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Phase Identification in a Series of Liquid-Crystalline TPP Polyethers and Copolyethers Having Highly Ordered Mesophase Structures. 4. Phase Structures and Order Evolution in TPP(n = 12) Thin Films

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ABSTRACT: A main-chain liquid-crystalline polyether has been synthesized from 1-(4-hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)propane and 1,12-dibromododecane, TPP(n = 12). In our previous report, the phase structures and phase transitions in bulk TPP(n = 12) have been identified. In this study, thin film samples of TPP(n = 12) have been prepared with thicknesses ranging from 10 to 100 nm on amorphous carbon coated substrates. Transmission electron microscopy and electron diffraction observations show that the liquid-crystalline chain molecules possess a tilted homeotropic orientation within monodomains at a structural formation temperature of 180 °C in the smectic F (S_F) phase. This is due to the surface-induced alignment effect. With increasing isothermal time, the lateral size and thickness of the monodomain increase, indicating that the formation of monodomains is initiated by a uniformly oriented molecular aggregate and is conceptually similar to the nucleation-controlled process of polymer crystallization. The growth stage reveals that large-scale molecular motion is required in order to transfer the chain molecules from an isotropic orientation to a tilted homeotropic structure. Electron diffraction results on the TPP(n = 12) thin films confirm the phase structures identified in bulk materials. When the thin film samples are quenched from the isotropic melt to lower structural formation temperatures, the samples no longer show the tilted homeotropic molecular orientation. This indicates that the amorphous carbon surface-induced alignment process is sensitive to the type of phase in which the structural formation occurs. It is not possible to access the tilted homeotropic orientation when the molecules have been in an ordered structure higher than the S_F phase. In the smectic crystal G phase, molecular mobility along the chain direction can still be expected, which is evidenced by an observation of significant morphological layer thickening during annealing in this phase. The regularity of morphological layers in the different ordered phases is also investigated.

Introduction

In a recent series of publications, we have reported that in a series of main-chain liquid-crystalline polyethers synthesized from 1-(4-hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)propane and different α,ω-dibromoalkanes [TPP(n = odd and even)] highly ordered smectic F and smectic crystal G and H phases (S_F, SC_G, and SC_H) exist.[1−4] These phase identifications are based on experimental results of structural analysis, thermodynamic transition properties, and morphological observations from differential scanning calorimetry (DSC), powder and fiber wide-angle X-ray diffraction (WAXD) patterns at different temperatures, and polarized light and transmission electron microscopy (PLM and TEM). The identification of these phases suggests that, although long-chain molecules possess covalent connectivity between mesogenic groups and methylene units, classification of the liquid-crystalline polymer phase behavior follows the concepts established for small-molecule liquid crystals.[5,6]

Furthermore, we have also found a surface-induced structural ordering process in thin films of TPP(n = 7).[4] In TPP(n = 7) bulk and fiber samples, three liquid-crystalline phases have been identified: nematic (N), S_F, and SC_G phases. Note that this series of smectic and smectic crystal phases possesses a tilted molecular direction with respect to the layer normal, and the tilt of the molecules is toward a side of the hexagonal lattice.[1−3] In thin film samples in which the film thickness is on the same order of magnitude as the molecular size (with a thickness ranging from 10 to 100 nm), the detailed structure and morphology of TPP(n = 7) have been studied by electron diffraction (ED) and TEM experiments on three different types of substrates. These include silane-grafted, amorphous carbon coated, and clean glass surfaces. Homeotropic molecular alignment in monodomains has been obtained by using the substrates with silane-grafted and amorphous carbon coated surfaces. Both surfaces can also induce structural ordering in TPP(n = 7) to form orthorhombic lateral packing which does not exist in bulk and fiber samples and usually only appears in TPP($n \geq 11$).[2] This phase has been identified as a SC_H phase. The clean glass surface does not induce orthorhombic packing, and only polydomain structures can be found in which a homogeneous alignment of the chain directors exists.[4]

The previous study of phase identifications in bulk and fiber samples for this series of TPP samples[1−3] has provided useful information for further investigation of structure and order evolution in the TPP thin films. In this study, the polymer chosen is TPP(n = 12), which possesses an even number of methylene units. This is a counterpart of the study of TPP(n = 7), which has an

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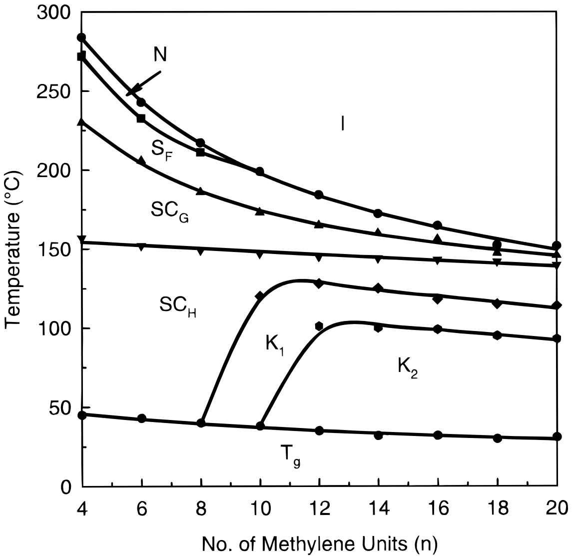
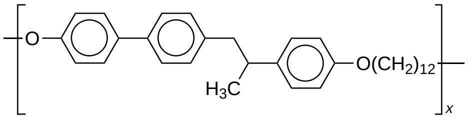


Figure 1. Phase diagram of TPP(n = even)s.

odd number of methylene units. The chemical structure of TPP(n = 12) is



Experimental Section

Materials and Samples. TPP(n = 12) was synthesized from 1-(4-hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)propane and 1,12-dibromododecane. The detailed synthetic procedure has been reported in an earlier publication.[7] The number-average molecular weight is 18 300 and the polydispersity is 2.9 as measured by gel permeation chromatography (GPC) in chloroform based on polystyrene standards.

TPP(n = 12) thin films (having thicknesses of 10−100 nm) on the amorphous carbon coated surfaces were prepared for TEM and ED experiments. The films were cast from a 0.1% (w/w) TPP(n = 12)/chloroform solution. After the solvent evaporated under vacuum, the samples were heated above the isotropization temperature (184 °C) for 10 min under a dry nitrogen atmosphere to eliminate previous thermal history. Samples were then rapidly cooled to a preset temperature for different annealing times. After annealing, the samples were quenched in liquid nitrogen before they were brought back to room temperature. The films were then stripped, floated onto the surface of water, and recovered with copper grids.

Instrumentation and Experiments. The structures and morphology of TPP(n = 12) thin films on the amorphous carbon coated surfaces were observed using a JEOL (JEM 1200 EX II) TEM with an accelerating voltage of 120 kV. The TPP(n = 12) thin films were shadowed with Pt and coated with carbon for TEM morphological observations. A tilting stage was used for the ED experiments to determine the molecular orientation on the carbon substrates. Calibration of the ED spacings was carried out using gold (Au) and thallium chloride (TlCl) (d-spacing < 0.384 nm, the largest spacing for TlCl). Spacing values larger than 0.384 nm were calibrated by doubling the d-spacings of those reflections based on the spacing of their first-order reflections.

Results and Discussion

Structure and Symmetry of TPP(n = 12) Monodomains. From our previous work, it was found that TPP(n = even)s show complicated phase behavior. A complete phase diagram has been reported in ref 3. Figure 1 is a reproduced phase diagram for the purpose of understanding the phase behavior in TPP(n = even)s. It is evident that highly ordered smectic and smectic crystal phases exist for TPP(n = 12) and the transition sequence from high temperature to room temperature is[3]

$$\mathrm{I} \xrightarrow[18.84\ \mathrm{kJ/mol}]{184\ ^\circ\mathrm{C}} \mathrm{S_F} \xrightarrow[6.45\ \mathrm{kJ/mol}]{165\ ^\circ\mathrm{C}} \mathrm{SC_G} \xrightarrow[11.20\ \mathrm{kJ/mol}]{148\ ^\circ\mathrm{C}} \mathrm{SC_H} \xrightarrow[2.96\ \mathrm{kJ/mol}]{128\ ^\circ\mathrm{C}} \mathrm{K_1} \xrightarrow[2.21\ \mathrm{kJ/mol}]{101\ ^\circ\mathrm{C}} \mathrm{K_2} \xrightarrow{40\ ^\circ\mathrm{C}} \mathrm{T_g}$$

The transition temperatures as well as heats of transitions are also given for complete information. Note that a nematic phase does not exist in TPP(n = 12). A necessary condition to observe the surface-induced ordering process in the TPP thin films is that the sample must potentially be able to develop a further ordered phase structure compared to the corresponding bulk sample. Since bulk TPP(n = 12) samples possess the orthorhombic crystal packing of SC_H and K_1 and K_2 crystal phases, we do not expect that TPP(n = 12) will show further ordered phase structures in its thin film form (or, at least, expect that further ordered structural identification using an ED pattern will be difficult). However, it is still interesting to observe the correlation between the ordered phase formation and morphology as well as the phase structure results obtained from the monodomains in this polymer.

A general principle is that in polymer liquid crystals the surface-induced ordering process is most likely to occur in low-ordered liquid-crystalline states such as the N, S_A, or S_C phase due to a relatively low viscosity and large degree of molecular motion in these phases. The new structure which appears in TPP(n = 7) thin films is an example of this process.[4] For highly ordered smectic phases, the molecular mobility is restricted due to the formation of highly ordered lateral packing. However, in TPP(n = 12), surface-induced molecular orientation can be achieved in the highly ordered S_F phase. When TPP(n = 12) thin film samples on the amorphous carbon substrate are cooled from the melt to the S_F phase and isothermally kept there for a prolonged period of time (a few to several tens of hours), sharp, single-crystal-like ED diffraction patterns can be obtained from a monodomain structure using a tilting stage (about 30°) as shown in Figure 2. This ED pattern possesses the [*00l*] zone. According to the *hk0* reflections of the ED pattern in Figure 2, the lateral packing symmetry is hexagonal with dimensions of $a = b = 0.52$ nm, suggesting that a S_F (or SC_G which may form during cooling of the sample to room temperature in order to conduct the ED experiments) phase exists. This is consistent with the previous WAXD experimental observations in TPP(n = 12) bulk and fiber samples as reported in ref 3, in which a monoclinic unit cell was deduced since the layer normal is tilted 35° away from the fiber axis.[3] In addition to the hexagonal lateral packing, a two-chain orthorhombic lateral packing can also be identified using 30°-tilted ED observations as shown in Figure 3. The orthorhombic lateral packing has lateral lattice sizes of $a = 0.84$ nm and $b = 0.53$ nm based on the *200* and *110* reflections. The orthorhombic packing has also been observed in the SC_H (possibly the K_1 or K_2) phase in TPP(n = 12) bulk and fiber samples.[3]

The monodomain morphologies of these two lateral packings are drastically different. Monodomains having the hexagonal packing generally show a close-to-circular shape (see below in Figure 4d), indicating isotropic growth of the monodomain along all of the lateral directions. However, monodomains having orthorhom-

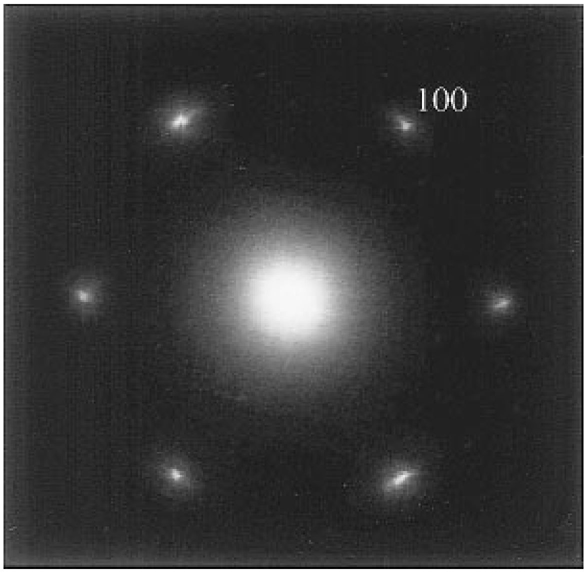


Figure 2. 30°-tilted ED pattern for TPP(n = 12) thin film samples on amorphous carbon coated substrate surfaces with hexagonal lateral packing obtained from the monodomain along the [*00l*] zone. The monodomain morphology can be seen in Figure 4d.

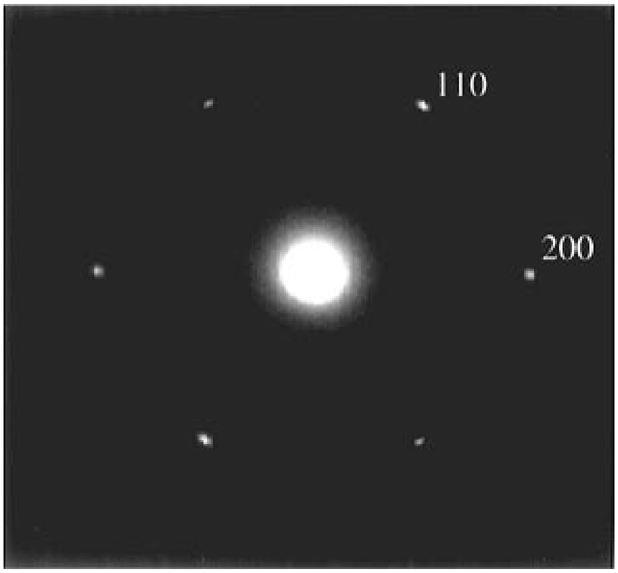


Figure 3. 30°-tilted ED pattern for TPP(n = 12) thin film samples on amorphous carbon coated substrate surfaces with orthorhombic lateral packing obtained from the monodomain along the [*00l*] zone.

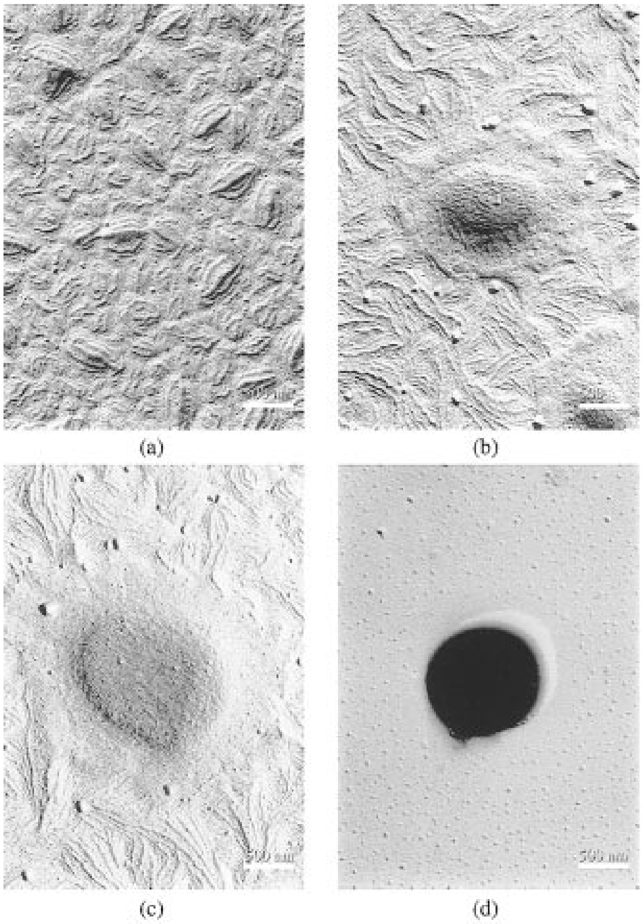


Figure 4. Set of TEM micrographs of the TPP(n = 12) monodomain on amorphous carbon coated surface formed at 180 °C for different times: (a) 3 min; (b) 1 h; (c) 3 h; (d) 50 h.

bic packing exhibit an elongated shape with the long axis always along the *b*-axis. This reveals that the development of the monodomain texture along the *a*- and *b*-axes is anisotropic. Similar observations have also been found in the case of monodomains in TPP(n = 7).[4]

Formation of TPP(n = 12) Monodomains: Nucleation and Self-Assembly Processes. The growth of the tilted homeotropic monodomains has been observed at 180 °C for different times. The lateral size of the monodomain increases progressively with time as shown in Figure 4a–d. In the initial stage of growth (for example, 3 min of annealing as shown in Figure 4a), only a polydomain texture is formed as observed under TEM. This is verified by polarized light microscopy (PLM) observations. A schlieren pattern is found after the sample is isothermally kept at 180 °C for a few seconds. The schlieren pattern corresponds to the polydomain texture. As further annealing takes place for 1 h, a small monodomain morphology with an irregular shape can be found as shown in Figure 4b. Parts b and c of Figure 4 show the growth of the monodomain with increasing the annealing time. After quenching, the polydomain texture can be observed surrounding the monodomains. From these figures, a zone area between the monodomain and polydomain texture exists, and molecules must cross through the zone before incorporation into the crystal. We speculate that the zone area is an intermediate stage of the molecules transferred from randomly oriented polydomains to uniaxially oriented monodomains. Both the monodomain and zone areas progressively grow with increased annealing time, as shown in these figures. However, the zone area appears to be everywhere when the annealing time is prolonged as shown in Figure 4d (for an annealing time of 50 h). The molecules are now almost extended in the monodomain. In this figure, the thickness of the monodomain drastically increases to reach a thickness with an order of magnitude of 100 nm (see below). Under PLM, no birefringence can be observed when the polarized light is parallel to the chain direction in tilted samples.

It may therefore be concluded that in the initial stage of the monodomain formation, TPP(n = 12) molecules possess the tendency to form tilted homeotropic orientation in molecular aggregates. This should most likely be due to the surface alignment effect as described in ref 4. We may describe this stage as a “nucleation” process. After the initiation of the monodomain, the surrounding molecules continue to migrate toward this

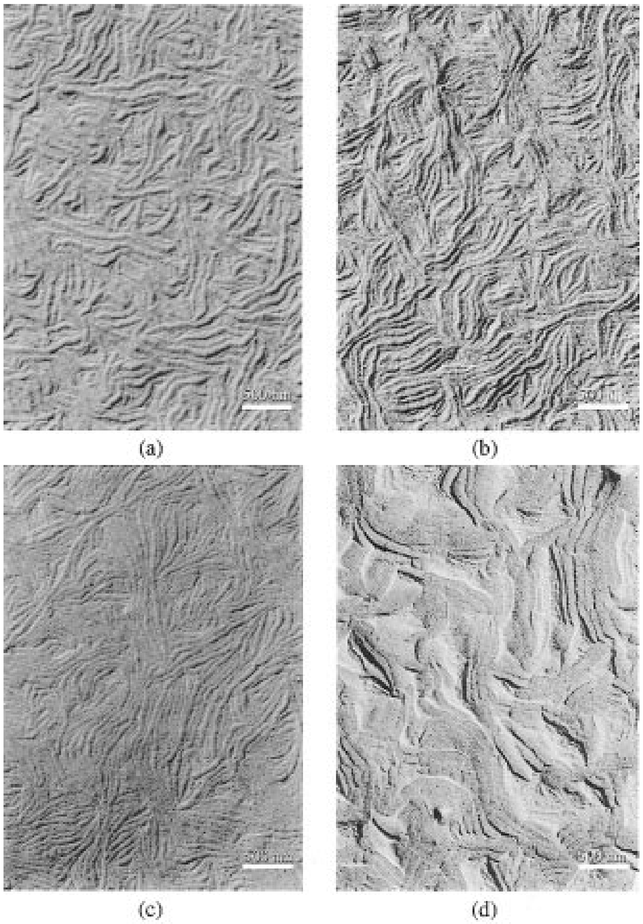

(a) (b) (c) (d)

Figure 5. Set of TEM micrographs of TPP(n = 12) thin film samples on amorphous carbon coated surfaces at (a) 90 °C for 15 h, (b) 120 °C for 3 h, (c) 140 °C for 3 h, and (d) 160 °C for 3 h.

domain, orient themselves, and become part of the domain's ordered structure. We suggest that this growth process is a self-assembly behavior for the evolution of the ordered structure in TPP(n = 12) monodomains.

Temperature Dependence of the Self-Assembly Ordering Process. Similar to polymer crystallization, the nucleation and self-assembly processes should be temperature (more precisely undercooling) dependent. TPP(n = 12) thin films kept isothermally at different temperatures below 180 °C on carbon-coated substrates exhibit significantly distinguished morphologies as shown in Figure 5a–d. Note that, for TPP(n = 12), the S_F phase is between 165 and 184 °C, the SC_G phase is between 148 and 165 °C, the SC_H phase is between 128 and 148 °C, the K_1 phase is between 101 and 128 °C, and the K_2 phase is between the glass transition temperature (40 °C) and 101 °C.[3] The structural formation temperatures chosen in this set of experiments are 160, 140, 120, and 90 °C, respectively, and, therefore, the thin film samples were isothermally annealed in the SC_G, SC_H, K_1, and K_2 phases. The results from annealing in the S_F phase at 180 °C are reported in Figure 4.

It is interesting that only when the samples are kept at 180 °C can tilted homeotropic molecular alignment be observed. Below this temperature, the majority of the chain molecules in most of the cases are close to homogeneous alignment parallel to the substrate surface. This indicates that the homeotropic surface alignment process is only effective in the S_F phase, in which TPP(n = 12) molecules retain a relatively high degree of mobility. It is expected that, for the molecules to be oriented by the surface-induced alignment effect, large-scale molecular motion must be required. When the molecules are quenched from the isotropic melt into the phases which possess order higher than S_F, the chain mobility is restricted and the molecules do not have enough time to assume tilted homeotropic alignment induced by the surface effect. Therefore, the morphological layer stacks are observed with homogeneous molecular alignment. At temperatures below 160 °C, ED experiments on the layer morphology show only a ring pattern attributed to polydomains. Annealing in the SC_G phase at 160 °C, the ED pattern shows long diffraction arcs similar to the TPP(n = 12) fiber pattern in the SC_G phase as reported in ref 3, indicating a certain degree of uniaxial orientation existed.

Furthermore, the morphological layer stacks are similar to edge-on lamellar crystals observed in many polymer crystals grown from the melt, such as in the case of poly(aryl ether ketone)s reported recently.[8,9] For the formation of edge-on lamellar crystals in polymer crystallization, the chain molecules are homogeneously oriented and the lamellar crystals are arranged parallel to each other to form stacks, the basic component in the construction of spherulites. With increasing crystallization temperature (*i.e.*, lower undercooling), the lamellar thickness increases, the edge-on arrangement becomes more regular, and the spherulitic size increases as well.

As shown in Figure 5a–c, we have found that in TPP(n = 12) thin films the layer structure becomes increasingly regular as the structural formation temperature increases. However, the morphological layer thickness is more or less constant. In Figure 5d, the layer thickness of the TPP(n = 12) thin film annealed at 160 °C increases drastically to a size approximately 2–3 times greater than that formed at temperatures below 160 °C. Note that annealing at 160 °C occurs in the SC_G phase, and in this phase molecular motion still seems to be possible along the chain direction. The direct consequence is thus that the morphological layer is thickened to about 100 nm although the molecules do not assume homeotropic orientation. It should be pointed out that the molecular length of TPP(n = 12) is on the same order of magnitude (around 100–400 nm). Therefore, the layer structure may consist of nearly extended chains of TPP(n = 12) macromolecules.

Finally, when we discuss the formation mechanism of tilted homeotropic aligned monodomains observed in Figure 4a–d, flat-on single lamellar crystals grown from the polymer melt are perhaps a good analog for comparison, such as in the cases of polyethylene (PE),[10–12] poly(ethylene oxide),[13,14] and syndiotactic polypropylene single crystals grown from the melt.[15,16] One discernible difference of the liquid-crystalline state is that, after the monodomain formation, the molecular mobility along the chain direction is still largely maintained. The permissible sliding motion arising from this mobility is analogous to extended chain crystal formation in PE with hexagonal packing at elevated pressure.[17,18] The important issue here is, however, the difference in the formation mechanisms between the monodomain in liquid-crystalline polymers and polymer single lamellar crystals. The experimental observations in this publication may serve as a starting point to quantitatively revisit these mechanisms.

Conclusions

We have reported the phase structure and order evolution of liquid-crystalline mono- and polydomains in TPP($n = 12$) thin film samples based on TEM and ED experiments. It has been found that both the monodomain lateral size and thickness increase over time when the samples are kept at 180 °C. At this temperature, the molecules show tilted homeotropic orientation due to the surface-induced alignment effect in the S_F phase. The tilted homeotropic aggregates may thus be viewed as analogous to a nucleus. Growth of the monodomains can be recognized as a self-assembly process facilitated by the large degree of molecular mobility. When the annealing temperature is below 180 °C, the melt-quenched thin films do not show tilted homeotropic molecular orientation due to the limited mobility in the phases with orders higher than that of the S_F phase. Instead, a more or less homogeneous orientation of the chain molecules can be found. It is interesting that the thickness of the morphological layer is constant with structural formation temperatures although the regularity of layer stacks improves. However, when the thin film samples are kept in the SC_G phase, a thickening process is obvious, indicating that molecular motion along the chain direction in this phase is still largely retained.

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References and Notes

(1) Cheng, S. Z. D.; Yoon, Y.; Zhang, A.-Q.; Savitski, E. P.; Park, J.-Y.; Percec, V.; Chu, P. *Macromol. Rapid Commun.* **1995**, *16*, 533.
(2) Yoon, Y.; Zhang, A.; Ho, R.-M.; Cheng, S. Z. D.; Percec, V.; Chu, P. *Macromolecules* **1996**, *29*, 294.
(3) Yoon, Y.; Ho, R.-M.; Moon, B.; Kim, D.; McCreight, K. W.; Li, F.-M.; Harris, F. W.; Cheng, S. Z. D.; Percec, V.; Chu, P. *Macromolecules* **1996**, *29*, 3421.
(4) Ho, R.-M.; Yoon, Y.; Leland, M.; Cheng, S. Z. D.; Yang, D.; Percec, V.; Chu, P. *Macromolecules* **1996**, *29*, 4528.
(5) Gray, D. G. *Polymeric Liquid Crystals*; Blumstein, A., Ed.; Plenum: New York, 1985.
(6) Pershan, P. S. *Structure of Liquid Crystal Phases*; World Scientific Publishing: Singapore, 1988.
(7) Percec, V.; Chu, P.; Ungar, G.; Cheng, S. Z. D.; Yoon, Y. *J. Mater. Chem.* **1994**, *4*, 719.
(8) Lovinger, A. J.; Davis, D. D. *J. Appl. Phys.* **1985**, *58*, 2843.
(9) Ho, R.-M.; Cheng, S. Z. D.; Hsiao, B. S.; Gardner, K. H. *Macromolecules* **1994**, *27*, 2136.
(10) Labaig, J. J. Ph.D. Dissertation, Faculty of Science, University of Strasbourg, 1979.
(11) Bassett, D. C.; Olley, R. H.; Al Raheil, I. A. M. *Polymer* **1988**, *29*, 1539.
(12) Keith, H. D.; Padden, F. J., Jr.; Lotz, B.; Wittmann, J. C. *Macromolecules* **1989**, *22*, 2230.
(13) Kovacs, A. J.; Gonthier, A. *Colloid Polym. Sci.* **1972**, *250*, 530.
(14) Cheng, S. Z. D.; Chen, J.-H. *J. Polym. Sci., Polym. Phys. Ed.* **1991**, *29*, 311.
(15) Lovinger, A. J.; Lotz, B.; Davis, D. D.; Padden, F. J., Jr. *Macromolecules* **1993**, *26*, 3494.
(16) Bu, Z.; Yoon, Y.; Ho, R.-M.; Zhou, W.; Jangchud, I.; Eby, R. K.; Cheng, S. Z. D.; Hsieh, E. T.; Johnson, T. W.; Geerts, R. G.; Palackal, S. J.; Hawley, G. R.; Welch, M. B. *Macromolecules* **1996**, *29*, 6575.
(17) Hikosaka, M.; Tsukijima, K.; Rastogi, S.; Keller, A. *Polymer* **1992**, *33*, 2502.
(18) Hikosaka, M.; Rastogi, S.; Keller, A.; Kawabata, H. *J. Macromol. Sci. Phys.* **1992**, *B31* (1), 87.

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