

Evidence of Liquid Crystal Texture in Slowly Solidified Films of Polystyrene-*block*-polyisoprene Diblock Copolymers

Wei Wang

Institute of Materials Research and Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260

Takeji Hashimoto*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan

Received January 12, 1999

When a given diblock copolymer, consisting of two incompatible blocks, is dissolved into an appropriate solvent at a concentration beyond a certain critical concentration, the block copolymer will self-assemble into ordered microdomain structures, such as spheres, cylinders, bicontinuous phases, and lamellae.^{1,2} The morphology may change with polymer concentration when a selective solvent is used.³ The ordered solution of diblock copolymers shows lyotropic liquid crystal (LC) textures as partially clarified experimentally.^{4–11} Here in this work we like to report a new, striking piece of evidence that the LC texture has been conserved in a bulk diblock copolymer film prepared by a solution casting with a neutral solvent. Before going into detailed descriptions and discussion of our results, it is important to point out that the experimental results reported in the literature have shown that the behavior of the ordered solution is highly dependent on the solubility of two blocks with a given solvent. Therefore, we shall first discuss the effects of solvent selectivity below.

In a system composed of a block copolymer and an extremely *selective* solvent, only one block can be dissolved so that the two blocks have very different chain conformations: the dissolved blocks are strongly expanded, while the insoluble blocks are densely packed. In this case the behavior of the block copolymer is quite similar to the behavior of a surfactant in water. The ordered solution having the lamellar or cylindrical microdomains exhibits a lyotropic smectic or columnar LC phase.^{3–9} It is necessary to emphasize that since the solvent selectivity leads to a different partition of solvent against the two blocks, the ratio of the volumes occupied by two blocks in the microdomains formed is altered with polymer concentration. The microdomain structures in such ordered solution can, in principle, vary from spheres, cylinders, to lamellae as a function of polymer concentration. Therefore, the microdomain structure in the bulk of the block copolymer may be different from those formed in the ordered solution. This gives a further implication that it is not always possible to solidify the mesophase structures formed in the ordered solution, due to the fact that the order–order phase transition(s) (OOT) among different symmetries will occur during solidification processes.

For a system composed of a block copolymer with a *nonselective* or *neutrally good* solvent, the two blocks

are equally swollen with the solvent.^{10–15} Thus, the ratio of the volumes occupied by the two blocks remains unchanged with polymer concentration, identical to that in bulk. As a consequence, the microdomain morphology is invariant with polymer concentration, but only the microdomain spacing increases.^{12,13} This means that, in this case, only the block copolymers having either lamellar or cylindrical microdomain in bulk can form a smectic or columnar lyotropic LC phase in the ordered solution.¹⁰ The phase diagram of this system is very simple: it consists of the isotropic and disordered (or single phase) solution and the anisotropic and ordered solution. The simple phase behavior means that it is possible to solidify the mesophase structures formed in the ordered solution, because there is no OOT when the polymer concentration is increased to bulk.

As for the LC texture conserved in bulk block copolymers having lamellar microdomains, there are some reports, based on observations of microdomain morphology under transmission electron microscopy (TEM), showing evidence that some defects, similar to those formed in liquid crystals, have been visualized in the bulk block copolymers.^{16,17} The length scale over which the similarity was found is of order of ~ 500 nm, corresponding to a few tens of lamellar spacing, a local feature of the LC texture. On the top of this local similarity, we should be able to find a global similarity, i.e., an optical texture in block copolymers similar to that found in lyotropic or thermotropic LC texture. The texture that we are interested in is typically on the order of micrometers which can be observed under conventional optical microscopy. For example, when the block copolymers form lamellar or cylindrical microdomain structures in bulk, they may show a fan-shaped texture. We believe it is very important to find out the direct and exact evidence to demonstrate that LC textures appearing in ordered solutions can be maintained in bulk block copolymers having either lamellar or cylindrical microdomain. If we can, we can further gain new insight into the formation of self-assembled structures at length scales much larger than the spacing of microdomains themselves, which we focus on to study intensively in this series of works.

One of the important characteristics of LC substances, in particular for low molar mass ones, is that their thin film samples are able to exhibit diverse optical textures, closely related to defects.^{18,19} Traditionally, it has been widely recognized that optical microscopy (OM) is one of the most powerful methods to study the textures of LC substances.^{18,19} It is also well accepted that by studying the textures we can directly identify whether a substance is a liquid crystal, and furthermore we can distinguish the type of liquid crystals to some extent. In this study, we will utilize OM to obtain the evidence to demonstrate that LC textures appearing in ordered solutions can be conserved in the bulk block copolymers having lamellar or cylindrical microdomain. Moreover, we can further obtain clear-cut evidence that the bulk block copolymers having the lamellar or cylindrical microdomain exhibit the texture characteristic of the smectic or columnar LC phase. However, up to now there are no reports that show the clear existence of the LC type textures in bulk block copolymers under OM.

* To whom correspondence should be addressed.

It is conceivable that the relatively low magnification of OM limits its application in studying the textures of bulk block copolymers, because bulk specimens usually have tiny "grains" within which a coherent order of microdomains exists.^{20,21} An essential requirement to circumvent this problem is to prepare a sample with large grains. Before running our experiment, therefore, we need to select a proper system and then to clarify the factors that strongly hamper the formation of large ordered grains in the bulk sample of a given diblock copolymer.

In this study we selected a system comprised of polystyrene-*block*-polyisoprene (PS-*b*-PI), a most commonly used block copolymer, and toluene, a well-defined neutrally good solvent for this block copolymer. It is in this system that the mesophase structures in the ordered solution can be solidified without changing the shape of microdomains, as discussed before. Now, the key to visualizing optical textures of block copolymers is finding an efficient way to prepare a sample with large grains (composed of lamellae or cylinders), larger than a few tens of micrometers. We can think of viscosity of solution, closely related to molecular weight of block copolymers, and of concentration change or evaporation rate of solvent as two crucial factors that will govern the size of optical textures.¹¹

We used a PS-*b*-PI with number-averaged molecular weight, $\bar{M}_n = 1.96 \times 10^4$, and a heterogeneity index, $\bar{M}_w/\bar{M}_n = 1.05$, determined with size exclusion chromatography calibrated by PS standard samples. The copolymer has a weight fraction of PS 0.54 and hence equilibrium morphology of lamellar microdomain in bulk. The relatively low molecular weight obviously gives a low solution viscosity, which will definitely facilitate to form large grains. In this study, the initial concentration of the block copolymer in the solution was 2 wt %.

Our previous study shows that a low evaporation rate of solvent will give the system enough time to self-assemble into large grains. This point becomes more and more crucial when the concentration increases, because the viscosity of the polymer solution is rapidly increasing with concentration. In this study the solution of the copolymer was prepared by dissolving the copolymer in toluene within a small glass bottle plugged with a polyethylene stopper. To reduce the evaporation rate of the solvent to a minimum, the solution was kept in the enclosed glass bottle, and the bottle was quiescently deposited in a dark box at room temperature for several months. The desired slow evaporation rate was achieved because of a slow leakage of toluene from the very small gap between the stopper and the rim of the bottle. After about 4 months, we observed a thin solid copolymer film solidified on the bottom surface of the glass bottle. Finally, we should point out that the sample should not be touched before ensuring that the sample has been totally solidified. Any mechanical disturbances of samples before solidification, especially in the stage reached to a high concentration, will blur or destroy the large grains or textures already well developed.

The optical textures appearing in the solid film sample were observed under a polarized light microscope (PLM) (Nikon Optophot-Pol) at room temperature and were recorded onto a photographic film. PLM micrographs a and b in Figure 1 show a typical texture that has been reproducibly observed in the thin solid film samples prepared by following the preparation

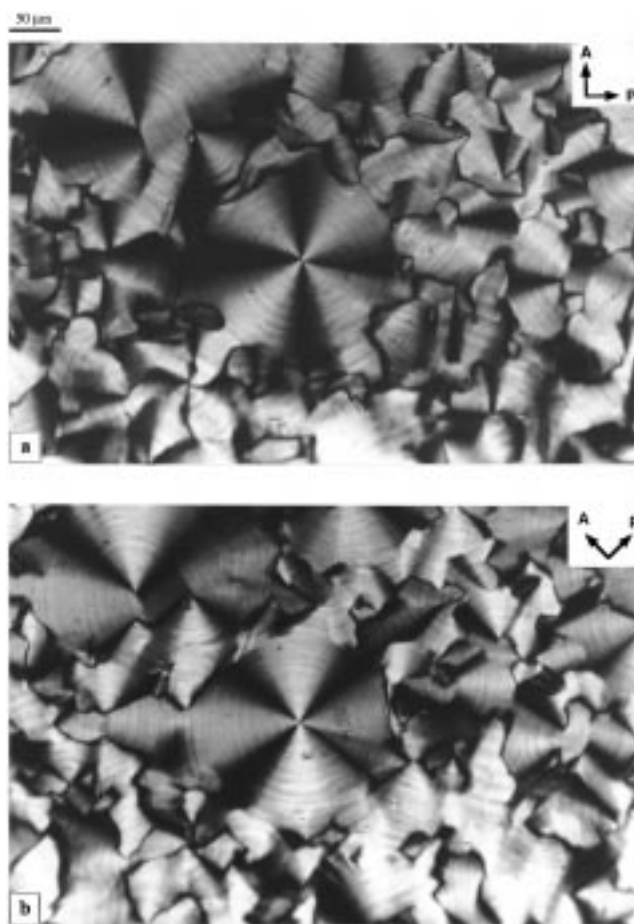


Figure 1. Two micrographs taken from a film sample with a thickness less than 30 μm of the diblock copolymer used and showing a typical fan-shaped texture that has been clarified to be a texture for liquid crystals having a lamellar structure. (a) Crossed polarizers. (b) Crossed polarizers rotated counterclockwise by 45°.

process described above. The thickness of this sample was strictly controlled in the range less than 30 μm . The orientation of the crossed analyzer, denoted by the arrow A, and polarizer, denoted by the arrow P, is indicated in the top-right side of each figure. Micrographs a and b were taken in the same area of the same sample with crossed polarizers but having different orientations as indicated. From micrographs a to b, the crossed polarizers were rotated counterclockwise by 45°. Without doubt, the texture shown in the figure is a typical fan-shaped texture.^{18,19} The optical texture presented in the micrographs provides exact evidence that the orientation of molecules or the lamellar microdomain in this solid film specimen is absolutely the same as that in the lyotropic or thermotropic low molar mass liquid crystals with a layer arrangement.^{18,19} The identity in texture implies an identity in property and also in structure at large scale between bulk block copolymers having lamellar microdomains and low molar mass smectic liquid crystals. Our results demonstrate that lyotropic LC textures well developed in the block copolymer solution have been successfully conserved and solidified in the films. Our success may elucidate that there is no OOT after formation of well-developed order in the solution with increasing polymer concentration to bulk. This is a feature that may not be easily attained in the solvent-cast films with a selective solvent.

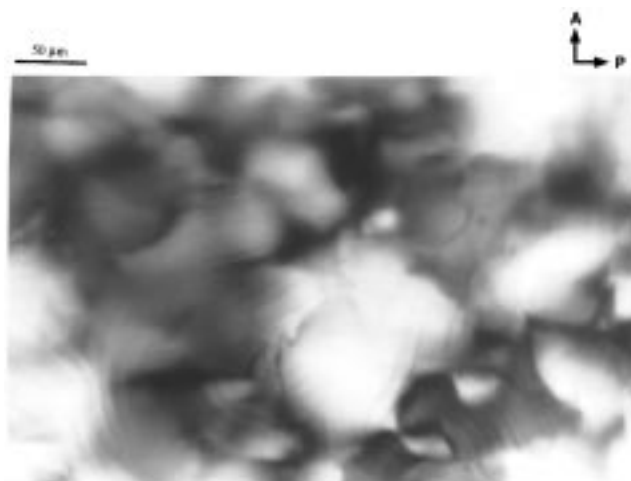


Figure 2. Blurred texture observed in the film sample with a thickness more than 60 μm .

In the POM image shown in Figure 1a,b, we can observe a pronounced fingerprint texture throughout the image. The Maltese cross (or discination with four dark brushes) rotated in the same counterclockwise direction as the polarizer and analyzer rotation. However, other dark brushes rotated in a complex way with the rotation of the crossed polarizers. Detailed analyses of the textures will be presented elsewhere.¹¹

The visualization of the optical textures depends very much on thickness. When the thickness of a sample is larger than the grain size, the optical texture now becomes very blurred, and it consists of only unshaped bright and dark regions, as evidenced by Figure 2 which was taken from a sample with a thickness more than 60 μm . The appearance of the blurred texture is believed to be due to the overlay of the textures along the thickness direction. In a sample of this diblock copolymer with a thickness of ca. 1 mm, we have observed that the sample appeared bright under crossed polarizers without any special texture features. This is an indication that many textures overlay each other along the thickness direction, and their optical axes change continuously in all directions.

The LC texture in Figure 1 has revealed a continuous and smooth change of the director, which may be taken along the lamellar normal, except the locations of some defects, in a sampling area of about $680\ \mu\text{m} \times 400\ \mu\text{m}$,²² being much larger than the sampling area normally observed by TEM. This is indicative of that the LC texture presented in this paper is not a local but global feature of such block copolymers. From Figure 1 to Figure 2 as well as the samples much thicker than 60 μm , a change in LC texture from 2D to 3D is demonstrated. These results unambiguously elucidate that the LC texture indeed exists in 3D samples of the block copolymers even on the length scale of order of 10 μm . More importantly, these results reveal a fact that the LC texture is inherent of block copolymers having lamellar (or cylindrical) microdomain. The features of LC-type defects are the key to determining the change in the director, and their number will control the "size" of the texture.^{18,19,23}

It should be noted here the LC texture observed in the solid films is not only a memory of the texture existed in the solution and conserved in the solid films but also a stable or metastable texture in the solid film. That is, the texture developed in the films does not

disappear even after a long annealing of the films at temperatures higher than the glass transition temperature of the polystyrene microdomains and lower than the order-disorder transition temperature (T_{ODT}) if $T_{\text{ODT}} < T_{\text{DEG}}$, the thermal degradation temperature, or T_{DEG} if $T_{\text{DEG}} < T_{\text{ODT}}$. We expect that the same texture might be developed via an ordering process from disordered block copolymer melts, if the systems have a mobility comparable to that encountered in the solvent evaporation process or if the systems have an enough time for the ordering into the large texture.

In summary, we have shown clear-cut evidence that the block copolymers having lamellar microdomain in the bulk show the LC texture strikingly similar to a smectic LC texture, owing to the success in preparing and studying the thin samples with large textures. This finding should provide an important link in the efforts to understand the evolution of structures at different levels of length scale and properties for block copolymers having lamellar or cylindrical microdomains. The LC texture of the bulk block copolymers having lamellar or cylindrical microdomain implies that the directors continuously change in three dimensions and that there are no grain boundary walls where the directors discontinuously change their orientation. The global texture will be determined by the features of LC-type defects existing in bulk block copolymers. Finally, it should be mentioned that in the texture of ordered block copolymers there are defects which are different from those found in the LC textures in low molar mass LC substances and in the LC texture we found in this work. For example, we can think of the defects developed in highly nonequilibrium situations, i.e., the grain boundaries created by impingement of the lamellar grains developed via nucleation-growth process. The grain boundary wall becomes defects where the lamellae having different orientations may be connected possibly through Scherker first surface.²⁴⁻²⁶ Relationships between this type of defect and the type of defect in the LC textures which are created by the thermal fluctuations should be clarified in the future.

References and Notes

- (1) Hashimoto, T.; Shibayama, M.; Fujimura, M.; Kawai, H. In *Block Copolymers: Science and Technology*; Meier, D. J., Ed.; MMI Press: New York, 1983 and references therein.
- (2) Hasegawa, H.; Hashimoto, T. In *Comprehensive Polymer Science—Second Supplement*; Aggarwal, S. L., Russo, S., Eds.; Pergamon: New York, 1996; Chapter 14, p 497.
- (3) De Gennes, P.-G. In *Liquid Crystals*; Liebert, L., Ed.; Academic Press: New York, 1978; p 1.
- (4) Sadron, C.; Gallot, B. *Makromol. Chem.* **1973**, *164*, 301.
- (5) Wittmann, J. C.; Lotz, B.; Candau, F.; Kovacs, A. J. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1341.
- (6) Candau, F.; Ballet, F.; Debeauvais, F.; Wittmann, J. C. *J. Colloid Interface Sci.* **1982**, *87*, 356.
- (7) Yang, J.; Wegner, G. *Macromolecules* **1992**, *25*, 1786.
- (8) Wanka, G.; Hoffmann, H.; Ulbricht, W. *Macromolecules* **1994**, *27*, 500.
- (9) Förster, S.; Antonietti, M. *Adv. Mater.* **1998**, *10*, 195 and literature therein.
- (10) Wang, W.; Hashimoto, T., submitted to *Polymer*.
- (11) Wang, W.; Hashimoto, T., manuscript in preparation.
- (12) Hashimoto, T.; Shibayama, M.; Kawai, H. *Macromolecules* **1983**, *16*, 1093.
- (13) Shibayama, M.; Hashimoto, T.; Hasegawa, H.; Kawai, H. *Macromolecules* **1983**, *16*, 1427.
- (14) Mori, K.; Hasegawa, H.; Hashimoto, T. *Polymer* **1990**, *31*, 2368.
- (15) Mori, K.; Okawara, A.; Hashimoto, T. *J. Chem. Phys.* **1996**, *104*, 7765.
- (16) Winey, K. I.; Patel, S. S.; Larson, R. G.; Watanabe, H. *Macromolecules* **1993**, *26*, 2542.

- (17) Amundson, K.; Helfand, E.; Quan, X.; Hudson, S. D.; Smith, S. D. *Macromolecules* **1994**, *27*, 6559.
- (18) Demus, D.; Richter, L. *Textures of Liquid Crystals*; Verlag Chemie: Weinheim, 1978.
- (19) Chandrasekhar, S. *Liquid Crystals*, 2nd ed.; Cambridge University Press: New York, 1992.
- (20) Sax, J. E.; Ottino, J. M. *Polym. Eng. Sci.* **1983**, *23*, 165.
- (21) Newstein, M. C.; Garetz, B. A.; Dai, H. J.; Balsara, N. P. *Macromolecules* **1995**, *28*, 4587.
- (22) Actually, the size of our sample has a diameter of 2 cm, and we observe the same texture in the whole sample.
- (23) Kléman, M. *Points, Lines and Walls*; John Wiley and Sons: New York, 1983.
- (24) Thomas, E. L.; Alward, D. B.; Henkee, C. S.; Hoffman, D. *Nature* **1988**, *334*, 598.
- (25) Gido, S. P.; Gunther, J.; Thomas, E. L. *Macromolecules* **1993**, *26*, 4506.
- (26) Nishikawa, Y.; Kawada, H.; Hasegawa, H.; Hashimoto, T. *Acta Polym.* **1993**, *44*, 192.

MA990030Q