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Persistence of Surface-Induced Alignment in Block Copolymers upon Large-Amplitude Oscillatory Shear Processing

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ABSTRACT: Subjecting lamellae-forming poly(styrene-*b*-isoprene) (SI) diblock copolymers to large-amplitude oscillatory shear (LAOS) offers a route to microstructural alignment. This study examines the spatial uniformity of both isotropic (unaligned) and LAOS-aligned states of an SI diblock copolymer and its blend with homopolystyrene. Unlike typical studies in this vein, we do not restrict our examination to the bulk but characterize the state of alignment near the shearing surfaces. Transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS) results reveal that lamellae near the surfaces adopt a parallel orientation, regardless of bulk orientation. This near-surface parallel region is uniform and extends ca. 2 μm into the bulk. In the case of perpendicular bulk alignment, the mutually orthogonal bulk and surface lamellae are separated by a boundary region containing defects similar to $+^1/_2$ and $-^1/_2$ disclinations. Our results indicate that the near-surface parallel region is created upon quenching through the order−disorder transition temperature. Furthermore, the near-surface parallel region persists, relatively unchanged, even when the bulk of the specimen becomes perpendicular.

Introduction

External shear fields applied to block copolymer melts[1−4] affect their miscibility behavior and mechanical properties. In the particular case of lamellae-forming block copolymers, shear fields can control macroscopic alignment of the microdomains.[5,6] These investigations of the large-amplitude oscillatory shear (LAOS) induced alignment in block copolymers typically assume that the lamellar orientation or orientations of a bulk specimen are uniform throughout a sample. Current models of block copolymer alignment also make this assumption and omit considerations of the surface.[5−8] Two unidirectional lamellar orientations have been observed and predicted as a result of shearing. In the parallel orientation, the layers are parallel to the shearing surfaces. The perpendicular alignment is characterized by layers perpendicular to the shearing surfaces with their normals along the neutral axis.[9] In contrast, many cases exist in which multiple lamellar orientations are found, which may or may not be stable with respect to LAOS.[6] Certainly, the isotropic state has multiple orientations coexisting and can be altered with LAOS. The coexistence of parallel and transverse has been found to be transient[6] or shear-stabilized.[4,10,11] Here, "transverse" refers to lamellae perpendicular to the shearing surfaces but with normals along the shearing direction. Other work in our group has identified the superstructure of parallel−transverse lamellae to be kink bands.[12,13] The coexistence of parallel and perpendicular has also been found as both transient[6] or nontransient[14,15] in the bulk.

In this study, we identify a region of parallel orientation residing near the shearing surfaces. This region is observed in otherwise isotropic or perpendicular bulk specimens that were produced by quenching from the disordered state and LAOS, respectively. This near-surface parallel (NSPL) orientation is identified by transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS) specifically targeted at

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the surface. The NSPL region may be a common, but undetected, feature of LAOS-aligned diblock copolymers and blends. The NSPL region has likely been overlooked because typical investigations of LAOS-aligned systems rely on small-angle scattering, birefringence, and rheological measurement of the entire specimen. Hence, only the average bulk alignment has been addressed experimentally.[1−6] We propose that, as a result of contrasting processing histories, the NSPL region could be a nonnegligible fraction of the overall alignment. We also compare this NSPL region to previously reported surface-induced parallel alignment in block copolymers produced by solvent-casting bulk specimens and spin-coating thin films.[16−23]

Experimental Section

Materials. A poly(styrene-*b*-isoprene) (SI) diblock copolymer of molecular weight $\bar{M}_w$ = 21 200 g/mol and low polydispersity (1.03) was obtained from Pressure Chemical Co. (Pittsburgh, PA). This copolymer is nearly compositionally symmetric (on a mass basis), having a styrene content of 53 wt %. A blend containing 60 wt % styrene overall was prepared with a low molecular weight (4100 g/mol) homopolystyrene (hS). Solvent-cast films of both the neat copolymer and blend were obtained from a dilute (3% w/v) toluene solution. After solvent removal over the course of 7−10 days, the blend was heated to 40 °C under vacuum for 1 day to remove residual solvent and annealed for 3 days at 120 °C. These materials are analogous to those used in previous studies[14] and are reported to have order−disorder transition temperatures (T_{ODT}) at 157 °C for the neat copolymer and 142 °C for the blend.[14,24,25] These materials exhibit the lamellar morphology at temperatures $T < T_{ODT}$.[26,27]

Processing. To provide an initial isotropic state comprised of randomly oriented lamellar grains, the specimens underwent further thermal treatment prior to LAOS processing. Following a protocol shown to reproducibly create an initial isotropic (bulk) state,[28] specimens were held for 5 min at ∼2 °C above T_{ODT} and then cooled to 110 °C for 15 min. This thermal treatment was performed in a Rheometrics RSA-II dynamic strain rheometer equipped with the shear sandwich geometry (0.5 mm gap). Perpendicular lamellar alignment was induced by LAOS in the rheometer for 1 h at 130 °C with a
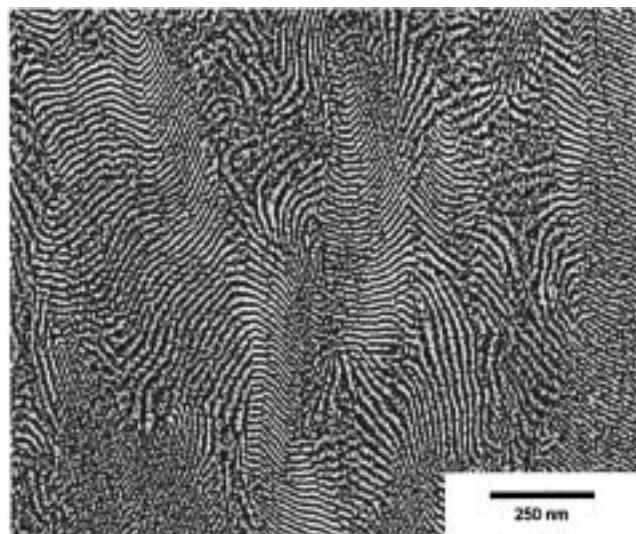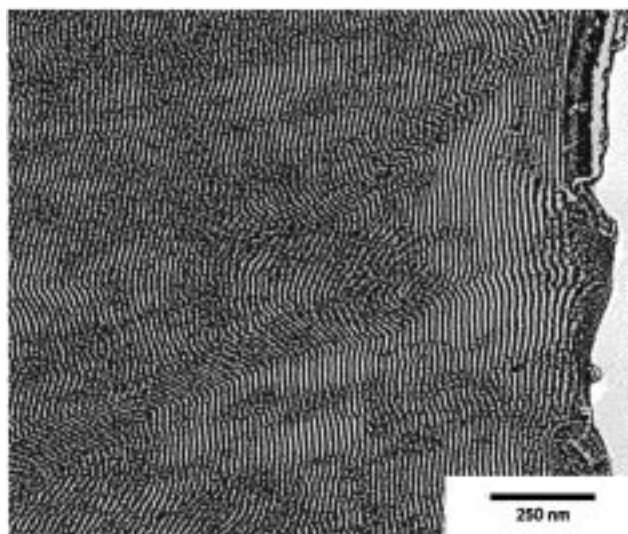
Figure 1. Transmission electron micrograph of the isotropic blend, obtained from the bulk. Numerous lamellar grains, 100−600 nm across, exist in different orientations. The projected periodicities vary with grain orientation, from 12 to 24 nm, because of their distinct orientations with respect to the electron beam. In this and all other micrographs presented, the **2**-axis is directed toward the right and the **3**-axis is vertical. Comparable results were found in the neat diblock copolymer.


Figure 2. Transmission electron micrograph of the isotropic blend, obtained from the surface of the specimen. A well-defined parallel orientation having a periodicity of 18 ± 0.5 nm is found to extend ca. 2 μm away from the surface. The surface is observed on the right side of the micrograph. Comparable results were found in the neat diblock copolymer.

frequency of 1 rad s^{-1} and strain amplitude of 98%. Aligned specimens were postannealed in the rheometer for 3 h at 110 °C to promote microstructural refinement.

Characterization. Periodicity and alignment information was obtained from TEM and SAXS performed on both the bulk material and near the shearing surfaces of the specimen. The SAXS apparatus[14] was operated using a 1 mm diameter beam of 40 kV Cu Kα X-rays and a sample-to-detector distance of 125 cm. Two-dimensional scattering patterns were collected with a Siemens Hi-Star position-sensitive detector. The patterns were radially integrated around the first-order maximum to characterize the intensity variations associated with preferential alignment. For TEM, the free surface of the specimen was marked with Au for identification using a Polaron Instruments coating unit operated at 120 kV and 20 mA in an Ar environment. After sectioning at −100 °C on a Reichert-Jung Ultracut S ultramicrotome, specimens were immediately exposed to the vapors of a 4% (aqueous) OsO_4 solution at room temperature for 90 min to enhance electron contrast by staining the isoprene microdomains. Images were collected on a Phillips 400T transmission electron microscope operated at 120 kV. Variations due to section thickness were digitally removed from the micrographs presented herein in order to aid interpretation.

Results

The neat copolymer and the blend exhibit similar morphologies; thus, only the blend will be discussed for the sake of brevity. Before considering the LAOS-aligned specimen, it is worthwhile to first examine the spatial uniformity of the initial isotropic starting state. Having been annealed at $T_{ODT} + 2$ °C in the rheometer and then quenched to 110 °C ($< T_{ODT}$), the specimen develops a bulk morphology of randomly oriented lamellar grains in the absence of an applied shear field. This bulk morphology is shown in the TEM micrograph of Figure 1. Numerous lamellar grains are observed to coexist in a variety of orientations. The size of each grain varies from 100 to 600 nm, while the lamellae within each grain have projected periodicities of 12−24 nm. Variation of projected periodicities arises because the isotropically oriented grains have been sectioned at

different angles relative to the electron beam. It is important to note the difference between this specimen and other unaligned initial states, wherein well-defined lamellar grains are not always achieved. A recent report by Chen and Kornfield,[6] for example, presents a TEM micrograph of an unaligned state in which lamellae do not exist in distinct grains.[29] Instead, their starting morphology has regions of well-defined but curved lamellae coexisting with regions of perturbed, nearly disordered layers. Such a state is certainly unaligned but not isotropic in the sense of Figure 1.

When imaged near the shearing surface, the isotropic blend is shown to possess parallel-oriented lamellae (Figure 2). By examining several sections, the NSPL region was found to extend ca. 2 μm into the bulk, on average. At this distance away from the free surface, misoriented lamellar grains protruding into the near-surface parallel region mark the boundary between the NSPL and bulk orientations. Unlike the isotropic grains of Figure 1, the lamellar periodicity of the NSPL region in Figure 2 is a uniform 18 ± 0.5 nm. It should be noted that the surface is not pristine, as removal from the rheometer and partial delamination of the Au coating during cryosectioning has altered the outermost layer.

Small-angle X-ray scattering from the bulk of the isotropic blend is characterized by peaks of uniform azimuthal intensity, essentially identical to that previously reported for the neat copolymer.[14] The lamellar periodicity in the blend is 17.7 nm, which is the same as the neat copolymer previously reported.[14] The radial integration of the first-order maximum is presented in Figure 3 and indicates that the scattered intensity is relatively uniform azimuthally. The absence of intensity variations confirms that the lamellar microstructure possesses no preferred orientation in the bulk of the specimen. This is not the case when SAXS is performed near the shearing surface of the same specimen (Figure 3). The near-surface region of the blend exhibits a well-defined maximum at 180° that corresponds to parallel lamellae.[14] The lamellar period measured by SAXS in this NSPL region is 17.5 nm, unchanged from the bulk.
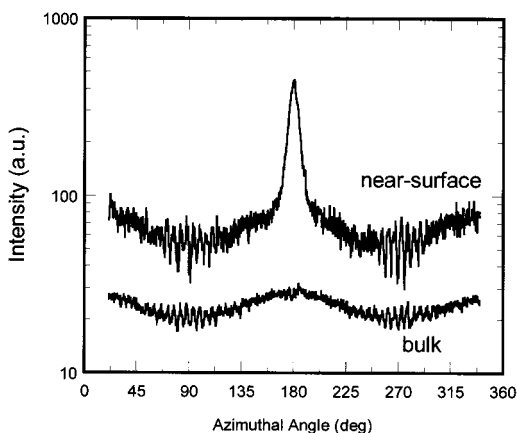
Figure 3. Scattered intensity as a function of azimuthal angle of the first-order SAXS peak from the isotropic blend. The X-ray beam is incident along the velocity direction (**1**-axis). SAXS performed near the shearing surface exhibits a maximum at 180°, indicating a preferred parallel lamellar orientation (upper curve). In the bulk, no significant intensity variations are observed, indicating no preferred orientation (lower curve). The lamellar periodicity measured by SAXS is 17.7 nm for both cases. Comparable results were found in the neat diblock copolymer. Curves have been shifted along the intensity axis for clarity.
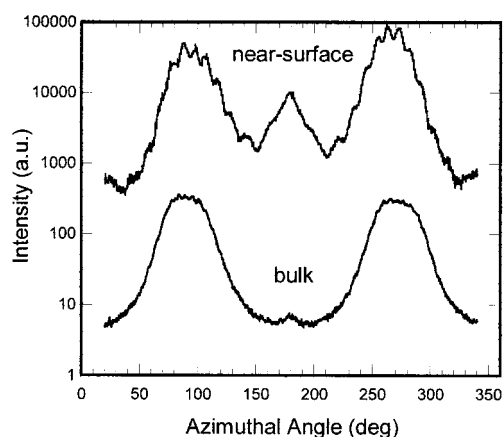
Figure 4. Lamellar orientations in a perpendicularly aligned blend. Scattered intensity as a function of azimuthal angle from the near-surface region (upper curve) indicates the existence of a parallel region, while the lamellae are perpendicularly aligned in the bulk (lower curve). Intensity maxima occur at 90° and 270° for the bulk (perpendicular), while an enhanced maximum at 180° (parallel) is found near the shearing surface. The X-ray beam is incident along the velocity direction (**1**-axis). Comparable results were found in the neat diblock copolymer. Curves have been shifted along the intensity axis for clarity.

The perpendicular blend also exhibits an NSPL region. SAXS performed on the bulk specimen indicates that the LAOS processing induced perpendicular alignment, as the intensity maxima occur at 90° and 270° (Figure 4). In contrast, SAXS performed close to the surface has an additional intensity maximum at 180°. Therefore, there is a distinct contribution to the scattered intensity from parallel lamellae near the surface of the specimen. The TEM micrograph (Figure 5) shows both the bulk perpendicular and NSPL regions. The boundary between the NSPL region and the perpendicular region appears qualitatively similar to a set of disclinations of strength $+1/2$ and $-1/2$. Such a characteristic boundary was not observed in the absence of LAOS alignment between the NSPL region and the bulk isotropic morphology. Furthermore, the fraction of

intermediate orientations within the boundary region is small as evident from Figure 4. The depth to which the NSPL region persists is, like the isotropic case, ca. 2 μm. Beyond the NSPL and boundary regions, only perpendicularly oriented lamellae are observed. Further, the lamellar periodicity is 17.7 nm in each region (NSPL, boundary, perpendicular), which is the same as the isotropic specimen.

Discussion

The TEM and SAXS results for the bulk (nonsurface) region of the isotropic copolymer and blend both reveal an ensemble of lamellar grains of varied orientation. Considering the volumes sampled by TEM and SAXS, the bulk results (Figure 1) indicate that this morphology exists over the $\sim$1 μm and $\sim$1 mm length scales. In this sense, the bulk isotropic state exhibits a high degree of spatial uniformity. Likewise, a similar observation is made for the bulk region of a perpendicularly aligned copolymer and blend (Figure 3). Consequently, it was reasonable in previous LAOS-alignment investigations to use only bulk-directed experimental methods to obtain microstructural information. However, the results discussed above clearly show that TEM and SAXS performed solely on the bulk region do not convey the state of lamellar orientation throughout the *entire* specimen. In both the isotropic and perpendicular specimens, a distinct near-surface parallel layer ca. 2 μm wide was observed at the surface. Similar parallel alignment at surfaces of block copolymers has been previously observed via TEM, neutron reflectivity, and secondary ion mass spectroscopy.[16-23]

Numerous experimental[16-21] and theoretical[22,23] efforts have addressed the surface orientation of block copolymers. In nearly all cases, alternating lamellae have been observed parallel to the surface of thick (>0.1 mm) solvent-cast[16-18] and thin (<2 μm) spin-cast[19-21] specimens of a variety of block copolymers. Hasegawa and Hashimoto[16] report a small region of perpendicular lamellae near the surface of a solvent-cast SI diblock copolymer, although most of the specimen exhibited parallel alignment. Even in the perpendicular regions, they find a layer of PI coating the outermost surface layer.[16] The primary driving force in interfacial alignment is the difference in interfacial energies of the two constituents, such that the lower-energy block prefers the air–polymer surface.[22,23] This migration induces density fluctuations normal to the surface and similarly normal to the polymer–substrate interface.[22] Hence, the parallel orientation is found to propagate into the bulk material for most block copolymer systems. In thin spin-cast films <2 μm thick, the interfacial-induced parallel alignment can persist through the entire film.[19-21] In films on the order of 1 mm thick, the parallel alignment has been shown to persist over large lateral dimensions of the film,[21] but no measurement of the depth of the NSPL region has been reported.

The existence of the NSPL region in our isotropic specimens indicates that near-surface lamellae adopt the parallel orientation upon cooling through T_{ODT}. This alignment is likely induced in the same manner as solvent-cast and spin-cast block copolymer films. A thermal gradient in the specimen during cooling may also contribute to surface alignment.[30] The thickness of the NSPL region will depend on material parameters (e.g., molecular weight) and processing routes but is 2 μm for our experiments. The lamellar period within the
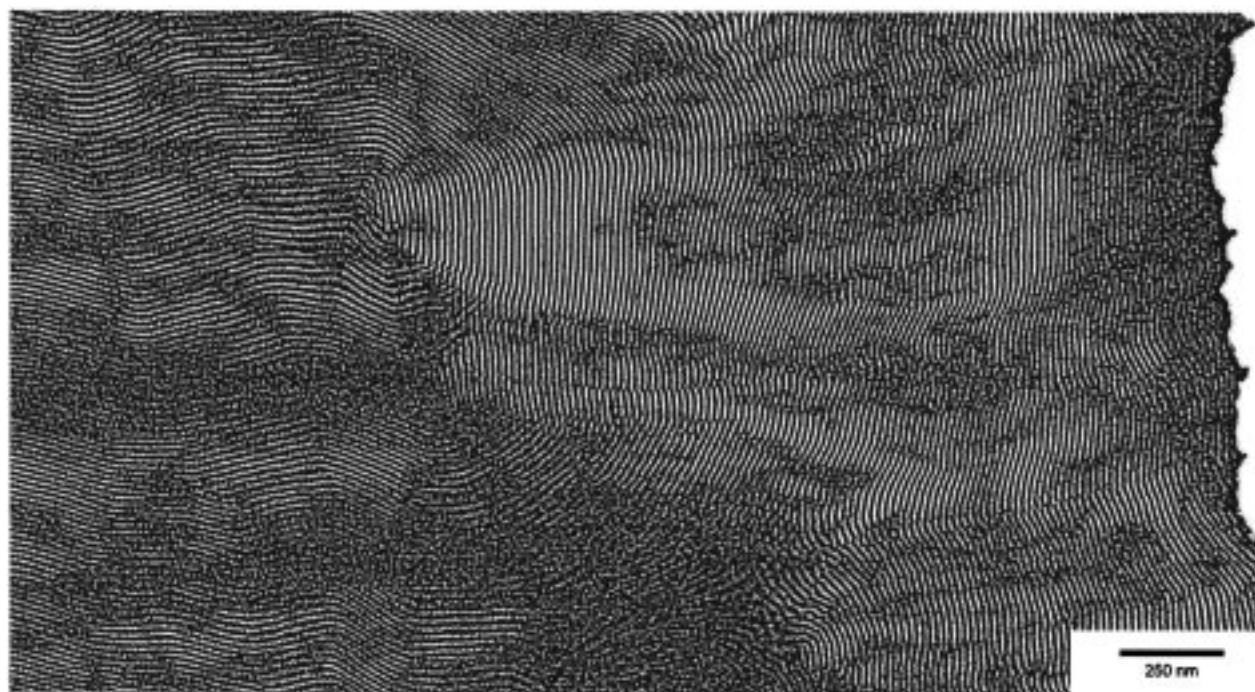
Figure 5. Transmission electron micrograph of the perpendicularly aligned blend, obtained near the surface. Lamellae are aligned parallel to the surface but become perpendicular away from the surface (i.e., in the bulk). The surface is observed on the right side of the micrograph. The NSPL−perpendicular boundary occurs approximately 2 μm from the surface and is visible in the micrograph. Comparable results were found in the neat diblock copolymer.

NSPL has been determined to be equal to that of the bulk. Polymer chains within the NSPL are therefore not significantly stretched or compressed relative to those in the bulk.

The perpendicularly aligned specimen also exhibits NSPL behavior. The NSPL orientation in Figure 5 maintains a 17.7 nm lamellar periodicity and persists ca. 2 μm into the bulk, as in the isotropic specimen. This NSPL region was formed during cooling from above T_{ODT} to produce the isotropic stating state. Therefore, the parallel-aligned region is invariant to subsequent LAOS processing, consistent with previous observations of bulk-parallel block copolymers.[6,7] Fredrickson et al.[5] have proposed mechanisms that stabilize the parallel orientation relative to perpendicular. Specifically, "reverse flipping," the conversion of parallel to perpendicular oriented lamellae via LAOS, is energetically unfavorable for SI diblock copolymers. Our observation that the NSPL region persists upon LAOS confirms the inability of shearing to reorient parallel lamellae to perpendicular lamellae, while the same shearing can reorient *other* orientations to perpendicular.

The boundary between the NSPL and nonparallel bulk has been shown to depend on LAOS processing. In the case of the quiescent isotropic specimen, the isotropic−NSPL boundary contains nonparallel lamellar grains protruding into the NSPL region. In contrast, the perpendicular−NSPL boundary contains curved lamellae. The schematic in Figure 6a illustrates this boundary as produced by $+^1/_2$ and $-^1/_2$ disclinations. Disclinations of this type have been observed in polymer nematic liquid crystals and are the subject of ongoing research in the area of microstructural defects.[31,32] The $+^1/_2$ defects observed in Figure 5 are not disclinations by rigorous definition, because lamellae change orientation by discrete steps, rather than by continuous curvature (Figure 6b). Lamellae between the neighboring $+^1/_2$ defects, visible in the lower portion of Figure 5, are less
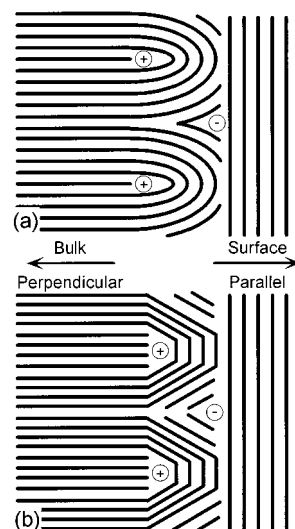
Figure 6. Schematic of the NSPL−perpendicular boundary. In (a), the boundary contains $+^1/_2$ and $-^1/_2$ disclinations. In (b), this boundary is modified by allowing nonconstant curvature of the lamellae, which is more consistent with experimental results in Figure 5.

well-defined in the TEM image but appear to be $-^1/_2$ disclinations.

For the present system, the NSPL region accounts for ca. 0.8% of the total specimen volume. Such a small parallel contribution is not expected to have a measurable effect on mechanical or rheological properties but could significantly influence permeability measurements. Furthermore, because LAOS studies use various initial states and processing temperatures, a much larger NSPL region could conceivably form in diblock copolymers. Finally, special processing procedures would need to be developed to completely eliminate the NSPL region.

Conclusions

A well-defined region of parallel alignment at the surfaces of an SI diblock copolymer and an SI/hS blend was observed and found to be ca. 2 μm thick. This near-surface parallel (NSPL) region is present in isotropic specimens prepared by cooling through T_{ODT}. It is likely that this alignment forms upon cooling due to contrasting block interfacial energies, the physical constraints imposed by the rheometer tools, and the thermal gradient in the specimen. Similarly, solvent-cast and spin-coated films have been reported to possess NSPL regions, although few efforts have reported the depth of the NSPL region in thick (0.5−1.0 mm) solvent-cast specimens. In this study, we observed that, once formed, the NSPL region persists during subsequent LAOS processing that produces an otherwise perpendicularly aligned specimen. Currently, there is no established LAOS route by which to remove the NSPL region in lamellar block copolymers.

Since theoretical and experimental studies of block copolymer defects are an active research area, it is appropriate to report that the LAOS processing examined herein is a novel method to systematically create $\pm^{1}/_{2}$ defects for quantitative investigation. The perpendicular−NSPL boundary in LAOS-aligned block copolymers is characterized by such defects and is experimentally accessible via TEM and SAXS.

References and Notes

(1) Maring, D.; Wiesner, U. *Macromolecules* **1997**, *30*, 660.
(2) Garetz, B. A.; Balsara, N. P.; Dai, H. J.; Wang, Z.; Newstein, M. C.; Majumdar, B. *Macromolecules* **1996**, *29*, 4675.
(3) Gupta, V. K.; Krishnamoorti, R.; Kornfield, J. A.; Smith, S. D. *Macromolecules* **1995**, *28*, 4464; **1996**, *29*, 1359.
(4) Zhang, Y.; Wiesner, U. *J. Chem. Phys.* **1995**, *103*, 4784.
(5) Fredrickson, G. H.; Bates, F. S. *Annu. Rev. Mater. Sci.* **1996**, *26*, 501.
(6) Chen, Z. R.; Kornfield, J. A. *Polymer* **1998**, *39*, 4679.
(7) Patel, S. S.; Larson, R. G.; Winey, K. I.; Watanabe, H. *Macromolecules* **1995**, *28*, 4313.
(8) Cates, M. E.; Milner, S. T. *Phys. Rev. Lett.* **1989**, *62*, 1856.
(9) In the standard LAOS coordinate system, the shearing direction is taken as the **1**-axis and the shear-gradient direction defines the **2**-axis, while the neutral **3**-axis completes the right-hand Cartesian system.
(10) Okamoto, S.; Saijo, K.; Hashimoto, T. *Macromolecules* **1994**, *27*, 5547.
(11) Pinheiro, B. S.; Winey, K. I.; Hajduk, D. A.; Gruner, S. M. *Macromolecules* **1996**, *29*, 1482.
(12) Polis, D. L.; Winey, K. I. *Macromolecules* **1996**, *29*, 8180; **1998**, *31*, 3617.
(13) Polis, D. L.; Smith, S. D.; Terrill, N. J.; Ryan, A. J.; Morse, D. C.; Winey, K. I. *Macromolecules* **1999**, *32*, 4668.
(14) Pinheiro, B. S.; Winey, K. I. *Macromolecules* **1998**, *31*, 4447.
(15) Riise, B. L.; Fredrickson, G. H.; Larson, R. G.; Pearson, D. S. *Macromolecules* **1995**, *28*, 7653.
(16) Hasegawa, H.; Hashimoto, T. *Macromolecules* **1985**, *18*, 589.
(17) Chen, X.; Gardella Jr., J. A.; Kumler, P. L. *Macromolecules* **1993**, *26*, 3778.
(18) Stocker, W. *Macromolecules* **1998**, *31*, 5536.
(19) Liu, Y.; Zhao, W.; Zheng, X.; King, A.; Singh, A.; Rafailovich, M. H.; Sokolov, J.; Dai, K. H.; Kramer, E. J.; Schwarz, S. A.; Gebizlioglu, O.; Sinha, S. K. *Macromolecules* **1994**, *27*, 4000.
(20) Coulon, G.; Russell, T. P.; Deline, V. R.; Green, P. F. *Macromolecules* **1989**, *22*, 2581.
(21) Anastasiadis, S. H.; Russell, T. P.; Satija, S. K.; Majkrzak, C. F. *Phys. Rev. Lett.* **1989**, *62*, 1852.
(22) Fredrickson, G. H. *Macromolecules* **1987**, *20*, 2535.
(23) Shull, K. R. *Macromolecules* **1993**, *26*, 2346.
(24) Balsara, N. P.; Perahia, D.; Safinya, C. R.; Tirrell, M.; Lodge, T. P. *Macromolecules* **1992**, *25*, 3896.
(25) Owens, J. N.; Gancarz, I. S.; Koberstein, J. T.; Russell, T. P. *Macromolecules* **1989**, *22*, 3388.
(26) Winey, K. I.; Thomas, E. L.; Fetters, L. J. *Macromolecules* **1992**, *25*, 2645.
(27) Hong, S.-K.; Laurer, J. H.; Zielinski, J. M.; Samseth, J.; Smith, S. D.; Duda, J. L.; Spontak, R. J. *Macromolecules* **1998**, *31*, 2174.
(28) Pinheiro, B. S. Ph.D. Dissertation, University of Pennsylvania, 1996.
(29) See Figure 11 (I) in ref 6.
(30) Hashimoto, T.; Bodycomb, J.; Funaki, Y.; Kimishima, K. *Macromolecules* **1999**, *32*, 952.
(31) Hudson, S. D.; Fleming, J. W.; Gholz, E.; Thomas, E. L. *Macromolecules* **1993**, *26*, 1270.
(32) Kléman, M. Defects and Textures in Liquid Crystalline Polymers. In *Liquid Crystallinity in Polymers: Principles and Fundamental Properties;* Ciferri, A., Ed.; VCH Publishers: New York, 1991; pp 365−394.