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Extended-Chain Lamellar Structure and Chain Segregation in Lyotropic Liquid Crystals of Poly{5,7-dodecadiyne-1,12-diol bis[((4-butoxycarbonyl)methyl)urethane]}

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ABSTRACT: The supermolecular structure of thin films of poly{5,7-dodecadiyne-1,12-diol bis[((4-butoxycarbonyl)methyl)urethane]} (P-4-BCMU), a soluble polydiacetylene, and mixtures of two P-4-BCMUs with different average lengths of molecules were investigated by means of transmission electron microscopy. An extended-chain lamella is observed in thin films of the polymer and mixtures. The influences of the weight fraction of a component and the difference between the average lengths of molecules on the supermolecular structure are discussed. Models describing structural features of extended-chain lamellae for the polymer and mixtures are suggested. The chain segregation according to the distribution of the extended-chain length of the rodlike macromolecules and the formation of the extended-chain lamella are discussed.

I. Introduction

Liquid crystalline (LC) polymers, in particular for the main-chain LC polymers without flexible spacers, supply an opportunity to investigate the new aspects of the morphology and supermolecular structure of polymers as the different kinds of defects, such as disclinations and inversion walls observed frequently in low molecular weight (LMW) liquid crystals but not in flexible-chain polymers, appear in the polymers. The much larger anisotropy and chain rigidity of main-chain LC polymers can result in some molecular arrangements much differing from the LMW liquid crystals and flexible polymers.

In the last decade investigations on the morphology and structure of LC polymers have rapidly increased. For thermotropic polymers, Windle and co-workers studied the morphology in thermotropic random copolyesters, mainly composed of 4-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA), that do not contain any flexible spacers in the main chain using transmission electron microscopy (TEM).[1-6] They suggested a model called a nonperiodic layer (NPL) crystallite to describe the crystallite in thermotropic random copolyesters. Roche et al.[7] studied the thin film morphology and the crystalline structure of poly(*p*-phenylene terephthalamide) (PPTA) coagulated from its lyotropic solution in concentrated sulfuric acid after shear. The influence of the coagulation on the PPTA polymorphs was investigated in great detail. In these studies the supermolecular structures, such as disclinations and thread lines, however, were not directly imaged by TEM in these LC polymers.

Disclinations and inversion walls were first imaged by Wood and Thomas[8,9] utilizing the TEM technique in thin samples of a main-chain LC polymer containing flexible spacers. Their studies show that the relative primary nucleation and growth rates of crystallites formed from a freezing-in liquid crystalline state are controllable. In the suitable condition folded-chain crystalline lamellae that are everywhere perpendicular to the director of molecules can be formed. In this case the defects appearing in the liquid crystalline state can be imaged via TEM.[8-12] The molecular arrangement in the folded-chain crystalline lamallae of this LC polymer is the same as that of flexible-chain polymers according to Thomas and co-workers.[8-12] This lamellar decoration technique has been widely used to image the supermolecular structures of thermotropic LC polymers.[13-16] It is worth noting that a thickness of lamellae observed by Mazelet and Kléman[13] and Ford et al.[15] is considerably larger than those of most conventional flexible-chain polymers.

In our previous works[17-22] we have systematically studied the properties and the textures of concentrated solutions of poly{5,7-dodecadiyne-1,12-diol bis[((4-butoxycarbonyl)methyl)urethane]} [IUPAC name: poly{5,7-dodecadiynediyl bis[*N*-((butoxycarbonyl)methyl)carbamate]}] (P-4-BCMU), a soluble polydiacetylene, in chloroform and the morphology of its thin solid film prepared from these solutions. The results show that a stable lyotropic liquid crystalline phase develops at room temperature when the concentration of the solution is higher than a critical concentration. In appearance a typical Schlieren texture was observed by polarized light microscopy (PLM). The disclinations with strengths of $s = \pm^1/_2$ were frequently observed. In thin solid films solidified from the annealed lyotropic state, however, a lamellar structure is observed directly by transmission electron microscopy (TEM) in a bright field.[17-22] The average thickness of lamellae is the same as the average length of the molecules and is controlled by the number-average molecular weight. This indicates that extended-chain lamellae are formed and further implies that the distribution of the lamellar thickness should be controlled by the distribution of the molecular length.[23] These results indicate that chains segregate in accordance with the molecular length in the lyotropic phase during annealing to form extended-chain lamellae of different thicknesses. We term this phenomenon "chain segregation" to emphasize the difference in the formation of the lamella between flexible and rodlike polymers.

In the present work we will further investigate the extended-chain structure and the chain segregation of P-4-

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Table 1. Number-Average Degree of Polymerization $\overline{DP}_n$, Molecular Weight Distribution $\bar{M}_w/\bar{M}_n$, and Average Molecular Length $\bar{l}$, of Samples Used in Mixtures Prepared for TEM Investigation

	$\overline{DP}_n$	$\bar{M}_w/\bar{M}_n$	$\bar{l}$ (nm)
polymer 1	425	2.38	210
polymer 2	270	2.65	130
polymer 3	145	5.52	70
polymer 4	110	7.20	55

Table 2. Relative Contents of Mixtures Used for TEM Investigation

sample	fraction of polymer 1	fraction of polymer 2	fraction of polymer 3	fraction of polymer 4
1	1.00			
2	0.50			0.50
3	0.50		0.50	
4	0.50	0.50		
5	0.25		0.75	
6	0.75		0.25	

BCMU lyotropic liquid crystals based on results obtained recently. These results emphasize the influence of the distribution of the molecular length on the supermolecular structure of the polymer. As reported in the previous works,[17-22] the electron microscopy technique was used to investigate supermolecular structures of thin films of P-4-BCMU and of mixtures prepared by mixing two polymers with different molecular lengths and distributions of the molecular length. Our purpose is to understand the molecular mechanism of this chain segregation in the lyotropic liquid crystalline state of P-4-BCMU.

II. Experimental Section

Molecular lengths and distributions of the molecular length for the different samples of P-4-BCMU are shown in Table 1. These parameters were determined by gel permeation chromatography in tetrahydrofuran solutions.[17,18] To study the influence of the molecular distribution on the supermolecular structures, five mixtures were prepared. The contents of the components in mixtures are shown in Table 2. Solutions in chloroform with a concentration of 1 g/L were prepared by dissolving the polymer or mixtures at room temperature. The solution was kept at least 4 days at room temperature to ensure a complete solubilization of polymers.

Thin films for the TEM study were prepared by casting solutions onto the surface of glass slides inside a Petri dish in which the evaporation of the solvent was slow. In this case the solution can stay in the lyotropic state during the evaporation of the solvent for a relatively long time. The samples of long molecular length were annealed in the lyotropic liquid crystalline state to obtain a clear morphological feature.

The morphology or supermolecular structure of thin solid films of polymers and of their mixtures was investigated by transmission electron microscopy (Zeiss EM 902) at 80 kV. The films are self-supporting and can be directly examined without further preparation in TEM. The details of the preparation of the sample for TEM investigation have been reported previously.[17-21]

III. Results and Discussion

1. Supermolecular Structure of a P-4-BCMU Polymer. Figure 1 shows a TEM micrograph of a thin film of sample 1 ($\overline{DP}_n$ = 425 and $\bar{M}_w/\bar{M}_n$ = 2.38). For obtaining this supermolecular structure the thin film was first annealed in the lyotropic state for awhile. The relationships between the annealing time and the texture for the P-4-BCMU films in the lyotropic state and between the annealing time and the supermolecular structure for the thin films solidified from the lyotropic state have been investigated in detail in a previous work.[20] From this micrograph we can find that the average thickness of lamellae is approximately 200 nm. It is the same as the average length of macromolecules of the polymer, as pointed out in the previous works,[17-21] indicating that an extended-chain lamella is developed in the LC polymer. (Note that the length of the repeating unit of P-4-BCMU is 0.49 nm.[24,25]) The individual lamellae are not of uniform thickness. A thick lamella may divide into two thin lamellae, as shown by circle A in Figure 1. Most of the lamellae are tapered; i.e., they end in sharp wedges. These results indicate again that the distribution of the lamellar thickness should reflect the distribution of the molecular length owing to an extended-chain conformation in the lamellae. Due to the formation of the extended-chain lamella the disclinations with strength $s = \pm^1/_2$ are imaged as pointed out by black arrows for $s = -^1/_2$ disclinations and white arrows for $s = +^1/_2$ disclinations in this micrograph. The areas near cores of the $s = +^1/_2$ disclination are darker and much easier to see than those near cores of the $s = -^1/_2$ disclination. Bright lines with an even breadth of about 10 nm are located between lamellae. The electron density in bright lines is lower than that in the lamella. This electron contrast results in the lamellar structure observed by means of TEM in a bright field. Some fine striations with a thickness of about 15 nm in width and normal to the lamellar direction can be seen in this micrograph. The variation of these fine striations is much smoother than that of bright lines between lamellae. Therefore, disclinations can be also distinguished easily according to the variation of these fine striations.

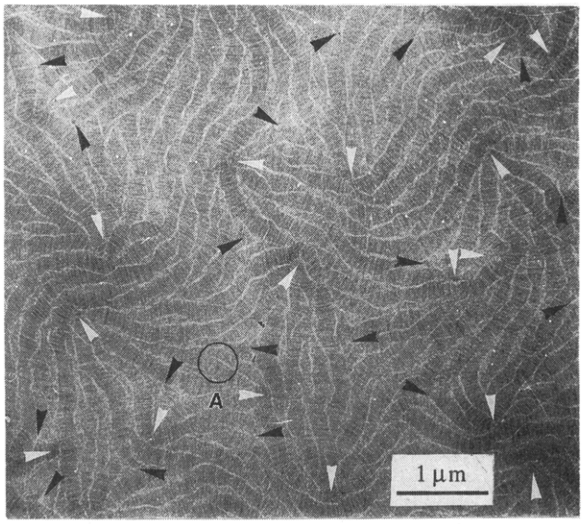

Figure 1. TEM micrograph of sample 1 in Table 2 showing a typical supermolecular structure of an extended-chain lamella with a thickness of approximately 200 nm. The sample was annealed in the lyotropic state for awhile. Different disclinations are imaged as indicated by white arrows for $s = +^1/_2$ and by black arrows for $s = -^1/_2$. The circle A shows a region where a thick lamella is split into two thin ones.

2. Supermolecular Structure of P-4-BCMU Mixtures. In Figure 2 three TEM micrographs show supermolecular structures of thin films for samples 2–4 in Table 2. Figure 2a shows the supermolecular structure of sample 2 in which the ratio of the average degrees of polymerization, i.e., the average lengths of the molecules, of two components is approximately 4 and the fraction of the polymer with a short molecular length is 0.50. Lamellae with an average thickness of about 50–55 nm can be easily observed. This size is close to the average length of short molecules but much shorter than the average length of long molecules. Thin lamellae with an average thickness of about 20–30 nm can be found between these thick

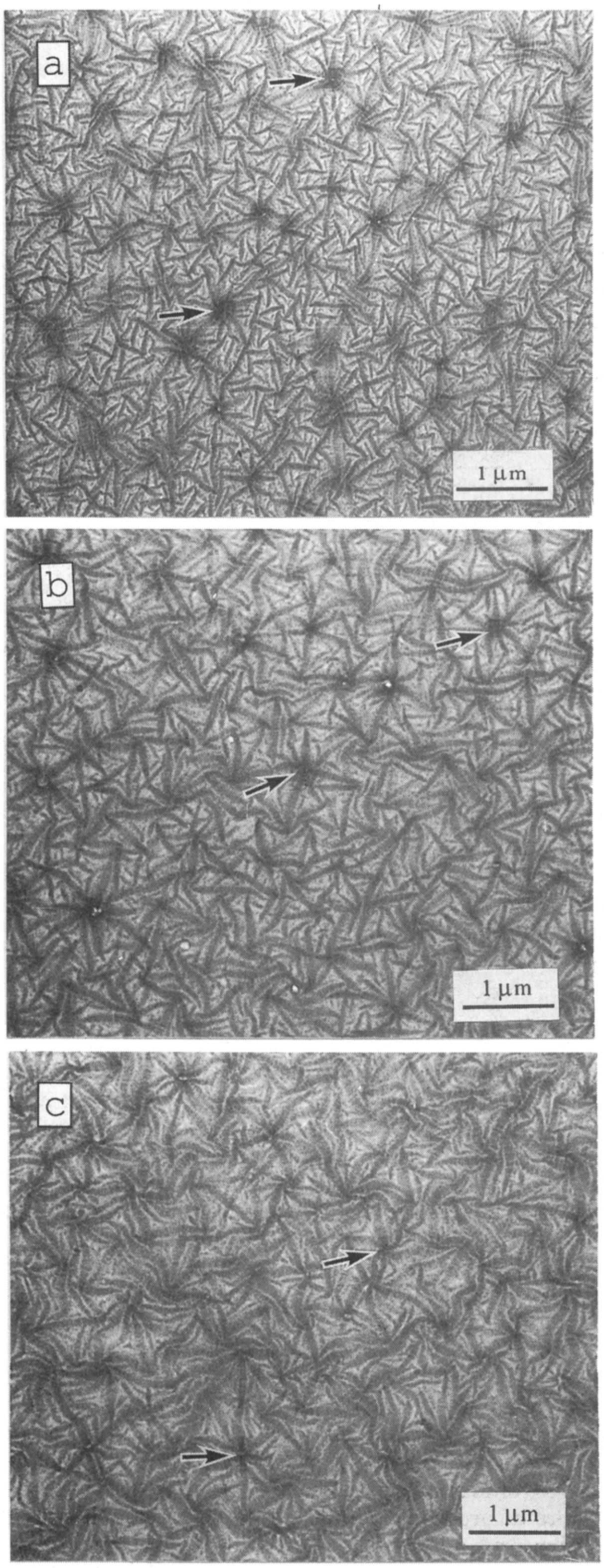

Figure 2. Three TEM micrographs demonstrating the influence of the difference, $\Delta\bar{l}$, between molecular lengths in mixtures on the supermolecular structure. Some disclinations with $s = +1$ are indicated by arrows. (a) Sample 2 with the largest $\Delta\bar{l}$. (b) Sample 3 with the middle $\Delta\bar{l}$. (c) Sample 4 with the smallest $\Delta\bar{l}$.

lamellae. The thickness of individual lamellae decreases frequently toward their ends. The orientation of these lamellae seems to be random in appearance. In this case it is difficult to identify disclinations according to the lamellar structure. It is worth noting, however, that some disclinations with $s = +1$, as indicated by arrows as an example, can be easily found from the micrograph. It should be noted that the $s = +1$ disclination was rarely observed for polymer 1 as shown in the previous work.[20] From this micrograph fine striations normal to the lamellar "director"[26] can be observed, but their shape is not as orderly as it is in Figure 1. The other important feature of sample 2 is that bright areas with a polygonal shape are located between lamellae instead of bright lines. They are disordered regions where the lamella cannot be formed. The ratio of the area occupied by lamellae to the area occupied by bright areas is larger than 0.5, indicating that the long molecules should be involved also in the formation of the lamella though the average molecular length is 4 times as long as the lamellar thickness.

Micrographs in parts b and c of Figure 2 show the supermolecular structures of thin films as-cast from the solutions of samples 3 and 4 in which the fraction of the polymer with a short molecular length is the same as that of sample 2, but the difference, $\Delta\bar{l}$ $(=\bar{l}_l - \bar{l}_s)$, between the average molecular lengths $\bar{l}_l$ and $\bar{l}_s$ (footnote l defines the component with a long molecular length and s the component with a short molecular length) is diminished in mixtures. In these cases some supermolecular structure features, such as the tapered shape of lamellae, are similar to those of sample 2 as shown in Figure 2a. Like sample 2, lamellae are divided into two groups according to their thickness: thick lamellae that form a main network and thin lamellae located between thick lamellae. The thicknesses of thick lamellae, 65–75 nm for sample 3 and 85–100 nm for sample 4, are close to the average molecular lengths of the component with a short molecular length in mixtures. In comparison with these TEM micrographs shown in Figures 1 and 2, the following observed evidences concerning the supermolecular structure are summarized: (1) with the decrease of $\Delta\bar{l}$ in mixtures, the area occupied by lamellae increases and the thickness distribution of lamellae tends to become more narrow; (2) at the same time bright polygons become bright lines; therefore, the shape of the lamella becomes more regular; (3) the variation of the lamellar director becomes more recognizable; therefore, the different kinds of disclinations can be easily distinguished.

Figure 3 shows two TEM micrographs of thin as-cast films of samples 5 and 6, showing the influence of the fraction in these mixtures on the supermolecular structure. The micrograph in Figure 3a corresponds to sample 5 containing 75% polymer 3 with a short molecular length. The lamellae are easy to see and are of a thickness in the range of 80–100 nm that is a little longer than the average molecular length of the polymer with short molecular length in the sample, but some thin lamellae with a thickness of around 20–30 nm can be seen between the thicker lamellae. On the contrary, the as-cast film of sample 6 displays a structural feature of blurred lamellae. For a thin film of the sample annealed in the lyotropic state for awhile, a supermolecular structure the same as shown in Figure 1 has been observed. With an increase of the fraction of the component with a short average molecular length, the lamellar structure is easily observed by means of TEM for the thin as-cast film. This seems to be because the short molecule has a short relaxation time; thus a short annealing time is needed to reorganize the extended-chain lamellae. In samples 5 and 6 the shape of the bright areas is close to a line. The fine striations can also be seen in these micrographs, and a few disclinations with $s = +1$ can be found as pointed out by arrows.

3. Models of Extended-Chain Lamellae. In the literature[17,18] a model of the extended-chain lamellae was suggested based on the experimental results obtained from the TEM observations for some P-4-BCMU samples with

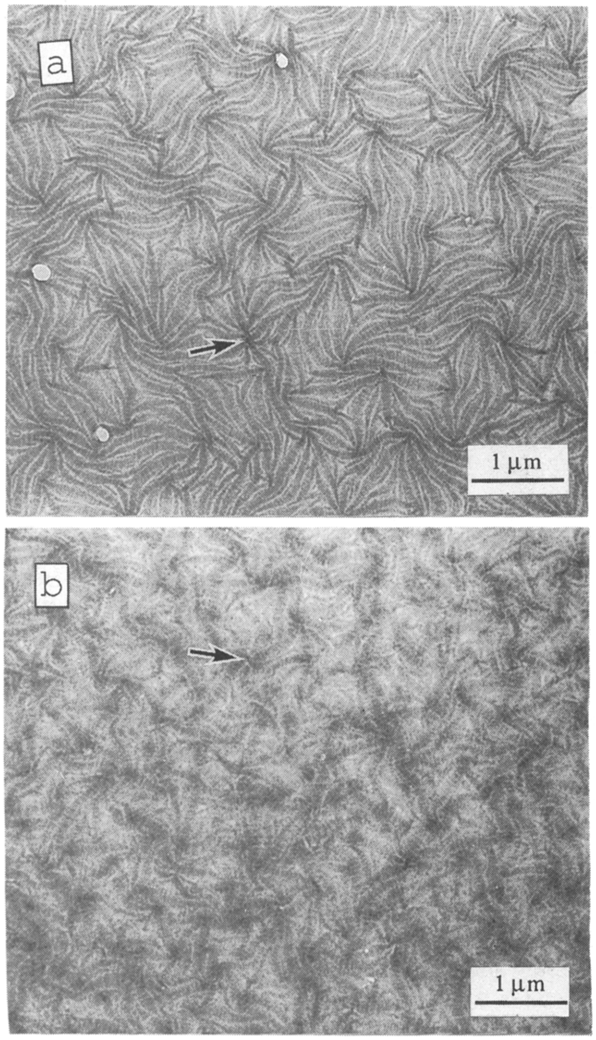

Figure 3. (a) TEM micrograph showing the supermolecular structure of sample 5. (b) TEM micrograph of sample 6 showing a blurred lamellar structure.

Figure 4. Suggested model describing the supermolecular structure of the extended-chain lamella observed in the thin film of P-4-BCMU with a relatively narrow distribution of molecular length.

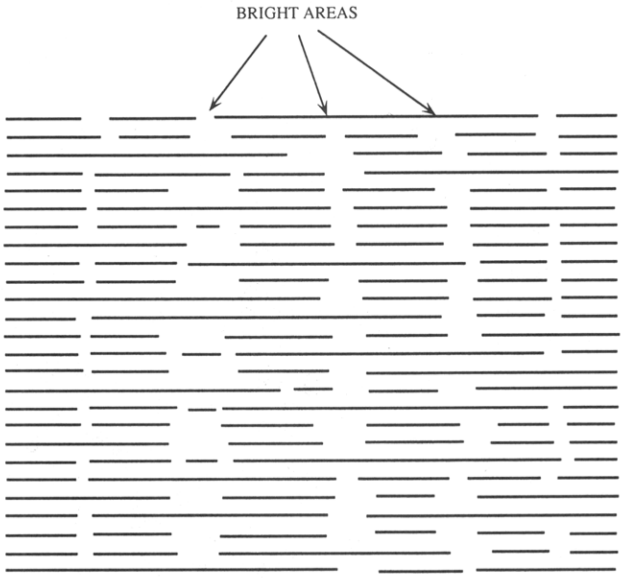

Figure 5. Suggested model describing the supermolecular structure of the extended-chain lamella observed in the thin film of mixtures of P-4-BCMUs with different lengths of molecules. Long molecules can run through a few lamellae whose thickness corresponds to the average length of the short molecules. The bright area is formed by a few segments of long molecules and some very short molecules, but lamella cannot be formed in this area due to the random distribution of long molecules along the transversal direction of lamellae.

a relatively narrow distribution of molecular weight, such as sample 1. This model as shown in Figure 4 indicates the characteristics of the extended chain in the lamellae. The areas between lamellae formed mainly by chain ends correspond to bright lines observed by means of TEM as the electron density in these areas is relatively low. For these samples the breadth of the bright line is approximately 10 nm (see Figure 1). This is related to a difference, $\Delta\bar{l}$, between molecular lengths in the formation of the lamella indicated in Figure 4. It should be emphasized that this difference is much smaller than that of the molecular length distribution.

This model cannot be used to describe the morphological feature observed in mixtures of P-4-BCMUs with different average molecular lengths. For these mixtures only the lamellae whose thickness is close to the average length of molecules of the short component are seen and the fraction of the area occupied by the lamella is much higher than the function of the short component, as shown in section 2. These results indicate that the long molecules in mixtures should be involved in the formation of the lamella. In this case a model, as shown schematically in Figure 5, is suggested for indicating the supermolecular structure of mixtures and the influence of $\Delta\bar{l}$ and of the relative content on it. Some important essentials of the model should be interpreted: (1) long molecules run through a few lamellae with a thickness close to the average length of the short molecules; (2) the long molecules cannot form the lamellae with a thickness corresponding to their average length because a much longer annealing time is needed for forming the relevant lamellae; (3) in these cases a more disordered boundary area between two lamellae can be formed when the content of the two components in the mixture is equal to one another. The model can interpret why the fraction of area occupied by the lamella is higher than the fraction of short molecules in the mixture and the bright area is much disordered in the case that the fraction of a component is equal to 0.5. $\Delta\bar{l}$ determines the lamellar number that the long molecule can run through.

These two models cannot explain the influence of the distribution of the molecular length on the lamellar structure formed by the extended chain. We will discuss the relationship between the supermolecular structure and the distribution of the molecular length in the next section.

4. Chain Segregation and Formation of Extended-Chain Lamellae. The experimental results obtained in

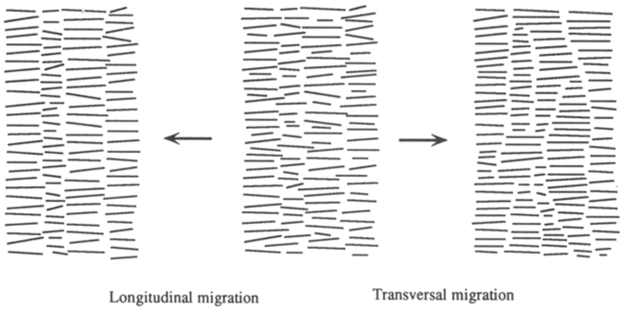

Figure 6. Schematic representation of the two kinds of chain migrations in the lyotropic state of P-4-BCMU macromolecules. The longitudinal migration leads to the formation of lamellae with different thicknesses, and the transversal migration leads to the formation of tapered lamellae.

the study distinctly demonstrate that rodlike P-4-BCMU chains segregate according to the molecular length to form extended-chain lamellae with different thicknesses in the lyotropic liquid crystalline state. In terms of the shape and the thickness distribution of lamellae in these micrographs and the results reported in the previous works,[17–22] two types of segregation processes can be inferred, as shown schematically in Figure 6. On the one hand, the longitudinal migration of molecules leads to the formation of the thick and thin lamellae whose thickness distribution is theoretically similar to the distribution of the macromolecular length. On the other hand, the transversal migration leads to the formation of the tapered lamellae. Both migrations occur in the lyotropic liquid crystalline state of P-4-BCMU. Due to the formation of some tapered lamellae, the short molecules are gathered in the two ends of the lamella, it is thus difficult to study the exact relationship between the thickness distribution of the lamella and the distribution of the molecular length. In this case the average thickness of the lamellae seems to be larger than the average length of the macromolecule (see Figures 2 and 3). The chain segregation can be explained by avoiding the formation of the elastic distortion in the lamella caused by the abrupt termination of the short molecules. This distortion can result in the increase of the free energy in the liquid crystalline system. In addition, due to the formation of the tapered lamellae the lamellar thickness around a dislocation gradually varies; therefore, an extremely small increase of the free energy caused by this dislocation can be achieved. It is easy to find this dislocation in TEM micrographs. This is a particular behavior of main-chain LC polymers related to the distribution of molecular length. This dislocation is quite different to that in the low molecular smectics.[27]

The formation of the extended-chain lamella of rodlike macromolecules, such as P-4-BCMU, in the lyotropic state is related to minimizing density change caused by the splay deformation in main-chain LC polymers, as was pointed out by de Gennes[28] in the study of the light scattering of main-chain liquid crystalline polymers and was further analyzed by Meyer in a review[29] in which a much detailed discussion can be found. Figure 7 shows a splay deformation of the rodlike macromolecules with a thickness of L ($=n\bar{l}$) before and after the formation of the extended-chain lamella. The density difference Δd is proportional to the length of the splay deformation. This relation can be shown as follows:

$$\Delta d \sim n\bar{l} \qquad (1)$$

where $\bar{l}$ is the average length of macromolecules and n is the integer. The smallest density difference is achieved when $n = 1$, namely, corresponding to a situation in which an extended-chain lamella should be formed. This is because long molecules have fewer ends available to fill the gaps opened up between molecules. However, the thickness of the splay deformation L has to be at least 2 times as long as the average length of the rodlike macromolecules $\bar{l}$, otherwise, the rodlike chain cannot segregate to form the extended-chain lamellae.

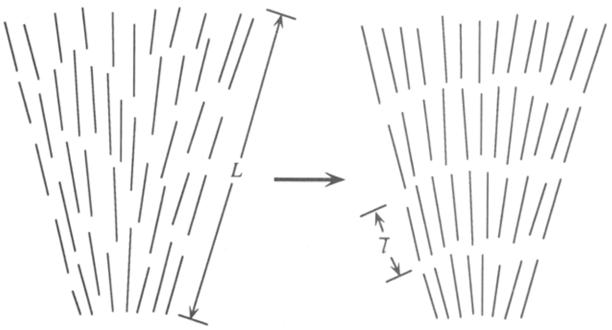

Figure 7. Schematic representation of the formation process of the extended-chain lamellae resulting from the splay deformation for requiring the smallest difference in density in the system of main-chain LC polymers.

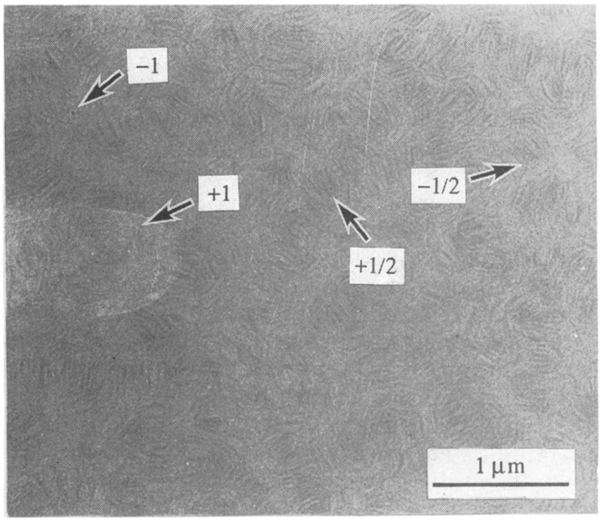

Figure 8. TEM micrograph showing the supermolecular structure of sample 1 at the state near the critical point. Different disclinations as shown by arrows can be seen. The distance between two adjacent disclinations is approximately 400–500 nm.

In a thin film of main-chain LC polymer, the splay deformation is caused by the distortion of defects, such as the disclination. In this case we can suppose that to form a structure of the extended-chain lamella, the critical distance between two disclinations in a thin film sample has to be twice as long as $\bar{l}$. The micrograph shown in Figure 8 shows the structural feature of the thin film of sample 1 at a state near the critical point at which the lamellae start to form. Many disclinations are imaged by fine striations in this case. The disclination strengths with $s = \pm{}^{1}/_{2}$ and ± 1 are indicated in the micrograph as an example. It is important to note that the distance between two adjacent disclinations is about 400–500 nm, approximately twice as long as $\bar{l}$ of the polymer. At this point the first sign of the formation of lamellae is already visible. The supermolecular structural feature of an earlier stage could not be characterized by TEM in a bright field in these experiments.

In the procedures of the formation of extended-chain lamellae and the chain segregation in the lyotropic state, a migration of whole molecules (not segments) occurs. The extended-chain conformation, i.e., without any entanglement between molecules, for this main-chain LC polymer enables that this migration possibly occurs in the liquid crystalline state. The energy required for moving these molecules is provided by the energy released possibly by the annihilation of two opposite disclinations. Before the annihilation the distance between two opposite disclinations decreases. At the same time the molecules located between disclinations are squeezed out. These molecules are naturally rearranged according to their length to form a new supermolecular structure for avoiding defects related to the length distribution of the molecules. In this case the chain segregation occurs, as shown schematically in Figure 6.

In this study the supermolecular structures observed in solid films were explained in accordance with the liquid crystalline properties of this polymer. In other words, we assumed that the supermolecular structure was preserved after the solidification from the lyotropic state to the solid state. It is impossible to study the supermolecular structure of these samples in the lyotropic state using TEM. We have noted that extended-chain lamellae have been observed in some flexible chain polymers, such as polyethylene and PTFE,[30,31] crystallized under a high pressure. (A typical pressure used was 5 kbar.) However, for the P-4-BCMU studied in this work, the thin films were solidified from its lyotropic state at room temperature and ambient pressure. In this case we believe that the extended-chain lamellae are formed and the chain segregation occurs in the lyotropic state. The solidification or crystallization does not affect these supermolecular structures too much. The reasons are as follows: first, the structure depends strongly on the annealing time in the lyotropic state but not on the solidification condition as reported in the previous work;[20] second, some special textures, such as oily streaks, that only appear in the layered liquid crystals, i.e., smectic A, have been observed in the LC polymer.[21] Finally, we believe that the fine striations appearing in these samples are related to the crystallization. Before a correct explanation for the fine striations can be given, more investigations should be done.

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