Polymer 41 (2000) 4729–4735

polymer

Lyotropic liquid crystal behavior of polystyrene-*block*-polyisoprene diblock copolymers in toluene as a truly neutral solvent

W. Wang[a], T. Hashimoto[b,*]

[a]*Institute of Materials Research and Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore, Singapore 119260*
[b]*Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan*

Received 23 June 1999; received in revised form 9 September 1999; accepted 13 September 1999

Abstract

We present our experimental observations concerning lyotropic liquid crystal behavior and textures of the solutions of the two polystyrene-*block*-polyisoprene block copolymers in a truly neutral solvent (toluene). The block copolymers used either lamellar or cylindrical microdomains in bulk and also in solutions above the critical concentration (c_c). The optical textures, such as fan-shaped texture, parabolic focal conic texture and oily streaks, which have been often observed in smectics or columnar phases of lyotropic low-molecular-weight liquid crystals, were observed in the solutions above c_c enclosed in between two glass slides. This demonstrates that the smectic or columnar lyotropic phases are formed in the ordered solutions. Further, we discuss the origin of the formation of the lyotropic phases of the block copolymer solutions in relation to the microdomain structures of the solutions. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Block copolymers; Polystyrene-*block*-polyisoprene; Lamellar morphology

1. Introduction

In 1978, de Gennes has proposed that when diblock copolymers form a lamellar or cylindrical microdomain structure in a *selective* solvent their solutions can form lyotropic liquid crystal (LC) phases [1]. Such lyotropic LC phases had been experimentally observed in the solutions of diblock, triblock or graft copolymers in some selective solvents [2–5]. Depending mainly on the concentration of copolymers, c, in the solutions, the lamellar or cylindrical microdomain structure can be formed. Hence the LC behavior of the solutions is expected to be much similar to that of smectics or columnar phases of liquid crystals, if one notices that the lamellar and cylindrical phases in block copolymer solutions correspond to the smectic and columnar phases in liquid crystals, respectively [1–5]. This has been evidenced in the observations of optical textures in the thin film samples of these copolymer solutions. The results show the same textures as those observed in smectics or columnar phases of low-molecular-weight (LMW) lyotropic liquid crystals [6–8]. It is important to notice that the solvents used in these studies are *selective*, good for one block chain, e.g. A but poor for other block chain, e.g. B. In such solutions, A block chains are strongly swollen with the solvent and stretched normal to the interface in the microphases rich in A and responsible for a strong optical anisotropy, while B block chains are not swollen and only weakly stretched and hence less optically anisotropic. Therefore, the block or graft copolymers in such solutions have characteristics much similar to LMW amphiphilic molecules in water [1]. In other words, formation of the lyotropic LC phases of the copolymer solutions has been thought to be primarily due to a *solvent selectivity effect*.

Nowadays it is well known that the formation of lyotropic LC phases for systems comprised of block or graft copolymers and selective solvents is due to the formation of the lamellar or cylindrical microdomains in the ordered solution. From a viewpoint that block copolymers can self-assemble into a similar lamellar or cylindrical microdomains in *non-selective or truly neutral* solvents as well beyond a critical concentration (c_c), it is worthwhile to further explore whether or not such block copolymer solutions can show lyotropic LC behavior. (The non-selective or truly neutral solvent is defined here as a solvent, which satisfies such a criterion, that the volume fraction of one of the microphases in the ordered solution is invariant with c.) To our best knowledge, there is no experimental evidence to clarify this matter for truly neutral solvents. If this is the case, the LC texture becomes quite general for the block copolymer solutions forming ordered lamellae or cylinders. If the LC texture is observed even for bulk

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* Corresponding author. Tel.: +81-75-753-5604; fax: +81-75-753-4864.
E-mail address: hashimoto@alloy.polym.kyoto-u.ac.jp (T. Hashimoto).

PII: S0032-3861(99)00665-5

Table 1
Molecular characteristics, critical concentration (c_c) and microdomain structures found in solution-cast samples of the copolymers

Sample code	$\bar{M}_n$	$\bar{M}_w\bar{M}_n$	PS/PI	c_c (wt%)	Morphology
H102	12.8×10^4	1.16	50/50	ca. 20	Lamella [15,16]
HS-6	8.59×10^4	1.14	39/61	34–44	PS-cylinder

block copolymer films having the ordered lamellae or cylinders [9], this phenomenon becomes even more general. In this study we aimed to further reinforce and generalize the earlier observations and conclusions [2–5] by investigating polystyrene-*block*-polyisoprene (PS-*b*-PI) in toluene as a truly neutral solvent. The study of the texture will help us to understand a higher order organization of lamellar and cylindrical block copolymers in bulk and in ordered solutions.

In order to ensure the criterion of block copolymers in truly neutral solvents, we selected a system comprised of PS-*b*-PI and toluene, a well-defined truly neutral solvent [10–13] to study its lyotropic LC behavior. This is because the Flory–Huggins interaction parameters of PS and toluene and of PI and toluene are, respectively, 0.44 and 0.40 [14], greatly satisfying the criterion of neutral solvent. For a better understanding of the relation between microdomain structure in bulk and lyotropic mesophase behavior, we selected two PS-*b*-PI copolymers having either lamellar or cylindrical microdomain in bulk and also in ordered solution in toluene. As usual, we selected optical microscopy (OM) to study LC behavior of the solutions, because OM is a simple and efficient method that has been widely accepted to identify LC behavior of LC substances through identification of optical textures. To overcome the resolution limit of OM, we aimed to develop LC textures that are large enough for OM characterization.

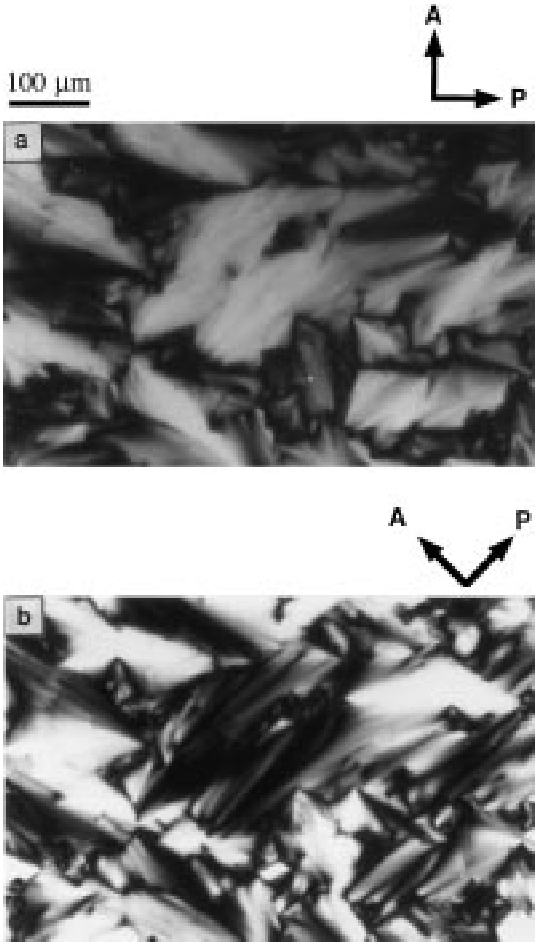


Fig. 1. Two POM micrographs showing the fan-shaped texture in the thin film specimen of the toluene solution of PS-*b*-PI diblock copolymer (H102) having a concentration slightly higher than C_c and having the lamellar microdomain structure in bulk and also in the ordered solution.

2. Experimental method

2.1. Materials

In this study we selected two PS-*b*-PI diblock copolymers, H102 and HS-6, which form lamellar or cylindrical microdomains in bulk to study their optical textures and hence their lyotropic LC behavior in the solutions prepared with a truly neutral solvent (e.g. toluene). H102 and HS-6 were synthesized in our laboratory. The molecular characteristics, c_c, and the microdomain morphology found in the as-cast samples with toluene as a solvent are listed in Table 1. The molecular weight, $\bar{M}_n$, and the heterogeneity index, $\bar{M}_w/\bar{M}_n$, of the copolymers were determined with size exclusion chromatography calibrated by PS standard sample. The critical concentrations were estimated based on the results published in the previous papers [10–13]. Their microdomain morphologies in bulk were identified by transmission electron microscopy (TEM) [15,16].

2.2. Preparation of solutions

The solutions of these two copolymers were prepared by dissolving the copolymers in toluene within a small glass bottle at room temperature for several days. The concentrations of the solutions were controlled in the range of 10–40 wt% copolymer.

2.3. Preparation of specimens for optical observations

Since optical textures of liquid crystals are usually investigated in their thin specimens, thin specimens of the solutions used for optical investigation were prepared by slightly pressing a small amount of the solutions in between two clear glass slides at room temperature. The glass slides were sealed immediately with epoxy resin that can be cured at room temperature. The thickness of the specimens was controlled by using the solutions having different initial concentrations, because the optical textures of liquid crystals in a specimen cell are dependent upon their thickness [8]. We found that the thickness is a function of the concentration of solutions under the conditions used in this study. Thin specimens with a thickness less than 10 μm can

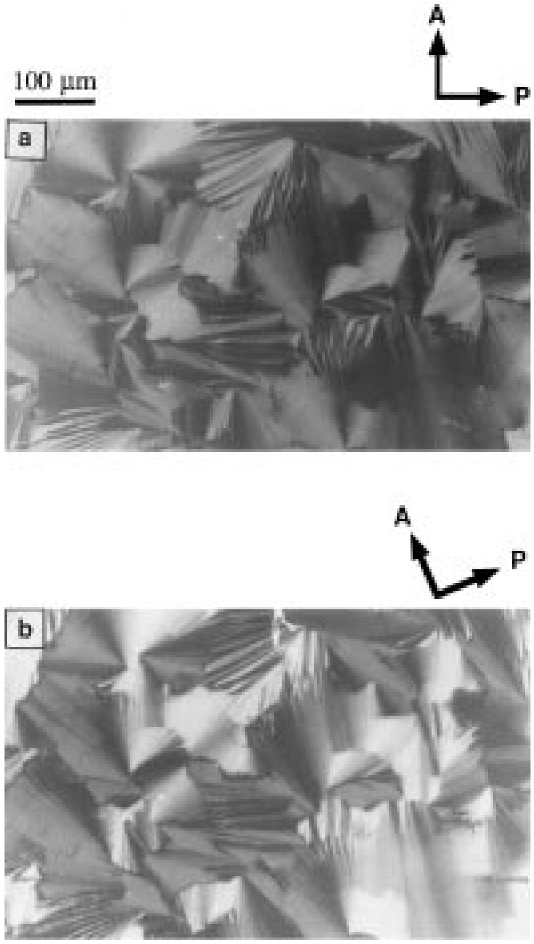


Fig. 2. Two POM micrographs showing the fan-shaped texture in the thin film specimen of the toluene solution of PS-*b*-PI diblock copolymer (HS-6) having a concentration slightly higher than C_c and having the cylindrical microdomain structure in bulk and also in the ordered solution.

be easily obtained if the solution has a concentration of 10–20 wt% copolymer. Thickness of the specimens prepared from the 30–40 wt% solutions is more than 20μm. The thickness of the solutions enclosed in such a cell as described above was evaluated roughly by using the optical microscope.

2.4. Optical observation

The optical textures appearing in the film specimens of the solutions were observed under a polarizing optical microscope (POM) (Nikon Optophot-Pol) at room temperature and were recorded by using a camera.

3. Experimental results and discussion

3.1. Optical textures

The POM micrographs in Figs. 1 and 2 show typical textures observed for the solutions of the two PS-*b*-PI block copolymers designated as H102 (Fig. 1) and HS-6 (Fig. 2) in toluene which have a concentration slightly higher than C_c. The orientation of the crossed polarizers is indicated by letters P (polarizer) and A (analyzer). Figs. 1 and 2 demonstrate first that the solutions are optically anisotropic. The specimens used for taking the micrographs were prepared from the solution with the initial concentrations of 12.5 wt% (Fig. 1) and 15 wt% (Fig. 2), respectively, thus their estimated sample thickness is less than 10 μm. It is worthwhile to indicate that these initial concentrations are below c_c of the block copolymers (Table 1). However the micrographs in Figs 1 and 2 were obtained for the solutions with their concentrations slightly higher than C_c. We will describe and further discuss the formation of the optical texture in the figures in detail in Section 3.2.

In the figures, some areas are bright and others dark. Their size can be a few hundred μm. In Figs. 1b and 2b the crossed polarizers were rotated counterclockwise by 45 and 22.5°, respectively. Comparing two micrographs *a* and *b* in Fig. 1 or Fig. 2, we can see that some bright areas in micrograph *a* become dark in micrograph *b*. This indicates that the optical axes in the bright areas are inclined with respect to the polarization direction of polarizer or analyzer, while in the dark areas they are parallel or normal to one of them. The dark and bright areas have vertices of a triangle-like shape. Within the bright or dark area, we can see some fine texture composed of thin ribbon-like or band-like structures. More precisely, we have observed a gradual variation of contrast from bright to dark within the bands or across the neighboring bands when rotating the crossed polarizers slowly. This indicates an internal structure with slightly mismatched director (or optical axis) orientation. All these optical features elucidate that the optical texture in the micrographs is a typical fan-shaped texture which was often observed in the thin specimens of LMW thermotropic smectics [17] and of LMW lyotropic smectics or columnar phases [6,7] as well as of the lyotropic LC solutions of some copolymers in the selective solvents [2,3].

The three micrographs in Fig. 3 were taken from the same specimen prepared from a solution of the lamella-forming block copolymer (H102) with an initial concentration of 40 wt%, higher than c_c (ca. 20 wt%). The orientation of the crossed polarizers is also indicated by letters P (polarizer) and A (analyzer). Owing to the initial concentration being increased to 40 wt%, we estimated that the thickness of the solutions is more than 20 μm. Several very bright spots, as indicated by arrows in Fig. 3, are anisotropic impurities. These POM micrographs also demonstrate that the solution is of optical anisotropy at this concentration. The textures shown in Fig. 3 have been frequently observed in the thick film specimens of LMW lyotropic smectics or columnar phases [18–23] as well as of the lyotropic LC solutions of some copolymers in the selective solvents [2,3]. Fig. 3a shows a typical parabolic focal conic texture. Fig. 3b shows a typical texture of oily streaks. Fig. 3c shows the multi-texture composed of the parabolic focal conic and oily streak textures. The dark regions between the oily streaks in Fig. 3b and c are the anisotropic solution in the homeotropic orientation. So far, we can confidently conclude that the system we are studying can form a lyotropic LC phase and the size and type of optical textures depends highly on the conditions used during sample preparation, such as initial concentration and sample thickness.

3.2. Formation of optical textures and critical concentration

In our experiment, we employed the solutions with different initial concentrations, some were higher than c_c but others were lower than c_c, to prepare our specimens. Our observations showed that optical textures could be observed immediately after enclosing the solution into the cell when the initial concentration is higher than c_c, for example, the case of Fig. 3. However, it took some time for us to discern the textures after enclosing the solutions with the initial concentrations being lower than c_c, the case of Figs. 1 and 2. Therefore, it is necessary to describe the details concerning the formation or appearance of the optical textures in these solutions.

Many factors, such as specimen thickness and interaction with substrate surface, are crucial to the formation of optical textures of a LC specimen. It is well known that some well-defined optical textures such as fan-shaped texture are usually observed in the thin specimen and can help us identify the feature of liquid crystals [8]. Due to the polymer characteristics, like relatively high viscosity, we can easily make solution specimens thinner than 10 μm from the solutions with the initial concentrations below 20 wt% without pressing the solution specimen between glass slides. In such specimen, the solution will not be oriented seriously. The thin solution specimens were optically isotropic when viewed under the crossed polarizers immediately after enclosing them into the cell. While the specimens were kept at room temperature for several days, we normally observed at first such optical texture in the periphery of the cell, i.e. in the area touched to the epoxy resin. The texture gradually grew up or spread toward the center of the specimen and eventually filled the whole specimen volume.

The formation of the optical texture with time after the enclosure of the solution into the cell is a consequence of the concentration gradually increasing and finally exceeding c_c due to a slow solvent leakage from the cell. This is because toluene could strongly affect the curing reaction of epoxy resin and then led to a swollen epoxy resin, possibly developing a small gap between glass slide and epoxy resin later on. The slow increase in the concentration may be favorable to formation of large optical textures, as evidenced in Figs. 1 and 2. In such a way the systems have an enough time for the ordering into the large textures. At the time when the texture in Figs. 1 and 2 was observed, we estimated that the concentration in the cell reached slightly above c_cs, i.e. $c \geq 20$ wt% for H102 and $c \geq 34$–44 wt% HS-6, respectively. The concentration at the time when the optical observation was made was determined by measuring the weight of the solution specimen.

3.3. Lyotropic LC behavior and microdomain structures

The optical textures shown in Figs. 1–3 provide a piece of definite evidence that the solutions of the PS-*b*-PI copolymers (H102 and HS-6) in toluene are in lyotropic smectics or columnar phases simply because the optical textures are totally same as those observed in LMW thermotropic smectics [17] and LMW lyotropic smectics or columnar phases

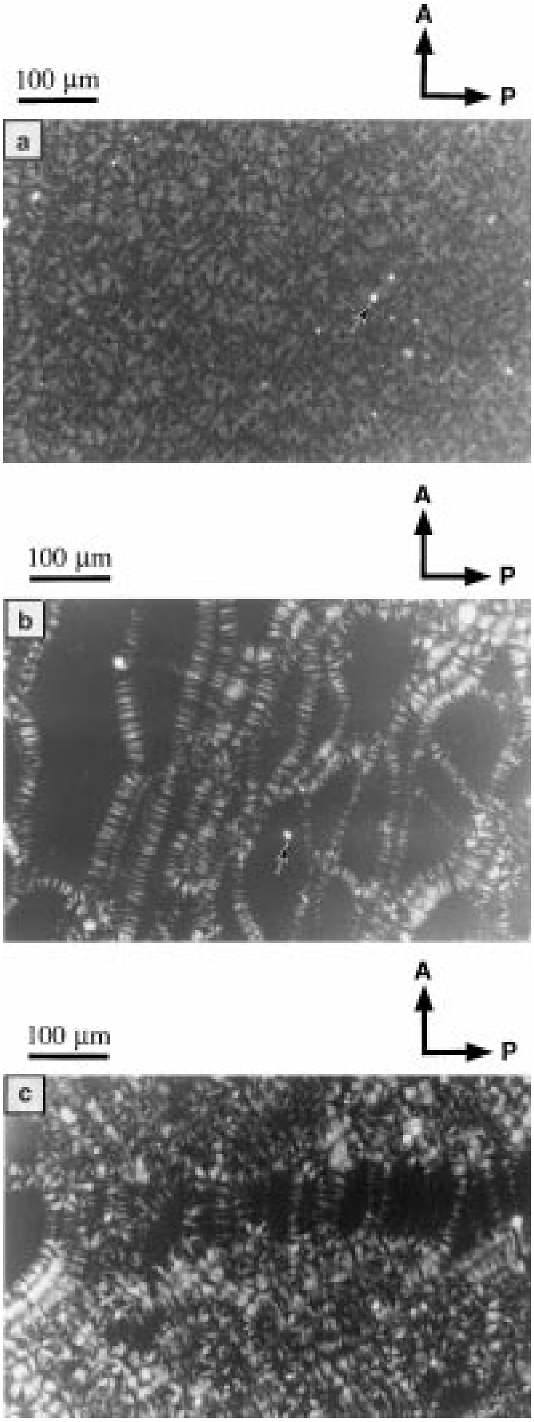


Fig. 3. Three POM micrographs showing the textures observed in the film specimen prepared from the toluene solution of PS-*b*-PI diblock copolymer (H102) at an initial concentration of 40 wt%. (a) A typical parabolic focal conic texture. (b) A typical texture of oily streaks. (c) The multi-texture composed of the parabolic focal conic texture and oily streaks.

[6,7,17–23]. This further implies that the formation of lyotropic liquid crystals should be due to the lamellar or cylindrical microdomain structure in the block copolymer solutions. In fact, our former studies [10–13] have definitely indicated that microphase separation between PS and PI blocks has occurred in the PS-*b*-PI block copolymer solutions in the truly neutral solvents (e.g. toluene) when $c > c_c$. Furthermore, microdomain shapes developed in the solutions are independent of c and the same as those of the copolymers in bulk, but only domain spacing increases with c, due to an increase of segregation power [10–13]. Therefore, we can say that above c_c, the H102 solutions form the microdomain structures composed of alternating lamellae of PS and PI swollen with toluene and the HS-6 solutions form the hexagonal cylinders of PS solution in the matrix of PI solution. These results indicate that formation of lyotropic liquid crystals is not necessarily ascribed to the *solvent selectivity effect*, as presented in previous works [1–5], but in a quite universal phenomenon for the ordered block copolymer solutions forming lamellar and cylindrical mesophases.

For a better understanding of the distinction between the systems comprised of selective and non-selective solvents for the same block copolymer, let us discuss the conformation of two block chains in solutions. We will concern the distinction in phase diagram of two systems caused by the different chain conformations. For the selective solvent good for A, but bad for B blocks, two microphases are composed of A lamellae and B lamellae which are swollen and unswollen with solvent, respectively, or A cylinder (or matrix) swollen with solvent in the B matrix (or cylinder) unswollen with solvent. Because only block A can be swollen with solvent, the ratio of the volume occupied per a single block A to the volume occupied per a single block B in the microdomain phases increases with increasing solvent fraction, the microdomain structures in solution can be quite different from that in bulk and will change, in general, from spheres in body center cubic lattice, hexagonal cylinder and finally to alternating lamellae with changing concentration of block copolymers [2–5,24]. At least five phases, isotropic, micelle, cubic, hexagonal cylindrical, and lamellar phases, have been observed experimentally in the earlier studies [2–5,24]. Lyotropic liquid crystals can be formed in the selective solvent solutions having the lamellar and cylindrical microdomain structures.

In contrast with the selective solvent system, in the truly neutral solvent, two microphases are composed of blocks A and B equally swollen with solvent. Thus the ratio of the volume occupied per single block A to the volume occupied per a single block B keeps a constant value independent of c. As a consequence the microdomain shape is invariant with c but only the domain spacing increases with c [10–12]. The corresponding phase diagram of the block copolymers having lamellar or cylindrical microdomain structures in bulk is simple: it consists of the isotropic, disorder solution phase and the anisotropic, order solution phase with either swollen lamellar or cylindrical microdomains for block copolymers forming lamellae or cylinders in bulk. The simple phase behavior means that the optical texture observed in ordered solutions will appear in bulk of the same block copolymers. This has been verified in our former work [9].

It is worthwhile to discuss in more detail the results for binary block copolymer–solvent systems presented in Ref. [2], because the authors mentioned that the best LC texture could be observed from a system consisting of block copolymers and truly neutral solvents. In that paper, Wittmann et al. [2] studied the LC textures of the binary systems consisting of either polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) or PS-*b*-PI with either ethyl formate or 2,4-pentanedione and stated that “solvents which are too selective for one or the other sequence are inadequate: the best results are obtained for solvents which partition equally well between the two sequences”. At the same time, they suggested that “in such binary copolymer–solvent systems, transitions from one mesophase to another can be induced by either concentration or temperature changes’. Thus the solvents employed in their studies may not be truly neutral, or at least not so neutral as toluene for PS-*b*-PI. This is because block copolymers can easily form different mesophases in selective solvents [1,3–5,24] and that there is no mesophase transition(s) in the non-selective solutions of copolymers.

The formation of the “lamellar mesophase” in the systems comprised of PS-*b*-PEO with either ethyl formate or 2,4-pentanedione is believed to be due to the solvent selectivity effect, because a copolymer used had PS weight fraction of 0.9 and should have spherical microdomains of PEO in the matrix of PS in bulk if crystallization is not encountered (see Figs. 1, 6 and 9 in Ref. [2]). Clearly, the solvent selectivity effect causes a change in microdomains from spheres in bulk to lamellae in solution. For the single-solvent system of PS-*b*-PI with a 34% polyisoprene content, unfortunately, they did not specify the solvent used in the caption of Fig. 5 and also in the text [2]. Hence, in this case it is impossible to justify whether the formation of LC phase for the system comes from the solvent selective effect or not. In Section 3, Wittmann et al. [2] stated that the solvents, such as, 2,4-pentanedione, which are good for the formation of LC phase for PS-*b*-PEO, are suitable for the PS-*b*-PI copolymers. But, we have evidence to indicate that these solvents (ethyl formate or 2,4-pentanedione) are not truly neutral for PS-*b*-PI block copolymers. First, we observed that the solutions of block copolymer H102 in the two solvents were not clear as it is in toluene. Secondly, TEM observation for O_sO_4-stained ultrathin sections of the H102 specimens prepared by a solution cast from 10 wt% polymer with ethyl formate or 2,4-pentanedione as a solvent did not show any alternating lamellar microdomains. Instead, it showed many small particles having a size in the range of 30–40 nm, as shown in Fig. 4. Therefore, we may state that the solvents employed by Wittmann et al. [2] in the binary systems are not necessarily truly neutral. However, our work presented here for truly neutral solvent further generalizes and reinforces their observations and conclusions.

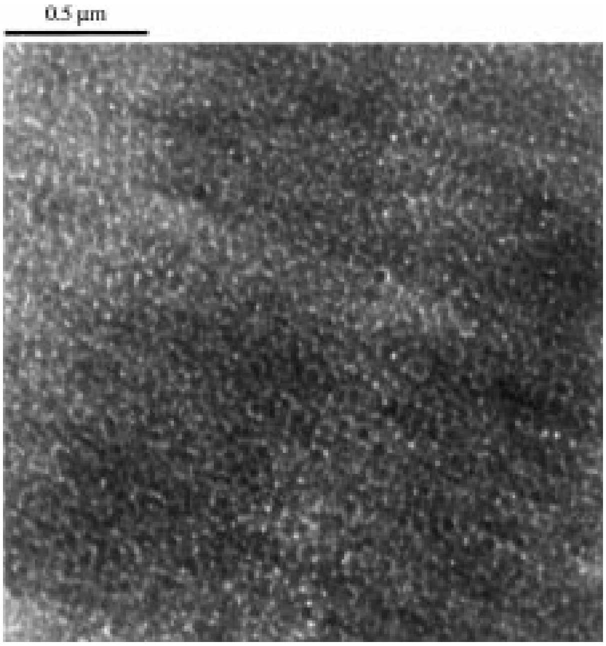
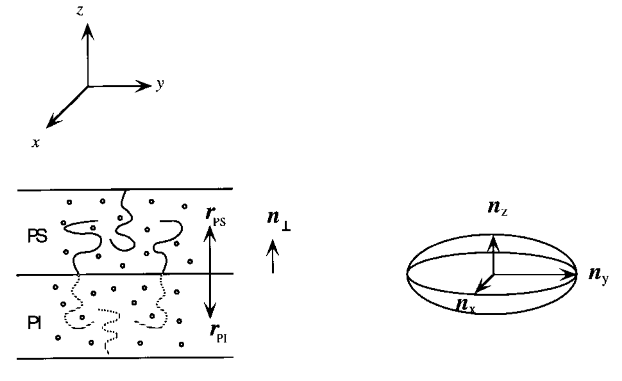


Fig. 4. A TEM micrograph of the block copolymer H102. The thin sample for TEM observation was prepared by microtoming a film cast from the pentanedione solution of H102 and then by O_sO_4 staining.

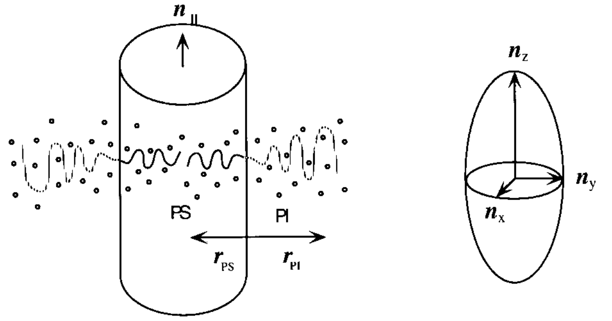
3.4. Origin of optical anisotropy

Normally, liquid crystals are formed by rod-like molecules with a high optical anisotropy. In this case it is easy to understand where the optical anisotropy of the LC textures comes from. This anisotropy arises from molecular orientations. For the lyotropic liquid crystals comprised of LMW amphiphilic molecules in water or of block copolymers in selective solvent, the stretched conformation of one part of molecules is the origin of the optical anisotropy which arises also from the molecular orientations. Considering the chain conformation of two blocks in the non-selective solvents, it is helpful to further discuss the optical anisotropy of the block copolymer solutions studied in relation to microdomain structure. As pointed out in our previous paper [25], intrinsic optical anisotropy of the block copolymer microdomains contains the following two contributions: orientational anisotropy and form anisotropy. The orientational anisotropy is the anisotropy due to molecular orientation of two kinds of chains (e.g. PS and PI chains) in the domain space. The form anisotropy is the anisotropy arising from the distortion of the electric field strength of the incident light wave at the phase boundaries between the two coexisting microphases when the microphases have anisotropy in shape and have a difference in their refractive indices [25–27]. The net intrinsic birefringence Δn_t of microdomains is given by a sum of intrinsic orientational birefringence Δ_orient and intrinsic form birefringence Δ_form

$$\Delta n_\mathrm{t} = \Delta_\mathrm{orient} + \Delta_\mathrm{form}. \tag{1}$$



(a) Lamellar case



(b) Cylindrical case

Fig. 5. Schematic diagrams showing lamellar (a) and cylindrical (b) microdomain structures of PS-*b*-PI block copolymer solutions with a truly neutral solvent (○) and the corresponding refractive index ellipsoids having negative and positive form anisotropy. Notice that $\mathbf{r}_\mathrm{PS}$ and $\mathbf{r}_\mathrm{PI}$ are parallel to $\mathbf{n}_\perp$ in the lamellar case, but are normal to $\boldsymbol{n}_\parallel$ in the cylindrical case.

Our earlier results have demonstrated that $\Delta n_\mathrm{t} \approx \Delta_\mathrm{form}$ or $\Delta_\mathrm{form} \gg \Delta_\mathrm{orient}$ and Δ_form is negative for PS-*b*-PI block copolymers having lamellar microdomains [25]. Therefore, the form anisotropy dominates the intrinsic optical anisotropy. Therefore the optical anisotropy of our block copolymer solutions arises from Δ_form and hence orientation of microdomains (lamellae or cylinders) rather than molecular orientations of PS and PI block chains.

In Fig. 5, we schematically represent the lamellar and cylindrical microdomain structures in the truly neutral solvent (marked by open circles) and the corresponding refractive-index ellipsoids. $\mathbf{r}_\mathrm{PS}$ and $\mathbf{r}_\mathrm{PI}$ are averaged end-to-end vectors of PS and PI blocks, respectively, and $\mathbf{n}_x$, $\mathbf{n}_y$ and $\mathbf{n}_z$ are the vectors showing semi-axes in the refractive-index ellipsoid. In the lamellar case, we have $|\mathbf{n}_z| < |\mathbf{n}_x| = |\mathbf{n}_y|$, $\mathbf{n}_z \equiv \mathbf{n}_\perp$ (refractive-index vector normal to the interface), and $|\mathbf{n}_x| = |\mathbf{n}_y| \equiv |\mathbf{n}_\parallel|$ (with $n_\parallel$ being refractive-index vector parallel to the interface), thus the unit vector of the optical axis $\mathbf{n}_z/|\mathbf{n}_z|$ is parallel to the unit vector of the the lamellar normal $\mathbf{n}_\perp/|\mathbf{n}_\perp|$. The negative birefringence $\Delta n_t (= n_\perp - n_\parallel < 0)$ comes dominantly from the form birefringence.[1] In the cylindrical case, we obtain $|\mathbf{n}_z| > |\mathbf{n}_x| = |\mathbf{n}_y|$, $\mathbf{n}_z \equiv n_\parallel$ (refractive-index vector parallel to the cylindrical axis), and $|\mathbf{n}_x| = |\mathbf{n}_y| \equiv |\mathbf{n}_\perp|$ (with $\mathbf{n}_\perp$ being refractive-index vector normal to the cylindrical axis), thus the unit vector of the optical axis $\mathbf{n}_z/|\mathbf{n}_z|$ is parallel to the unit vector along the cylinder axis $\mathbf{n}_\parallel/|\mathbf{n}_\parallel|$. Again the form anisotropy is expected to dominate the orientational anisotropy. The net optical anisotropy in this case has a positive anisotropy. The optical axis $\mathbf{n}_\perp/|\mathbf{n}_\perp|$ of the lamellar microdomains corresponds to the director of the smectic LC phase and the optical axis $\mathbf{n}_\parallel/|\mathbf{n}_\parallel|$ of the cylindrical microdomains corresponds to the director of the columnar LC phase. Because the microdomain shape is invariant with c, the sign of the intrinsic optical anisotropy is independent of c. However, the magnitude of the anisotropy increases with c, because the refractive index difference between the PS and PI microphases increases with c and the interface between the two microphases become sharp [25].

In the selective solvent case, however, the averaged end-to-end vectors of two blocks are quite different each other because only one block can be swollen by the solvent. This difference will lead to the large orientational anisotropy and form anisotropy and hence a large net anisotropy compared with the corresponding anisotropy in truly neutral solvent. Thus the LC textures may be more easily seen in selective solvents rather than neutral solvents as long as well-ordered lamellae or cylinders are formed in the solutions.

Finally we note the following observations. (1) The contrast between bright and dark areas in Fig. 1 (lamellar microdomains) is higher than that in Fig. 2 (cylindrical microdomains). (2) Exposure times for taking POM micrographs in Fig. 1 were much shorter than those in Fig. 2 for a nearly identical sample thickness. These observations appear to indicate that the optical anisotropy in the lamellar system is higher than that in the cylindrical system.

4. Summary

We investigated the lyotropic LC behavior of the toluene solutions of the two polystyrene-*block*-polyisoprene diblock copolymers with either lamellar (H102) or cylindrical (HS-6) structure in bulk through their optical textures. Different optical textures, like fan-shaped, parabolic focal conic and oily streak textures, have been observed in the thin specimens of the solutions when their concentrations are above the critical concentration for the microphase separation. This demonstrates that the solutions exhibit the same texture as lyotropic liquid crystals. Since toluene is a *truly neutral solvent* for both PS and PI blocks, the two blocks are equally swollen with the solvent in the corresponding microphases. Under this situation, the microdomain shapes in the solutions are the same as those in bulk [10–13]. Thus we expect that in the solutions alternating lamellae of PS and PI swollen with toluene are developed for H102 and hexagonal cylinders of PS swollen with toluene are formed in the matrix of PI swollen with toluene for HS-6. The form anisotropy of these microdomains is the origin of the optical textures observed. Therefore, the ordered solution of H102 block copolymer has a texture inherent in smectic lyotropic liquid crystal, while the ordered solution of HS-6 block copolymer has a texture inherent in lyotropic columnar liquid crystals. The results obtained in the present study together with those in the earlier reports [2–5] universally elucidate that the textures in ordered block copolymer solutions are identical to those in lyotropic liquid crystals.

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[1] Orientational anisotropy is small, because the degree of segmental orientation of block chains with respect to the lamellar normal itself is small for both PS and PI block chains. Moreover, the orientational anisotropy of the PS microphases and that of the PI microphases tend to cancel each other, giving rise to even smaller net orientational anisotropy. This is because the PS block chains give negative orientational anisotropy with respect to the lamellar normal i.e. the refractive index parallel to the interface is greater than that normal to the interface but the PI block chains give positive orientational anisotropy, i.e. the refractive index parallel to the interface is smaller than that normal to the interface is the case of lamellar microdomains. A similar cancellation occurs in the cylindrical microdomains, because the PS chains and PI chains have a positive and negative orientational anisotropies with respect to the cylinder axis.