Thermotropic homopolyesters: 5. Investigation of the smectic phase of polyesters based on *p,p'*-bibenzoic acid

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We report a study of the mesophases of the homologous series of polymers prepared from *p,p'*-bibenzoic acid and the tetra-, hexa-, octa-, and decamethylene glycols. These polymers are designated BB*n*, where *n* is the number of methylene units in the diol. The BB4 and BB6 polymers form a thermotropic smectic phase which was independently identified as S_A by mutual miscibility studies with a known low molecular weight mesogen, TBBA, and by X-ray diffraction studies of oriented samples. The enthalpy change for the smectic–isotropic transition is only 1.4 Kcal mol^{-1} a value consistent with a smectic phase of low order. The smectic layer spacing is shorter than the fully extended length of the repeating unit for both BB4 and BB6. Low molecular weight samples of BB6 exhibit three crystal modifications. The two higher temperature forms have the same *c*-axis spacing as the smectic layer spacing, 18.7 Å, while the polymorph stable at room temperature has a fibre repeat of 32 Å, indicating a still smaller distance per repeating unit, 16 Å. All of these values are smaller than the 20 Å length of the fully extended repeating unit. Shearing the smectic hase of BB6 polymers having $\eta_{inh} < 0.45$ dL/g produces a highly oriented sample in which the repeating units are perpendicular to the direction of flow. Shear of the smectic phases of polymers having higher intrinsic viscosities breaks up the smectic structure, and leads to less perfect orientation of the molecules parallel to the shear direction.

Keywords Thermotropic smectic polyesters; mutual miscibility; orientation; shear; thermodynamics of transitions: X-ray diffraction

INTRODUCTION

In 1975 de Gennes[1] suggested that polymers exhibiting thermotropic mesomorphism, and having controlled melting temperatures, might be prepared by incorporating a rigid and a flexible segment in the repeating unit. In the same year Roviello and Sirigu[2] reported the properties of three polyesters based on *p,p'*-dimethylbenzalazine, perhaps the first example of this class of polymer. Since that time a number of laboratories have reported the synthesis and characterization of a variety of semiflexible polymers of this type that exhibit thermotropic mesomorphism. Previous papers in this series described polyesters based on 4,4'-dihydroxybiphenyl[3,4], and 4'-hydroxybiphenyl-4-hydroxycinnamate[5]. These polymers have melting temperatures in a convenient range for study, and are interesting for the variety of mesophases they exhibit.

Part of the impetus for the study of nematogenic polymers undoubtedly arises from the possibility of preparing high modulus fibres from a thermotropic nematic phase. The polymers described in the first two papers of this series were spun[6], but gave poor fibre properties. Two explanations can be offered for this outcome.

Polymers that form a lyotropic nematic phase at moderate concentrations must have highly extended chain conformations, as demonstrated by Flory's classical treatment[7] of semi-flexible polymer that form a lyotropic nematic phase. Flory noted that parallelism in the nematic phase imposes the constraint that any bending of the adjacent chains occurs in a correlated fashion. Hence, he assumed that semi-flexible molecules will adopt the lowest energy, rodlike conformation in a lyotropic nematic phase. By contrast, the treatment of Flory and Ronca[8] indicated that a thermotropic nematic phase is possible only if the axial ratio is below a critical limit. Thus, polymers forming thermotropic nematic phases are characterized by smaller persistence lengths than those which form only lyotropic phases. Whether such semi-flexible molecules adopt a rodlike form in a thermotropic nematic phase is therefore more problematical. We found[4] that for the poly(*p,p'*-biphenylene azelates), in common with small molecule nematogens, the entropy change at the crystal–nematic transition is much larger than that at the nematic–isotropic transition. The opposite outcome would have been expected if the molecules were rodlike in the nematic phase. Hence, we conclude that semi-flexible polymers are not rodlike in a thermotropic nematic phase. This circumstance will limit the perfection of crystallite orientation in fibres spun from these polymers, and lead to poorer initial modulus and tensile properties.

Secondly, it has been our experience that those semi-flexible polymers that form a thermotropic nematic phase characteristically exhibit low crystallinity and poor crystal perfection, while polymers forming a thermotropic smectic phase crystallize more completely and with higher

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crystal perfection. Although the reason for this striking difference remains obscure, the low crystallinity and poor crystal perfection of this type of nematogenic polymer is undesirable if the objective is to obtain high modulus fibre properties.

Semi-flexible polymers may exhibit various types of thermotropic smectic phases. For example, the polyesters based on 4,4'-dihydroxybiphenyl form a smectic phase when the number of methylene units is even, and predominantly a nematic phase when the number is odd[3]. Thus, poly(*p,p'*-biphenylene sebecate) forms a highly ordered S_H phase, while the azelate exhibits a nematic phase, and an unidentified type of smectic phase of lower order[4]. We earlier reported[9] that some of the polyesters prepared from *p,p'*-bibenzoic acid and aliphatic diols exhibit thermotropic smectic phases of undetermined type. Meurisse *et al.*[10] also reported a study of these polymers, as well as the poly(terphenyl-4,4''-dicarboxylates) and poly(stilbene dicarboxylates). Here we present the results of a more extensive investigation of the four polymers based on *p,p'*-bibenzoic acid and the diols $HO{-}(CH_2)_n{-}OH$ with $n=4$, 6, 8 and 10. These polymers are designated BB*n*, where *n* is the number of methylene units in the diol.

EXPERIMENTAL

Some of the polymer samples used in this investigation are the same as those used in the previous study[9]. A series of BB6 polymers, and a BB8 sample, were newly synthesized. These polymers were prepared by the procedure previously described[9] from the diethyl *p,p'*-bibenzoate and the appropriate diol using isopropyl titanate as a catalyst. Inherent viscosities were determined at 25°C using 0.50 g/dL solutions in a 60/40 mixture by weight of phenol and tetrachloroethane. Differential scanning calorimetry (d.s.c.) data were collected using a DuPont 1090 at a scanning rate of 10°C/min unless otherwise noted. Sample weights were in the range of 5 to 10 mg, and indium was used for calibration. Texture studies were performed with an Olympus BH-2 polarizing microscope equipped with a Mettler FP52 hot stage. Photomicrographs at an original magnification of 60 × were taken using a Nikon PMF photo attachment. X-ray diffraction patterns were recorded with a flat plate camera using nickel filtered CuKα radiation. A modified Koefler hot stage was used to collect diffraction data at elevated temperatures. The sample temperature could be maintained to within about ±2°C, and was monitored with a chromel–alumel thermocouple using a Fluke Model 801BR differential DC voltmeter.

RESULTS

Differential scanning calorimetry

Results of the d.s.c. measurements on the different polymers are collected in *Table 1*. Column 2 lists the inherent viscosities of the samples, while columns 3–6 give the transition temperatures. We have recorded the temperature corresponding to the extremum of an endotherm in the heating curve, or of an exotherm in the cooling curve. In general, the heating curves exhibit several endotherms. These are labelled t_1, t_2 and t_3 (usually in the order of appearance of the endotherms in the heating curve), while t_i refers to the temperature of the transition to the isotropic state. The first transition for polymer BB4

Table 1 Transition temperatures and enthalpies for poly(*p,p'*-bibenzoates)

Polymer	η_{inh}	t_1	t_2	t_3	t_i	ΔH_1	ΔH_2	ΔH_3	ΔH_i	ΔH_{total}
BB4	0.28		273 (246)	–	296 (293)	–	1.05	–	1.65	2.70
BB6-1'	0.21	181	195 (169)	204	216 (207)	0.50	⟵ 2.30 ⟶		1.45	4.25
BB6-2'	0.42	183 (142)	201	209 (191)	219 (203)	0.40	⟵ 1.85 ⟶		1.50	3.75
BB6-1	0.21	190	199 (188)	205 (192)[b]	213	–	–		–	4.90
BB6-2	0.25	194	204 (186)	210 (193)	219	–	–		–	4.45
BB6-3	0.34	200 (186)	213 (197)		220 (207)	0.55	⟵ 2.15 ⟶		1.40	4.10
BB6-4	0.39	200 (178)	214 (197)		218 (207)	0.60	⟵ 2.10 ⟶		1.30	4.00
BB6-5	0.46	192 (170)	209 (190)		215 (198)	0.50	⟵ 1.95 ⟶		1.35	3.80
BB6-6	0.50	192 (173)	207 (188)		215 (207)	0.40	⟵ 1.90 ⟶		1.30	3.60
BB8	0.23	111 (95)	166[b] (153)	176 (160)	188	0.35	⟵	3.75	⟶	4.10
BB10	0.18	96 (83)	135[a]	154[a]	159 (141)	0.30	⟵	4.45	⟶	4.75

[a] Very small peak
[b] Broad shoulder

is placed in the column t_2 due to the magnitude of its enthalphy change. The temperatures of the corresponding exotherms in the cooling curves are listed in parentheses. In general, there are fewer exotherms than the number of endotherms, so placement of the former temperatures in the columns is somewhat arbitrary. It is even possible that some of the phases encountered on cooling have no counterpart in the heating curve, but we have assumed this not to be the case. The same subscript notation is used to designate the enthalpy changes in columns 7–10, while $\Delta H_{\mathrm{total}}$ in column 11 refers to the sum of the enthalpy changes on going from the semi-crystalline sample at room temperature to the isotropic liquid state. The heating and cooling curves usually gave $\Delta H_{\mathrm{total}}$ values which agreed within the experimental error. In several cases the peaks overlapped so extensively that values of ΔH for the individual transitions could not be determined reliably. The enthalpy changes are given in the units Kcal mol^{-1} of repeating units.

The endotherm temperatures observed for these polymers appear plotted in *Figure 1* against the number, *n*, of methylene units in the diol. Polymer BB4 exhibits only two transitions, while four transitions are found for the other polymers. As expected, the transition temperatures decrease smoothly, and rather strongly, with increasing length of the flexible segment. It should be noted that this study involves only polymers having an even number of methylene units in the diol. These have higher transition temperatures than the members of the odd-numbered series, as shown in our earlier study[9].

Figure 2 illustrates the dependence of the endotherm temperatures for the BB6 series with inherent viscosity, η_{inh}. The two intermediate transitions merge for BB6-3 and polymers of higher inherent viscosity. Examination of column 2 reveals that most of the *p,p'*-biphenylene polymers have low inhereint viscosities. Hence, it is likely that fewer transitions would have been encountered if only polymers of higher inherent viscosity had been studied. Also, our previous experience has indicated[4] that is is more difficult to obtain reliable ΔH values for polymer samples of low η_{inh}. The temperatures of the three transitions show a decreasing trend for $\eta_{\mathrm{inh}} > 0.35$ dL/g. This is unexpected, since the transition temperatures increased toward asymptotic limits for both the even and odd series of polyesters based on 4,4'-dihydroxybiphenyl[3], and those prepared from 4'-hydroxyphenyl-4-hydroxycinnamate[5].

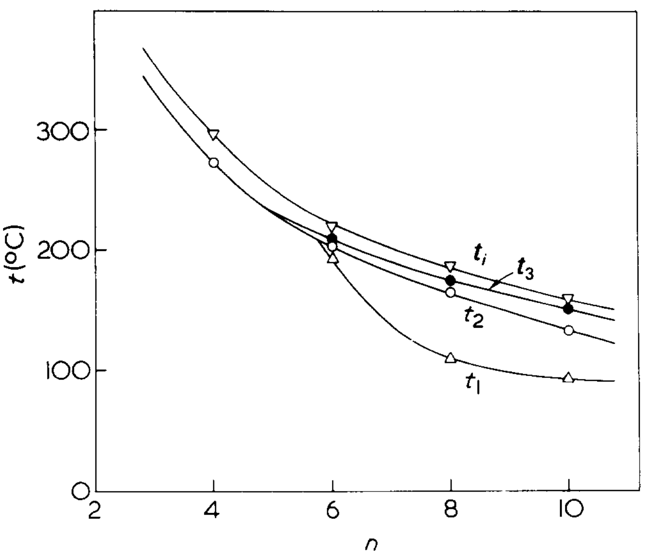


Figure 1 Transition temperatures observed on heating the poly(*p,p'*-bibenzoates) vs. the number of methylene units in the diol

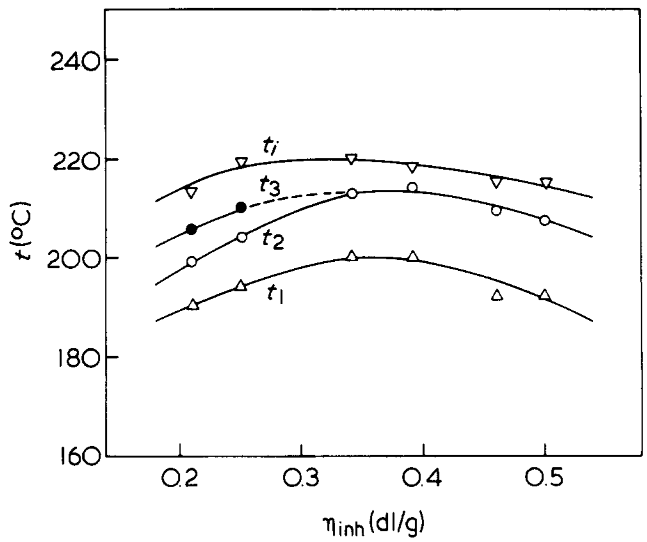


Figure 2 Dependence of transition temperatures for the BB6 polymers upon inherent viscosity

The enthalpy changes, ΔH, measured for the *p,p'*-bibenzoate polymers appear in *Figure 3* plotted against the number of methylene units in the diol. Similarly, the ΔH values for the BB6 series appear plotted against η_{inh} in *Figure 4*. The two polymers appearing in the earlier study are labelled BB6-1' and BB6-2' in *Table 1*. These differ significantly in thermal properties from the polymers more recently synthesized. As shown in *Table 1*, the temperature t_1 is lower for the earlier polymers, and BB6-2' shows a fourth endotherm in its heating curve which is not found for polymers in the unprimed series having that η_{inh}. For this reason, the earlier polymers are not included in *Figures 2* and *4*. The different thermal behaviour might be due to differences in the molecular weight distribution, or to the presence of some impurity in the monomers. Our d.s.c. results stand in reasonable accord with those reported by Meurisse *et al.*[10]. They observed two endotherms in the heating curve of BB4, and four in the case of a BB6 sample having $\eta_{\mathrm{inh}} = 0.94$ dL/g. This latter observation is more in line with the results reported here for the earlier BB6 samples designated in *Table 1* with a prime.

Figures 3 and *4* indicate that $\Delta H_{\mathrm{total}}$ increases substantially as the number of methylene units in the diol is increased, and decreases for the BB6 series with η_{inh}. These trends probably parallel changes in the degree of crystallinity of the samples at room temperature. If so, the trend for the BB6 polymers with η_{inh} is the reverse of that reported for the PB7 and PB8 series based on 4,4'-dihydroxybiphenyl. One can also see from the Figures that ΔH_1 is small (about 0.5 Kcal mol^{-1}), and decreases somewhat with *n*, and with η_{inh} for the BB6 series. This transition was not noticed in our earlier study[9], probably due to the lower sensitivity of the Perkin–Elmer DSC-IB used for those measurements. The X-ray diffraction data to be presented below will demonstrate that BB6 exhibits several polymorphic crystalline forms. Hence, we assign the transition at t_1 to a $K_\alpha \rightarrow K_\beta$ transition involving two crystal forms. In view of the small magnitude of ΔH_1, and the fact that ΔH_1 does not parallel the change in the degree of crystallinity with n, the samples cooled to room temperature may be mixtures of the K_α and K_β forms. As seen in *Figure 1*, the temperature span between t_2 and t_1 is broad for BB8, but quite narrow for BB6, while BB4 exhibits only one crystal modification. The (t_2-t_1) difference also increases with η_{inh} for the BB6 series, as indicated in *Figure 2*.

The enthalpy change at the smectic-isotropic transition, ΔH_i, averages about 1.4 Kcal mol^{-1}. This is much smaller than the average value, 4.8 Kcal mol^{-1}, reported[4] for the S_H phase of the polymers PB6, PB8, PB10 and PB12 based on 4,4′-dihydroxybiphenyl. It is also smaller than the values for the corresponding transition in the PB7 series, which increased from 1.9 to 2.25 Kcal mol^{-1} as η_{inh} ranged from 0.45 to 1.90 dL/g. These comparisons indicate that the smectic phase of the *p,p*′-bibenzoate esters is one of low order.

The transitions at t_2 and t_3 may represent transformations through two additional crystal forms, followed by melting to form the smectic phase. Unfortunately, these endotherms overlap so severely for BB6-1 and BB6-2 that the separate areas could not be measured. We cannot be certain which crystal modification is involved for BB6-3 and the higher polymers of that series, nor for BB4. We have rather arbitrarily assigned these as $K_\beta \rightarrow S$ in both cases.

Identification of the type of smectic polymorph

Eleven smectic polymorphs have been identified for small molecule mesogens using the method of mutual miscibility developed by Sackmann and coworkers[11,12]. These polymorphs are designated by the symbols S_A through S_K in the chronological order of their identification. The same procedure has been used successfully to identify nematic[13], S_A[14], and S_C[15] phases in polymers, but we were unsuccessful in our attempt[4] to identify the S_H phase of poly(*p*-biphenylene sebecate) by this procedure. It appears that, for the identification of polymeric mesophases, mutual miscibility is the method of choice for smectic phases of low order, while X-ray diffraction may be required for the more ordered smectic phases.

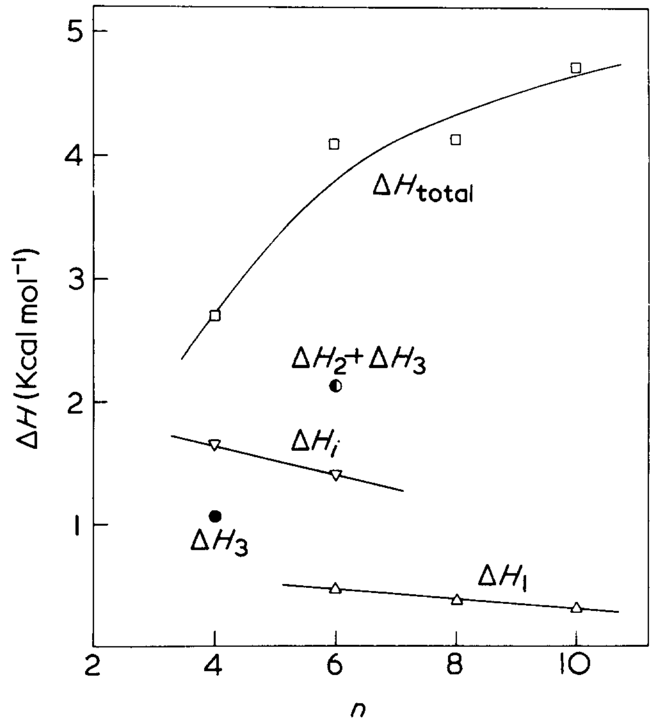


Figure 3 Enthalpy changes for the poly(*p,p*′-bibenzoates) plotted as a function of the number of methylene units in the diol

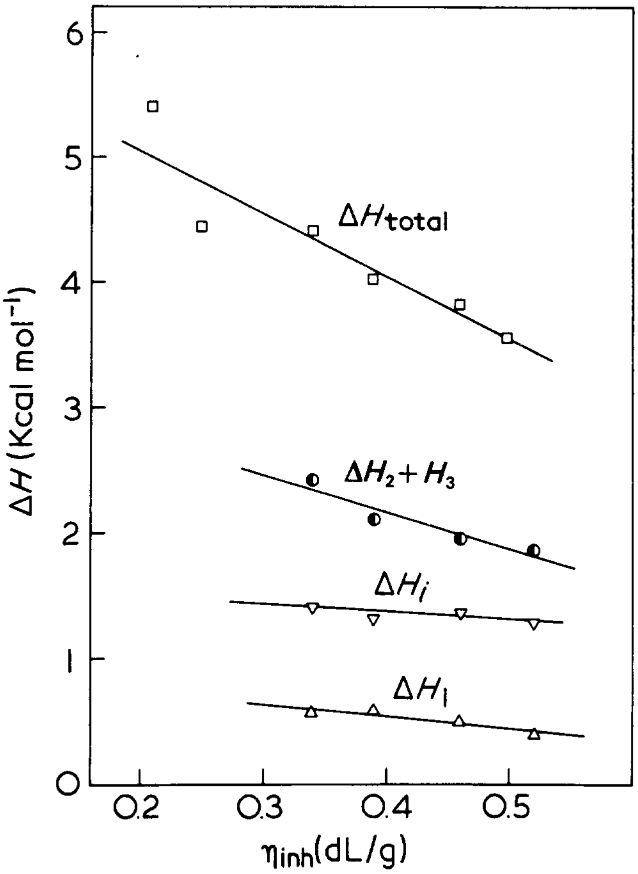


Figure 4 Transition enthalpies vs. inherent viscosity for the BB6 series

The d.s.c. data suggest the smectic phase in this case is one of low order, hence we have applied the mutual miscibility method using terephthalidene-bis(4-n-butylaniline), TBBA, as a known mesogen. This exhibits, on heating, the successive mesophases S_H, S_G, S_C, S_A, and nematic. Weighed mixtures of BB6-1′ and TBBA were heated to the isotropic state, and the phase boundaries were determined on cooling, either by observing texture changes in the polarizing microscope or from the location of exotherms in the cooling curves. The binary phase diagram shown in *Figure 5* clearly indicates that the smectic type is S_A, since this phase is miscible over the entire composition range.

The small magnitude of the enthalpy change accompanying the smectic–isotropic transition is compatible with this assignment, as are the textures observed in the polarizing microscope. When a sample of BB6-1′ was cooled from the isotropic phase to about 207°C, a birefringent phase appeared after several seconds in the form of very small spheres, as illustrated in *Figure 6a*. After a few minutes at this temperature, the spheres coalesced to form small rod-shaped particles, as shown in

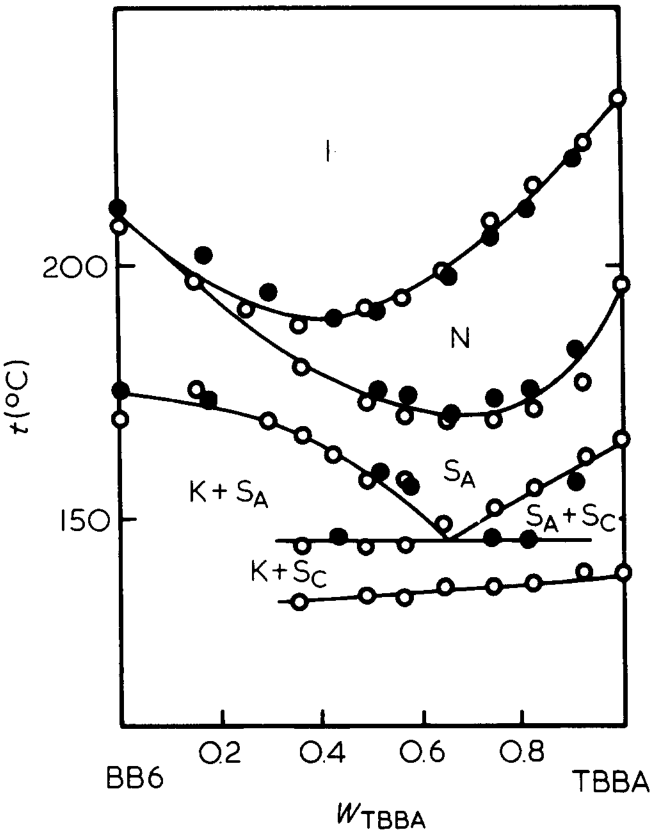


Figure 5 Phase diagram for the binary system BB6-1′-TBBA as determined on cooling by d.s.c. (open circles) and texture changes (filled circles)

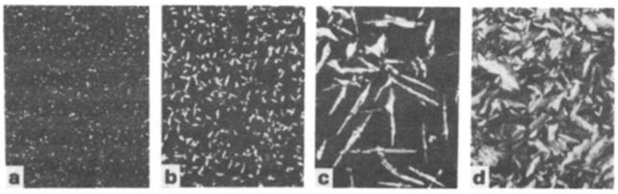


Figure 6 Development of smectic texture on cooling BB6-1′ to 207°C (left to right): (a) first appearance of birefringent spherical particles, (b) coalescence of spheres to form rod-shaped particles, (c) development of bâtonnets, and (d) fan-shaped texture on cooling sample to 195°C

Figure 6b, which transformed over a longer period of time to well-formed bâtonnets (*Figure 6c*). When the same sample was cooled to 192°C, the fan-shaped texture shown in *Figure 6d* appeared. Bâtonnets and the fan-shaped texture are characteristic of the S_A and S_C phases. Similar bâtonnets were observed for BB4, but not for BB-2′, BB6-5, BB6-6 or BB8. The higher viscosity of the smectic phases of the BB6 polymers having η_{inh} above 0.4 dL/g evidently precludes formation of bâtonnets, while for BB8 the small separation of the transition temperatures on cooling may have been responsible for our failure to observe bâtonnets in that case. Cooling BB8 to 110°C produced a sample showing no fluidity. This is presumably the K_β polymorph.

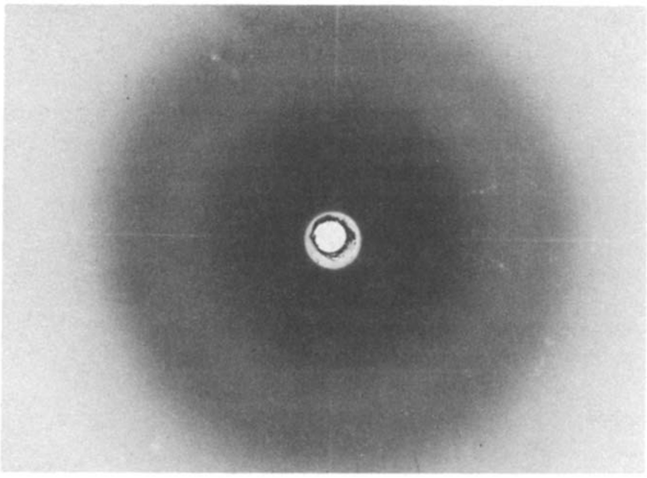


Figure 7 X-ray diffraction pattern recorded for the smectic phase of BB6-1′ on cooling to 185°C

Meurisse *et al.*[10] inferred from texture studies that the bibenzoate polyesters form some type of smectic phase. They reported only a poorly defined texture for BB2, a focal-conic texture for BB4, and bâtonnets and a focal-conic texture for BB6. These results are compatible with the smectic polymorphs S_A and S_C. They also reported that transition stripes appeared in the focal conic texture of a BB6 sample when it was cooled below 200°–205°C, suggesting the existence of a second smectic modification. The phase diagram shown in *Figure 5* gives no evidence for another smectic form; however, it should be noted that their sample had a higher inherent viscosity than any of ours.

X-ray diffraction

Both the crystalline and smectic phases of the poly(*p,p*′-bibenzoates) were examined by X-ray diffraction. A sample of BB6-1′ held in a Mark capillary was cooled from the isotropic phase to 185°C, and the diffraction pattern of the smectic phase shown in *Figure 7* was recorded at that temperature. This consists of a weak, but sharp, inner reflection and a diffuse outer halo. The inner ring, which was barely visible in the original photograph, became more evident in an oriented smectic sample produced by quenching. The sharp inner ring corresponds to the spacing of the layers in the smectic phase, while the diffuse outer halo indicates that the lateral arrangement of the molecules is disordered. These features are typical of the S_A, S_C and S_F polymorphic forms. The repeating units are normal to the layers in the S_A structure, and tilted in the S_C and S_F polymorphs. As shown in column 1 of *Table 2*, the inner reflection corresponds to a smectic layer spacing of 18.7 Å, while the fully extended length of the repeating unit is 20.0 Å. Hence, either the repeating units are tilted with respect to the layer normal, or the hydrocarbon portion of the repeating unit does not have its fully extended all-*trans* conformation. The miscibility study indicated that the smectic type is S_A, and the diffraction data obtained for an oriented sample (to be discussed below) offers independent evidence that the repeating units are normal to the smectic layers. The 15.5 Å smectic spacing determined for BB4 is also less than the 17.5 Å length of the fully extended repeating unit. Hence, some of

Table 2 Bragg spacings (Å) of polymer BB6-1′

Smectic phase at 185°C	Quenched from 190°C	Annealed at 190°C after quench	Slow cooled from 190°C	Sample at 25°C after shearing smectic phase
18.7	18.7 s	18.8 m		
		7.29 w	7.31 m	7.32 m ($l = 2$)
	6.47 w			6.46 vw ($l = 1$)
		6.11 vvw		
		5.72 w	5.72 m	5.72 m ($l = 0$)
	5.52 w	5.51 m		
	5.14 w	5.12 m		
~4.8		4.89 m	4.92 s	4.92 s ($l = 2$)
	4.51 w	4.49 w	4.51 m	4.50 m ($l = 0,3$)
	4.21 m			
		3.87 m	3.89 m	3.89 m ($l = 0,1$)
	3.68 w	3.63 s	3.67 s	3.66 s ($l = 0,1$)
		3.48 vw	3.50 w	3.49 w ($l = 0,1$)
	3.32 vw			
		3.08 vvw	3.10 w	3.10 w ($l = 0,1$)
			3.01 vvw	

The symbols are: s = strong, m = medium, w = weak, vw = very weak. etc.

the bonds in the methylene chains of both BB4 and BB6 must be in the *gauche* rotational state. The outer halos of both BB4 and BB6-1′ correspond to Bragg spacings of approximately 4.8 Å.

Bosio *et al.*[15] report a spacing of 21.7 Å for the S_A phase of poly(hexamethylene terphenyl-4,4″-dicarboxylate), a polymer which they designate as T6. This is somewhat smaller than the fully extended length of that repeating unit, indicating that the alkyl portion of that polyester departs from the all *trans* conformation.

We had earlier suggested[4] that the observation of an even–odd alteration of the isotropization temperatures for an homologous series might indicate that the methylene chain takes the all-*trans* conformation in the mesophase. Since the t_i values of the poly(p,p'-bibenzoates) exhibit such an alternation, these diffraction data demonstrate that this is not a valid assumption.

Diffraction data obtained for the poly(p,p'-bibenzoates) at room temperature consist of a number of sharp reflections, indicating a well-ordered crystal structure and a relatively high degree of crystallinity. This furnishes another example supporting our earlier observation that semi-flexible polymers that are smectogenic have higher crystallinity, and better crystalline perfection, than nematogenic polymers.

We next sought evidence for the existence of various crystal forms by varying the cooling rate or annealing conditions. *Figure 8a* illustrates the diffraction pattern obtained for a BB6-1′ sample which had been cooled to 190°C to produce the smectic phase and then rapidly quenched in ice water. The fact that the pattern shows several rings indicates that it is crystalline, although the intensities of the rings are rather weak. The Bragg spacings measured for these rings are given in column 2 of *Table 2*. The 18.7 Å spacing of the smectic layers is retained, and seven additional rings appear. We assume this represents the highest temperature K_γ modification.

When this sample was heated at 190°C for 30 min the diffraction pattern shown in *Figure 8b* was recorded. Since this temperature is between t_1 and t_2, this should represent the K_β crystal modification. Comparison of *Figures 8a* and *8b* shows that annealing has increased the crystallinity, as expected, but it has also altered the crystal modification. This is indicated by comparison of the Bragg spacings listed in columns 2 and 3 of *Table 2*. The longer spacing is still evident, but the 6.46, 4.21 and 3.32 Å spacings of the quenched sample are no longer present, and the annealed sample exhibits additional rings with spacings of 7.29, 5.72, 4.89, 3.87, 3.48 and 3.08 Å.

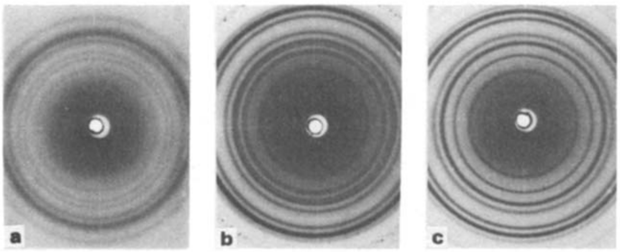


Figure 8 Diffraction diagrams of various crystal modifications of BB6-1′: (a) (left) K_γ formed on quenching from 190°C into ice water, (b) (middle) K_β obtained on annealing the quenched sample at 190°C for 30 min, (c) (right) K_α modification formed upon slow cooling from 190°C

Finally, *Figure 8c* shows the diffraction pattern of a sample of the same polymer which had been slowly cooled from 190°C. We believe this should represent the K_α modification, or perhaps a mixture of the K_α and K_β forms. The long period spacing observed for both the quenched and annealed samples is no longer evident, and the reflections at 6.11, 5.51 and 5.12 Å in the annealed sample are not present, while an additional inner ring at 3.01 Å is observed. As will be indicated below, it was possible to determine the fibre identity period of an oriented sample in the low temperature crystal form. This value, 32 Å, probably represents two repeating units, so each repeating unit contributes only 16 Å to the fibre repeat period. This is less than the 18.7 Å spacing of the smectic phase, and is substantially smaller than the 20 Å length of the fully extended repeating unit.

The fibre repeat distance reported by Bosio *et al.*[14] for T2 indicates the repeating unit is fully extended, but the fibre repeats of T4, T6 and T10 are shorter than the fully extended lengths of the corresponding repeating units. They point out that these observations are somewhat similar to those made for the terephthalate polyesters, which have been extensively studied[16-25]. The methylene portions of the 2GT and 6GT polyesters are found to be in the all *trans* conformation, while those of 3GT, 4GT and 5GT contain some *gauche* conformers. Both 4GT and 5GT are transformed to a second, all *trans* crystal modification by strain.

Figure 9 illustrates how the exotherm temperatures in the cooling curve of BB6-1′ depend upon the cooling rate (plotted on a logarithmic scale). It is probable that the K_β crystal modification nucleates from the smectic phase under these conditions. The transition from the low order smectic S_A phase to the crystal exhibits a larger supercooling, and the supercooling is more dependent upon the cooling rate, than the transition from the isotropic to the smectic phase.

Orientation of the smectic A phase in shear flow

In the smectic S_A phase of a low molecular weight compound, the lath-like molecules are arranged in planar layers, and their long axes tend to be perpendicular to the layers. Rotational motion of the molecules is fairly free, there is no long range order within any layer, and the position of molecules in successive layers is uncorrelated. Hence, apart from the constraints imposed by the layered structure, the molecules are in a liquid-like environment. The diffraction pattern of the S_A phase of BB6-1′ suggests a similar structure. The sharp inner ring indicates that the repeating units are arranged in a layer structure, while the diffuse outer halo implies that the lateral packing of chains within the layers has no long range order.

In the small molecule system the layer boundaries mark the locations of ends of the molecules. No covalent bonds extend through these boundaries, so that one layer easily flows past its neighbours. Shear flow should orient the layers parallel to the shearing direction, leaving the molecules perpendicular to that direction. By contrast, the repeating units are the building blocks of the polymeric S_A phase, and each polymer molecule must pass through many smectic layers. The chain ends are defects in the polymeric mesophase. Even if they congregate at the layer boundaries, the broad molecular weight distribution makes it quite unlikely that any pair of molecules will have their chain ends in the same two layers. Hence, unlike the small molecule case, motion of one layer of a polymeric S_A phase with respect to its neighbours will be highly impeded. We were surprised to find that fibres spun from low molecular weight poly(*p*,*p*′-biphenylazelate) showed a preferred crystallite orientation perpendicular to the fibre axis[6]. We therefore investigated the effect of shear flow upon a polymeric smectic phase.

A sample of BB6-1′ was placed on a microscope slide, heated above t_i, cooled into the smectic range, and covered with a cover slip. In time the sample developed a fan-shaped texture, as seen in the polarizing microscope, similar to that shown in *Figure 6d*. Shear was then applied by moving the cover slip. Flow occurred as easily as in the case of a nematic phase. The fan-shaped texture was destroyed, but a few moments after the flow ceased, the texture shown in *Figure 10a* appeared. This texture, resembling a cluster of bâtonnets with their long axes perpendicular to the shearing direction, did not disappear over a period of thirty minutes (at constant temperature). When the sheared sample was crystallized by slow cooling to room temperature, long cracks appeared perpendicular to the flow direction, as illustrated in *Figure 10b*. In order to investigate the crystallite orientation, a rectangular sample 1 × 1 × 0.02 mm was stripped from the glass surface and X-ray diffraction patterns were recorded successively with the beam entering along three mutually perpendicular directions.

Figure 11a shows the diffraction pattern obtained through face A in the sketch (when the incident beam was perpendicular to the film surface). The direction of flow is horizontal, and the sample thickness is 20 μm. This is a well oriented fibre-like pattern showing many reflections on the equator and on the layer lines. The Bragg spacings for this sample are listed in column 5 of *Table 2*. From this photograph one can determine that the fibre repeat distance is 32 Å, as mentioned earlier. It also demonstrates that the chains are perpendicular to the direction of the smectic layer planes, a further con-

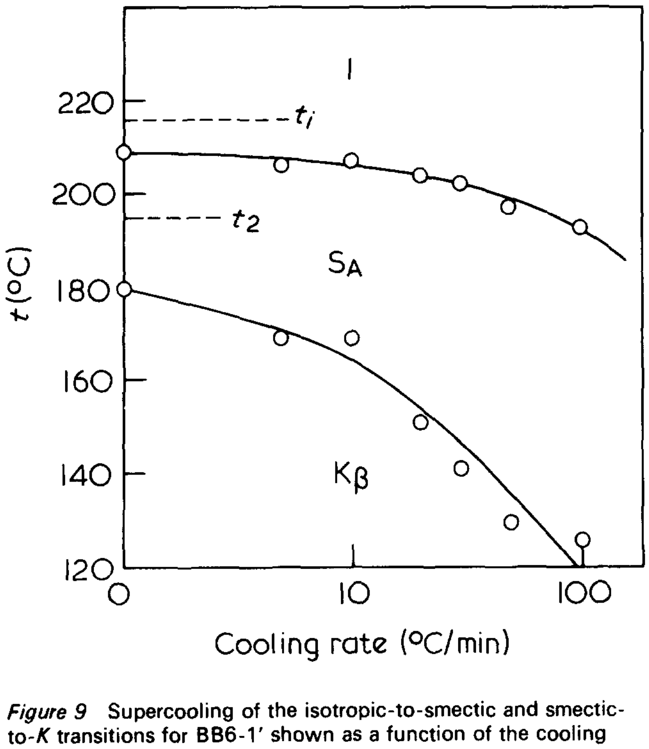


Figure 9 Supercooling of the isotropic-to-smectic and smectic-to-*K* transitions for BB6-1′ shown as a function of the cooling rate (logarithmic scale)

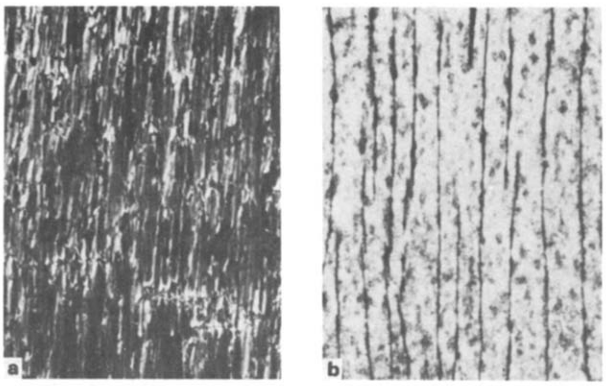


Figure 10 Effect of shearing the smectic phase of BB6-1′: (a) (left) bâtonnet-like texture observed in the sheared smectic at 192°C, (b) (right) crystallized sample at 25°C. (Shearing direction is horizontal in both photographs)

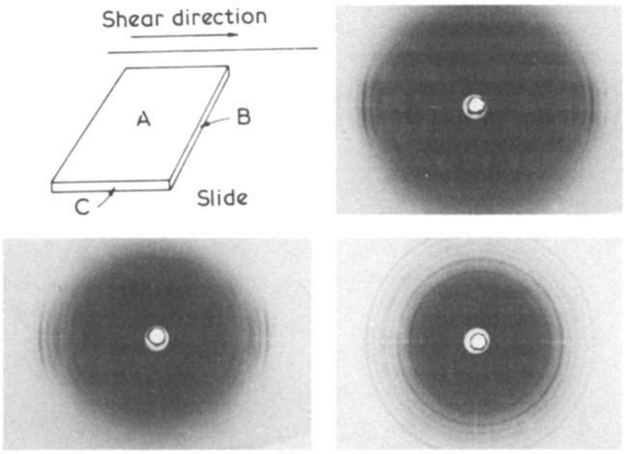


Figure 11 Diffraction patterns of a 20 μm thick sheared smectic phase after crystallization: (a) (top right) through face A, (b) (bottom left) through face B, (c) (bottom right) through face C

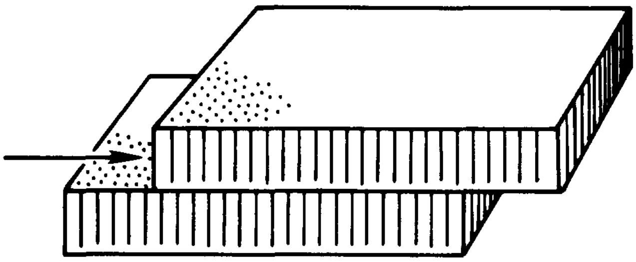
firmation that the smectic type is S_A. Finally, the high degree of orientation of the chains perpendicular to the direction of flow explains the ease of crack growth parallel to the chain direction.

Figure 11b represents the diffraction diagram of the same sample taken parallel to both the film surface and the direction of shear (beam entering face B). The pattern is similar to the previous one, but the arcs are longer, signifying less perfect alignment of the chains. Comparison of eight sheared smectic samples ranging in thickness from 10 to 50 μm indicates that, with increasing sample thickness, the orientation as measured through the A face is nearly constant, while that through the B face decreases. This follows from the dimishing tendency of the molecules to lie parallel to the glass surface for thicker samples. Only Debye–Sherrer rings are found in *Figure 11c*, which was recorded with the incident beam entering face C (parallel to the film surface and perpendicular to the shearing direction). This result indicates that, as expected, there is no preferred oriention in the plane perpendicular to the chain axes.

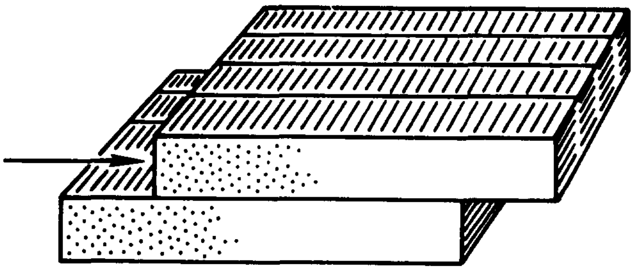
Polymer samples through BB6-4 ($\eta_{inh} = 0.39$ dL/g) gave a similar type of preferred orientation upon crystallization of the sheared smectic phase. BB6-5 and polymers having higher inherent viscosities showed a much weaker preferred alignment of the chains *parallel* to the shearing direction. This trend is similar to that observed in spun fibres of poly(p,p'-biphenylene azelate)[6]. A fibre spun from the polymer having $\eta_{inh} = 0.18$ dL/g showed chain orientation perpendicular to the fibre axis, while a weaker preferred orientation parallel to the fibre axis was observed when the polymer having $\eta_{inh} = 0.82$ dL/g was spun using a conical die. Shear of BB6-1$'$ in the isotropic state produced the expected alignment of molecules parallel to the shearing direction, although the degree of orientation is much less than that obtained by shearing the smectic phase.

Shear of both small molecule and polymeric smectic A phases produces what appears to be the same type of alignment, although the mechanism of shear flow must be different in the two cases. To explain this observation, we postulate that the chains initially have a preferred alignment parallel to the glass surface. For a thin sample (less than 50 μm) this preference extends, with some attenuation, throughout the sample thickness. Hence the smectic layers are predominately perpendicular to the glass surface, but their directions are random in the plane. Upon application of a shear stress, the smectic structure either rotates, or breaks up and reforms, so that the smectic layers are parallel to the shearing direction (but still perpendicular to the glass surface). Flow causes the formation of domains in the form of thin rectangular slabs. If the glass slide is taken to be horizontal, the thinnest dimension of the domain is the vertical one, while the width of the domain must be much larger than the smectic layer spacing. Since the molecules remain aligned horizontally, no covalent bonds join successive vertical layers. The molecules at the interface of two domains pass side-by-side, rather than end-to-end as in the case of flow of a small molecule smectic. These two situations are contrasted in the schematic drawing shown in *Figure 12*.

If an entire horizontal layer of the smetic sample moved uniformly, the connected nature of the smectic layers would play no role in the process. However, there must be some relative motion of one region of the sample with respect to its neighbours in the same horizontal plane. If the molecular weight is low enough, this requirement can be accommodated by creating flow domain boundaries by pulling chains out of the adjacent smectic structure. Since the lateral packing is liquid-like, the work to extract a chain end may not be prohibitive, and these chains can fold and re-enter the domain to which they are attached. Once such flow domains are formed, they can move quite easily along the shearing direction. Note that the lateral boundaries of the flow domain lie along the smectic layers in this case. If the molecules were aligned parallel to the flow direction, side-by-side passage of the molecules could still occur, but the lateral boundaries of the flow domains would now cross the smectic domains perpendicularly. Formation of such lateral boundaries would probably disrupt the smectic structure. Returning to the model



Flow of small molecule smectic A



Flow of polymeric smectic A

Figure 12 Schematic comparison of the flow of small molecule and smectic S_A phases shown in *Figure 12*, if the molecular weight is too high, the work to pull through the longer chain segments to create flow domain boundaries becomes too large, and the smectic structure is disrupted instead.

CONCLUSIONS

Various types of evidence lend support to the conclusion that poly-(hexamethylene-*p,p*′-bibenzoate) forms a thermotropic smectic S_A phase. The small enthalpy change for the smectic–isotropic transition, 1.4 Kcal mol^{-1}, is consistent with a smetic phase of low order. The bâtonnets and the fan-shaped texture observed in the polarizing microscope are characteristic of the S_A and S_C polymorphs. The X-ray diffraction patterns of unoriented samples is consistent with the low order smectic phases S_A, S_C and S_F. The mutual miscibility study with TBBA as a known mesogen unambiguously identifies the type as S_A, and this is independently confirmed by the X-ray diagram of an oriented sample.

Most of the poly(*p,p*′-bibenzoate) homologues exhibit in their heating curves two transitions in addition to the crystal–smectic and smectic–nematic transitions. The evidence presented indicates there are three crystal polymorphs for low molecular weight BB6 samples, which suggests that these additional transitions involve different crystal modifications. The transition temperatures for the BB6 series decrease with inherent viscosity for $\eta_{\text{inh}} > 0.35$ dL/g. This trend was not seen in the other types of polyesters we have investigated. Also, ΔH_{total} decreases with η_{inh} for the BB6 series, probably reflecting a decrease in the degree of crystallinity.

Since the repeating units are known to be perpendicular to the layer spacings in the S_A phase, this has the advantage that the layer spacing gives an unambiguous measure of the length of the repeating unit in the smectic phase. For both BB4 and BB6 the smectic layer spacing is shorter than the fully extended length of the repeating unit. Of the three crystal modifications identified for the latter polymer, the two higher temperature polymorphs have the same *c*-axis spacing as the smectic layer spacing, 18.7 Å, but the 32 Å fibre repeat of the room temperature modification indicates a still shorter length per repeating unit. Thus, the expectation that the molecule should adopt the lowest energy conformation in both the crystalline and smectic phases is not borne out by this example: Also, as mentioned above, we had assumed that an even–odd alternation of the isotropization temperatures of an homologous series might indicate that the hydrocarbon portion of the repeating unit adopts the fully extended all-*trans* conformation. Since the poly(*p,p*′-bibenzoates) exhibit such an alternation, the study of this series disproves that assumption.

Shear flow of the smectic phase of BB6 polymers having $\eta_{\text{inh}} < 0.45$ dL/g produces a high degree of alignment of the molecules perpendicular to the flowing direction. The aligned smectic structure is stable under isothermal conditions for at least a period of 30 min, and cooling produces a well oriented crystalline sample. Since a magnetic field has only a modest effect in aligning a smectic phase, its use in producing aligned smectic phases is restricted to those compounds having a nematic phase at higher temperature. For this reason the technique of producing aligned smectic samples by shear flow may have some interest.

Shear flow of polymeric smectic *A* phases of low molecular weight produces a perpendicular alignment of the molecules with respect to the direction of flow. The same effect would be anticipated for a small molecule smectic *A* phase, but the flow mechanisms must be different in the two cases. We believe that alignment of the polymer molecules parallel to the glass surface plays an important role in the shear flow process of the polymeric smectic phase. We suggest that flow occurs by passage of the polymer molecules side-by-side, rather than end-to-end as in the case of small molecule smectics. Some chain ends must be pulled out of adjacent regions in order to create flow domains. This process apparently can occur if the molecular weight is low enough, but if the molecular weight is too high the smectic structure is disrupted by shear, leading to a weaker alignment of the molecules parallel to the shearing direction.

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