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Regular Formation of Chain Folding in Smectic Phase of Main-Chain BB-3(2-Ph) Polymer Followed by Columnar Association of Phenyl Side Group in Propane Spacer

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ABSTRACT: The main-chain type of liquid crystal (LC) polymer was prepared with a combination of bibenzoate mesogen and 2-phenyl propane spacer. It forms the fluid smectic LC. However, the smectic phase has a two-dimensional frustrated structure with a (parallel to the layer) = 12.9 Å, c (along the polymer chain) = 20.6 Å and $\beta = 70.0°$. The occurrence of such a characteristic frustration is due to the bulky phenyl group sticking out of the propane spacer that is incompatible with a conventional smectic structure. The polymer assumes the regular chain folding conformation excluding the obstructive phenyl groups within a limited column-like space, and the resulting columns embedded in a smectic matrix are aligned with a two-dimensional positional order.

1. Introduction

The chain folding conformation in main-chain type of polymer has been one of contemporary topics,[1−10] and has been studied by treating twin dimers as a model compound.[11−13] The twin dimer has three different skeletal units: alkyl tail, aromatic mesogen, and alkyl spacer. When the dimers form a smectic LC, the mesogenic groups gather together to form the smectic layer as in monomeric molecules, and three types of smectic structure are possible with different accommodations of the alkyl group in the tail and spacer into a smectic layer.[14−16]

Most reliable smectic structure may be constructed by random mixing of both the alkyl spacer and tail groups to gain the mixing entropy. However, such a structure can be envisaged only when the length of spacer is comparable to that in the tail group. When their lengths become significantly different, we have to consider two other packing modes of twin dimers into smectic layer phase. One of them is constructed by a segregation of the spacer and tail groups because of their steric incompatibility, which results in bilayer smectic phase with two mesogenic layers in a repeat length. Such a bilayer smectic phase is particularly interesting when it is formed from the dimers which possess odd-carbon numbered spacers.[15,17] It is called $S_{CA}{}^{b}$, in which mesogenic groups in each layer are tilted to the layer normal, but their tilt directions are opposite between neighboring layers.[18,19] Each bilayer in a repeat unit possesses spontaneous polarization parallel to the layer and along the tilt direction of molecule, resulting in ferroelectric or antiferroelectric smectic phase as has been first found by our group.[15,16,20−22] Another smectic phase is also possible which can accommodate comfortably the alkyl tail group fairly longer than the spacer group. It is constructed by the molecules with folded U-shaped conformation; the twin molecules are folded so that two alkyl tails within a molecule are closely associated. It should be noted that such a U-shaped conformation is not unusual. The conformational analysis by isomeric-state model has shown that the U-like conformation is possible for dimers with the odd-numbered carbon spacer.[5,23] In the previous study,[13] we found that the dimeric *m*OAM5(3-Me)AMO*m* compounds with 3-methyl pentane spacer assume the folding conformation and form the U-shaped SmA phase (U−S_A) when the carbon number of alkyl tail group (m) is larger than 12. Since the homologous dimers with linear pentane spacer have not assumed such a U-shaped conformation, the methyl group sticking out of the spacer plays a significant part in the induction of the U-sheped conformation.[13] This is reasonably envisaged because there is a packing difficulty of the methyl group sticking out of the spacer. Thus, U-shaped conformation in twin dimers offers another way to accommodate the tail groups fairly longer than the spacer group, showing new potentiality in spontaneous molecular organization in dimers and polymers.

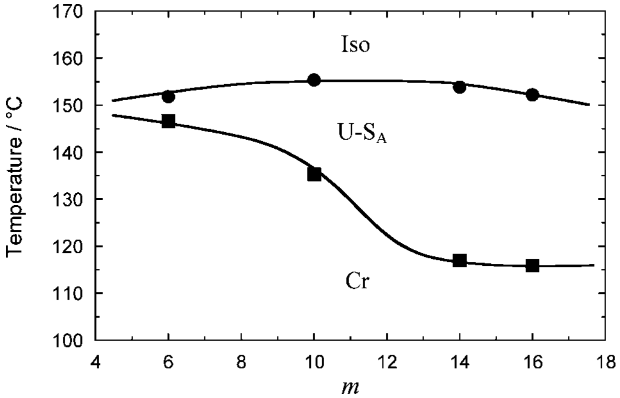
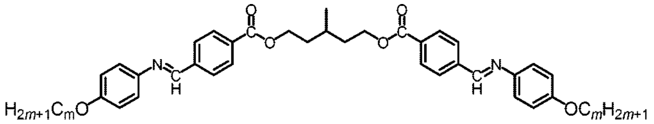
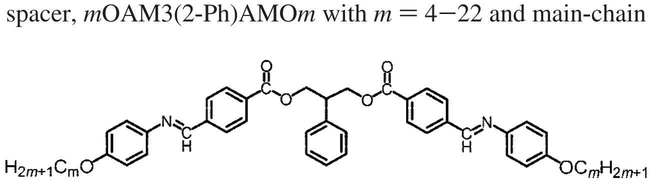
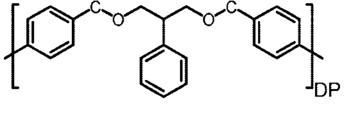


Figure 1. Phase behavior of *m*OAM3(2-Ph)AMO*m*. Transition temperatures were collected by DSC thermograms.



In this study, we prepared twin dimers with 2-phenyl propane spacer, *m*OAM3(2-Ph)AMO*m* with m = 4−22 and main-chain type of polymer, BB-3(2-Ph), with a combination of bibenzoate mesogen and 2-phenyl propane spacer.





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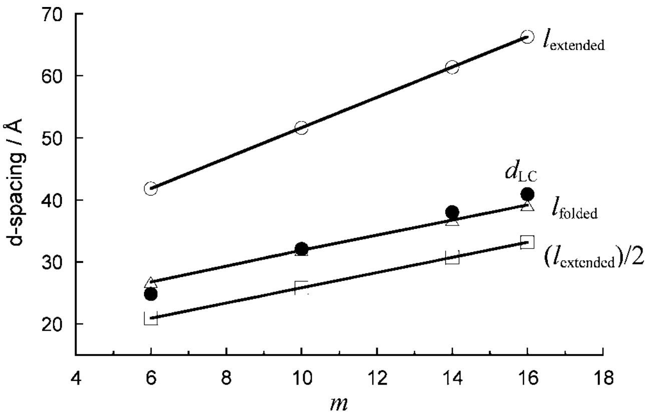

Figure 2. Variation of smecic layer spacing (closed circles) observed for *m*OAM3(2-Ph)AMO*m* with the carbon number of the tail group, *m*. Open circles and squares indicate the molecular length and half a molecular length of most-extended chain, respectively, and open triangles are the molecular length of folded one. The molecular lengths were calculated on the basis the models illustrated in Figure 3.

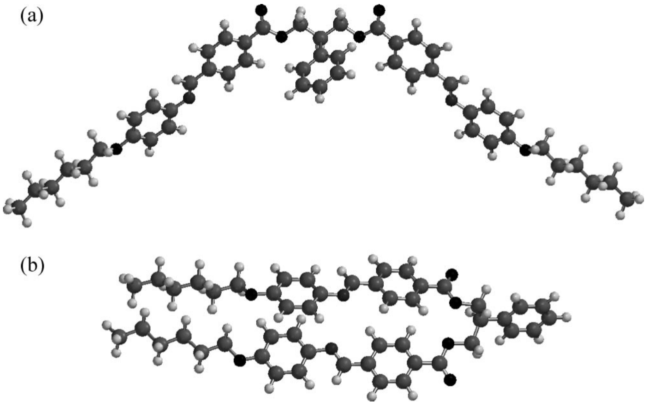

Figure 3. Two possible conformations of *m*OAM3(2-Ph)AMO*m*. (a) most-extended conformation and (b) folding conformation attained by trans, gauche +, gauche −, trans sequence of the propane spacer.

As suggested from a significant packing difficulty in lateral direction due to the bulky phenyl group, dimers assumed the folded U-shaped conformation in their smectic A phases. On the other hand, the BB-3(2-Ph) polymer formed the characteristic smectic phase with density modulated two-dimensional lattice along the layer, which can be constructed by the polymer taking regularly folded conformation and excluding the obstructive phenyl group into the limited columnar domain.

2. Experimental Section

2.1. Materials. The dimers were synthesized according to the synthetic route previously reported.[13] The polymer was synthesized by melt transesterification from dimethyl *p*,*p*′-bibenzoate as a mesogenic moiety and 2-phenyl-1,3-propanediol as a spacer with isopropyl titanate as catalyst. Molecular weight and molecular

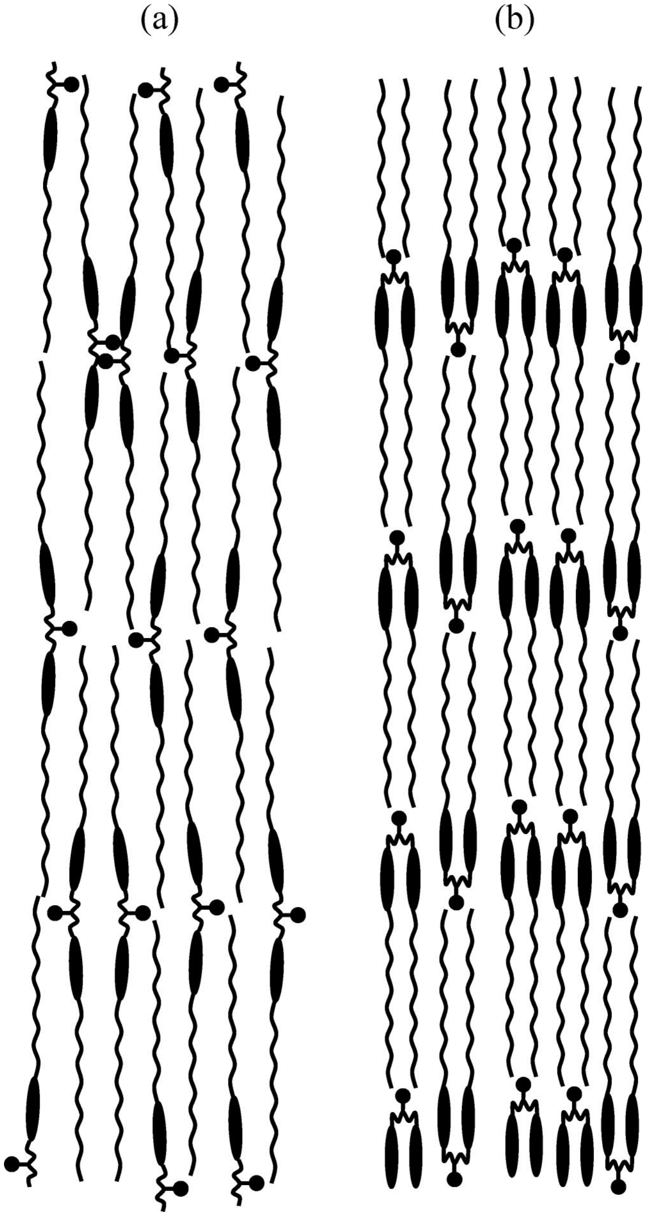

Figure 4. Two possible S_A structures formed from *m*OAM3(2-Ph)-AMO*m* with the tail groups fairly longer than the spacer group; (a) single layer S_A phase with random mixing of spacer and tail groups and (b) the S_A phase constructed by U-shaped folded molecules. In part a, one knows that the molecules cannot form the smectic layer structure since the microsegregation of mesogens and alkyl groups hardly occurs.

Table 1. Thermodynamic Date, Molecular Length, and Smectic Layer Spacing Observed for the *m*OAM3(2-Ph)AMO*m* Series

	transition temperature/°C (ΔH/kJ mol^{-1}) [ΔS/J mol^{-1} K^{-1}]							
M	Cr		U−S$_A$		I	d_{obs}/Å[a]	d_{calc}/Å[b]	d_{calc}/Å[c]
6	•	147 (41.0) [97.6]	•	152 (17.2) [40.6]	•	24.8	41.8	25.0
10	•	135 (46.9) [115]	•	155 (21.8) [50.6]	•	32.1	51.6	29.8
14	•	117 (61.5) [157]	•	154 (22.6) [53.6]	•	38.0	61.4	34.7
16	•	116 (74.1) [191]	•	152 (23.0) [54.0]	•	40.9	66.3	37.2

[a] Observed in U−S$_A$ phase. [b] Based on extended conformation in Figure 3a. [c] Based on folded conformation in Figure 3b.

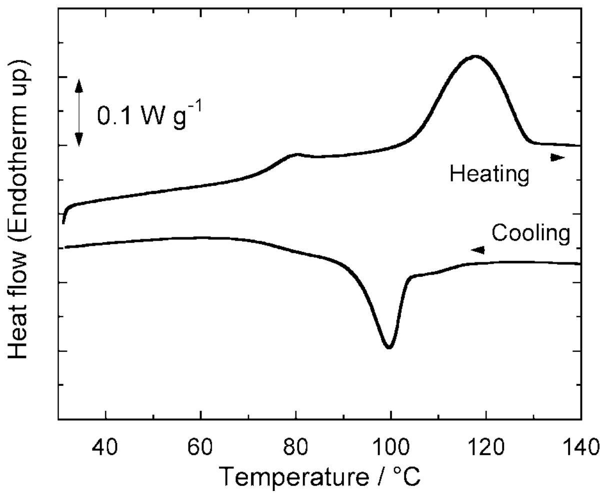

Figure 5. DSC thermogram of BB-3(2-Ph) polymer observed on second heating and cooling process at a scanning rate of 10 °C/min.

weight distribution were determined as $M_w = 7500$ and $M_w/M_n = 2.5$ from GPC curve which was calibrated with a polystyrene standard.

Table 2. X-ray Data for the Smectic Phase of BB-3(2-Ph) Polymer

*h*0*l*	d_{obs}/Å	intensity	d_{calc}/Å^{a}
001	19.4	vs	19.4
102	9.22	vvw	9.27
103	6.74	w	6.74
104	5.16	m	5.15
105	4.13	w	4.13
205	3.93	vvw	3.93
206	3.38	vw	3.37
207	2.93	vw	2.93

[a] Based on the two-dimensional lattice with $a = 12.9$ Å, $c = 20.6$ Å, and $\beta = 70.0°$.

2.2. Methods. Differential scanning calorimetric (DSC) measurements were carried out with a Perkin-Elmer Pyris 1 DSC at a scanning rate of 10 °C min^{-1} under a flow of dry nitrogen. Wide-angle X-ray diffraction measurements were performed at ambient temperature by using a Rigaku-Denki RINT-2500 X-ray generator with monochroic Cu Kα radiation (40 kV, 50 mA) from graphite crystal of monochromator and flat-plate type of imaging plate.

Steady shear alignments were performed on a UBM Rheosol-G3000 rheometer equipped with cone-plate fixture with 25 mm in diameter and 0.09847 rad (5.642°) in cone angle within its torque range (∼2 kg cm) until the steady viscosity was observed. After the shear was stopped, the sample was cooled to the room temperature at a rate of 10 ° min^{-1} and then removed from the rheometer fixture by putting it into liquid nitrogen. The orientation

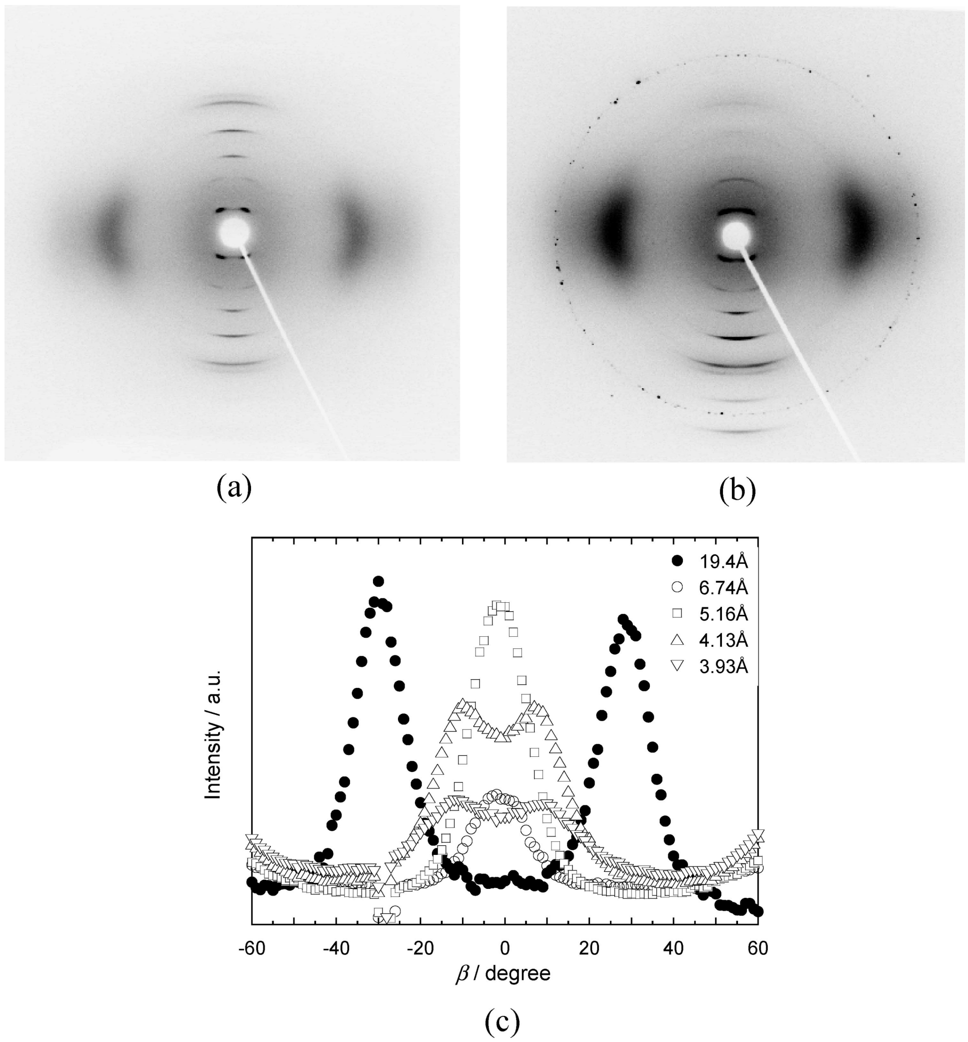

Figure 6. Oriented X-ray patterns of the LC fiber of BB-3(2-Ph). Here, the fiber was spun from the isotropic melt and then annealed at 85°. Its fiber axis is placed in a vertical direction. Pattern a was taken with the X-ray beam perpendicular to the fiber axis. In pattern b, the fiber axis was tilted by 10° to the beam. Pattern c is the azimuthal β-scans of the reflections with spacings of 19.4, 6.74, 5.16, 4.13, and 3.93 Å in pattern b. It should be noted that the 19.4-Å reflection is located at an azimuthal angle of 27° from the meridian.

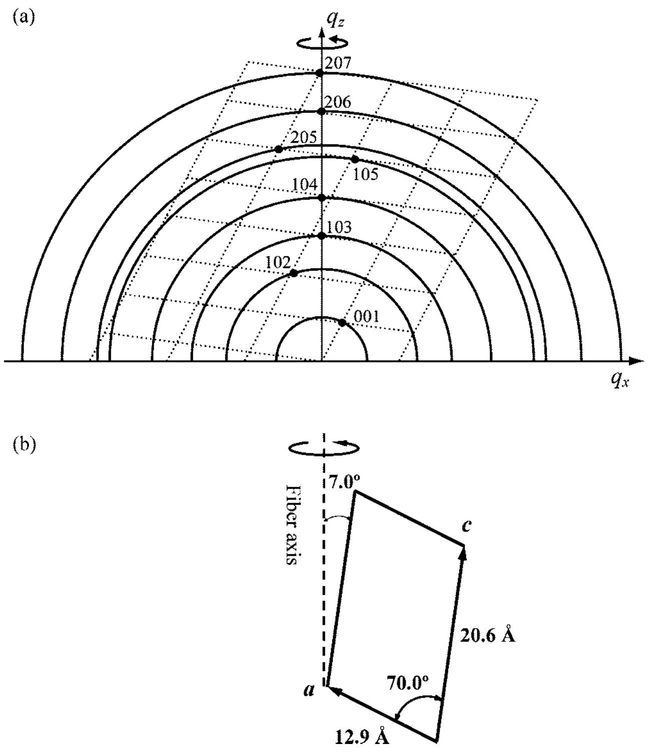

Figure 7. (a) Reciprocal lattice that satisfies the observed diffraction pattern (closed circles) and (b) corresponding real lattice in fiber specimen. The diffraction geometry in (a) is based on the azimuthal β-scanning data of Figure 6c. The angle of 7° between the fiber axis and *c*-axis in real lattice was determined from the azimuthal angle of 27° for the (001) reflection with a spacing of 19.4 Å (refer to Figure 6c).

of the polymer in sheared sample was determined by X-ray diffraction profile.

3. Results and Discussion

3.1. Chain Folding Conformation of Twin Dimers Observed in Smectic Phase. We first refer to twin dimers. Figure 1 shows their phase behavior. The thermodynamic data are listed in Table 1. All the dimers form enantiotropic smectic phase.

The smectic phase appears as typical batonnets upon cooling from the isotropic melt and finally develops to well-defined fan texture. In homeotropically aligned sample obtained on surface-treated glass, texture becomes completely dark. In the X-ray diffraction pattern taken with a beam parallel to the layer for this homeotropically aligned sample, the inner layer reflections appear on the meridian and outer broad ones on the equatorial line. All these observations identify the smectic A (S_A) structure. Layer spacings estimated from the first layer reflection are listed in Table 1.

In Figure 2, the layer spacings are plotted against the carbon number of tail group, *m*, and compared with the molecular length and half a molecular length which were calculated for the most extended twin molecules (refer to Figure 3a). The observed spacing increases continuously with the increase of *m* as expected. However, these are significantly smaller than the molecular length, but somewhat larger than half a molecular length.

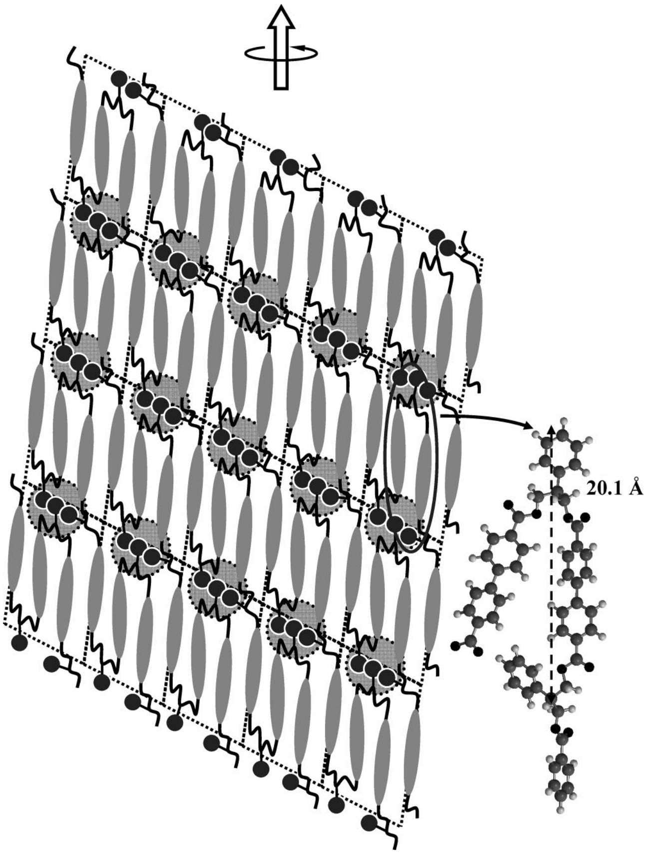

Figure 8. One of the most reliable models of molecular packing into the two-dimensional lattice (shown by dashed lines) in oriented fiber. The mesogens lie parallel to the fiber axis and the polymer is folded in each second unit. The averaged axes of polymer chain and mesogens are tilted by 27° to the layer normal so that the smectic liquid crystal is essentially S_C phase. The repeating unit illustrated in the inset gives the unit length of 20.1 Å, which corresponds to the observed one (20.6 Å). The bulky phenyl groups sticking out of the spacer are accommodated into the limited space to form a columnar type of domain (dotted circles) which develops parallel to the layer, and perpendicular to the tilt direction of mesogens. It is a kind of columnar phase with the columns embedded within a S_C matrix.

Here, two possible models for S_A structure are likely as discussed in the Introduction. These are illustrated in Figure 4, parts a and b. One is constructed by the extended molecules in which two mesogenic groups are parallel to each other. In this case, the observed layer spacing that is nearly equal to half a molecular length requires the random mixing of the tail and spacer groups. However, the smectic layer structure may be hardly built up by such a random mixing as illustrated in Figure 4a, because the length of the propane spacer group is remarkably shorter than the alkyl tail length with a carbon number of 4−22. The resulting liquid crystal should be nematic. Another model is constructed by the folded U-shaped molecules. In this case, the molecules can easily form the S_A phase. The molecular lengths calculated for one possible folded conformation of Figure 3b, are listed in Table 1and plotted against *m* in Figure 2. Good correspondence can be found between the calculated and observed values, leading to the conclusion that the 2-phenyl propane spacer forces the U-like association of two mesogens within a molecule. Such a U-shaped conformation may be the best way to accommodate the bulky phenyl group sticking out from the alkyl spacer into a smectic layer structure. Two mesogens within a molecule closely associated by folding may work as one mesogen to form smectic structure as illustrated in Figure 4b.

3.2. Smectic Structure Constructed by BB-3(2-Ph) Polymer with Regular Chain Folding Conformation. Figure 5 shows DSC data for BB-3(2-Ph). It shows only an LC to isotropic phase transition peak with an enthalpy of 4.3 kJ mol^{-1} at 121°. The LC phase is fluid and on cooling to room temperature, it is solidified at the glass transition temperature of 75°.

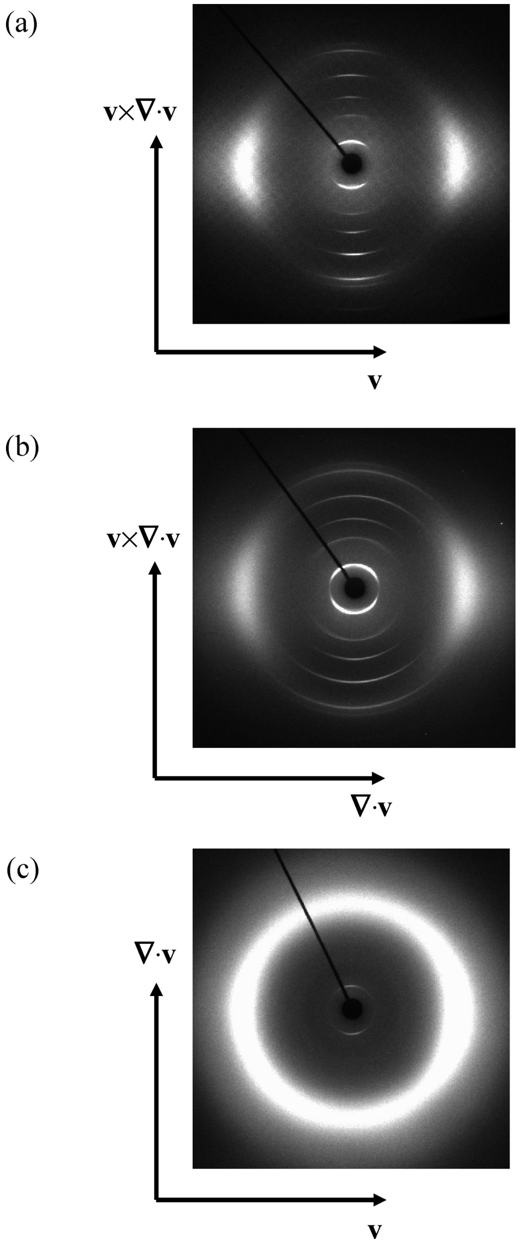

Figure 9. X-ray patterns for BB-3(2-Ph) films oriented by shearing at 5.3×10^{-3} s^{-1} at 105 °C, taken by the irradiation along (a) the velocity gradient ($\nabla\cdot\mathbf{v}$), (b) the velocity ($\mathbf{v}$), and (c) the vorticity ($\mathbf{v} \times \nabla\cdot\mathbf{v}$) directions.

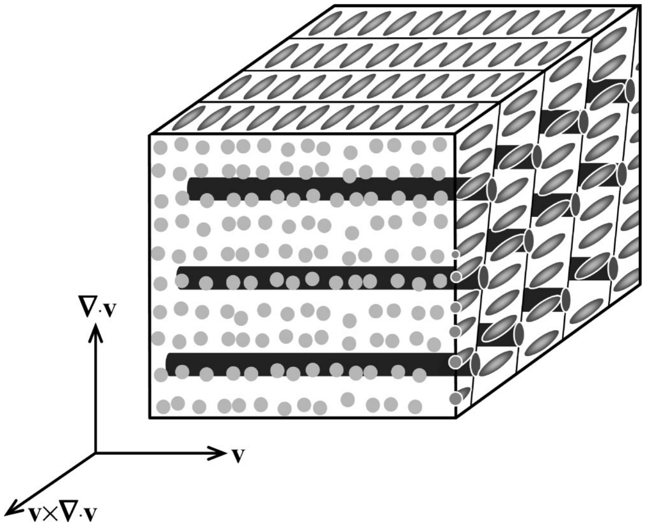

Figure 10. Schematic illustration of shear-flow orientated smectic phase. Mesogens and polymer chains are oriented parallel to the $\mathbf{v} \times \nabla\cdot\mathbf{v}$ direction, that is perpendicular to the $\mathbf{v}-\nabla\cdot\mathbf{v}$ plane. The mesogens are tilted within a $\nabla\cdot\mathbf{v}-(\mathbf{v} \times \nabla\cdot\mathbf{v})$ plane and columns formed by the phenyl groups are aligned parallel to the $\mathbf{v}$ direction.

Figure 6 shows the oriented X-ray pattern of the LC phase. Here, the polymer is spun from the isotropic melt and then annealed at 85°. The X-ray pattern was taken with the fiber axis set in a vertical direction. The reflection pattern includes outer hallow with a spacing of 4.5 Å on the equatorial line and several inner reflections around the meridional line. The outer halo indicates a liquid-like association of mesogens in their lateral direction and its location on the equator means that the long axes of mesogens are parallel to the fiber axis. On the other hand, the inner reflections cannot be explained by a simple layer structure, but by the type of frustrated structure with two-dimensional lattice.[16,17,21,24,25,26] The spacings of these reflections are listed in Table 2. All these reflections can be interpreted as a two-dimensional lattice with $a = 12.9$ Å, $c = 20.6$ Å, and $\beta = 70.0°$; c is the layer periodicity and a the density-modulated periodicity along the layer. Figure 7a illustrates the orientation of the reciprocal lattice that satisfies the observed diffraction pattern with respect to both the spacing and diffraction geometry. Figure 7b illustrates the corresponding orientation of real lattice in the fiber specimen. Here, the tilt angle (7°) of c-axis to the fiber axis was determined from the azimuthal angle (27°) of (001) reflection from the meridian (refer to Figure 6c).

Considering that the lateral spacing between neighboring mesogens is around 4.5 Å, one can assume that three mesogens are included within a unit lattice length of $a = 12.9$ Å (along the layer plane). On the other hand, length of $c = 20.6$ Å is fairly larger than 15.1 Å of the fully extended repeating unit.[5] Such characteristics of two-dimensional lattice can be produced when each second spacer takes up the folding conformation as observed in twin dimers. Most reliable model is illustrated in Figure 8. In this model, averaged axes of polymer chain and mesogens are tilted by 27° to the layer normal so that the smectic liquid crystal is essentially S_C phase. The possible repeating unit is illustrated in the inset, the calculated length of which is 20.1 Å, nearly equal to the observed one. The bulky phenyl groups sticking out of the spacer[27,28] are accommodated into the limited space to form a kind of columnar domain which develops parallel to the layer, and perpendicularly to the tilt direction of mesogens. This is a kind of columnar phase with the columns embedded within a S_C matrix.

Here, a question arises on whether it is a kind of crystal or liquid crystal. For the following reasons, it is surely a liquid crystal. First, it shows a broad outer reflection of 4.5 Å, indicating the liquid-like packing of mesogen within a layer as mentioned above. Second, it shows a clear glass transition. Third, it is really fluid so that the molecular orientation can be achieved by shear flow as follows.[6]

Steady shear alignment was performed by a cone-plate type of rheometer at 105 °C in LC phase and at a shear rate of 0.005 rpm (5.3×10^{-3} s^{-1}). After stopping shear flow, sample was cooled to room temperature and then removed from rheometer fixture. X-ray patterns were recorded by irradiation to three characteristic directions, velocity gradient ($\nabla\cdot\mathbf{v}$), flow ($\mathbf{v}$) and vorticity ($\mathbf{v} \times \nabla\cdot\mathbf{v}$) directions, as shown in Figure 9a−c. At a glance, one can recognize that the well orientation can be achieved and then that the phase is surely fluid liquid crystal.

Let us consider the orientation behavior, referring at first to the outer broad reflection with a spacing of 4.5 Å. On $\mathbf{v}-(\mathbf{v} \times \nabla\cdot\mathbf{v})$ and $\nabla\cdot\mathbf{v}-(\mathbf{v} \times \nabla\cdot\mathbf{v})$ planes, the broad reflection is observed in a direction of $\mathbf{v}$ and $\nabla\cdot\mathbf{v}$ directions, respectively, while on $\mathbf{v}-\nabla\cdot\mathbf{v}$ plane it appears as ring. Since the broad reflection arises from the lateral packing of mesogens, this means that the mesogens, i.e. polymer chains, are oriented in a $\mathbf{v} \times \nabla\cdot\mathbf{v}$ direction, that is perpendicular to $\mathbf{v}-\nabla\cdot\mathbf{v}$ plane. Such a perpendicular orientation is reasonable since in polymeric smectic phases the flow preferentially occurs within a layer or perpendicularly to the polymer chain axis.[6,7,10] On the other hand, sharp reflections attributable to the two-dimensional lattice also appear differently on the three planes. On the $\mathbf{v}-(\mathbf{v} \times \nabla\cdot\mathbf{v})$ plane, all of the reflections lie just on the $\mathbf{v} \times \nabla\cdot\mathbf{v}$ direction. On the $\nabla\cdot\mathbf{v}-(\mathbf{v} \times \nabla\cdot\mathbf{v})$ plane, the reflections are somewhat spread around $\mathbf{v} \times \nabla\cdot\mathbf{v}$ axis, and some of the inner reflections, for example (001) and (102) reflections, are split as observed in the oriented fiber. On the $\mathbf{v}-\nabla\cdot\mathbf{v}$ plane, only a (001) reflection with a very weak intensity can be detected in a direction of $\nabla\cdot\mathbf{v}$. All these profiles can be explained by the alignment of columns illustrated in Figure 10 where the columns lie parallel to the $\mathbf{v}$ direction and with (001) plane nearly parallel to $\mathbf{v}-(\mathbf{v} \times \nabla\cdot\mathbf{v})$ plane. Such a parallel alignment of columns is also preferable because it is only a way which does not deform the two-dimensional lattice as observed in the LC block copolymer with cylindrical microdomain.[26]

4. Conclusion

In this study, we have shown that the phenyl group attached on the propane spacer induces the chain folding conformation for dimeric molecules and main-chain type of LC polymer. The dimeric compounds behave as chain folded U-shaped molecule and form the S_A phase. On the other hand, the polymer taking up the regular chain folding conformation in each neighboring unit, form the S_C phase. In this S_C phase, the bulky phenyl groups are excluded within a limited space, resulting in the columnar like domain running along the layer with its axis perpendicular to the tilt direction of mesogens. Such columnar domains are regularly formed to produce the regular density modulation along the layer. In other words, the columns embedded in a smectic matrix are aligned with two-dimensional positional order, showing the new potentiality in spontaneous nano-organization in LC polymers.

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