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Thermotropic Liquid Crystals of Polyesters Having a Mesogenic *p,p′*-Bibenzoate Unit. 7. Chain Folding in the Smectic Phase of BB-6

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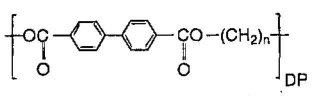
ABSTRACT: The solid state morphology of the main-chain liquid crystal BB-6 polyester was studied by the small angle X-ray scattering (SAXS) method. The BB-6 polyester forms isotropic, smectic A, and crystal phases in the order of decreasing temperature; thereby its crystallization is taking place from the smectic A phase. The SAXS for the crystalline specimens prepared by cooling the isotropic melt at a rate of 10 °C min^{-1} shows the well-defined reflection maxima which are attributable to the stacked lamellar structure. The lamellar spacings are distributed around 250 Å so that an appreciable number of chain foldings are included in a chain. The lamellar size is increased by annealing the crystal like in other crystallizable polymers. In contrast, it is not essentially altered by annealing the smectic A phase. The results show that the chain foldings exist at a thermodynamic equilibrium in the smectic A phase. The correlation length between the chain foldings is assumed approximately to be 250 Å, which corresponds to 15 times the length of the repeat unit.

Introduction

The introduction of flexible alkylene spacers between the rigid aromatic units in the polymer backbone is a proven method for obtaining liquid crystalline phases. The resulting polymers are termed main-chain liquid crystalline polymers (LCPs). These main-chain LCPs have generated much interest in recent years both because of the challenge of understanding such systems and because of their many industrial and commercial applications.

In this series of studies,[1−6] we have treated the following main-chain LC polyesters designated as BB-*n*



where *n* is the carbon number of the methylene spacer. These BB-*n* polyesters invariably form smectic mesophases when *n* varies from 3 to 9. In BB-*n* with an even *n*, a S_A phase is formed with both the axes of the polymer chain and the biphenyl mesogen lying perpendicular to the layers. In contrast, the smectic structure of BB-*n* with an odd *n* was identified as a new type of smectic phase, S_{CA}, in which the tilt direction of the mesogenic group is the same in every second layer but opposite between neighboring layers.[2,3,6] This odd−even alteration of the smectic structures results from the conformational constraint in which the polymethylene spacer, assuming the more extended conformation, forces the neighboring mesogens to arrange with the characteristic angular diaplacement that depends on the odd−even parity of *n*.[6] Thus, we can picture that the polymer takes up the extended configuration at least in a local space of the smectic LC field. However, it has not been clarified if the polymer chains are extended along the entire length or not.

This important structural aspect of polymer chain configuration in the LC field has been extensively debated theoretically.[7−9] The complexity and subtlety in the main-chain LCPs come from the interplay between long-range orientational order of the liquid crystal and the polymeric tendency to maximize entropy. de Gennes[7] first pointed out that a semiflexible long chain in the nematic phase may recover some part of the entropy lost due to the ordering of the mesogenic units by forming hairpin foldings where the chain executes a counter-reversal (180°) with respect to the director. The existence of one or two hairpin foldings was recently established by small-angle neutron scattering measurement for poly(4,4′-dioxy-2,2′-dimethylazoxybenzene alkanedioyl)s in their nematic phases.[10−13] On the other hand, Takahashi and Nagata[14] have studied the morphology of BB-6 crystals by small-angle X-ray and electron microscopic measurements and found that the stacked lamellar structure is formed. This study is interesting since it suggests that the chain folding may exist in the preceding smectic phase.

In this paper, we have studied in more detail the solid state morphology of BB-6 by the small-angle X-ray scattering (SAXS) method to discuss the chain configuration of the main-chain LCP in the smectic A phase.

Experimental Section

BB-6 polymers were synthesized by melt transesterification from dimethyl *p,p′*-bibenzoate and hexamethylenediol with isopropyl titanate as catalyst. The inherent viscosities of the samples, η_{inh}, were measured at 30 °C by using 0.5 g dL^{-1} solutions in a 60/40 w/w mixture of phenol and tetrachloroethane. The number average molecular weights, M_n, were determined by gel permeation chromatography (Polymer Laboratories Mixed-C with a JASCO 830-RI detector) in a 25/75 v/v mixture of pentafluorophenol and chloroform at 50 °C on the basis of calibration of standard polystyrene. Differential scanning calorimetric (DSC) measurements were carried out with a Perkin-Elmer DSC II at a scanning rate of 10 °C min^{-1} under a flow of dry nitrogen. The wide-angle and small-angle X-ray measurements were performed using a Rigaku-Denki X-ray generator with Ni-filtered Cu Kα radiation. The lamellar spacings from the small-angle X-ray measurement were evaluated with a possible error of ± 5 Å.

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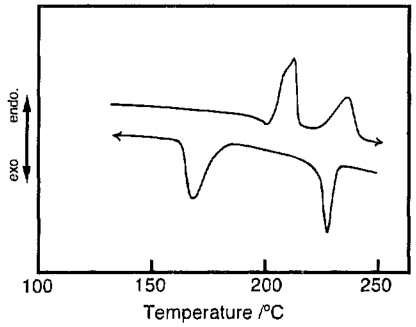

Figure 1. DSC heating and cooling thermograms of BB-6-III measured at a rate of 10 °C min^{-1}.

Results and Discussion

Characterization of the Polymers. Seven specimens with different molecular weights, BB-6-I to BB-6-VII, were prepared by controlling the reaction period of melt transesterification. All the polymers exhibit the well-defined transition behavior, as found in the DSC thermogram of Figure 1 where the two enantiotropic transitions are included. The two transitions at T_m and T_i can be assigned to the crystal melting to smectic A and the isotropization of the smectic A phase, respectively.[2] The inherent viscosities, M_n, M_w/M_n, and thermodynamic data are listed in Table 1.

Parts a and b of Figure 2 show the wide-angle X-ray patterns taken for the oriented smectic A and crystalline phases of BB-6-III, respectively. The oriented smectic A phase exhibits the characteristic X-ray pattern which includes the sharp inner reflection with a spacing of 18.3 Å on the meridian and the outer broad reflection with a spacing of around 4.5 Å on the equator. The smectic type of structure has been identified from this characteristic reflection geometry.[2]

For the crystal prepared by cooling the smectic A phase of Figure 2a, the X-ray pattern is also highly oriented and ordered, as shown in Figure 2b; the amorphous halo is nearly absent, and significant peaks are measurable up to $2\theta = 30°$ with about 20 peaks. The unit cell of the crystal has been reported to be monoclinic with $a = 10.98$ Å, $b = 11.47$ Å, $c = 19.62$ Å, and $\beta = 89.7°$.[15]

Stacked Lamellar Structure in the Crystalline Phase. Figure 3 shows the SAXS pattern taken for the same oriented crystal as in Figure 2b. Clear reflection maxima with a spacing of around 250 Å can be seen on the meridian, showing that the long period exists along the chain axis. The spacing of the long period, L, is obviously smaller than the entire extended molecular length of the polymer, l (see Table 2). These results show that the lamellar type of crystal structure with the chain foldings is formed. Takahashi and Nagata[14] have reported a similar observation for the same BB-6 sample and concluded the formation of the stacked lamellar structure by giving more decisive evidence from electron microscopy in which the 250 Å thick lamellae showing characteristic smectic-like texture and defects are observed with high contrast and resolution. Thomas et al.[16,17] and Kleman et al.[18] have also reported a similar morphology for the other type of main-chain LC polymer. The stacked lamellar structure with chain foldings is common in linear polyesters, poly(ethylene terephthalate) and poly(butylene terephthalate), so it is reasonable that the present BB-6 polyester could accommodate folds.

The long spacings by SAXS were determined for all the polymers. Those are listed in Table 2 and plotted against the molecular weight in Figure 4. In an effort to prevent a thermal prehistory, the data were collected for the crystals cooled at a rate of 10 °C min^{-1} after 5 min of annealing in the isotropic melt. The long spacing, L, is distributed around 250 Å, increasing somewhat with an increase of molecular weight. The correlation length between foldings thus corresponds to approximately 15 times the length of the repeat unit. The values for the average number of foldings in a chain, F, are listed in Table 2 as calculated from the equation, $F = l/L - 1$. It was found that several foldings are included in a chain.

Figure 5 shows the dependence of the lamellar spacing on annealing time at respective temperatures below T_m. Initially, the spacing increases very rapidly in the first 10 min of annealing and thereafter changes very little. Figure 6 shows the temperature dependence of L values which were collected at a constant annealing time of 60 min. As with other crystalline polymers,[19,20] the long spacing increases with the increase of annealing temperature. These features are also expected for chain-folded lamellar crystals.

Chain Folding in the Smectic A Phase. What is interesting here is that the crystallization of the present BB-6 polymer takes place from the smectic melt. This situation is completely different from that encoutered in the conventional polymers in which the crystallization takes place from the isotropic liquid. In a liquid state, a polymer molecule is capable of assuming a large number of configurations because of the freedom of rotation of the individual chain atoms about their connecting bonds. There is no significant correlation between the configurations assumed by the individual molecules so that the liquid state is characterized by random, haphazard arrangements of the polymer chain units. On the other hand, the smectic A phase has a long range orientational order due to the extended configuration of polymer molecules. Further, it has an additional one-dimensional positional (smectic layer) order with the layer spacing nearly equal to the repeat length of the polymer in a fully extended form.[1,21] We can thus envisage that the crystallization to achieve full three-dimensional order takes place more easily and steadily from the smectic melt than from the isotropic melt, since it does not require a significant migration of the molecules and significant change of the molecular configuration. From a comparison of the X-ray patterns in Figures 2a,b, in practice, one can recognize that the orientational order of the smectic phase is completely sustained on crystallization and the resulting crystal has a high degree of crystallinity. Solid state morphology of the crystalline phase, hence, should reflect the morphology of the preceding smectic A phase, and it can be concluded that the chain folding observed in the crystalline phase already existed in the preceding smectic A phase.

A significant question arises as to whether the chain folding in the smectic A is thermodynamically stable or is attributable to kinetic factors arising at the isotropic to smectic phase transformation. To examine this point, the lamellar spacing was measured for the crystal specimens of BB-6-III which were annealed for a certain period in the smectic A phase and then cooled down at a rate of 10 °C min^{-1}. In Figure 7, the lamellar spacings thus determined are plotted against the annealing time. Here, the crystal specimens with various lamellar sizes were initially prepared by annealing at temperatures below T_m (refer to Figure 6) prior to heating to the smectic A phase for annealing. For the specimens with the lamellar spacings larger than 250 Å, the lamellar

Table 1. Characterization of BB-6 Polyesters

				calorimetric data					
				transition temp					
				heating process		cooling process		transition enthalpy[a]	
sample	η_{inh}/dL g^{-1}	$10^{-4}M_n$	M_w/M_n	T_m/°C	T_i/°C	T_m/°C	T_i/°C	ΔH_m/kcal mol^{-1}	ΔH_i/kcal mol^{-1}
BB-6-I	0.26	1.28	2.41	210	231	187	218	3.12	1.99
BB-6-II	0.34	1.36	2.39	213	238	167	228	2.09	2.31
BB-6-III	0.40	1.52	2.03	216	239	166	227	2.09	1.97
BB-6-IV	0.49	1.70	2.46	214	240	165	229	1.90	2.01
BB-6-V	0.67	2.15	2.38	220	241	161	227	1.84	2.13
BB-6-VI	0.79	3.28	1.58	220	238	177	223	2.17	2.15
BB-6-VII	0.92	3.23	2.30	210	239	155	224	1.96	2.15

[a] Based on cooling DSC data.

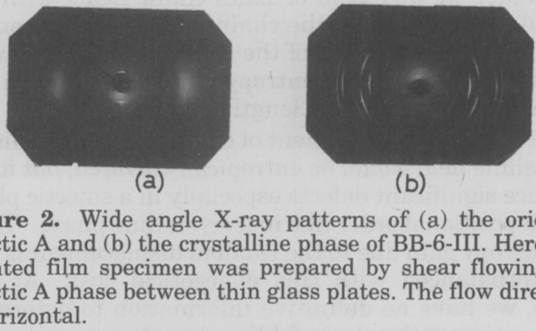
(a) (b)

Figure 2. Wide angle X-ray patterns of (a) the oriented smectic A and (b) the crystalline phase of BB-6-III. Here, the oriented film specimen was prepared by shear flowing the smectic A phase between thin glass plates. The flow direction is horizontal.

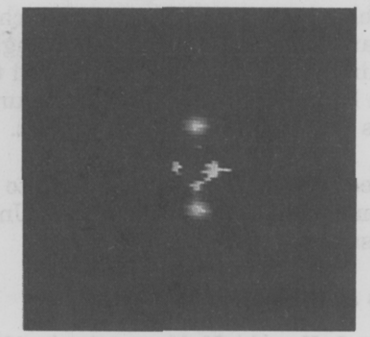

Figure 3. Small angle X-ray pattern for the oriented crystal of Figure 2b.

Table 2. Parameters for the Lamellar Structure Formed by Folded Chains of BB-6

sample	chain length l^a/Å	lamellar size L^b/Å	number of chain foldings F^c
BB-6-I	7.8×10^2	225	2.5
BB-6-II	8.3×10^2	244	2.4
BB-6-III	9.2×10^2	251	2.7
BB-6-IV	1.0×10^3	247	3.2
BB-6-V	1.3×10^3	267	3.9
BB-6-VI	2.0×10^3	261	6.6
BB-6-VII	2.0×10^3	294	5.5

[a] Calculated by using the repeating length of 19.6 Å[15] in the crystalline phase. [b] Observed for the crystal sample which was cooled from the isotropic melt at a rate of 10 °C/min. [c] $F = l/L - 1$.

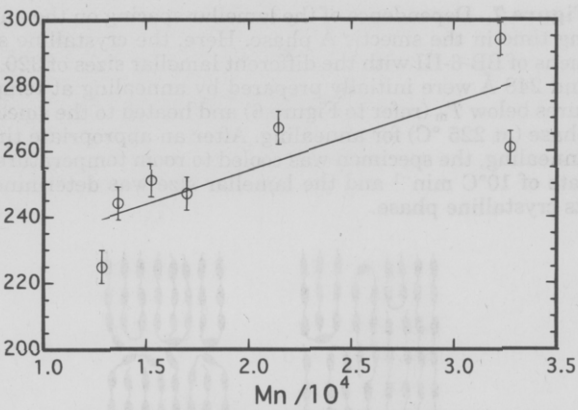

Figure 4. Molecular weight dependence of the lamellar spacing elucidated for the crystalline specimens which were prepared by cooling the isotropic melt at a rate of 10 °C min^{-1}.

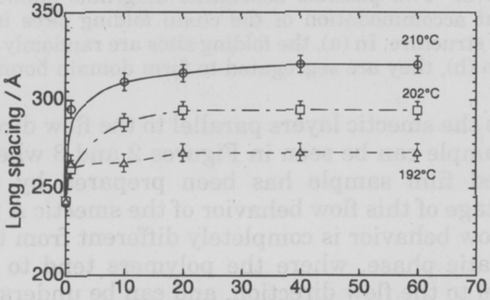

Figure 5. Dependence of the lamellar spacing on the time of annealing in the crystalline phase. The crystalline specimens of BB-6-III were initially prepared by cooling the isotropic melt at a rate of 10 °C min^{-1} and annealed at respective temperatures below T_m.

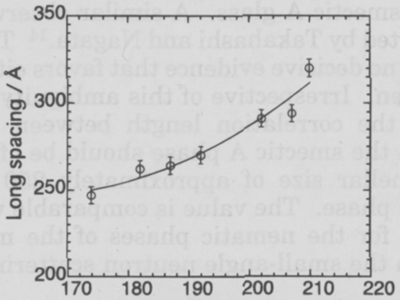

Figure 6. Dependence of the lamellar spacing on the annealing temperature below T_m. The data were collected after 60 min of annealing (refer to Figure 5).

spacings changed drastically for the initial 5 min of annealing and finally reached a constant value of around 250 Å. This result leads to a significant conclusion that the chain foldings exist as a thermodynamic equilibrium state in the smectic A phase.

The next question that arises is, how are the chain foldings accommodated in the smectic A phase? Are the chain foldings positioned randomly or segregated in a certain confined position to result in the lamellar type of domain boundaries like in the crystalline phase? The two possible schematic diagrams reflecting the key features of the respective models are shown in Figure 8a,b. To this argument, it is interesting to note that the smectic A phase of the main-chain polymers shows the anomalous orientation behavior on applying shear flow deformation which was first observed by Krigbaum and Watanabe.[21] Shear flow orients the polymer chains perpendicular to its flow direction; in other words it

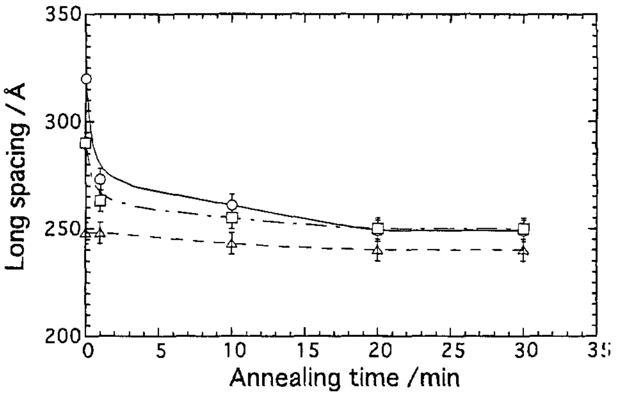

Figure 7. Dependence of the lamellar spacing on the annealing time in the smectic A phase. Here, the crystalline specimens of BB-6-III with the different lamellar sizes of 320, 290, and 248 Å were initially prepared by annealing at temperatures below T_m (refer to Figure 6) and heated to the smectic A phase (at 225 °C) for annealing. After an appropriate time of annealing, the specimen was cooled to room temperature at a rate of 10°C min^{-1} and the lamellar size was determined in its crystalline phase.

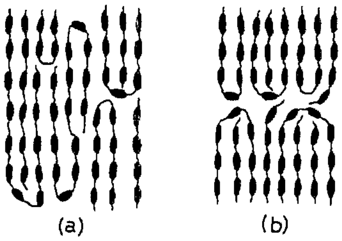

Figure 8. Two possible schematic diagrams showing the different accommodation of the chain folding sites into the smectic structure. In (a), the folding sites are randomly placed, while in (b), they are segregated to form domain boundaries.

orients the smectic layers parallel to the flow direction. An example can be seen in Figures 2 and 3 where the oriented film sample has been prepared by taking advantage of this flow behavior of the smectic A phase. This flow behavior is completely different from that in a nematic phase, where the polymers tend to orient parallel to the flow direction, and can be understood if the lamellar type structure exists such that the chain folding parts are limiting the boundaries of the flow domains,[21] as illustrated in Figure 8b. However, it should also be noted that the reflection maxima in SAXS leading to the lamellar type domains have never been observed in the smectic A phase as well as in the quenched smectic A glass. A similar observation has been reported by Takahashi and Nagata.[14] Thereby, at this stage, no decisive evidence that favors either model can be given. Irrespective of this ambiguity, it can be said that the correlation length between the chain foldings in the smectic A phase should be of the order of the lamellar size of approximately 250 Å in the crystalline phase. The value is comparable with those elucidated for the nematic phases of the main-chain LCPs from the small-angle neutron scattering.[11-13]

Concluding Remarks

The solid state morphology was studied for the main-chain LC polyester, BB-6, which forms the smectic A phase preceding the crystalline phase. The well-defined lamellar structure was detected from the SAXS method. For the specimens prepared by cooling at a rate of 10 °C min^{-1} from the smectic A phase, the lamellar spacing was observed to be around 250 Å, although it tends to somewhat increase with an increase of the molecular weight. From a comparison of the lamellar spacing with the length of entirely extended chain, the correlation length of about 250 Å between the chain foldings is approximately 15 times the length of the repeating unit of polymer and several chain foldings are included within a chain.

The most significant result obtained here is that the chain folding is formed at thermodynamic equilibrium in the foregoing smectic A phase. To produce the orientational and positional orders in a smectic A phase, the obvious configuration for a polymer molecule to assume in order to minimize its energy is for it to lie entirely along the director. On the other hand, it is also reliable that the energy penalty due to the chain folding is smaller in this type of main-chain LCPs with the flexible spacer. Thus, the chain folding can be considered to arise as a result of the counterbalance between its energetical cost and entropy gain of where it can be placed along the chain's length.[8,9]

The random displacement of chain foldings in a liquid crystalline field would be entropically favored, but it can produce significant defects especially in a smectic phase with a positional order like in a crystalline phase. Thus, the entropy gain due to the random displacement is also counterbalanced with this energetical cost. At this stage, we have no definitive information to determine the location of the chain folding, but the characteristic shear flow behavior in which the polymer chains orient perpendicular to the shear direction strongly suggests that the chain folding sites are segregated to form the flow domain boundaries, as shown in Figure 8b. Further study is required to clarify this point.

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