Rigid-Rod Polyesters with Flexible Side Chains. 6. Appearance of Hexagonal Columnar Phase as a Consequence of Microsegregation of Aromatic Main Chains and Aliphatic Side Chains

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There have been several recent reports in the literature on the thermotropic phase behaviors of rigid-rod polymers with long flexible alkyl side chains.[1-13] The most interesting property of these materials is their ability to form layered structures in crystals and liquid crystals when the alkyl side chains reach a critical length. The α-helical poly(γ-alkyl L-glutamates) were the first examples of this type of material,[1] and recently, aromatic polyesters and polyamides with long alkyl side chains have also been examined.[2-13] The layered mesophases are characterized by a lateral packing of the rigid-rod main chains into layers, with the fluidlike side chains occupying the space between the layers. It has been postulated that the driving force for the adoption of such a structure is a type of microphase separation of the aliphatic and aromatic domains.[2,5,6,12] In these layered structures, liquid crystallinity is the result of a partial or total lack of positional order with respect to the main-chain packing within a layer and the fluidlike disordered alkyl side chains between the layers.[12] In the crystalline phases with a layered structure, it has been found from X-ray and NMR analyses that the main chains and side chains crystallize in a cooperative fashion.[10,12,13]

In this report, we study the thermotropic phase behavior and structures of the rigid-rod poly(*p*-biphenylene terephthalate) main chain with flexible dodecyloxy side chains on the terephthalate moiety,
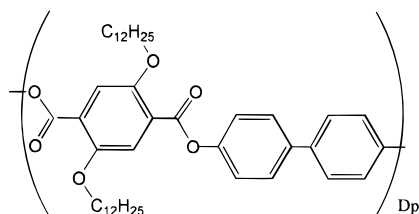
Two polymers with inherent viscosities of 0.45 and 1.80 dL/g were prepared by different methods; the lower molecular weight polymer, designated PBpT-O12(I), was synthesized by polycondensation of 4,4′-dihydroxybiphenyl with 2,5-bis(dodecyloxy)terephthaloyl chloride in dry pyridine at 60 °C while the higher molecular weight PBpT-O12(II) was prepared by polycondensation of the same materials in the melt at 290 °C. The significant result obtained here is that the polymers do not form the well-known layered mesophase, but form the hex-
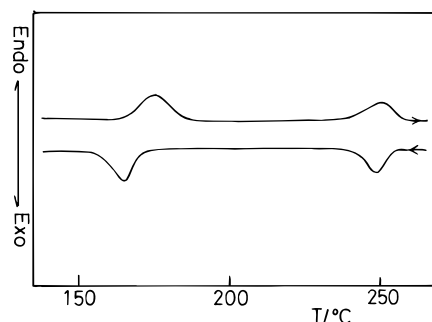
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Figure 1. DSC thermograms of PBpT-O12(I) measured at a rate of 10 °C/min.

agonal columnar phase. The structure of the hexagonal columnar phase can be described as a new type of morphology resulting from a microsegregation of aliphatic side-chain and aromatic main-chain domains.

Figure 1 shows the DSC thermogram of PBpT-O12-(I). In order to avoid any thermal prehistory, the sample was first heated to the isotropic melt above T_i and reproducible data were collected on cooling and heating as shown in Figure 1. Two small transitions can be observed at $T_1 = 175$ °C and $T_i = 250$ °C. The enthalpies of the T_1 and T_i transitions are 0.22 and 0.14 kcal/mol of repeat unit, respectively.

Optical microscopy indicates that there exist two mesophases. One is the nematic phase with a fairly low viscosity, which appears in the temperature region between T_1 and T_i. The nematic nature was evident from the schlieren or inversion wall textures (see part a of Figure 2). The other is a mesophase observed in the temperature region below T_1. On cooling the nematic to this phase, the texture became fine (see part b of Figure 2) and the viscosity increased as well although it is still fluid. No crystallization has so far been observed on cooling to room temperature even though the sample is annealed for a prolonged time.[12] PBpT-O12(II) shows a similar transition behavior, although the T_1 and T_i temperatures increased to 212 and 287 °C, respectively, because of its higher molecular weight.

The structural features of the two mesophases were analyzed by X-ray diffraction. The X-ray patterns are shown in Figure 3, where the highly oriented fiber was prepared by pulling up the nematic melt and its axis is placed in the vertical direction. In the nematic phase, the pattern includes two broad reflections with spacings of ~20 and 4.5 Å (see part a of Figure 3). These are expected of a nematic mesophase where the former broad reflection reflects a somewhat disordered lateral packing of rods and the latter may result from the alkyl side chains in a molten state.

The lower temperature mesophase exhibits a distinct X-ray pattern as observed in part b of Figure 3. It includes one reflection on the meridian and several sharp reflections on the equator. The meridional reflection has a spacing of 16.6 Å, which corresponds to the repeating length of the polymer in a fully extended form.[8] Its appearance as a streak shows that the polymer chains are randomly placed with respect to each other along the fiber axis.[14,15] On the other hand, the well-distributed reflections on the equator indicate a somewhat ordered packing of molecules in their lateral direction. From Figure 4, where the intensity profile is measured along the equator, one can recognize at least four sharp reflections. The lattice spacings of the
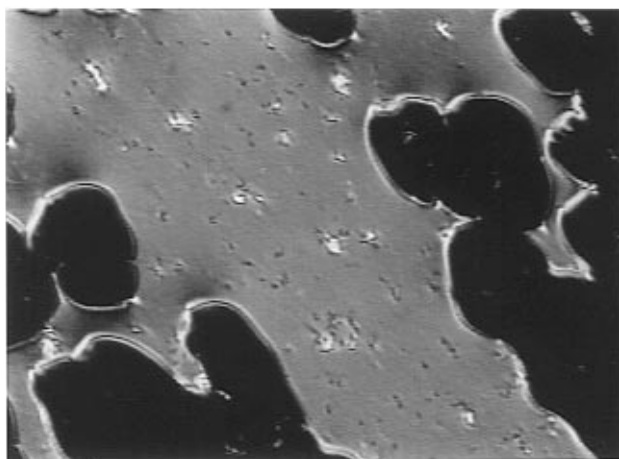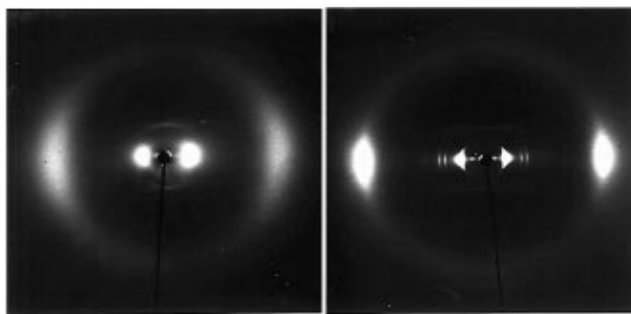
(a)
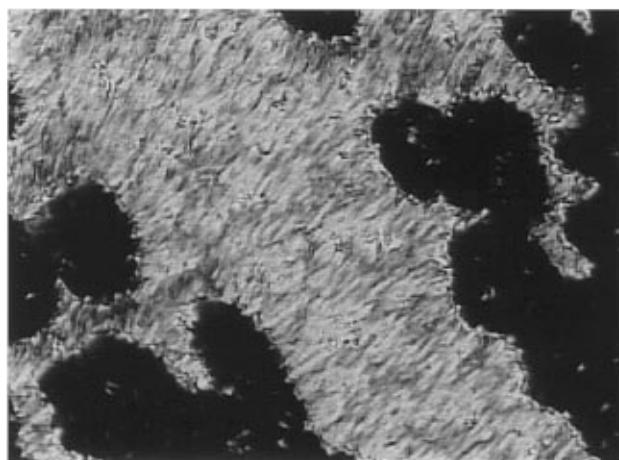
(b)

Figure 2. Optical microscopic photographs for (a) the nematic phase exhibiting an inversion wall texture and (b) the hexagonal columnar phase.

(a)   **(b)**

Figure 3. Oriented X-ray patterns of (a) the nematic phase and (b) the hexagonal columnar phase of PBpT-O12(II). Here, the oriented fiber was spun from the nematic melt and the fiber axis corresponding to the polymer chain axis is placed in the vertical direction.

reflections are 23.3, 13.5, 11.6, and 8.82 Å. These are in the ratio $1:1/\sqrt{3}:1/\sqrt{4}:1/\sqrt{7}$, indicating that the polymers are packed in a two-dimensional hexagonal lattice with $a = b = 26.9$ Å and $\gamma = 120°$. Figure 4 also shows the outer broad reflection of around 4.4 Å that can be attributed to the molten side chains. The molten state was also confirmed by ^{13}C NMR.[13] From the above structural features, we can conclude that the hexagonal
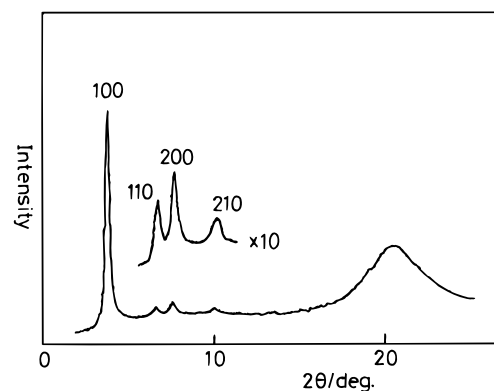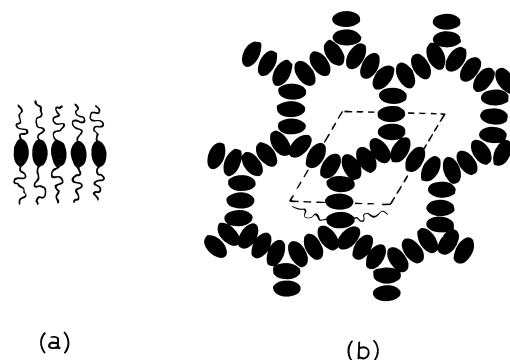

Figure 4. Intensity profile for the hexagonal columnar phase of Figure 3b, measured along the equator.

(a)   (b)

Figure 5. On the basis of the segregation of the aromatic main chains (closed ellipsoids) and aliphatic side chains into a layer form of (a), the hexagonal columnar phase can be illustrated as in (b) where the molten side chains are accommodated within a cylindrical domain and the aromatic main chains form a honeycombed network to surround the side-chain domains. The dashed lines show the hexagonal unit cell.

columnar mesophase is formed. The observed density of 1.07 g/mL suggests the presence of a large number of molecules, approximately 9−10 on average, within a lattice. The structural transformation from the columnar phase to the nematic phase is completely reversible on heating and cooling. The lattice parameters of the hexagonal phase remain constant subject to the thermal history and the molecular weight of the sample.

In the case of rodlike molecules with long alkyl side chains, formation of the nematic liquid crystal is rather easily understood. A disordered sheath, due to the molten side chains, is formed around the backbone that screens off the periodic nature of the polymer chains from its neighbors. Thus the intermolecular positional order, both parallel and perpendicular to the chain direction, is lost.

The mesophase that draws immediate attention in this study is the hexagonal columnar phase. This is the first example of a hexagonal columnar phase in these aromatic polyesters with flexible side chains. Although several examples of the columnar phase have so far been reported in the polymeric system,[1,16−19] the above columnar phase is especially interesting because approximately 9−10 molecules are included in the hexagonal lattice. Such a large number indicates that there exists a specific association of molecules. As the side chains are still conformationally disordered in this phase, a molecular association can be visualized only on the basis of a microsegregation such that the aromatic main chains closely associate with each other to form a layer and the side chains are sticking out of both sides of the layer[2,5,6,12] (see part a of Figure 5). In

analogy with the amphiphilic molecule[20] and block copolymer systems,[21] such a microsegregation of two components can lead to mesophases with two fundamental morphologies. One is the well-known layered (lamellar) mesophases which have so far been observed. The other is a hexagonal (cylindrical) phase such as the one observed here. A cubic phase cannot be expected in this system, since the main chains are fully extended and can hardly be accommodated in a cubic domain. In order to satisfy the condition of all the side chains spaced with an equivalent environment and the main chains packed within reasonable distances of each other, a unique structure of the hexagonal phase can be illustrated as in part b of Figure 5. Here, the molten side chains form a cylindrical domain and the aromatic main chains form the honeycombed network that surrounds the side-chain domains. The distance between the aromatic main chains can be calculated to 4.3 Å, which is similar to those observed in the layered mesophases.[8,12]

More recently, we have prepared a series of PBpT-On polymers with the carbon number of side chain, n, varying from 6 to 20 and found that the two types of morphology, the layered and columnar ones, appear depending on the length of the side chain. The polymers with $n \leq 12$ form a hexagonal columnar phase while those with $n \geq 18$ form a layered phase. This dependence of the side-chain length is similar to that observed in the block copolymer system in which the morphologies are determined primarily by the component of the copolymer.[21] More details of the phase behavior and structures in these homologues will be described in a future report.

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