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Thermotropic Liquid Crystals of Polyesters Having a Mesogenic *p*,*p*′-Bibenzoate Unit. 1. Smectic Mesophase Properties of Polyesters Composed of *p*,*p*′-Bibenzoic Acid and Alkylene Glycols

In a previous paper,[1] Krigbaum and Watanabe reported a study of smectic A phase (S_A) of the homologous series of polyesters prepared by *p*,*p*′-bibenzoic acid and its tetra-, hexa-, octa-, and decamethylene glycols. These polymers are designated BB-*n*, where *n* is the number of methylene units in the diol. The BB-4 and BB-6 polymers form a thermotropic smectic phase which could be identified as S_A by mutual miscibility studies with a known low molecular weight mesogen, TBBA. The S_A structure is also supported by the X-ray observation that the smectic layer spacing is slightly shorter than the fully extended length of the repeating unit for both BB-4 and BB-6.

We here investigated the polymeric smectic mesophase by extending the study to the homologous series BB-4, BB-5, BB-6, BB-7, BB-8, and BB-9. Interestingly, all polymers invariably form the smectic phase and its isotropization temperature, T_i, and entropy, ΔS_i, exhibit an even–odd oscillation with the number of intervening methylene units, *n*, which has been generally observed for the nematic mesophases.[2-4] The even–odd nature of methylene units is also reflected in the thickness of the smectic layer. Some discussion will be made on a relation between the smectic mesophase properties and the even–odd nature of methylene units.

All the polymers used here were synthesized by melt transesterification from diethyl *p*,*p*′-bibenzoate and the appropriate diol with isopropyl titanate as catalyst. Inherent viscosities, as determined at 25 °C by using 0.50 g/dL solutions in a 60/40 w/w mixture of phenol and tetrachloroethane, ranged from 0.2 to 0.4 dL/g for all polymers.

In Figure 1, the representative DSC curves of polymers are shown for BB-4 and BB-5. Both indicate two peaks on heating and cooling; the peak at lower temperature (T_1) corresponds to the crystal to liquid crystal transition and the higher temperature (T_2) peak to the liquid crystal to isotropic transition. The mesophase on heating arises in a narrow temperature region and this trend becomes remarkable as *n* increases. Hence, there is a monotropic appearance of mesophase in BB-7, BB-8, and BB-9, in which the mesophase is observed only on cooling.

Data obtained from the cooling curves, concerning the temperature range of the mesophase and the enthalpy and entropy changes upon isotropization, are collected in Table I. In Figure 2a is shown the behavior of the two transition temperatures as a function of the number, *n*, of methylene units in the alkanediol. Both temperatures exhibit the usual even–odd oscillation, and the vertical spacing of the two points, which represents the temperature span of the mesophase, becomes narrow as *n* increases. Similarly, an even–odd oscillation is observed in the isotropization entropies, ΔS_i, as shown in Figure 2b, and for the isotropization enthalpies with higher values in the even-membered polymers (see the fourth and fifth columns in Table I). It seems unlikely that the entropies of the isotropic phases of the even and odd members would differ by this magnitude, leading to the conclusion that the mesophase of the even-membered series is more highly ordered.

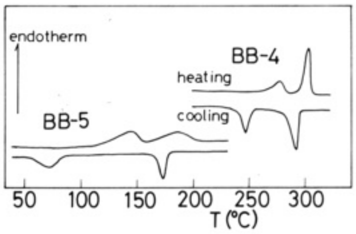

Figure 1. DSC thermograms of BB-4 and BB-5.

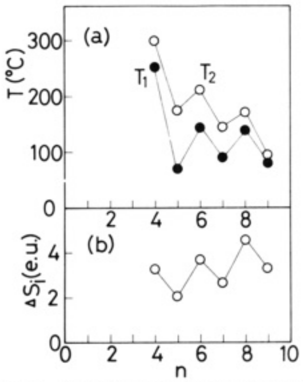

Figure 2. Variation of (a) transition temperatures (T_1 and T_2) and (b) transition entropy (ΔS_i) with the number (*n*) of methylene units.

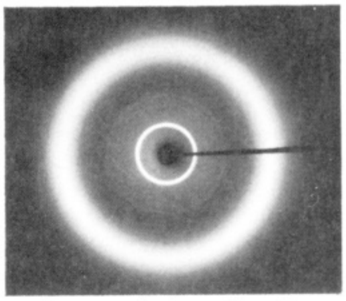

Figure 3. X-ray photograph of unoriented mesophase of BB-5 taken at 150 °C.

In optical microscopic observation, the mesophases of even-membered polymers appear as batonnets on cooling from the isotropic melt and they coalesce to make a well-developed fan-shaped texture with focal-conic domains. Batonnets and the fan-shaped texture are characteristic of the layer structure of smectic mesophase. In the odd-membered mesophases, a similar fan-shaped texture is observed, although it is composed of the finer focal-conic domains than those in the even members.

X-ray diffraction clarifies the smectic mesophase in both series. Here, the diffraction pattern of the mesophase was recorded for the polymer held in a capillary which was cooled from the isotropic phase to the mesophase. The diffraction pattern, as representatively shown for BB-5 in Figure 3, consists of one or two sharp inner reflections and

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Table I
Characterization of BB-*n* Polyesters

polymer	T_1,[a] °C	T_2,[a] °C	ΔH_i,[a] kcal/mol	ΔS_i,[a] cal/(mol K)	d_{obsd}, Å	d_{c1},[b] Å	d_{c2},[b] Å	d_{c3},[b] Å
BB-4	251	298	1.87	3.30	15.8	17.2	15.9	16.3
BB-5	70	173	0.92	2.07	15.5	17.2	15.9	14.6
BB-6	143	211	1.79	3.70	18.2	19.6	18.1	17.7
BB-7	89	144	1.11	2.67	17.4	19.7	18.2	15.8
BB-8	139	171	2.03	4.57	20.6	22.0	20.4	18.9
BB-9	80	95	1.22	3.30	18.7	22.2	20.6	16.8

[a] Based on cooling data. [b] Based on the models described in the text.

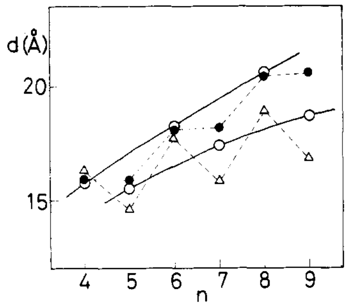

Figure 4. Variation of the smectic layer thickness (d) with the number (n) of methylene units: (○) the observed thickness (d_{obsd}) at the temperature 10 °C lower than T_2; (●) the calculated thickness (d_{c2}) by the diffuse cone model; (△) the calculated thickness (d_{c3}) by the rotational isomeric state model (see text).

a diffuse outer halo. The sharp inner ring (varying from 15 to 20 Å with n) is attributable to the piling of the layers. On the other hand, the diffuse outer halo of around 4.5 Å indicates that the lateral arrangement of molecules in a layer is disordered. These features are typical of the S_A or S_C form. The reflection pattern remains unchanged over a whole mesophase temperature range and the spacing of inner reflection is not very dependent on temperature. The spacings of inner reflection (d_{obsd}) are listed in sixth column of Table I and plotted by open circles against n in Figure 4. Interestingly, the spacing, that is the smectic layer thickness, also exhibits the remarkable even–odd oscillation with the larger value in even members.

In the polymeric smectic phase, each mesogen participates in each layer,[1,5,6] and so the polymer molecule must adopt a conformation or packing which 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.

We first consider that the smectic phase is composed of molecules in a fully extended conformation. By comparison of BB-6 and BB-5 chains in parts a and b of Figures 5, the even-membered polymer is seen to have a transoid arrangement of the mesogenic biphenyl groups, whereas in odd membered chains the neighboring mesogens in a chain are inclined toward each other. Under the assumption that these extended molecules construct a layer structure of S_A type with their molecular axes perpendicular to the layer, one can estimate the layer thickness (d_{c1}) as listed in seventh column of Table I. In comparison of sixth and seventh columns of Table I, it is found that the values thus calculated are larger than those observed.

The same situation has generally arisen in a S_A system of low molar mass compounds. de Vries et al.[7] showed according to their diffuse cone model that a difference between the observed and calculated values may be attributed to the average tilting of molecules against the layer normal which is caused by orientational disorder. For an orientational order parameter $S = 0.8$ as usually observed for the low molar mass S_A, the diffuse cone model gives an averaged value of $\langle \cos \theta \rangle$ of 0.927 and an averaged tilt angle $\langle \theta \rangle$ of 19°.[7] Applying this for the present polymeric system, we calculated the spacings (d_{c2}) in eighth column of Table I and plotted them as closed circles against n in Figure 4. However, an appreciable difference with the larger value in calculation still remains for the odd-membered polymers. As one possible explanation for the latter disagreement, we suggest that the molecules of odd membered polymers adopt an appreciable amount of the gauche conformer so as to reduce the layer thickness. This may lead to a less favorable orientation of mesogens in the mesophase which can be partly responsible for the lower value of ΔS_i in the odd series of polymers. We can also offer another explanation, that in odd-membered polymers there is formed S_C mesophase in which the averaged molecular axes of polymer chain are tiled with respect to the layer normal; the tilting angles of 12.9°, 17.1°, and 24.8° are estimated for BB-5, BB-7, and BB-9, respectively. However, such an ordinary S_C seems less likely from the reason mentioned below.

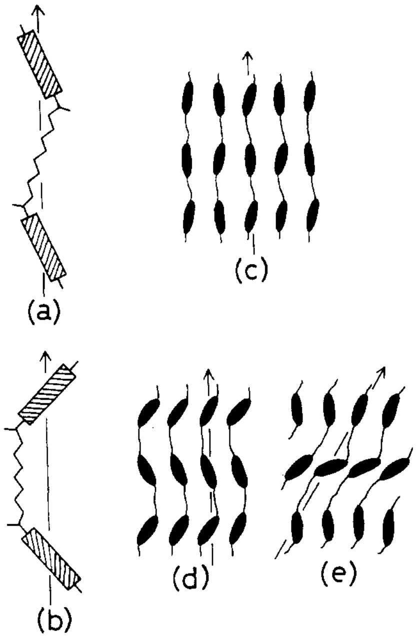

Figure 5. Illustration of the fully extended chains of (a) BB-6 and (b) BB-5 and their proposed packing arrangements into a smectic layer structure ((c)–(d)) (see text). The arrow indicates the molecular axis of the polymer.

The different structural aspect in the smectic mesophase of odd and even membered polymers is also expected with respect to a packing of molecules into a layer structure. In even-membered polymers, the neighboring biphenyl mesogens in a chain are parallel to each other with their long axes approximately parallel to a chain axis (see Figure 5a). In this case, therefore, one can easily envisage the normal S_A structure as illustrated in Figure 5c which is similar to the low molar mass S_A. In odd-membered polymers, however, it is not simple to determine the S_A structure since the mesogenic groups are alternatively tilted toward each other by about 60° as in Figure 5b. One possible smectic structure like S_A can be imagined such that the molecular axis of polymer chain is normal to the layer but the mesogens in neighboring layers are inclined toward each other, having the same tilt angle of around 30° to the layer normal. Such a smectic structure, as illustrated in Figure 5d, may be realistic only in the polymeric system with the mesogens linked together, although it is not obvious whether this type of smectic should be classified into a S_A, S_C, or a new type of smectic phase. On the other hand, the ordinary S_C form, having the tilting of the polymer chain axes to the layer normal, is less accepted for the odd-membered mesophase as long as the all-trans conformation model is adopted, since the angular correlation of the mesogens appears inconsistent from layer to layer (for example, see Figure 5e).

We tried to explain above the even-odd appearance of smectic properties by assuming the all-trans conformation of the flexible spacer. In a real system, however, the appreciable amounts of gauche conformers should be included. This was originally pointed out in a polymeric system by Abe et al.[8,9] and Yoon et al.[10] and examined by the conformational analyses due to the rotational isomeric state model. Their conformational analyses by computation indicate that the angular correlation between the neighboring mesogenic cores appears different between the odd- and even-membered polymers. For the present kind of polyesters with n = even, the angle θ, made by long axes of two successive mesogens, was found to be distributed in the range 0–30° (30–40%) and 85–130° (60–70%). For the odd-membered polymers, the major portion is located in the region 50–90°, and orientations are also permitted in the range $\theta > 160°$ (10–20%). Since the uniaxial orientation of mesogens is required in a mesophase, Abe[8] considered that only a nearly parallel orientation of the successive mesogenic groups (with the angle $\theta = 0$–30°) is allowed in even-membered polymers, while in the odd-membered mesophase two successive mesogens are inevitably inclined with each other at the angle in the range 50–90°; this indeed explains the odd–even oscillation observed in the orientational characteristics of the nematic mesophase.[9] According to this treatment,[8] we calculated the layer thickness (d_{c3}) which may correspond to an averaged distance between the neighboring mesogens (in the ninth column of Table I). As found in Figure 4, the layer thickness (open triangle) is significantly reduced in odd-membered chains and the observed extent of oscillation can be qualitatively reproduced, although a further analysis of conformation is necessary to attain a better correspondence.[11] Finally, it should be noted that even in this model, having an appreciable amount of gauche conformers, the angular correlation between neighboring mesogens in a chain cannot be essentially altered from that expected in an all-trans conformation model.

We now continue the study of the polymeric S_A mesophase by preparing the oriented mesophase and by proceeding with the conformational analyses to elucidate the molecular orientation in mesophases and explain the observed layer thickness. The details will be published in a succeeding paper.[11]

Registry No. BB-4 (copolymer), 81197-17-3; BB-4 (SRU), 29088-02-6; BB-5 (copolymer), 81197-18-4; BB-5 (SRU), 81192-66-7; BB-6 (copolymer), 81197-19-5; BB-6 (SRU), 50602-05-6; BB-7 (copolymer), 111409-85-9; BB-7 (SRU), 111409-88-2; BB-8 (copolymer), 88190-05-0; BB-8 (SRU), 88189-21-3; BB-9 (copolymer), 111409-86-0; BB-9 (SRU), 111409-89-3.

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