixtures of cresol and chlorinated aliphatic hydrocarbons, using Ubbelohde dilution viscometers.

Phase transition measurements were made using a Perkin Elmer DSC-2C differential scanning calorimeter and a Mettler hot stage Leitz-Ortholux Polarizing Microscope.

The samples were either unannealed (*in situ*) or annealed as follows: The polymer was held under nitrogen for 2 h at a temperature exceeding by 20°–30°C the TMA softening temperature, then cooled slowly to room temperature (0.625°C/min). The d.s.c. instrument was calibrated with standard samples of indium and benzil. Heating rates were 10, 30 and 40°C per min. The melting temperatures were corrected for the effect of the heating rate on the instrumental time lag.

The peak areas for unannealed samples were strongly dependent on the history of the sample. Annealing considerably enhances the reproducibility of the measured values of transition enthalpies. The peak areas under overlapping peaks were determined as in ref 11.

The thermomechanical properties were determined by means of a Perkin Elmer Thermomechanical Analyzer (TMA-1) on polymers pressed into a standard-size 200 mg pellet.

Flow was assumed to occur at temperatures at which an easy displacement of the cover glass could be made under the microscope (or at which flow could be observed directly).

X-ray diffraction patterns were recorded by means of a flat plate camera (Warhus) provided with a sample heater and mounted on a Norelco Generator (Ni filtered Cu radiation). The sample holder consisted of three brass rings of ~2 mm thickness and ~1 cm diameter. Both ends of the centre ring were sealed with mica. A ring was placed on each side of the centre ring and all three rings were tightened by means of screws. The assembled cell was placed in the camera mounted heater at the desired temperature. The temperature was controlled to within ±2°C. In other cases, the sample was contained in a glass capillary (for X-ray specimen) placed in the oven. The relative error involved in the determination of spacings is of the order of 1% (±0.03–0.04 Å) for wide angle diffraction at 25°C. This error becomes larger at high temperatures (line broadening). For small angle diffraction it may in some cases reach up to approximately (±0.5–0.8 Å).

Electron diffraction patterns were obtained from single crystals of SEB-1 formed upon slow cooling of dilute solution of the polymer in 1,1,2-trichloroethane. These crystals were deposited on carbon substrates by transfer of a drop of suspension and subsequent solvent evaporation. They were examined in JEM 100 transmission electron microscope.

RESULTS

The structure of a series of polymers with mesogenic moieties in the backbone has been varied by

independently altering the nature of the rigid mesogenic moiety and the length and composition of the flexible spacer. Because of the linear nature of these polymers it was expected that nematic order would prevail in the thermotropic liquid-crystalline phases. However, as can be seen below, the X-ray diffraction patterns in a number of cases point toward the existence of lamellar mesophases in the interval of temperatures between crystalline melting and transition to the isotropic melt. In what follows the main characteristics of selected polymers will be described and discussed. The polymers will be grouped as follows: (A) Polymers which give lamellar mesophases (SEB-1, SEB-2); (B) Polymers which give potentially nematic melts (SEB-5, SEB-7, SUC-5); (C) Crystalline polymers (MEA-2, SUC-2).

(A) Polymers with lamellar mesophases

1. SEB-1 (Poly(p,p'-benzylidene aminophenylsebacate))
Synthesis: Interfacial Polymerization.

Solubility: Soluble in hot *m*-cresol, slightly soluble in hot 1,1,2-trichloroethane.

Viscosity: $\eta_{red}^{30} = 0.35 \text{ dl g}^{-1}$ (0.2 wt% solution at 30°C in 1:1 (v/v) *m*-cresol and 1,1,2-trichloroethane). A gradual degradation of SEB-1 in the above solvent was observed.

Microscopy: A thin film of polymer, moulten and pressed between a glass slide and a cover slip gave a birefringent 'lacy, thread-like' texture. The phase transitions are difficult to observe except for the isotropic phase transition which sets in gradually above 220°C. At this temperature the polymer appeared to have a significant flow.

Thermal properties: The *in situ* polymer shows a TMA softening temperature of $154 \pm 7^\circ\text{C}$, and three d.s.c. transitions: T_1 at 124°C, followed by an exotherm; T_2 at 150°C; and T_3 , a broad peak centred around 220°C. SEB-1 annealed at 200°C for 2 h showed a peak at $T_1 = 201^\circ\text{C}$, and two broader overlapping peaks centred at $T_2 = 230^\circ\text{C}$ and $T_3 = 245^\circ\text{C}$, respectively. The value of ΔH_1 was found to be 1.05 kJ mol^{-1} of repeating unit and $\Delta H_2 + \Delta H_3$ was 7.54 kJ mol^{-1} of repeating unit. (2.76 J g^{-1} and 19.89 J g^{-1}).

Table 2 gives X-ray diffraction data for the *in situ* polymer at 25°C and for the polymer at 180°C.

The nature of the unit cell has not yet been determined, but it is noted that the 18.8 and 14.8 Å spacings are considerably shorter than the fully extended repeating unit which is 26 Å long. Some of the X-ray peaks faded at temperatures above 100°C. This is attributed to loss of order in the methylene chains at the elevated temperatures. The two lines observed at higher temperatures are compatible with a layered organization in the mesomorphic domains.

Figure 1 (a, b, c) shows electron diffraction patterns taken at room temperature on crystals grown from a dilute solution in 1,1,2-trichloroethane (a), after heating to 160°C and quenching (b), and from a monocrystal with the same heat treatment (c). It is apparent that a lamellar structure of crystals characterizes the crystalline domains

Table 2 X-ray diffraction spacings of SEB-1

t (°C)	Spacing (Å)
25	3.15(w); 3.78(w); 4.08(s); 4.35(s); 4.57(s); 9.92(m); 18.8(s)
180	4.36(s); 14.8(w)

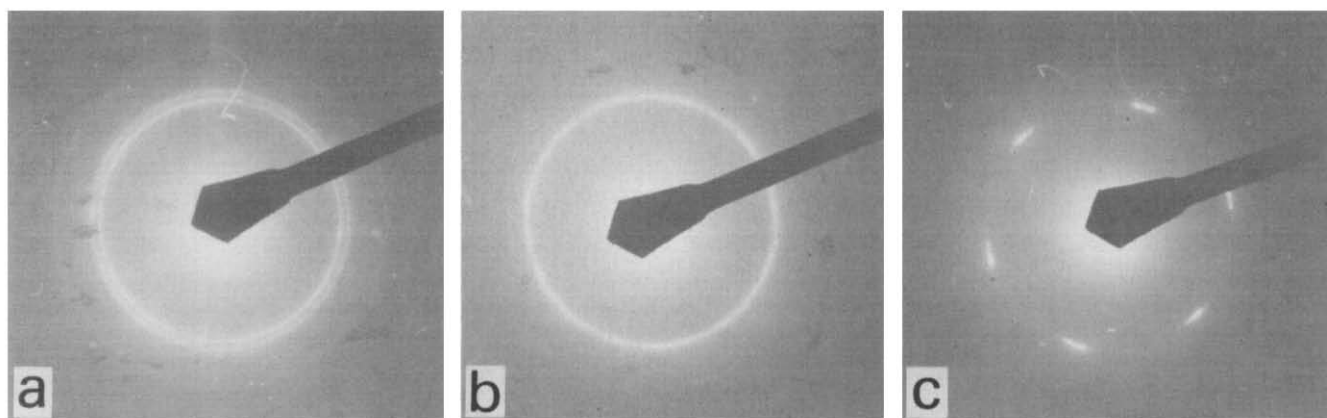


Figure 1 Electron diffraction pattern from SEB-1. (a) Lamellar crystals grown from a dilute solution in 1,1,2-trichloroethane; (b) after heating crystals shown in (a) to 160°C and quenching to 25°C; (c) diffraction from a few crystals with nearly identical orientation, indicating a hexagonal structure. Crystals heated as in (b)

Table 3 T.m.a. and d.s.c. results for different samples of SEB-2

	Polymer <i>in situ</i>			Annealed polymer		
	(a)	Sample (b)	(c)	(a)	Sample (b)	(c)
T_1 (°C)	200	208	209	201, 203**	202	213
ΔH_1 $\frac{\text{kJ}}{\text{mru}^*}$	3.85	4.31	6.70	5.44***	6.28	4.10
ΔH_1 (J/g)	10.92	12.22	19.00	15.20	17.83	11.64
T_2 (°C)	248	262	280	255	262	278
ΔH_2 $\frac{\text{kJ}}{\text{mru}^*}$	x	2.97	13.4	0.50	5.44	14.65
ΔH_2 (J/g)	x	8.41	38.01	1.42	15.45	41.62
$\Delta H_1 + \Delta H_2$ (J/g)	x	20.64	56.98	16.87	33.28	53.26
$T_{\text{softening}}$ (t.m.a. °C)	149	182	185			

* Mole of repeating unit

** Two overlapping peaks; samples (b) and (c), also gave closely overlapping peaks, at slow heating rates

*** Combined overlapping peak areas

x Difficult to measure reproducibly

of SEB-1. Such crystals can generate lamellar (smectic) mesophases. It is probable that we deal here with lamellar mesophases of higher order (such as Smectic B or B₁), as witnessed by the sharp 4.36 Å X-ray spacing at 180°C. X-ray patterns of an oriented mesophase will be necessary to substantiate the nature of the mesomorphic domains in SEB-1.

2. SEB-2 (Poly(4,4'-diphenylsebacate))

This polymer was prepared by several methods including interfacial (sample a), solution (sample b), and melt (sample c) polymerization. Interfacial polymerization was similar to the technique used in the case of SEB-1. Solution polymerization was carried out in sulfolane with pyridine as proton acceptor. The melt polymerization was done at 270°C by transesterification of *p,p'*-biphenoldiacetate with sebacic acid in presence of magnesium. Infra-red spectra and elemental composition of the polymer were independent of the method of preparation.

Solubility: samples (a) and (b) are sparingly soluble in hot 1,1,2-trichloroethane; sample (c) in hot *m*-cresol.

Viscosity: sample (a) $\eta_{\text{red}}^{30} = 0.22 \text{ dl g}^{-1}$ (0.1% solution in 1:1 (v:v) *m*-cresol and trichloroethane); sample (b): $\eta_{\text{red}}^{33} =$

$= 0.28 \text{ dl g}^{-1}$ (solution as above); sample (c): $\eta_{\text{red}}^{45} = 0.67 \text{ dl g}^{-1}$ (0.1% solution in *m*-cresol).

Microscopy: The polymers display a 'lacy, thread-like texture'. Easy displacement of the cover glass occurs above 200°C for samples (a) and (b), and at 245°C for sample (c). Birefringence disappears at 264°, 274° and 295°C for samples (a), (b) and (c), respectively.

Thermal properties: The polymers were annealed at 200°C for 2 h. The results of d.s.c. and t.m.a. analysis are summarized in Table 3.

Table 3 shows that T_1 and T_2 increase with molecular weight and that little change is introduced by annealing. The t.m.a. softening temperature also increases with molecular weight. The t.m.a. softening temperature of sample (a) is abnormally low, compared to samples (b) and (c). It is possible that sample (a) contains oligomers which act as plasticizers, since this sample (as well as all the others) is unfractionated.

Both ΔH_1 and ΔH_2 appear also to increase with molecular weight. Interpretation of d.s.c. results, however, should be approached cautiously. Multiplicity of peaks, their position and magnitude of peak areas, may be affected by factors such as method of sample preparation,

Table 4 X-ray diffraction data for some samples of SEB-2

Temperature (°C)	Spacings (Å)
25 (annealed, sample b)	3.47(w); 3.92(w); 4.25(s); 4.69(m); 4.96(m); 7.60(w) 9.78(w); 15.8(m); 19.2(s)
170 (sample a); (sample b)	4.33(s); 15.8(w) 4.35(s); 14.6(w); 19.5(s)
220 (sample a)	4.46(s); 16.4(w)
194 (sample b)	4.46(s); 17.0(s)

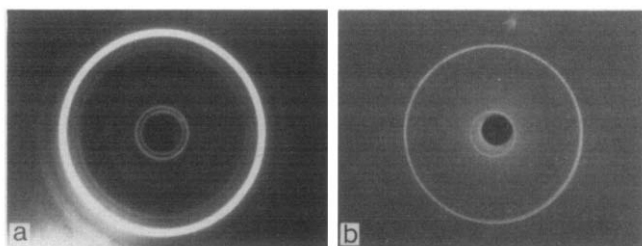


Figure 2 X-ray diffraction pattern from SEB-2. (a) Room temperature diffraction, after annealing at 220°C; (b) diffractogram obtained at 215°C (Sample a)

molecular weight and dispersity¹², rate of heating and thermal history, including temperature and time of annealing^{11,13,14}.

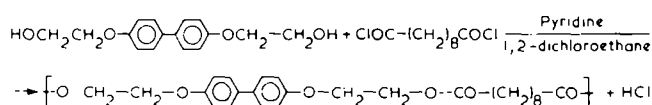
Table 4 lists X-ray diffraction spacings for selected samples of SEB-2. In considering the X-ray diffraction patterns as a function of temperature, one should not expect a close correlation with the phase transition temperatures obtained by d.s.c. The d.s.c. scans are obtained under dynamic conditions, whereas X-ray spacings are measured from films developed after 24 h of isothermal exposure. Results from X-ray diffraction, then, reveal the organization which the polymer develops during extensive annealing at the temperature indicated.

The X-ray spectra of SEB-2 (Figure 2) are qualitatively similar to those of SEB-1. Here again the crystalline 3-dimensional order seems to collapse upon transition to the mesophase. The two remaining lines suggest a layered organization of chains with a fair amount of order within layers. As previously in the case of SEB-1, the small angle spacing of 16.7 Å observed at higher temperatures is shorter than the fully extended repeat unit. Contrary to a recent statement by D. Van Luyen and Strzelecki²⁰ who report SEB-2 to be nematic we found this polymer to be smectic.

(B) Polymers displaying potentially nematic melts

1. SEB-5: poly(bisethylenoxy-p,p'-diphenylsebacate)

Method of synthesis: Solution polymerization:



Solubility: Soluble in *m*-cresol at room temperature, soluble in hot dichloroethane.

Viscosity: $\eta_{\text{red}}^{20} = 0.47 \text{ dl g}^{-1}$ (0.2% solution in 1:1 v/v *m*-cresol trichloroethane).

Microscopy: Birefringence persisting up to 165°C. Isotropic transition at 165.6°C, observable flow at 157°C. Birefringence reappears on cooling at 160°C.

Thermal properties: The t.m.a. softening temperature is 149°C. Figure 3 shows a d.s.c. thermogram of SEB-5 and the results are summarized in Table 5. An exotherm is observed between T_1 and T_2 at heating rates below $20^\circ\text{C min}^{-1}$. At the present time we do not have a satisfactory explanation for the presence of this exotherm which might be due to a recrystallization following T_1 . Subsequent melting of the recrystallized material might overshadow the nematic to isotropic ($N-I$) transition at T_2 .

Magnetic birefringence measurements²¹ are in agreement with this interpretation. We have tentatively classified SEB-5 as a potentially nematic polymer, that is one in which there appears to be competition between nematic alignment and crystallization.

At heating rates above $20^\circ\text{C min}^{-1}$ no exotherm was observed between T_1 and T_2 on d.s.c. scans. Calorimetric data (Table 5) are in agreement with the existence of a nematic phase between T_1 and T_2 . For low molecular weight liquid crystals the relative magnitudes of ΔH_1 and ΔH_2 usually provide quantitative information on the partitioning of order among the various phases^{15,16,17}. The enthalpy change associated with the crystal \rightarrow nematic transition is generally about an order of magnitude higher than the nematic \rightarrow isotropic transition enthalpy. In the case of SEB-5, the values of ΔH (Table 5)

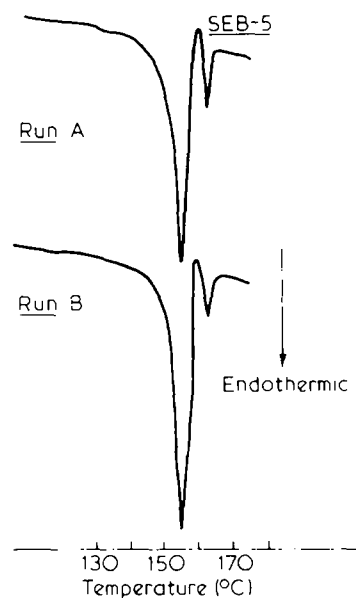


Figure 3 D.s.c. scan of SEB-5. Run A — SEB-5 *in situ*. Heating rate 10°C/min ; Run B — after heating at 175°C for 20 min, cooling to 80° at 0.625°C/min and reheating at 10°C/min

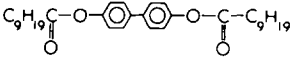
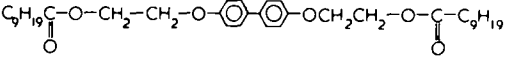
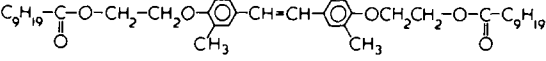
Table 5 D.s.c. data for SEB-5 (heating rate $20^\circ\text{C min}^{-1}$ **)

	Run a (see Figure 3)	Run b (see Figure 3)
T_1 (°C)	155	155
ΔH_1 (kJ/mru*)	22.19	23.0
ΔH_1 (J/g)	50.4	52.3
T_2 (°C)	162	163
ΔH_2 (kJ/mru*)	3.06	1.72
ΔH_2 (J/g)	6.90	3.89
$\Delta H_1 + \Delta H_2$ (J/g)	57.32	56.23

* mole of repeating unit

** no exotherm between T_1 and T_2

Table 6 Transition temperatures and enthalpies of model compounds

	Temperature (°C)	ΔH_1^*	Corresponding polymers	ΔH_1^*
I. 	K $\xrightarrow{92}$ S $\xrightarrow{119}$ I	(362.6)	SEB-2:	(205.15)
II. 	K $\xrightarrow{100.5}$ I	(2428.3)	SEB-5:	(1046.7)
III. 	K ₁ $\xrightarrow{72}$ K ₂ $\xrightarrow{77.5}$ I	(1163.9)	SEB-7:	(401.9)

* In J mol⁻¹ of backbone atoms

are in keeping with this ratio, but, as already mentioned, it would be imprudent to base one's structural interpretation solely on calorimetric data, especially for polymers for which this ratio may not hold because ΔH_1 does not represent the enthalpy of melting ΔH_m ($\Delta H_1 = W_c \Delta H_m$ where W_c is the fraction of crystalline material).

The room temperature X-ray pattern for SEB-5 annealed at temperatures slightly above its softening point gives a multiplicity of X-ray lines which seem to persist up to 140°. Due to the narrow interval between T_1 and T_2 it is difficult to estimate the extent of crystallinity in this interval, beyond the presence of some very weak reflexions. Above 160 only 2 halos (centred around 4.9 Å and 14 Å) can be observed.

2. *SEB-7: poly(bisethylenoxy-p,p'-(2,2'-dimethyl)stilbene sebacate)*

Method of synthesis: Solution polymerization using pyridine and tetrachloroethane as solvents.

Solubility: Soluble in dichloroethane and chloroform at room temperature.

Viscosity: $\eta_{red}^{30} = 0.28$ dl g⁻¹ (0.2% solution in *m*-cresol and trichloroethane). ($M_n = 4.5 \times 10^3$ mol g⁻¹ as determined by vapour phase osmometry in chloroform at 29°C).

Microscopy: Flow can be observed at 125°C. Birefringence persists till 134°C.

Thermal behaviour: The t.m.a. softening point is 115°C. The d.s.c. thermogram is qualitatively similar to that reported for SEB-5 (Figure 3), with T_1 at 114 and T_2 and 129°C. However, the exothermic peak area between T_1 and T_2 is much larger than for SEB-5 and the two transition enthalpies are of comparable magnitude for heating rates below 20°C/min. For a heating rate of 20°C/min $\Delta H_1 = 18.8$ J/g, $\Delta H_2 = 2.09$ J/g and the exotherm between T_1 and T_2 vanishes.

The X-ray pattern of SEB-7 (annealed at a temperature slightly above its softening point of 115°C) gives a multiplicity of X-ray lines almost up to its isotropic transition temperature. At 135°C, only a diffuse halo at 4.5 Å persists.

3. *SUC-5: poly(bisethylenoxy-p,p'-diphenylsuccinate)*

Method of synthesis: Melt polymerization at 230°-235°C in the presence of litharge.

Solubility: Soluble in *m*-cresol, slightly soluble in hot diacid trichloroethane.

Viscosity: $\eta_{red}^{30} = 0.28$ dl g⁻¹ (0.2% solution in 1:1 v/v *m*-cresol and trichloroethane).

Microscopy: Birefringent up to 201°C; observable flow at 196°C.

Thermal behaviour: A t.m.a. softening temperature was found at 183°C. The unannealed sample shows two d.s.c. transitions: $T_1 = 191^\circ\text{C}$ ($\Delta H_1 = 44.38$ J/g) and $T_2 = 196^\circ\text{C}$ ($\Delta H_2 = 25.96$ J/g). The X-ray pattern of SUC-5 is similar to those of SEB-5 and SEB-7.

(C) Crystalline polymers

The polymers poly(*p,p'*-diphenylsuccinate) (SUC-2) and poly(*p,p'*-diphenyl-3-methyladipate) (MAA-2) were prepared by interfacial polycondensation between 4,4'-bisphenol and the corresponding acid chloride.

The polymer SUC-2 is sparsely soluble in *m*-cresol and insoluble in other common solvents; MAA-2 is soluble in *m*-cresol and chloroethane. The inherent viscosity of MAA-2 was found: $\eta_{inh}^{31.9} = 0.40$ dl g⁻¹ (1:1 v/v *m*-cresol and 1,1,2-trichloroethane). The polymers showed neither d.s.c. transitions nor t.m.a. softening point and decomposed before melting could be observed. Both were birefringent and strongly crystalline.

(D) Model compounds

In Table 6 are listed transition temperatures and enthalpies for three model compounds synthesized following the method described in the Experimental section. The value of ΔH_1 represents the enthalpy measured for the first transition, crystal \rightarrow mesophase, for model compound I and polymers SEB-2, SEB-5 and SEB-7. Model compounds II and III do not display a mesophase and ΔH_1 is simply the measured value of the enthalpy change corresponding to the crystal \rightarrow isotropic phase transition.

We have used the ratio (ΔH_1 polymer)/(ΔH_1 model compound) as a rough measure of the degree of crystallinity W_c of the polymer.

The units, J mol⁻¹ of backbone atoms¹⁸, are used to eliminate the effect of different lengths of structural units. Assuming the validity of the above approach, we can estimate the degree of crystallinity as ranging from some 35%, in the case of SEB-7, to above 55% in the case of SEB-2.

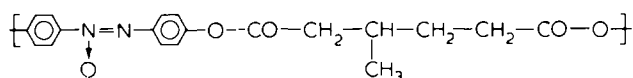
DISCUSSION

Phase transition data for polymers investigated here are summarized in Table 7.

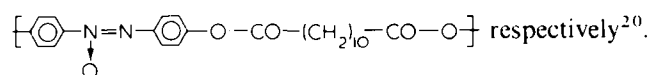
Table 7 Summary of phase transition data

Polymer	No. of atoms in spacer unit	T_1 (°C)	T_2 (°C)	Nature of mesophase
SUC-2	6	Polymer decomposes before melting		
MAA-2	8	Polymer decomposes before melting		
SEB-1	12	201	230–245	smectic
SEB-2	12	202	262	smectic
SUC-5	12	191	196	potentially nematic
SEB-5	18	155	163	potentially nematic
SEB-7	18	114	129	potentially nematic
MAA-8	8	221	295	nematic
DDA-8	14	216	265	nematic

Polymers MAA-8 and DDA-8¹⁹ are:



and



Influence of length of spacer on phase transition temperatures is illustrated by the difference between SUC-2, MAA-2 and SEB-2, in which the mesogenic unit is a biphenyl moiety. Influence of the nature of the mesogenic unit can be observed by comparison of polymers MAA-2 and MAA-8; in the former rigidity of the biphenyl mesogene leads to decomposition prior to melting, in the latter influence of the nematogenic azoxybenzene moiety leads to a nematic range of some 70°C.

Length of spacer and nature of the mesogenic moiety are clearly important. In addition, the striking difference in behaviour between SEB-2 and SUC-5 suggests the influence of other structural parameters. Polymers SEB-2 and SUC-5 both have a biphenyl core and 12 atoms in the spacer unit. SEB-2, in which the ester group is directly linked to the biphenyl moiety, has a mesophase extending over a temperature range of approximately 65°C. In SUC-5, where the ester group is three atoms removed from the biphenyl core, the mesophase has collapsed to a narrow interval.

A similar effect is observed for SEB-5 and SEB-7. On the basis of d.s.c., X-ray diffraction and magnetic birefringence experiments, polymers SEB-5, SEB-7 and SUC-5 are considered as potentially nematic. The competition of crystallization and of mesophase formation in SEB-7 is described elsewhere²¹.

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