Macromolecules **2000,** *33,* 8367−8370

Aromatic Polyesters with Flexible Side Chains. 8. Studies on Long Periodical Structure Observed in Layered Crystalline Phase

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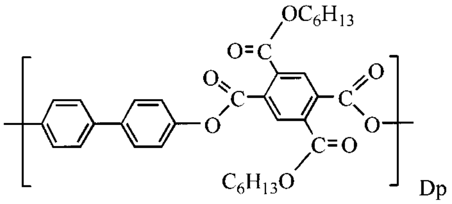
Received June 19, 2000

ABSTRACT: Long periodical structure was studied for the crystal of a rigid-rod liquid crystalline BC-6 polyester composed of the 1,4-dihexyl ester of pyromellitic acid and 4,4′-biphenol with small-angle X-ray scattering (SAXS) and transmission electron microscope (TEM) measurements. The highly oriented crystalline fibers which were prepared by spinning a nematic melt of the sample and succeeding annealing showed well-defined scattering maxima with a spacing in the range of 250−300 Å in the SAXS pattern and the corresponding clear stripes in the TEM photograph. The long spacing is attributed to the crystalline lamellae stacked along the chain axis. This is the first example of long periodical structure in the fully aromatic polymer systems. The origin of the long periodic structure is discussed.

There are many papers treating the rodlike polyesters with flexible alkyl side chains.[1−9] The purpose of the studies was to develop liquid crystallinity in the polymeric materials, which have lower melting temperatures and greater solubility than the simple aromatic polyesters with no side chain group. Easy processability for the polymer in the liquid crystalline state has led to not only the finding of the interesting structural feature in liquid crystalline phases but also the well organization of the aromatic polyesters into highly oriented crystals.

In this report, we demonstrate the crystalline morphology of the BC-6 polyester composed of 1,4-dihexyl ester of pyromellitic acid and 4,4′-biphenol. BC-6 forms isotropic liquid, nematic, and crystalline phases in order of decreasing temperature. In the crystalline phase, the aromatic main chains pack into layers, and the flexible alkyl side chains occupy the space between the layers.[2,4] Recently, we found that in the layered crystal phase the lamellar structure with long spacings of 200−300 Å is regularly formed along the aromatic main chain. As far as we know, the lamellar structure has never been observed for the fully aromatic polyesters. Thus, the lamellar morphology will be described in detail, and its origin will be considered.



BC-6

BC-6 polymers were prepared by a reaction of 2,5-bis(hexyloxycarbonyl)terephthaloyl and 4,4′-biphenol.[1] Five samples (BC-6/1 to BC-6/5) with different molecular weights were synthesized by controlling the reaction conditions. Before all of the characterization and the measurements, the cast films of the polymers were prepared by using tetrahydrofuran (THF) as a solvent and preheated to the nematic temperature of 230 °C. The inherent viscosities and the molecular weights determined by GPC are listed in columns 2−5 of Table 1.

Every member of the polymers exhibits the well-defined transition behavior. Figure 1 shows the typical DSC thermogram measured for BC-6/4 by a Perkin-Elmer DSC-II with a scanning rate of 10 °C min^{-1}. There are two transitions at 218 °C (T_m) and at 299 °C (T_i) on heating. On cooling, the corresponding transitions were observed at 164 and 275 °C. The large broad peaks of heating and cooling cycles are assigned to the crystal melting to nematic phase, and the other small peaks correspond to the isotropization of the nematic phase. As seen in columns 6 and 8 of Table 1, both of the transition temperatures increase with an increase of M_w, but saturated at a finite value for the higher molecular weight samples. Polymers are thermally stable so that only 5% loss of the weight takes place even at high temperature up to 350 °C in the TG-DTA measurement. Thus, the samples were handled comfortably without decomposition at the nematic temperatures below 230 °C.

The X-ray pattern of the oriented nematic liquid crystal of the BC-6 includes only a few broad reflections.[4] In the small-angle region, one broad equatorial reflection with a spacing around 16 Å was observed as well as a weak meridional arc with a spacing of 15.5 Å. In the wide-angle region, only a broad arc with a spacing of approximately 4.4 Å could be distinguished on the equator. Under the polarized optical microscopy, the nematic phase exhibits a schlieren texture (Figure 2) in areas with a free surface on one side, as well as an inversion wall texture. These optical textures undoubtedly show the nematic character of the mesophase.

Figure 3a shows the wide-angle X-ray diffraction (WAXD) pattern for the as-spun fiber of BC-6/4 taken at room temperature using a Rigaku Denki RU-200BH X-ray generator with Cu Kα radiation and a flat imaging plate. The fiber was spun from the nematic phase of 230 °C with a rate of approximately 10 m min^{-1}. The fibrous WAXD pattern is identical with that for the nematic phase, showing that the nematic struc-

10.1021/ma001056g CCC: $19.00

Table 1. Characterization of BC-6 Polyester

		GPC data[b]			calorimetric data[c]					
sample	η^a(dL/g)	M_n(×10^4)	M_w (×10^4)	M_w/M_n	T_m (°C)	ΔH_m (kcal/mol)	T_i (°C)	ΔH_i (kcal/mol)	lamellar spacing L^d(Å)	chain length l^e(Å)
BC-6/1	0.25	0.60	1.15	1.9	190	2.74	248	0.75	232	174
BC-6/2	0.35	0.71	1.59	2.2	195	2.69	263	0.71	236	206
BC-6/3	0.38	0.88	3.06	3.5	213	2.90	284	0.79	252	255
BC-6/4	1.02	1.52	7.59	5.0	218	2.81	299	0.88	252	441
BC-6/5	1.71	2.53	12.7	5.0	217	2.58	302	0.90	252	733

[a] Measured in THF solutions at 30 °C. [b] Measured by GPC, which was carried out using a Hitachi L-7100 pump, a Hitachi L-7300 column oven, and a Hitachi L-7400 UV detector fixed at 254 nm at 40 °C. Molecular weights are quoted with respect to monodisperse polystyrene standards. [c] Based on DSC data measured at a scanning rate of 10 °C/min. [d] Observed for the crystal fiber which was spun from the nematic melt and then crystallized at 120 °C for 1 h. [e] Calculated by using the M_n in column 3 and the repeating length of 16.6 Å.

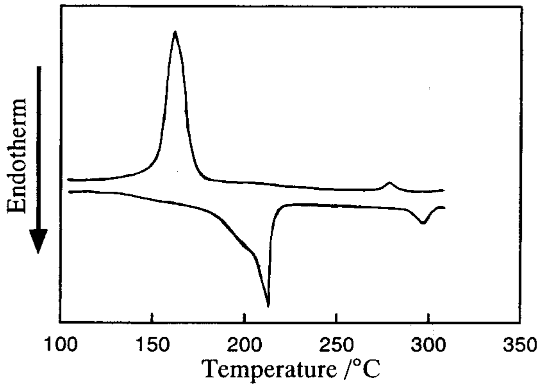


Figure 1. DSC thermogram for heating and cooling cycle of the BC-6/4 measured at a rate of 10 °C min^{-1}.

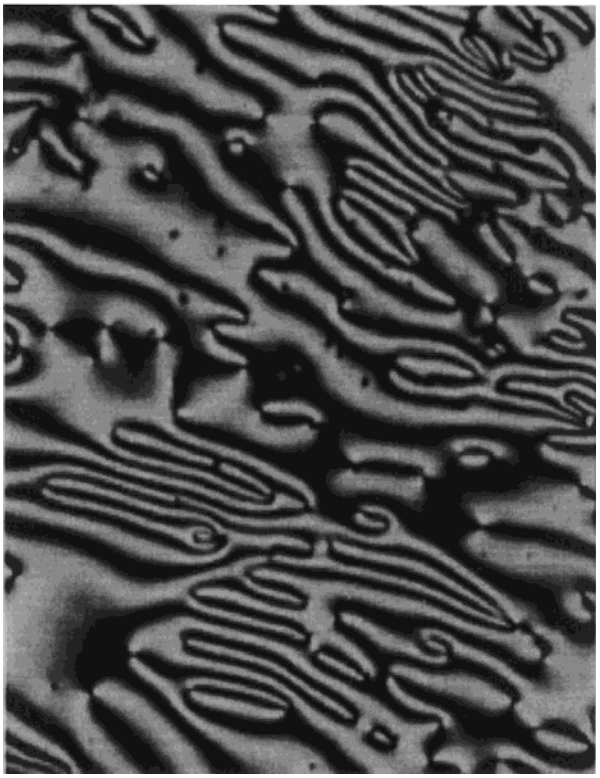


Figure 2. Optical micrograph for the nematic schlieren texture of BC-6-1.

ture is glassified in the as-spun fiber. The crystalline fiber was prepared by annealing of the as-spun fiber at 120 °C for 1 h. The crystalline fiber is also highly oriented as seen in the WAXD pattern of Figure 3b, which includes many sharp reflections. Although the precise three-dimensional crystal lattice has not yet been determined, the equatorial reflections can allow the umambiguous determination of the two-dimensional packing structure with lattice constants of $a = 10.0$ Å, $b = 4.55$ Å, and $\gamma = 103.1°$.[4] Within the lattice, the molecules adopt the layered structure in which the aromatic main chains are packed into a layer with a lateral spacing of b, and the side chains occupy the space separated by the layers at intervals of $a \sin \gamma$. The main chains in the layer take an extended conformation with a repeat length of 16.6 Å which can be determined from the height of the first layer line from the equatorial one.

Figure 3d shows the small-angle X-ray scattering (SAXS) pattern taken for the same crystal fiber as in Figure 3b. Clear reflection maxima with a spacing of around 250 Å can be seen just on the meridian, showing that the long period exists along the chain axis. More insight of the lamellar structure was interpreted from transmission electron microscopy (TEM) observation of the ultrathin sections cut along the fiber axis. Figure 4 shows a typical TEM photograph taken by a Hitachi H-500 TEM with 100 kV of acceleration voltage for the same fiber as in Figure 3d. The sections were stained with ruthenium tetraoxide (RuO_4), so the staining agent can be assumed to enter into the disordered region. The bright parts, therefore, correspond to the crystal lamellae and the dark areas to the disordered regions. The photograph indicates that the crystal lamellae with the large lateral size are well separated by the disordered regions and regularly piled up at regular intervals of approximately 250 Å, which corresponds to the spacing determined by SAXS measurement. It should be noted that such a long period can be detected only for the crystalline specimen (compare parts c and d of Figure 3).

The long period does not change with crystallization time. In column 10 of Table 1, the long spacings for the polymers crystallized at a constant temperature of 120 °C are listed. These are observed in a range from 230 to 250 Å, showing that the long spacing is not significantly affected by the molecular weight. Figure 5 shows the crystallization temperature dependence of the long spacing, where all the samples were quenched from the nematic melt and then crystallized at certain temperatures for each sample for 1 h. The long spacing is the increase function of the crystallization temperature.

Our basic conclusion is that the stacked lamellar structure with the long period of 200−350 Å is formed in the layered crystal of the fully aromatic polyester with the alkyl side chains. The lamellae with the large lateral size are regularly piled up in a direction parallel to the main chain axis, and their thickness increases with an increase of crystallization temperature. Instantaneously, one would visualize the chain-folding lamel-

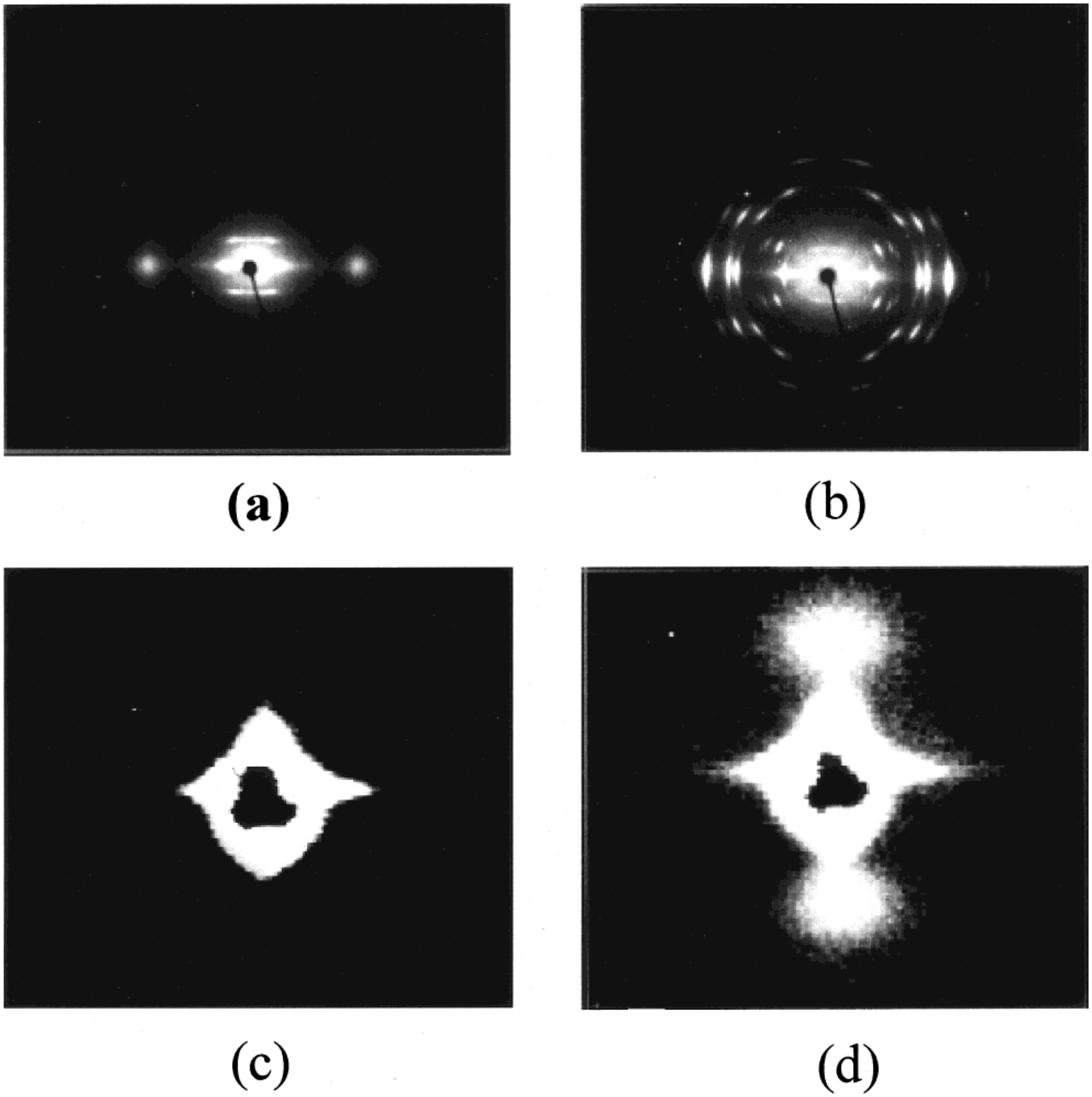


Figure 3. Wide-angle X-ray patterns [(a) and (b)] and small-angle X-ray patterns [(c) and (d)] of BC-6/4 fibers. (a) and (c) were observed for the fiber as-spun from the nematic melt, while (b) and (d) were observed for the crystal fiber crystallized at 120 °C. The fiber axis is in the vertical direction.

lar crystals as has been observed for the conventional flexible polymers. However, the restriction of conformational variety seems not to allow the chain-folding structure for this type of fully aromatic polyester.

To estimate the conformation of the present polymer, we first consider to the Mark−Houwink relations. From the plots of logarithm of inherent viscosity ($[\eta]$ in dL/g) and M_w, the following Mark−Houwink relation was obtained.

$$[\eta] = 1.51 \times 10^{-4} M_w^{0.80} \text{ (in THF at 30 °C)}$$

The exponential value of 0.80 is located in a range typical for semiflexible polymers,[10] the Kuhn lengths of which are approximately 100−200 Å.[11,12]

Such a semiflexible character of BC-6 can be understood from the M_w dependence of the transition temperature of bulk polymer. Truly hard rod polymers would exhibit divergent transition temperatures as can be inferred from studies of oligomeric compounds.[13] In the present BC-6 polymer, the transition temperature increases with the initial increase of the molecular weight but reaches a finite value at around M_w = 30 000. This indicates that the persistence length in bulk possesses the same order of magnitude as in solution.[11,14]

Even if the present polymer is nonrigid, but semiflexible, it is still difficult to illustrate the folding lamellar structure. In fact, according to the computer MD simulation,[15,16] only a loose loop comprising more or less than 10 repeating units is allowed. Formation of such a loop would significantly disturb the uniaxial orientational order and so is energetically unfavorable in the nematic liquid crystals.[17,18] Even if the loop exists, spinning the fibers in the nematic state, as has been done here, forces the polymer chains to assume the

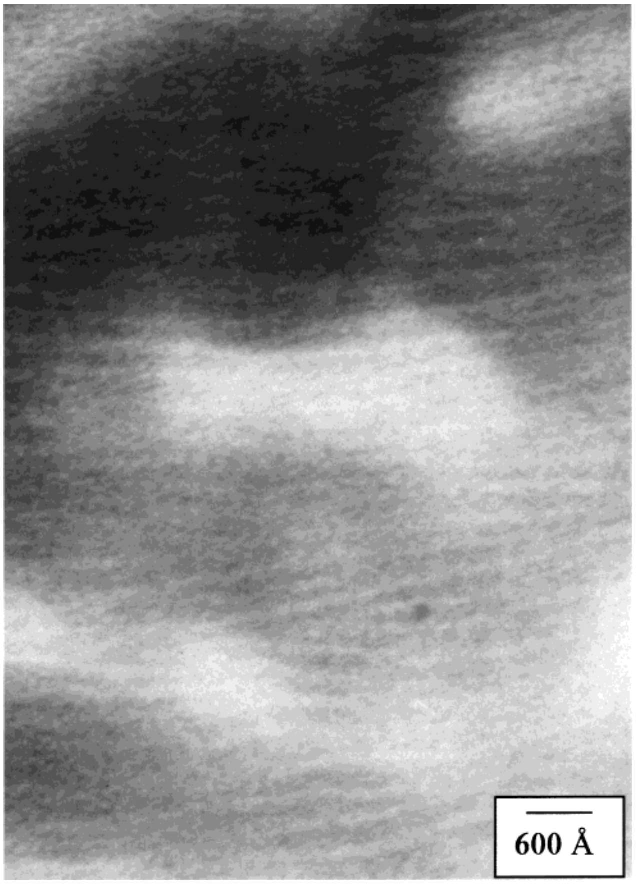


Figure 4. TEM photograph observed for the microtomed film cut along the crystal fiber same as in Figure 3d. The fiber axis is in the vertical direction.

extended form. Thus, no chain folding would exist in the crystalline phase. The possibility of the chain-folded lamellae is also ruled out from a comparison of the whole chain length of polymer and lamellar thickness. As found in columns 10 and 11 of Table 1, the lamella thickness obviously exceeds the length of the extended chain in BC-6/1 and BC-6/2.

Here we have to depict the morphology of the BC-6 crystalline fiber consisting of separate crystalline and amorphous regions regularly piled along the chain axis. The crystalline part ambiguously consists of the crystallized alkyl side chain. Thus, the alkyl chain crystallized periodically in the direction perpendicular to the chain axis. The resulting morphology is strange for the chain molecules which form long periodicity always in the direction parallel to the chain axis. Moreover, the lateral size of the crystalline lamella of the alkyl side chain is significantly large so that the lamella crystalline penetrates many aromatic layers. We speculate that the aromatic main chain may play important role in the periodic crystallization. For the BC-*n* polyesters, a high-resolution ^{13}C NMR study suggests that the conformations of main chain and side alkyl chain in BC-*n* polyesters are related to each other both in the liquid crystal and in the crystal.[5] The peculiar crystalline morphology in the alkyl side chains thus may be related with the conformation of the rigid-rod main chain. The studies are now proceeding to illustrate the detailed morphology and to present the reason for the occurrence of the lamellar type of crystallization in this kind of polymer.

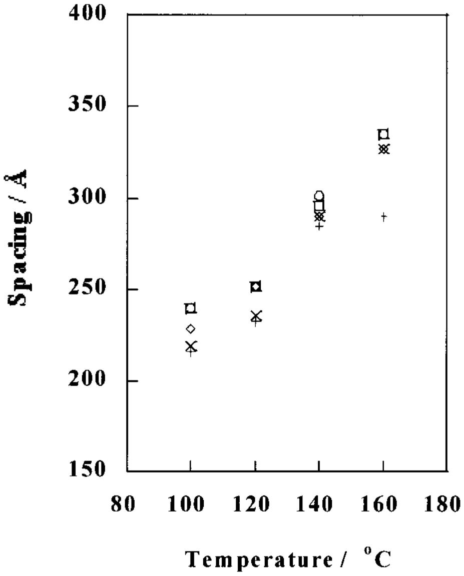


Figure 5. Temperature dependence of long SAXS periods observed for the crystal fiber of BC-6/1 (+), BC-6/2 (×), BC-6/3 (□), BC-6/4 (◇), and BC-6/5 (○). The fibers were spun at the nematic temperature of 230 °C, and the data were collected after the crystallization for 1 h.

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