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Thermotropic Liquid Crystals of Polyesters Having a Mesogenic *p,p'*-Bibenzoate Unit. 2. X-ray Study on Smectic Mesophase Structures of BB-5 and BB-6

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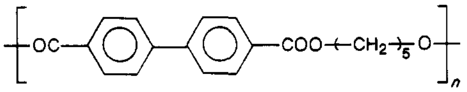
ABSTRACT: X-ray studies were performed for the oriented smectic mesophases of BB-5 and BB-6 polyesters, which were prepared from *p,p'*-bibenzoic acid and penta- and hexamethylene glycols, respectively. Well-oriented X-ray patterns were observed, offering sharp inner and broad outer reflections. From the diffraction geometry of both reflections, it could be concluded that different types of smectic mesophase are formed between BB-6 and BB-5. In BB-6, an average axis of the mesogenic group as well as the polymer chain axis lies perpendicular to the smectic layer planes. In BB-5, in contrast, the mesogenic groups are oriented with a tilt angle of about 25° to the layer normal within a layer, while the polymer chain axis lies perpendicular to the layer planes. The packing of mesogenic groups and polymer chains into a smectic layer structure was examined by selecting the conformations of polymer so as to conform to the orientational order of the mesophase. The selected conformations appear with a different arrangement of mesogenic groups to the polymer chain axis between BB-5 and BB-6. As a result, the smectic layer structures satisfying the X-ray observations could be described such that in BB-6 the normal smectic A mesophase is formed, while in BB-5 a new type of smectic C structure is obtained in which the tilt direction of mesogenic groups is invariable in every second neighboring layer but opposite to each other between neighboring layers.

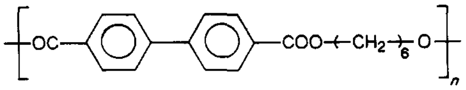
Introduction

In the first paper of this series,[1] we reported the thermotropic liquid crystal nature of main-chain polyesters that can be constructed by an alternative arrangement of the *p,p'*-bibenzoate unit as a mesogenic group and the alkanediol as a flexible spacer. The polyesters are designated BB-*n* where *n* is the number of methylene units in the diol. This homologous series of BB-*n* (*n* = 3–9) invariably forms smectic mesophases whose isotropization temperatures, T_2, and entropies, ΔS_i, exhibit an even–odd oscillation with the number of intervening methylene units, *n*, which has been generally observed for the nematic mesophase.

The even–odd nature of the methylene units also reflected the thickness of smectic layers, with a larger layer thickness in the even series.[1] Comparing the observed layer thicknesses with the calculated ones based on the diffuse cone model and the rotational isomeric state model, we suggest that the even–odd nature is strongly related to the polymer chain conformations and that different types of smectic structures should be formed between the two. In even-membered polyesters there may be formed a normal smectic A phase in which both axes of the polymer chain and the mesogenic group lie perpendicular to the layers. In odd-membered ones, in contrast, the smectic structure was assumed such that the average chain axis of the polymer may be perpendicular to the layer, but the mesogenic groups may be tilted with respect to the layer normal. The purpose of this study is to clarify these structural features through X-ray examination for the oriented smectic mesophases of BB-5 and BB-6 polyesters:



BB-5



BB-6

Experimental Section

The polymers were synthesized by melt transesterification from diethyl *p,p'*-bibenzoate and the corresponding diols with isopropyl titanate as catalyst.[1,2] High molecular weight samples of BB-5 and BB-6 were prepared with inherent viscosities of 1.09 and 0.94 dL/g, respectively, which were determined at 25 °C by using 0.5 g/dL solutions in a 60/40 w/w mixture of phenol and tetrachloroethane. Thermogram data obtained from the DSC cooling curves, concerning the transition temperatures (T_1 for crystal–mesophase transition and T_2 for mesophase–isotropic phase transition) and the enthalpy and entropy changes upon isotropization (ΔH_i and ΔS_i), are listed in Table I.

X-ray diffraction photographs were taken at different temperatures by using Ni-filtered Cu Kα radiation. The temperature was measured and regulated with an accuracy of 0.2 °C by using a Mettler FP-80 heater. The sample was kept in a glass capillary tube. Flat-plate photographs were taken at different temperatures within 20 min. The film-to-specimen distance was determined by calibration with silicon powder. The photographs were scanned by an optical densitometer and the optical densities obtained were converted to X-ray intensities. Photographs of the oriented smectic phase were taken by heating the polymers to the desired temperature. Here, the oriented fiber (~50 μm in diameter) was prepared by pulling up the highly viscous isotropic melt with tweezers and succeedingly elongating it with a speed of 1 m/s at a temperature 20 °C higher than T_2. Hence, in the resulting fibers the average chain axis of the polymer corresponds to the fiber axis. The X-ray photographs of fibrous smectic mesophases are shown in Figures 1a and 2a for BB-6 and BB-5, respectively, and their intensity contour maps in Figures 1b and 2b.

Results

A. Description of the X-ray Diffraction Pattern. As in Figures 1 and 2, highly oriented patterns are observed for both of the BB-5 and BB-6 mesophases. The patterns exhibit sharp inner reflections and diffuse outer halos. Obviously, these reflect the smectic character of mesophases; the sharp inner reflection is attributed to the regular piling of the smectic layers and the diffuse outer halo exhibits the packing of molecules in an unstructured way into a layer. The diffraction pattern is not significantly affected by temperature. Likewise, the spacings of the inner reflection and the outer halo are constant against temperature within experimental error.

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Table I
Characterization of BB-6 and BB-5

polymer	η_{inh}, dL/g	T_1,[a] °C	T_2,[a] °C	ΔH_i,[a] kcal/mol	ΔS_i,[a] cal/(mol K)	d_{obsd},[b] Å	d_{c1},[c] Å	d_{c2},[c] Å	d_{c3},[c] Å
BB-6	0.94	169	229	2.38	4.74	18.3	19.6	18.1	17.7
BB-5	1.09	83	198	1.29	2.73	15.4	17.2	15.9	14.6

[a] Based on cooling data. [b] Collected at the temperature 20 °C lower than T_2. [c] Based on the models in the text.

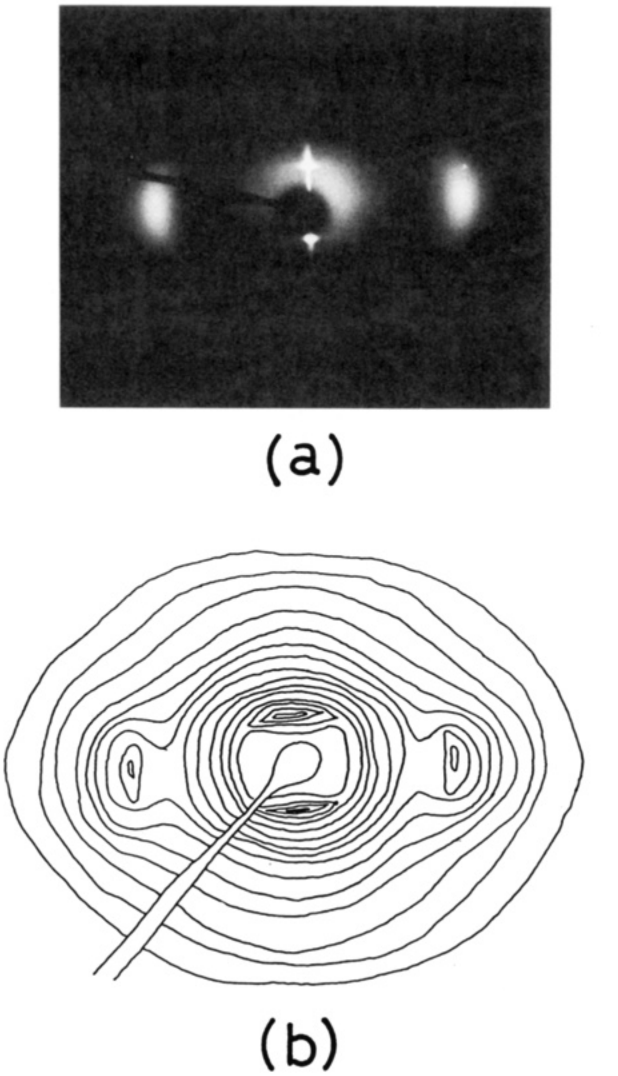


Figure 1. (a) X-ray photograph of the fibrous BB-6 smectic mesophase taken at 210 °C and (b) its intensity contour map. The fiber axis is in the vertical direction.

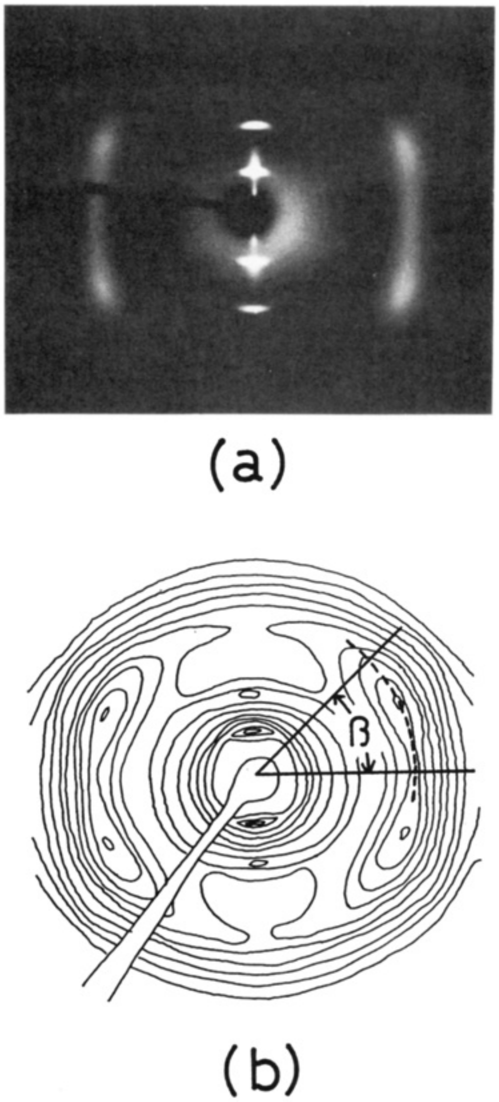


Figure 2. (a) X-ray photograph of the fibrous BB-5 smectic mesophase taken at 180 °C and (b) its intensity contour map. The fiber axis is in the vertical direction.

Inner Reflection. At first, we are concerned with the smectic layer character deduced from the inner reflection. As can be seen in the seventh and eighth columns of Table I, the spacing of the innermost reflection (d_{obsd} is 18.3 Å for BB-6 or 15.4 Å for BB-5) is approximately the molecular length (d_{c1} is 19.6 Å for BB-6 or 17.2 Å for BB-5) of the repeating unit of polymer in the fully extended form. The smectic structure in the polymeric system, thus, can be recognized such that each repeating unit (or each mesogenic group) is an element comprising each layer and a polymer chain passes through many layers, depending on a degree of polymerization. Since the inner layer reflections for both specimens are exactly observed on a meridional line, it can be concluded that the smectic layers are regularly formed with their planes perpendicular to the fiber axis.

It should be noted that there is a remarkable difference in the intensity distribution of the 00l layer reflections between BB-6 and BB-5. BB-5 shows three sets of reflections in a series of 00l, but in BB-6 only the 001 reflection can be observed. This dictates that the distribution function of positions of mesogenic groups in a direction (z-axis) normal to the smectic layer planes is remarkably different between the two. The distribution function $f(z)$ may be written

$$f(z) = (1 + \sum_l 2\tau_l \cos 2\pi l z/d)/d \qquad (1)$$

where $\tau_l = \langle \cos 2\pi l z/d \rangle$ is a smectic layer order parameter, which ranges from 1 for the perfect layer structure to 0 for no layer structure (for example, the nematic mesophase).[3,4] Then, the intensity of the 00l layer reflection is related to τ_l by the equation

$$I(00l) = C\tau_l^2 \langle F(00l) \rangle^2 \qquad (2)$$

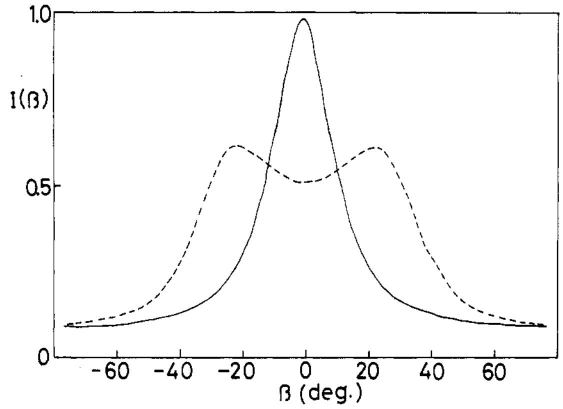


Figure 3. Intensity distribution $I(\beta)$ measured as a function of azimuthal angle β at a diffraction angle $2\theta = 20.5°$; the solid curve is for BB-6 smectic phase, and the dashed curve for BB-5 smectic phase.

where $F(00l)$ is the structure factor for a perfect layer and C is a constant. In the smectic phase of BB-5, the intensities for first- and second-layer reflections were precisely measured on a powder specimen at a temperature 20 °C below T_2. The ratio after correction for Lorentz and polarization factors is

$$I(002)/I(001) = 0.12 \tag{3}$$

The structure factors $\langle F(00l)\rangle$ were calculated for a simple model in which some extended molecule was given so as to just fit the observed layer thickness (15.4 Å). The result was

$$\langle F(002)\rangle / \langle F(001)\rangle = 0.73 \tag{4}$$

which is not sensitive to the fine details of the model. Use of eq 2 gives $\tau_2/\tau_1 = 0.47$ and the assumption of a Gaussian distribution for $f(z)$ gives the smectic layer order parameter $\tau_1 = 0.78$. On the other hand, BB-6 shows only the first reflection, so that the value of τ_1 may be smaller than that of the BB-5 mesophase.[4] This demonstrates that the smectic layer character of BB-6 is rather weaker than that for BB-5.

Outer Reflection. The broad outer reflection is attributed to the average distance between the neighboring molecules or between the neighboring mesogens within a layer; the elongated mesogenic groups are relatively free to assume any orientation about their long axis and so may act as cylindrically symmetric rods. Its spacing of around 4.3 Å is approximately equal to the value commonly observed for low molar mass mesophases.[5]

It is interesting that the outer reflections appear with different orientation to the layer reflections between BB-5 and BB-6 mesophases. In BB-6, the outer reflections are centered on the equator, while those in BB-5 are split into two intense portions lying above and below the equator. These can be directly observed in Figure 3, which exhibits the intensity distribution $I(\beta)$ measured as a function of azimuthal angle β at a diffraction angle ($2\theta = 20.5°$), corresponding to the maximum of diffracted intensity along the equatorial line (see Figure 2b). As it is likely that the broad reflection results mainly from the rigid mesogenic groups of bibenzoate units, these results indicate the different arrangement of mesogenic groups to the fiber axis between the two; in BB-6, the mesogenic groups lie parallel to the fiber axis, while in the BB-5, the mesogenic groups are arranged with an appreciable tilt to the fiber axis. The tilt angle β relative to the layer normal for the latter is seen to be around 25° from Figure 3.

It is noteworthy that there is a wider intensity distribution $I(\beta)$ in BB-5 than in BB-6 (for example, see Figure 3). This qualitatively indicates that the orientational order parameter in BB-5 is lower than that in BB-6, this being in contrast with that seen with respect to the smectic layer order. The details will be reported in another article.[6]

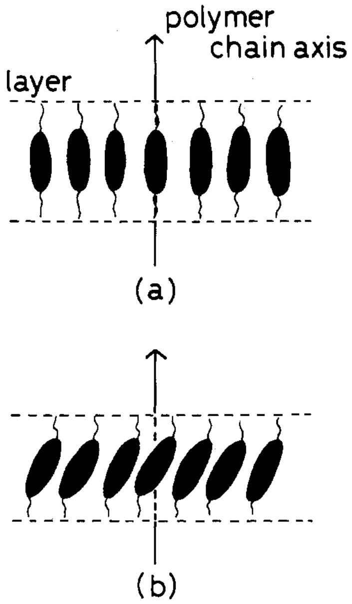


Figure 4. Orientation of polymer chain and mesogenic group to a smectic layer plane satisfying the X-ray data: (a) BB-6 and (b) BB-5.

B. Structural Features of BB-5 and BB-6 Smectic Mesophases Elucidated from the X-ray Data. Since the oriented specimens were prepared from the isotropic melt, there is no doubt that the average chain axis of the polymer corresponds to the fiber axis. The appearance of the layer reflections on a meridional line for both smectic phases thus indicates that the layers are formed with their planes perpendicular to the polymer chain axis. Within a layer, the lateral distribution of the mesogenic groups is random and so the smectic A or C phase with a lower structural order is likely for the present mesophases. As deduced directly from the diffraction geometry of inner reflections and outer halos (see Figures 1 and 2), there is a remarkable difference in the orientation of mesogenic groups within a layer between BB-5 and BB-6 mesophases. In BB-6, the mesogenic groups lie perpendicular to the layer planes, while those in BB-5 are tilted by about 25° to the layer normal.

Since the polymer chains pass through many layers perpendicular to the layer planes, the above facts also indicate different alignments of mesogenic groups along a chain; polymer chains of BB-6 compatible with the smectic layer structure should have an average conformation in which the mesogenic groups are parallel to the chain axis, while in the BB-5 polyester the mesogenic groups are tilted with respect to the chain axis. The fundamental packing structure of polymer chains into the layers and the alignment of mesogenic groups within a layer can thus be illustrated as in Figure 4. According to the classification elucidated for the low molar mass smectic phases, the BB-6 mesophase can be assigned to the smectic A phase while the BB-5 mesophase may be of the smectic C type.

More recently, we found that these two types of smectic phases appear, depending on the even–odd nature of intervening methylene unit.[6] For instance, BB-4 and BB-8 polyesters exhibit the smectic A phase as in BB-6, while the smectic phases of BB-3 and BB-7 are classified into the type of smectic phase seen in BB-5. This indicates that the smectic structure is formed in close relation to the polymer chain conformations, which appear with a different feature depending on the even–odd nature of flexible spacer linking the mesogenic groups, as discussed below.

Discussion

A. On the Conformation of the Polymer, Which Conforms to the Orientational Order of the Mesophase. In the polymeric smectic phase, each mesogenic group incorporated into a main chain participates in each layer, and so the polymer molecule must adopt a conformation or packing that is compatible with the smectic layer structure. Hence, the polymeric and mesogenic properties are closely coupled, which may cause the properties of the mesophase to depart from those of the low molar mass mesogen. Conversely, the formation of a mesophase may affect the conformation of the main-chain liquid crystal polymer. In a previous paper[1] reporting the smectic mesophase properties of the BB-*n* series, the argument on this point was made in order to explain the even–odd oscillation of the smectic layer thickness with remarkably larger values in even members.

To reproduce the even–odd oscillation of observed layer thicknesses (d_{obsd}), two models were applied. One is the diffuse cone (DC) model proposed by de Vries[7] where the constituent molecules take up a fully extended conformation and pack into the smectic layer structure with some orientational disorder. Another is the rotational isomeric state (RIS) model examined by Abe[8] in which an appreciable amount of gauche conformers can be allowed as long as the resultant conformations conform to the orientational order of the mesogens. In both models, the line connecting the centers of two succeeding mesogens was considered to be perpendicular to the layer planes and the layer thickness was identified as its average length.

In the DC model, we took the same situation as applied for the low molar mass smectic phase,[7] in which the orientational order parameter is around 0.8, giving an average value of $\langle \cos \beta \rangle$ of 0.927 and an average tilt angle $\langle \beta \rangle$ of 19°. The calculated spacings (d_{c2}) based on this model are listed in the ninth column of Table I. These are in good agreement with d_{obsd}; d_{c2} = 18.1 Å and d_{obsd} = 18.3 Å for BB-6 and d_{c2} = 15.9 Å and d_{obsd} = 15.4 Å for BB-5. It should, however, be noted that a significant deviation between d_{obsd} and d_{c2} has been observed, especially for the odd-membered polyesters with long flexible spacers when the examinations were extended for a homologous series of polyesters with four to nine methylene units.[1]

The DC model is a tentative model, since it is unlikely that the long polymer chains are packed with an orientational disorder while maintaining their fully extended conformation. On this point, the RIS model, where all possible configurations are enumerated within a framework of the RIS approximation, is realistic for the polymeric system. Extensive studies were performed by Abe et al.,[8-12] by examining the angular correlation between the neighboring mesogens along a chain, discarding the conformations that do not conform to the orientational order of the mesophase, and matching the macroscopic thermodynamic properties of transition entropies of isotropization as well as the microscopic deuterium NMR spectra of labeled chains. The conclusions were obtained such that only a nearly parallel orientation of the successive mesogenic groups (with the angle of 0–30°) is allowed in the even-membered polymer, while in the odd-membered mesophase two successive mesogens are inclined to each other at angles in the range 50–90°. For the present system, the same mesophase assemblies selected in ref 8 were treated. Interestingly, we have found that these mesophase assemblies give a fairly narrow distribution of distances connecting the centers of mesogenic groups and are compatible with the smectic layer structure, in comparison with a case where all possible conformations are allowed.[6] The calculated thicknesses (d_{c3}) are given in the last column of Table I. These qualitatively agree with the observed thicknesses, although the calculated values are somewhat smaller than the observed ones, suggesting that the more extended conformations are preferred in a real system.

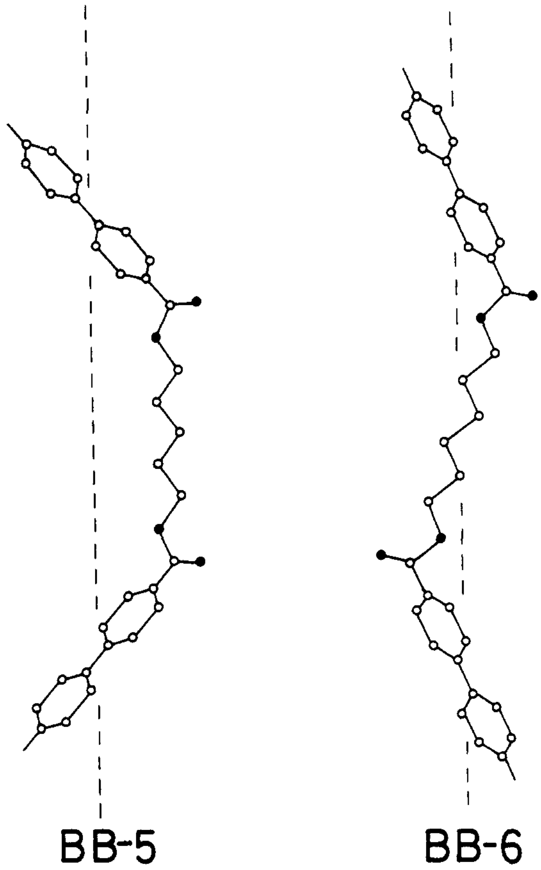
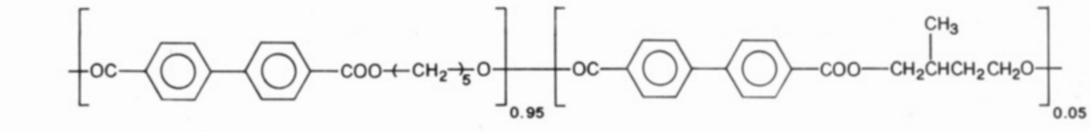


Figure 5. Comparison of the extended-chain structures of BB-6 and BB-5.

The RIS model as well as the DC model thus reproduce well the observed layer thickness and its even–odd oscillation, and as a result, one concludes that the smectic layers are constructed of highly extended chains and that there is a rather remarkable difference in the arrangement of mesogenic groups along the polymer chains in the mesophases of even- and odd-membered polyesters. In the polymer chains of even-membered polyesters, the mesogenic groups are approximately parallel to the chain axis, while in odd-membered polyesters the mesogenic groups are tilted by about 25–45° to the chain axis, their tilt directions being opposite between the mesogenic groups that are next to each other along the polymer chain. Such a situation can be well understood by looking at the arrangement of mesogenic groups for all-trans polymer chains as depicted in Figure 5.

B. Possible Smectic Structure To Reproduce the Oriented X-ray Pattern. We next show that the smectic layer structure satisfying the X-ray observations can be constructed by the polymer chains in the above selected conformations.

Smectic Structure of BB-6. In BB-6, the present X-ray data exhibited that the axes of both the mesogenic groups and the polymer chains are approximately parallel to the layer normal. A similar situation can be seen for the constituent molecules selected above. Therefore, in this case, only the side-by-side association of mesogenic



A

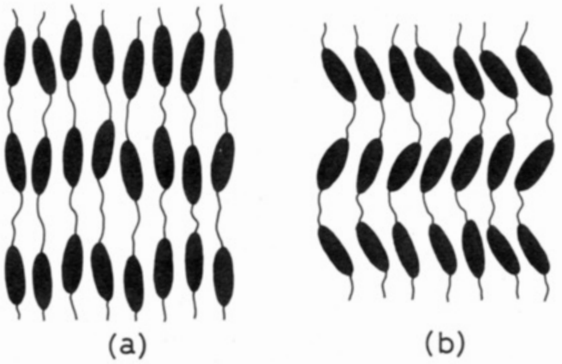


Figure 6. Layer structures proposed for (a) BB-6 and (b) BB-5 smectic mesophases. Here, BB-6 forms the normal smectic A while BB-5 assumes a new type of smectic C in which the mesogenic groups in each layer are tilted by about 25° to the layer normal but their tilt direction is opposite to each other between neighboring layers.

groups from the different polymer chains is required to reproduce the observed smectic layer structure (see Figure 6a). This type of smectic mesophase can be assigned as a smectic A that has the same character as a low molar mass smectic A.

Smectic Structure of BB-5. The X-ray pattern exhibited that in BB-5 the mesogenic groups are arranged with an appreciable tilt angle of around 25° within a layer and that the polymer chain axis is perpendicular to the layer planes. As far as the arrangement of mesogenic groups within a layer is concerned, the mesophase is considered to be of the smectic C type. For the strict identification of smectic C, however, further attention needs to be given to another important feature, that is, the alignment of c-directors (or tilt directions of long axes of mesogenic groups).[3] Are the c-directors random or aligned with some correlation on moving from layer to layer? If the c-directors are random the mesophase can be assigned a smectic A,[13-15] while in the smectic C an orientation correlation of c-directors should exist. Unfortunately, the present X-ray data offer no information on this structural feature.

The answer to this question was given by the recently obtained fact that the introduction of a small trace of chiral 2-methylbutanediol into BB-5 as a comonomer unit can induce the chiral smectic C liquid crystal.[16] Here, the helical structure of chiral smectic C could be confirmed by a microscopic observation of retardation lines superimposed on the smectic fan-shaped textures, a typical example of which is shown in Figure 7, as observed for the copolyester: copolyester A. This finding obviously indicates that the original BB-5 mesophase is essentially of smectic C type in which orientation correlation of c-directors persists from layer to layer, since the uniform helical twist can be induced only for the aligned c-directors.

For BB-5 smectic C, one might initially conceive the normal smectic C structure, as observed in a low molar mass system, in which the tilt direction as well as the tilt angle are invariable through a succession of layers within a given domain. This structure, however, is unlikely since the polymers in this case must assume the average conformation with a transoid arrangement of mesogenic groups, and the above discussion can eliminate this possibility. An alternative smectic C model, proposed here in relation to the above selected conformations which have a zigzag arrangement of mesogenic groups, is such that the tilt directions of mesogenic groups in neighboring layers are opposite to each other. In other words, the c-directors are tilted in the same direction in the 2nth or (2n + 1)th layers but in the opposite direction between 2nth and (2n + 1)th layers. The structure is illustrated in Figure 6b. This model is plausible since the observed tilt angle (β = 25°) corresponds approximately to the average tilt angle of mesogenic groups (25–45°) to the chain axis in the polymer chains selected above and can be expected if the mesogenic groups are regularly packed into layers in a zigzag fashion as in Figure 6b.

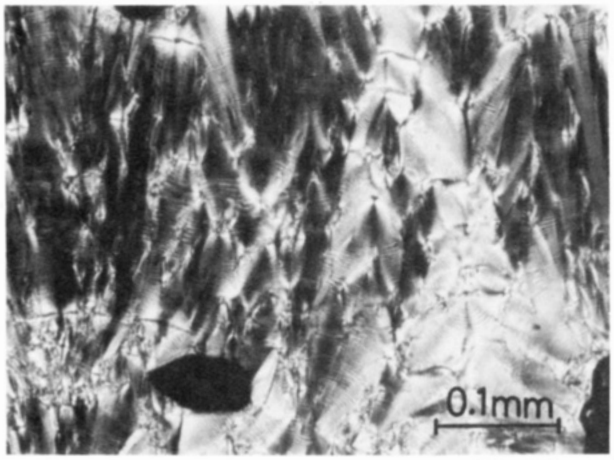


Figure 7. Microphotograph of a chiral smectic C liquid crystal observed for the copolyester (presented in the text) in which a trace of chiral 2-methylbutylene unit as a comonomer component was introduced into BB-5. Here, equally spaced lines are observed, which can be attributed to the helical repetition of chiral smectic C.

In relation to this characteristic structure, it is noteworthy that the chiral smectic C based on this smectic mesophase is not ferroelectric.[16,17] This fact also indicates that the BB-5 smectic C structure is unusual; probably in the chiral smectic C induced in this structure, the helical twistings may arise for two sets of antiparallel c-directors, the doubling of helical periodicity may occur with the phase difference of π, and two antiparallel c-directors may cancel the spontaneous polarizability within a domain. Such a curious smectic C phase seems to be formed as a direct polymeric effect and to our knowledge has not been observed experimentally, although the possibility of this structure has been reported by Michelson et al.[18]

In the mesophase structures proposed above, it is very reasonable that the BB-5 smectic phase has the higher layer order than the BB-6 one. In the BB-6 mesophase, translational motion of polymer chains along the layer normal would easily occur. In BB-5, in contrast, the similar thermal motion can be interrupted because of the zigzag packing of mesogenic groups into the layers, and hence the thermal fluctuation of mesogenic groups from the layer center should be reduced in comparison to that of the BB-6 mesophase. In this sense, the even–odd nature of the flexible spacer would also reflect a smectic layer order, which in practice has been recognized by treating a series of BB-*n* polyesters.[6]

Conclusion

Two distinct smectic layer structures were observed for BB-5 and BB-6 smectic mesophases. In the BB-6 mesophase, both the axes of the polymer chain and the mesogenic group lie perpendicular to the smectic layer planes. This type of smectic mesophase can be classified as smectic A. In BB-5, the mesogenic groups are tilted by about 25° to the layer normal, although the polymer chains lie parallel to it. The mesophase in this case is a new type of smectic C in which the tilt direction of mesogenic groups is invariable in each second neighboring layer but opposite to each other between the layers of nearest neighbors. Such a different formation of smectic layer structure between BB-5 and BB-6 can be appreciated by the average conformation of the polymer chain, which conforms to the orientational order of the mesophase and so appears with different features, depending on the even–odd parity of the carbon numbers in the flexible spacer.

Registry No. BB-5 (SRU), 81192-66-7; BB-5 (copolymer), 81197-18-4; BB-6 (SRU), 50602-05-6; BB-6 (copolymer), 81197-19-5.

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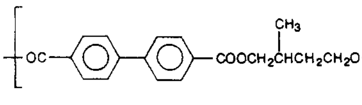

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Phase Behavior of a Semiflexible Polymer with both Thermotropic and Lyotropic Properties[1]

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ABSTRACT: A semiflexible polymer, comprising rodlike groups connected by spacer groups in alternating succession in the main chain and also rigid side groups attached to each backbone rodlike unit via a spacer, has been found to exhibit both thermotropic and lyotropic behavior. The polymer shows isotropic–nematic biphasic separation over a wide concentration range of 20–100% by volume in the temperature range of 25–268 °C. The resulting phase diagram therefore has a strongly bent chimney shape, in contrast to the nearly vertical chimney obtained with rigid rodlike polymers. Comparison of experimental results with the predictions of Flory and Warner on rodlike molecules with orientation-dependent interactions shows that the spacer groups in the main chain do not behave like free joints. The unique phase behavior is therefore attributed to the strong influence of the degree of flexibility of the spacer groups on the cooperative alignment of neighboring rodlike moieties in the ordered state.

Introduction

Isotropic–anisotropic biphasic equilibria have been investigated extensively for a number of liquid-crystalline systems, and their phase behavior characteristics are described satisfactorily by molecular theory.[3] These examples include rodlike polymers and mixtures of rods in solution,[4] mixtures of thermotropic rodlike molecules of different lengths,[5,6] mixtures of rodlike polymers and flexible polymers,[3,7] and semiflexible polymers in solution.[3,8] Flory and his collaborators, in particular, have been quite successful in describing these diverse systems with a molecular theory that employs a lattice model and thus emphasizes the major contributions of steric repulsions, augmented by soft orientation-dependent attractions.[9]

Recently, much attention has been focused on a new class of liquid-crystalline polymers comprising rodlike and flexible groups in alternating succession in the chain backbone, due to the appearance of isotropic–anisotropic transitions of polymer melts at experimentally accessible temperatures.[10-13] There are now a large number of experimental results on the thermotropic phase behavior of these semiflexible polymers. Theoretical understanding, however, is just beginning and is limited to some empirical descriptions of thermodynamic and molecular phenomena.[14] There exists virtually no experimental work on the phase behavior and the molecular order of these semiflexible thermotropic polymers in the presence of solvents. Experiments on lyotropic systems of this class of polymers, covering a wide concentration range, should provide much deeper insights into their order–disorder phase behavior and will also provide a stringent test for any emerging theoretical work.

In this paper we present the experimental results of isotropic–nematic biphasic separation of such a semiflex-

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