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Parallel and Perpendicular Orientations Observed in Shear Aligned S_{CA} Liquid Crystal of Main-Chain Polyester

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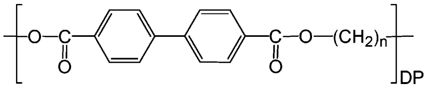
ABSTRACT: Shear alignment behavior was examined for smectic CA (S_{CA}) phase of main-chain BB-5(3-Me) polyester using a cone-and-plate fixture. In the smectic temperature region from 100 to 140 °C, two distinct orientations have been identified by wide-angle X-ray diffraction. At temperatures lower than 130 °C, the smectic layers arrange with unit normal perpendicular to the shear direction and parallel to the velocity gradient direction (so-called parallel orientation). Shearing at high temperatures near the isotropization temperature leads to the orientation of smectic layers with unit normal perpendicular to both the flow and velocity gradient directions (perpendicular orientation). At the intermediate temperatures, both orientations coexist. The SR-SAXS profile of the parallel oriented sample measured with irradiation along the vorticity direction includes a small peak with a spacing of around 80 Å in the velocity gradient direction that is parallel to the chain axis. The long spacing is roughly 5 times larger than the length of repeat unit, i.e., the smectic layer thickness (16.4 Å), showing the existence of chain-folded lamellae. The parallel orientation is attributed to mutual slide of the chain-folded lamellae. At higher smectic temperatures, on the other hand, the flow of the molecules within a smectic layer takes place preferentially to the mutual slide of lamellae, which is responsible for perpendicular orientation.

Introduction

Layered phases are an important group of structures formed simultaneously by condensed matters such as liquid crystals, block copolymers, and surfactant membrane liquids. They exhibit a surprising degree of complexity in the presence of shear flow. When shear rate and temperature in steady shear and amplitude, frequency, and temperature in oscillatory shear are changed, several orientations have been observed. Though simple arguments predict that the layers simply slide over each other with their normal parallel to the velocity gradient in the shear flow (i.e., parallel orientation), lamellae phase of block copolymer[1−9] and thermotropic smectic mesophases[10−14] usually show another orientation where their layer normal points in the vorticity direction (perpendicular orientation).

Main-chain liquid crystalline polymer treated in this study can also form the layered structure at the smectic phase, but its structure is more complicated. Each smectic layer is constructed by mesogenic moieties, which are connected to each other through flexible alkyl spacers. Hence, the polymer chain runs through several smectic layers, giving the completely different layer character from that of low molecular weight materials. We have explored this characteristic smectic structure with the following main-chain polyesters designated as BB-*n*[15−25]



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. A more interesting characteristic is that the smectic structure appears different depending on the odd−even parity of *n* (odd−even effect). BB-*n* with an even *n* form a smectic A (S_A) phase while BB-*n* with an odd *n* form a smectic CA (S_{CA}) phase where the mesogenic groups are tilted to the layer normal with their tilt direction opposite between neighboring layers.[15−17,25] This odd−even alternation of the smectic structures results from the conformational constraint in which the methylene spacer assumes the more extended conformation to arrange the neighboring mesogens at the characteristic angular displacement that depends on the odd−even parity of *n*.

Thus, it is no doubt that the polymer chain taking up the extended configuration penetrates many smectic layers, but the question arises as to whether the polymer chain is fully extended over a whole chain length. The answer has been brought from two experimental results which suggest the existence of chain-folded lamellar structure. One of them is that small-angle X-ray scattering maxima attributed to the stacked chain-folded lamellae have been observed for the solid BB-*n* polyesters crystallized from the smectic phase.[20−22] The scattering spot appears along the smectic layer normal, and its spacing is in the range 220−300 Å. Interesting is that the spacing decreases with increase in the crystallization temperature. This trend is opposite to that generally observed for the conventional polymer crystals, but in this specific system it is reasonably explained if the chain folding exists already in the preceding smectic phase as an entropy effect and its folding length is maintained on the crystallization.[22] The chain-folded lamellar structure was also suggested from unusual orientation behavior of smectic melt also.[23,24] When the fiber of BB-*n* is span from the smectic melt, the smectic layers arrange parallel to the fiber axis; in other words, the polymer chains lie perpendicular to the fiber axis. More interesting is that even at ambient temperature enough below the glass transition temperature of 50 °C, this oriented fiber can be further elongated to twice without changing both the smectic

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structure and its orientation. Such unusual flow of the smectic melt and elongation of the fiber are believed to result from mutual slipping of the chain-folded lamellae.

In this study, we examined from X-ray measurement on how the main-chain polymers are oriented in the S_{CA} liquid crystal under steady shear flow. The synchrotron radiation small-angle X-ray scattering (SR-SAXS) method was also employed for detection of the chain-folded lamellar structure which is expected to be arranged by the shear flow.

Experimental Section

The BB-5(3-Me) polyester was synthesized by melt condensation of dimethyl-4,4′-biphenyl dicarboxylate and 3-methyl-1,5-pentanediol with isopropyl titanate as catalyst. The inherent viscosity of the polymer, η_{inh}, was measured as 0.69 dL g^{-1} at 30 °C by using 0.5 g dL^{-1} solution in a 60/40 w/w mixture of phenol and tetrachloroethane. The number-averaged molecular weight (M_n) and polydispersity (M_w/M_n) were determined as 4.17×10^4 and 1.85, respectively, from gel permeation chromatography in chloroform solution on the basis of calibration of standard polystyrene. In this BB-5(3-Me), S_{CA} phase is formed on cooling from the isotropic melt and finally solidified without crystallization. From the DSC thermograms recorded with a Perkin-Elmer Pyris 1 DSC at a scanning rate of 10 °C min^{-1}, the glass transition is detected at around 30 °C, and smectic−isotropic phase transformation is observed at 150.1 °C on heating and 133.5 °C on cooling.

Shear alignments of the smectic melt were conducted on a Rheosol-G3000 (UBM Co., Ltd., Kyoto, Japan) using cone-and-plate fixture within its torque range (~2 kg cm). The plates were 25 mm in diameter, and the cone had a 0.098 47 rad (5.642°) angle. The sample was raised to 180 °C enough above the isotropization temperature for 3 min to produce the same disordered state. To ensure complete liquid crystal formation, the sample was cooled to 130 °C at once before shearing it at temperatures below and above 130 °C. The liquid crystalline sample was sheared at a predetermined shear rate and temperature. During the shearing, the stress showed rapid increase followed by abrupt decrease to a steady value within 60 min, and hence 60 min was adopted as an ample time to conduct the shearing experiments.

The orientation of the smectic structure was determined by wide-angle X-ray patterns for the film specimen which was removed from the rheometer fixture by putting it into liquid nitrogen. The WAXD patterns were recorded on a flat imaging plate by irradiating Ni-filtered Cu Kα radiation (Rigaku RU200BH) to the film sample in the three characteristic velocity gradient, flow, and vorticity directions. The SR-SAXS profile was measured at a BL-10C beamline in a synchrotron radiation facility, Photon Factory at National Laboratory for High Energy Physics, Tsukuba, Japan. The details of the optics and the instrumentation are described elsewhere.[26] The incident X-ray intensity of wavelength 1.488 Å was monitored by an ionization chamber. The scattering intensity was measured with a one-dimensional position-sensitive proportional counter (PSPC) having 512 channels with the camera length of about 2 m. The number of the counter channel is connected to the wave vector $q = 4\pi \sin \theta/\lambda$ with using the sixth reflection of a collagen. The scattering profile was obtained by normalization for minor decrease of the primary beam intensity during the measurements, subtraction of a background scattering, and Lorentz correction.

Results

Orientation of the Smectic Layers under Shear Flow. Two distinct orientations of the smectic layers were estimated by wide-angle X-ray diffraction patterns taken by irradiating the X-ray beam along three characteristic directions of the film specimen. In any orientation, the smectic layer spacing takes a constant value of 16.4 Å, indicating that smectic layers themselves are undergoing constant shear flow whereas the position of the layer's center of mass does not change. The X-ray diffraction patterns revealing the two characteristic orientations are shown in Figures 1 and 2, and the molecular orientations estimated from these patterns are depicted schematically in Figure 3.

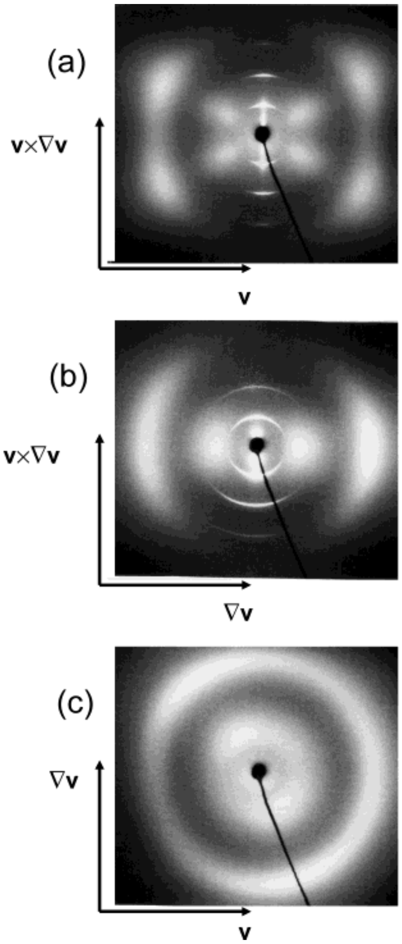

Figure 1. Wide-angle X-ray diffraction patterns for the BB-5(3-Me) sheared at a rate of 0.214 s^{-1} at 140 °C. These patterns indicate a perpendicular layer orientation. The broad inner hallows with the spacing of around 8 Å appearing in (a−c) are scattering due to continuous X-rays remaining in Ni-filtered X-ray. The intensity inequality in the outer broad halo in (c) was inconsistent over the measurements.

One of the characteristic orientations is the perpendicular orientation where the smectic layer normal points to the vorticity direction. Figure 1a−c shows the X-ray diffraction patterns typical for the perpendicularly oriented sample sheared at a rate of 0.214 s^{-1} at 140 °C. Intensity profiles of the layer reflections and the outer broad halo included in these three X-ray patterns appear different depending on the direction of X-ray irradiation. In the photographs of Figure 1a,b, the beam was irradiated parallel to the velocity gradient direction and the flow direction, respectively. Both X-ray patterns include layer reflections on the vorticity direction. In contrast, no layer reflection is found in the X-ray pattern of Figure 1c that is taken by irradiation along the vorticity direction. From these profiles of the layer reflection, we can illustrate the smectic layer structures with the layer normal preferentially orienting parallel to the vorticity direction in Figure 3a. The outer broad halos with a spacing of 4.5 Å also give the useful information. They are split above and below the equator in the photograph of Figure 1a, while they concentrate

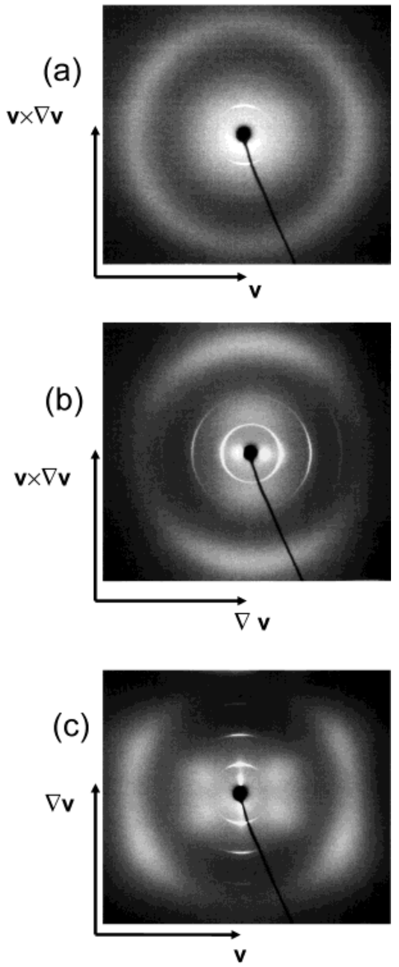

Figure 2. Wide-angle X-ray diffraction patterns for the BB-5(3-Me) sheared at a rate of 6.38×10^{-3} s^{-1} at 130 °C. These patterns indicate a parallel layer orientation. The broad inner hallows with the spacing of around 8 Å in (b, c) are scattering due to continuous X-rays remaining in Ni-filtered X-ray.

on the equator in the photograph of Figure 1b. These diffraction profiles show the biaxial orientation of the S_{CA}; the zigzag tilting of mesogenic groups preferentially takes place in the flow direction, as illustrated in Figure 3a.[16,25] For X-ray irradiation parallel to the vorticity direction, the diffraction intensity is not uniform in the azimuthal direction, and its maximum position is inconstant in the pieces of the perpendicularly oriented samples. We cannot find any reason for this phenomenon.

The second type of orientation is the parallel orientation where the layer normal points to the velocity gradient direction. Figure 2a–c shows the X-ray diffraction patterns typical for the parallel oriented specimen sheared at a rate of 6.38×10^{-3} s^{-1} at 130 °C. In the photographs of Figure 2b,c, where the beam is irradiated parallel to the flow direction and the vorticity direction, respectively, the layer reflections are observed with the maximum intensity in the velocity gradient direction. These patterns dictate that the smectic layers arrange parallel to the flow direction. However, the degree of orientation of the smectic layers along the vorticity direction are relatively low since the weak layer reflections are observed even in the vorticity direction in Figure 2a. Possibly, the smectic layers are likely to undulate along the vorticity direction. The structure is illustrated in Figure 3b.

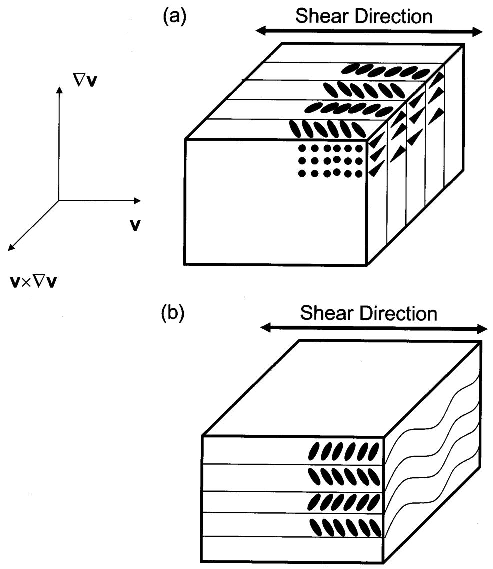

Figure 3. Illustration of the perpendicular (a) and parallel (b) orientations in the shear oriented S_{CA} specimen. In (a), the arrows depicted in the side of the rectangular parallelepiped mean that the mesogens are tilted with respect to the layer normal in the shear plane as seen in the upper face. In (b), the wave lines in the side of the rectangular parallelepiped represent that the smectic layers undulate along the vorticity direction.

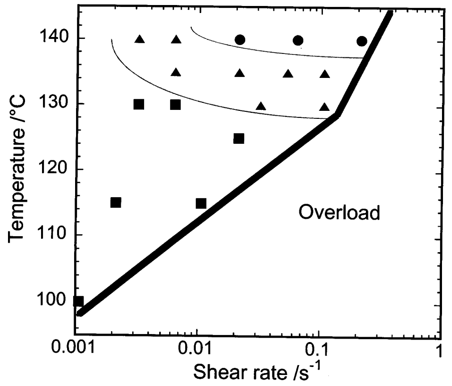

Figure 4. Shear rate–temperature diagram in smectic layer orientation for the S_{CA} mesophase of the BB-5(3-Me) subjected to steady shearing. Circle and square symbols refer to the perpendicular and parallel orientations, respectively. Triangle symbols indicate the intermediate orientation in which both the parallel and perpendicular orientations coexist. The shear rates and the temperatures in the lower right-hand region in the figure were not accessible because the apparent torque was over the mechanical range of the rheometer.

Dependences of Orientation on Temperature and Shear Rate. Figure 4 reveals how the two types of orientations appear as functions of temperature and shear rate. It is found that the parallel orientation is favored in sample sheared at lower temperature and at lower shear rate, while the perpendicular orientation appears at high temperature close to the isotropization point and higher shear rate. In the middle of these conditions, the oriented film shows the X-ray patterns with the layer reflections concentrated on meridian both in the vorticity–velocity and in velocity gradient–velocity planes, but with ring-shaped one in the velocity gradient–vorticity plane. As such, the corresponding smectic structure is depicted with its layer normal pointing to all directions in the plane perpendicular to the flow direction.[11] This is considered to be due to the coexistence of the perpendicular and parallel orientations.

The data in Figure 4 were collected for the samples prepared by shearing the polydomain smectic melt. Here, the question arises on what occurs when the sample with the certain orientation is sheared under a condition which produces another type of orientation, i.e., whether the subsequent shearing alter the kind of orientation. To examine this, we selected shearing rate of 0.0213 s^{-1}. At this rate, as found in Figure 4, the two different orientations can be achieved by changing the temperature; the perpendicular orientation is observed at a high temperature around 140 °C, while the parallel orientation at the temperatures lower than 130 °C. Thus, the transformation between the two orientations can be detected by a temperature jump between 125 and 140 °C. The results simply indicate that a subsequent shear flow can alter the orientation of a sheared sample if the shear flow is applied for a fully prolonged period. This two-way alternation of these two orientations has not been observed for other systems.[1]

Discussion

Shear orientation of smectic layers of thermotropic liquid crystals has been examined for a monomeric material,[10,11] main-chain polymers,[12,13] and a side-chain polymer[14] where the perpendicular orientation preferentially appears.

The shear orientation behavior observed here can be closely related to recent developments for the lamellar phases involving diblock copolymer lamellar phases.[1−9,27,28] In these lamellar phases, the parallel orientation is expected to appear under shear flow instinctively since there are two components with sufficiently different viscosities.[27] On the other hand, hydrodynamics of the lamellar phase has also predicted that the shear flow, which hardly affects individual lamella, can arrange the lamellae with the perpendicular orientation.[28] The experimental results observed for the smectic phase of BB-5(3-Me) are consistent with the theoretical prospects and the experimental results as observed in the lamellar systems.[1,27]

At first, we refer to the structure factor that produces the parallel orientation. In the smectic phase of the low molecular weight system, each smectic layer is constructed by individual molecules so that the smectic layers can slide from each other as in the conventional lamellar system. In the main-chain polyester, however, the mutual slide of smectic layers is prohibited because each layer is constructed by the repeating unit of polymer, and hence the extended polymer chains penetrate the smectic layers. To account for the parallel orientation, thus, we have to figure the chain-folded macroscopic layer (so-called lamella) having less interlayer connectivity as has been proposed by us.[20−23] Then, the two components with different viscosity are readily associated with the boundary and the center in the chain-folded lamella.

To confirm this lamellar structure, SR-SAXS profiles of the sample in the parallel orientation were measured by irradiating the X-ray beam in the vorticity direction. In the parallel oriented sample, the normal of the lamella should be in the velocity gradient direction, in other words, parallel to both the smectic layer normal and the chain direction. The scattering profiles in the velocity gradient direction are shown in Figure 5. It includes a small scattering maximum at around $q = 0.8$ nm^{-1}, indicating that the long-period structure with a spacing of around 80 Å exists along the chain axis. The spacing is 5 times larger than the smectic layer thickness of 16.4 Å. The lamella spacing of 80 Å is much smaller than those of around 250 Å proposed for the S_A phase in our previous works,[20−23] suggesting that shear flow in the smectic liquid crystal may affect the lamellar thickness. On the other hand, it is valuable to state that the spacing of 80 Å is comparable to the value estimated by a theoretical treatment of the effects of shear flow on the parallel oriented lamellae at a microscopic level where the lamellar spacing (d) is connected with the critical stress for the layer collapse (disorientation) ($(\eta\dot{\gamma})_c$) and the lamellar binding energy (K) as[1,29]

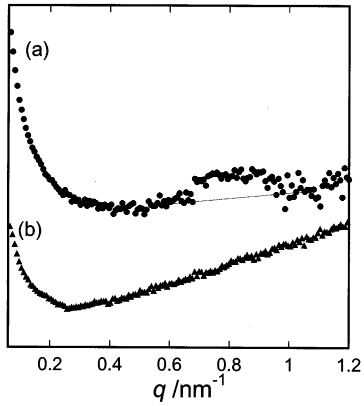

Figure 5. SR-SAXS profile of the parallel oriented BB-5(3-Me) (a) in the velocity gradient direction and (b) in the shear flow direction recorded by irradiating X-ray beam in the vorticity direction. The specimen was prepared by shearing the smectic melt at 6.38 × 10^{-3} s^{-1} at 130 °C.

$$(\eta\dot{\gamma})_c \cong \frac{(k_B T)^{5/2}}{K^{3/2} d^3} \tag{1}$$

Here we assume that $K \sim k_B T_i$ (T_i is the isotropization temperature of BB-5(3-Me), 423 K) and that $(\eta\dot{\gamma})_c$ equals the maximum stress of 3.0 × 10^3 Pa appearing on shearing the parallel oriented sample to transform to the perpendicular oriented one at 140 °C and obtain $d \sim 120$ Å. The calculated lamellar spacing of 120 Å is comparable to the lamellar spacing of 80 Å rather than the smectic layer spacing of 16.4 Å. Thus, the parallel orientation of the main-chain polymer smectic liquid crystal is reasonably attributed to the mutual slide of the chain-folded lamellae.

The smectic CA phase is the fluid smectic phase where the mesogens' centers of mass have a one-dimensional layer order along the director but are isotropically distributed within a smectic layer. In other words, it is a two-dimensional liquid so that an internal flow of the mesogens is also possible within the layer. Typical flow of mesogens is observed in the nematic liquid crystals which includes only the orientational order and results in the orientation with the polymer chains lying parallel to the shear direction. In the smectic phase, however, this type orientation is excluded because it leads the transverse orientation of the smectic layers where the dilation and compression of the preferred smectic layer spacing follow. The possible orientation is the perpendicular orientation where the molecules can flow maintaining the positional layer ordering.

It depends on the temperature or shear rate whether the molecules adopt the parallel or perpendicular orientation. In other words, it should be connected to change in the friction of the mesogens within the layer: the packing of mesogens within a layer is liquidlike at high smectic temperatures, but it may become solidlike at low temperatures. Thus, at low temperatures, the shear gradient prefers the mutual slide of the chain-folded lamellae whose boundary may possesses more fluidity to the internal flow with hard friction of mesogens within a smectic layer. This expected trend is surely observed in Figure 4. The relationship between the shear condition and the produced orientation in the smectic liquid crystal will be realized with product of shear rate and characteristic time for chain stretching, mesogen flow within a smectic layer, and mutual sliding of the chain-folded lamella (so-called Deborah number).

Finally, we shall comment on the orientations observed in the uniaxially stretched fiber or film of main-chain polymer smectic liquid crystals. Most characteristic orientation is so-called “anomalous orientation” where the chain axis lies perpendicular to the fiber axis; in other words, the smectic layer arranges parallel to the stretching direction (i.e., flow direction) as has been reported by us[23,24] and other groups.[30−33] Comparing this orientation to the orientations observed in this study, one would notice that there are two mechanisms to produce the anomalous orientation since the anomalous orientation is apparently identical to the perpendicular and parallel orientations produced by shear flow. Thus, we reasonably speculate that when the fiber or film is stretched from the smectic melt at high temperature close to the isotropization temperature the anomalous orientation is caused by the internal flow of the mesogens within the layer. On the other hand, the stretching at lower temperatures near the glass transition temperature should be attributed to the mutual slide of the chain-folded lamellae as we have discussed so far.[23] We have to keep in mind this different mechanism producing the anomalous orientation when we stretch the fiber or film of smectic polymers.

Conclusion

We have found that two types of orientations are generated when smectic liquid crystal in the main-chain BB-5(3-Me) polyester is subjected to a steady shear deformation. One is the parallel orientation where the smectic layers arrange with unit normal perpendicular to the shear direction and parallel to the velocity gradient direction, and the other is perpendicular orientation with unit normal perpendicular both to the flow and velocity gradient directions. These two types of orientations transform to each other by changing the temperature at a constant shear rate. At lower temperatures, the parallel orientation is preferentially observed, but on heating to the temperature close to T_i, it is altered to the perpendicular orientation. For the parallel oriented sample, a weak scatter maximum corresponding to a spacing of 80 Å was found in the SR-SAXS profile along the chain direction. The spacing of 80 Å is approximately 5 times larger than the unit length of 16.4 Å and is comparable to that of 120 Å estimated by the mechanical response for shearing the parallel oriented lamellae. It is thus concluded that the chain-folded lamellae are formed here, and the characteristic parallel orientation results from their mutual slide. With the increase of temperature, the mesogens within a layer become more fluid so that the shear gradient causes preferentially the two-dimensional liquid flow of mesogens to the slide of the chain-folded lamellae. This internal flow of mesogens within a layer results in the perpendicular orientation.

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