Notes

Morphology of a Lamellar Diblock Copolymer Aligned Perpendicular to the Sample Plane: Transmission Electron Microscopy and Small-Angle X-ray Scattering

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Received December 21, 1992
Revised Manuscript Received April 27, 1993

Introduction

Researchers have known for more than 2 decades that mechanically deforming a block copolymer influences the global alignment of the microdomains of the copolymer. In the case of lamellar diblock copolymers, the lamellar planes are typically observed within the plane of the sample.[1–7] For example, in our earlier rheological studies, a poly(styrene-*b*-isoprene) (SI) diblock copolymer was effectively aligned from a molded sample at a temperature far below the order–disorder transition (ODT) temperature by applying many cycles of oscillatory shear within the nonlinear regime.[7] This method produces very well-aligned lamellae in the plane of the sample as evidenced by observations in three orthogonal directions using small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). We introduced three length scales of block copolymer order. The local, intermediate, and global length scales of copolymer order correspond to the presence of microphase separation, the perfection of microdomains, and the orientation of microdomains with respect to the sample, respectively.

In addition to producing lamellae in the sample plane, researchers have recently observed lamellae perpendicular to the sample plane such that the normal of the lamellae is parallel to the neutral direction of the shear field.[8–10] Our previous work with large- and small-molecule smectic systems shows qualitatively similar rheological responses.[8] A lamellar diblock copolymer above its order–disorder transition temperature and a smectic liquid crystal molecule above its isotropic temperature exhibit terminal or liquidlike rheological behavior, $G' \sim \omega^2$ and $G'' \sim \omega$. Below, but near, their transition temperatures, the large- and small-molecule smectic systems initially show nonterminal behavior. However, applying large-amplitude oscillatory shear can permanently decrease the magnitude of the moduli and increase the frequency dependence of the moduli.

This paper contains morphological data for a lamellae diblock copolymer corresponding to (1) quenched from a temperature above the ODT temperature and (2) quenched from a temperature below the ODT temperature after large-amplitude oscillatory shearing. The first sample has slightly ordered lamellar microdomains on the intermediate length scale and randomly oriented, or unaligned, grains on the global length scale. The second sample exhibits lamellae of moderate global alignment perpendicular to the sample plane, and extensive wall defects exist on the intermediate length scale.

Experimental Methods

The lamellar poly(styrene-*b*-isoprene) diblock copolymer, SI 12/9, used in this study was synthesized by Watanabe via anionic polymerization.[11] The PS and PI block molecular weights are 12 500 and 9500, respectively. The sample was solvent cast and molded at room temperature, as described previously.[7] A Rheometrics System IV was used to measure the dynamic mechanical properties of the diblock copolymer in a parallel-plate geometry with applied rotational, oscillatory strain. The majority of the rheological results are presented elsewhere,[7–9] and the pertinent results are shown in Figure 1.

Samples were quenched within the rheometer without shearing from two elevated temperatures, 155 and 144 °C, by turning off the heating element of the rheometer and allowing the temperature to drop below the glass transition of the polystyrene block, 78 °C.[7] This quenching procedure occurred in ~4 min. The morphologies were subsequently investigated. TEM images of orthogonal planes and SAXS patterns from orthogonal directions were collected, as described previously.[7] The directions within the sample disk are labeled as follows: 1 corresponds to the velocity or shear direction (tangential to the disk), 2 corresponds to the gradient direction (through the disk), and 3 corresponds to the neutral direction (radial to the disk). For further clarification, please refer to the schematic in ref 7. Because these three directions are mutually orthogonal, their reciprocal space directions are parallel to the real space directions. We have indicated the reciprocal directions in the SAXS patterns with an asterisk.

Results and Discussion

As shown by the circles in Figure 1, the rheological response of SI 12/9 at 157 °C is characteristic of a disordered block copolymer or a liquid, because the order–disorder transition temperature is 152 °C.[8] Figure 2 shows a TEM image of the 1–2 plane, that is, an edge-on view, of SI 12/9 as quenched from 155 °C. The quenching procedure was sufficiently slow to allow microphase separation to occur, thus leading to order on the local length scale. On an intermediate length scale (1–10 μm), the lamellar microdomains are only slightly aligned, because the lamellae are not spatially extensive as evidenced by a grain size of ~200 nm. The grains appear to be randomly oriented with relation to neighboring grains, as indicated by lamellae in different directions and the range of projected interlamellar spacings. (The observed lamellae spacing in a projected TEM image is due to both the actual lamellae spacing within a bulk sample and the orientation of the lamellae relative to the electron beam within the microscope.) The SAXS patterns in Figure 3a show weak,

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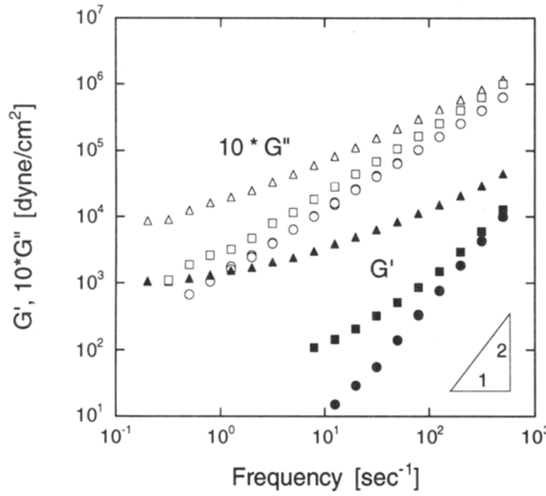

Figure 1. Frequency dependence of the elastic (filled symbols) and loss (open symbols) moduli of SI 12/9 at three experimental conditions: (●,○) T = 157 °C, which is above the ODT temperature of 152 °C. (▲,△) T = 144 °C, as quenched from above the ODT. (■,□) T = 144 °C, after prolonged oscillatory shear.

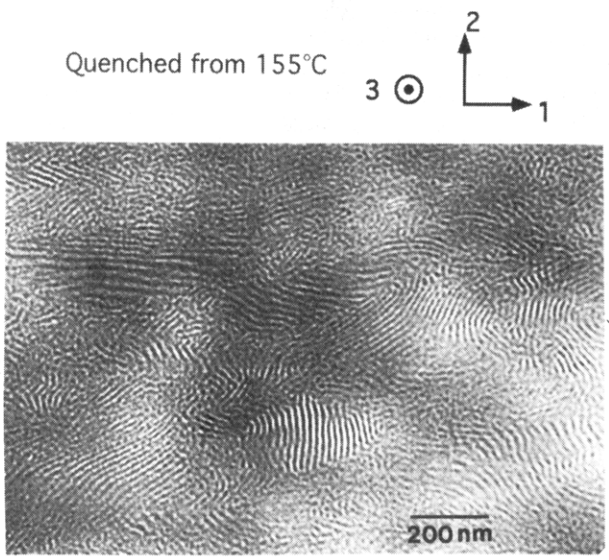

Figure 2. Transmission electron micrograph of SI 12/9 as quenched in the rheometer from 155 °C to room temperature. A variety of lamellar repeat distances are observed, because the lamellae are oriented differently with respect to the direction of image projection. The polyisoprene microdomains are stained dark via OsO_4.

uniform rings of intensity at three orthogonal directions, which further support the claim of randomly oriented, or unaligned, lamellae on a global length scale.

The second morphological state studied was produced by initially annealing above the ODT temperature and then reducing the temperature to 144 °C. This procedure of annealing above the ODT and then quenching into the ordered state for further investigation produces microphase-separated lamellae in randomly oriented grains, as discussed above, and is more reproducible than room temperature molding, which we previously used.[7] Upon quenching from above the ODT to 144 °C, the moduli increase and exhibit a weaker frequency dependence; compare the circles and triangles in Figure 1. At 144 °C, SI 12/9 was subjected to prolonged oscillatory shear (100% strain at 10 rad/s for a total of ~7.5 h). Subsequent frequency sweeps at smaller amplitude strains show that the moduli dropped and the frequency dependence increased; compare the triangles and squares in Figure 1.

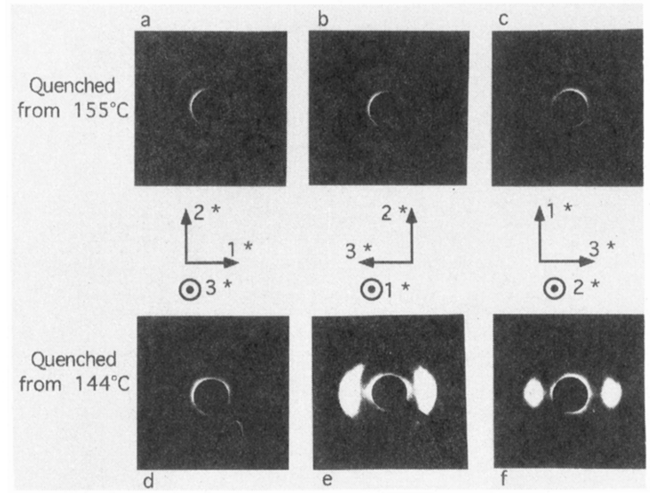

Figure 3. Small-angle X-ray scattering patterns from three orthogonal directions for SI 12/9 (a–c) as quenched from 155 °C and (d–f) as sheared at 144 °C and then quenched. Reflections correspond to a 17 nm lamellae thickness.

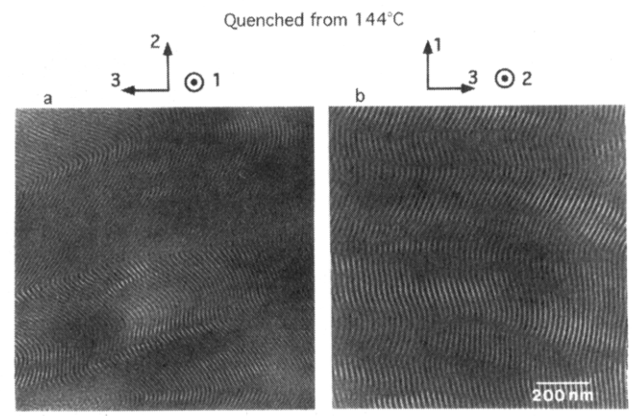

Figure 4. Two orthogonal planes imaged via transmission electron microscopy of SI 12/9 as sheared at 144 °C and then quenched. Both the 2–3 plane and the 1–3 plane indicate primarily lamellae with their normal in the **3** direction, but the 2–3 plane has a higher concentration of wall defects.

The three orthogonal SAXS patterns for the sample quenched from 144 °C (see Figure 3d-f) indicate imperfect global alignment in which the majority of lamellar microdomains have their normal parallel to the **3** direction, or the neutral direction, of the shearing field. This perpendicular global orientation corresponds to lamellae primarily in the 1–2 plane which is perpendicular to the sample plane (the 1–3 plane) and has been observed previously.[9,10] However, the lamellae exhibit only moderate alignment on a global length scale, as evidenced by the broader peak in the 2*–3* SAXS pattern (Figure 3e) as compared to the 1*–3* SAXS pattern (Figure 3f). The TEM images of this sample (see Figure 4) exhibit moderate alignment on the intermediate length scale.[7] Wall or bend defects, as defined previously,[7] are more prevalent and of a larger bend angle in the 2–3 plane, as compared to the subtler wall defects in the 1–3 plane. These data are consistent with the understanding that the least stable orientation during shearing is lamellae with their normal parallel to the **1** direction, that is, the shearing direction.

Table I summarizes the morphological alignments of the two samples of this study. For comparison, we refer the reader to our previous paper describing a method to produce lamellae in a parallel global orientation.[7] TEM images of that orientation exhibit very few defects, and SAXS patterns exhibit sharp peaks in both the 1*–2* plane and the 2*–3* plane (see Figures 9b and 10d-f). Though

Table I. Summary of Alignment for Two Preparations

preparation	intermediate	global
quench from 155 °C	slightly aligned	unaligned
shear at and quench from 144 °C	moderately aligned	moderately aligned

we have established methods to produce two types of global orientation in SI 12/9, currently the parallel orientation is of greater perfection.

Conclusions

Quenching diblock copolymers from the disordered state to the ordered state appears to be a reliable method for producing a morphology of global misalignment, having randomly oriented microphase separated grains. Applying oscillatory shear to SI 12/9 at 144 °C (10 rad/s) produces moderately aligned lamellae on the global length scale, such that the lamellae normals are parallel to the 3 direction. On the intermediate length scale, the sample contains a considerable number of wall defects. In contrast, we previously reported that applying oscillatory shear at 98 °C (0.1, 10, or 100 rad/s) produces lamellae in the parallel global orientation (lamellae normal parallel to the 2 direction) with very few defects. We refer the readers to a forthcoming publication for a more complete description of global orientation in block copolymers as a function of temperature and frequency.[9]

Acknowledgment. The authors thank D. D. Davis for experimental assistance. K.I.W. acknowledges the National Science Foundation's MRL Program, under Grant No. DMR 91-20668, at the University of Pennsylvania.

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