

Role of Strain in Controlling the Orientation Distribution in Oscillatory Shear of Diblock Copolymers as Studied by SAXS¹

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Small-angle X-ray scattering is used to examine quantitatively the distribution of lamellar orientation in shear aligned diblocks as a function of strain amplitude at constant shear duration, frequency, and temperature. At all strains, predominantly perpendicular alignment is observed with some parallel alignment. Also, there is a small amount of transverse alignment. This suggests that alignment by shear occurs at the expense of intermediate alignments followed by reducing transverse alignment. Increased strain at constant time increases the sharpness of the distribution of perpendicular alignment.

KEY WORDS: block copolymer; orientation; shear; small-angle X-ray scattering.

1. INTRODUCTION

Diblock copolymers are interesting materials due to the microphase transition these materials undergo, forming nanoscale patterns in the ordered state. Much recent work has been devoted to the microscopic nature of the order-disorder transition, concentrating on the structure of the ordered state as viewed within a single grain and in the absence of applied fields [1, 2]. As the nature of the ordered state becomes better understood, there has been an increase in the attention given to the larger-scale structure of

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these materials, that is, the overall orientation of the domain structures in the bulk sample. An understanding of methods of manipulating the orientation of the bulk sample is important as a means of both producing orientated samples for practical use and understanding the ordering process of these materials. One established approach to controlling the orientation is the use of flow [3, 4].

Recently, there has been much work done to explore the effect of shear on the orientation of lamellar domains in polystyrene-*block*-polyisoprene (SI) and polystyrene-*block*-poly(ethylene-*alt*-propylene) (SEP) diblock copolymers [5–15]. There are three defined directions for alignment: perpendicular alignment, where the lamellar normal is parallel to the vorticity direction; transverse alignment, where the lamellar normal is parallel to the flow direction; and parallel alignment, where the lamellar normal is parallel to the shear gradient direction. It has been reported that high-amplitude oscillatory shear can bring about both “perpendicular” and “parallel” alignment in these materials, depending on the maximum strain, shear frequency, and temperature [5–7]. By the use of *in situ* birefringence measurements during shear, a route to final alignment has been proposed [5]. Real-time small-angle X-ray scattering (SAXS) has also been used to observe the orientation of styrene-SEP diblocks under large-scale oscillatory shear [8].

Through the use of SAXS measurements, we can quantitatively observe the distribution of lamellar orientations in a sample. While such measurements cannot easily be done *in situ*, and thus there is the concern of changing internal structures of the sample during the sample preparation process (i.e., cutting from the shear tool, mounting in X-ray holder), they provide valuable information to extend the birefringence results reported by other groups, which measure the average orientation of the lamellar domains, but not the orientation distribution.

2. EXPERIMENTAL METHOD

2.1. Specimens

An SI diblock copolymer was synthesized by anionic polymerization. The polystyrene (PS) block has a number-average molecular weight of 1.12×10^4 and the polyisoprene (PI) block, a molecular weight of 1.46×10^4 . The heterogeneity index for the molecular weight distribution of the block copolymer, M_w/M_n , is less than 1.05. By SAXS measurements on the sample, the order-disorder transition (ODT) temperature was determined to be 172.5°C. Details of the procedure for determining ODT are

described elsewhere [16, 17]. Samples were first cast from toluene solutions (ca. 5 wt% polymer). Less than 1% antioxidant (Irganox 1010) was added to the polymer to prevent degradation. The samples were then annealed under vacuum to remove residual solvent. Finally, they were annealed above the ODT temperature and quickly cooled to ensure random alignment of grains by erasing the effect of solvent casting on orientation.

2.2. Procedure

Shear experiments were performed with an oscillatory shear device at 153°C with a sample thickness of 1 mm and under nitrogen flow to prevent degradation. The shear can be described by $\gamma = \gamma_0 \sin(\omega t)$, where γ is the strain experienced by the sample, γ_0 is the strain amplitude, ω is the angular frequency, and t is time. The shear frequency was 0.1 Hz, giving an angular frequency of 0.2π (0.628) $\text{rad} \cdot \text{s}^{-1}$. The samples were sheared for 1.5 h each. They were then quenched with liquid nitrogen and carefully cut from the machine for further analysis by SAXS. We define the axes of our coordinate system as follows: x is the flow direction, y is the velocity gradient, and z is the vorticity (neutral) direction.

SAXS measurements were performed with an 18-kW rotating anode X-ray generator (Mac Science Co. Ltd., Japan) with a graphite crystal monochromator, a He gas-filled scattering path, and a two-dimensional imaging plate detector. The sample center-to-detector distance was 800 mm. Beam collimation was achieved by two 0.5-mm pinholes in series. Results were corrected for background scattering and sample absorption. The edge view is the view obtained with the incident X-ray beam parallel to the z axis (neutral direction) and the through view is that obtained by making a measurement with the incident X-ray beam parallel to the y axis (velocity gradient direction).

3. RESULTS AND DISCUSSION

In Figs. 1a and b, we show the 2-D scattering patterns from the through and edge views of this diblock after shearing at 153°C for 1.5 h at a frequency of 0.1 Hz and a strain amplitude of 1.50. The inset in each figure shows the alignment of the sample with respect to the X-ray beam. The first-order peak clearly shows the orientation of the sample, and from Fig. 1a, the through view, we see that the sample shows predominantly perpendicular alignment, that is, lamellar normals parallel to the vorticity direction. In Fig. 1b, the edge view, we observe evidence for both parallel alignment and weak transverse alignment.

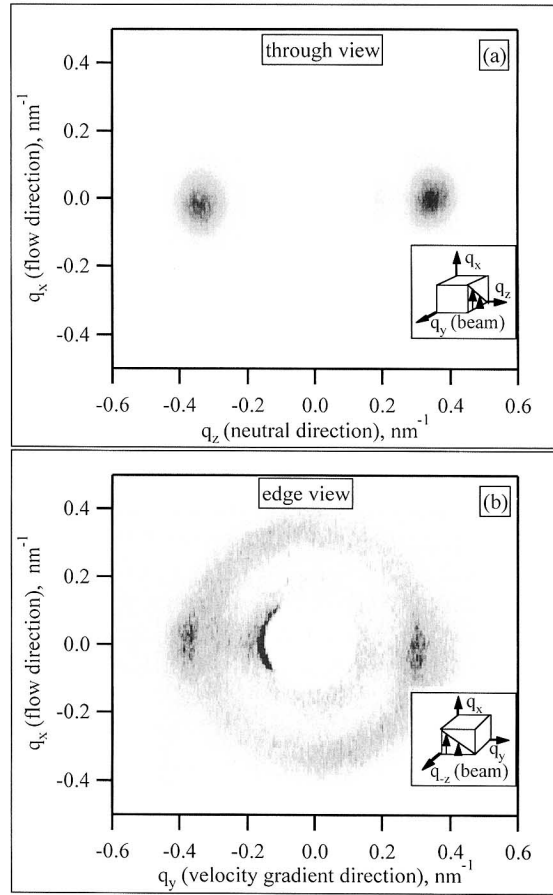


Fig. 1. (a) 2-D scattering pattern from a shear-oriented sample, $\gamma_0 = 1.50$, through view. (b) 2-D scattering pattern from a shear-oriented sample, $\gamma_0 = 1.50$, edge view.

We can show the orientation more clearly by showing the azimuthal angle dependence of the first-order maximum, $I_{\text{int}}(\mu)$, which we define by

$$I_{\text{int}}(\mu) = \int_{q_1}^{q_2} I(q, \mu) d\mu \quad (1)$$

where q is the magnitude of the scattering vector and q_1 and q_2 are the upper and lower bounds of q for the first-order scattering maximum. $q = 4\pi/\lambda \sin(\theta/2)$, where λ is the wavelength of the X-ray and θ is the scattering angle. Note that the angle $\mu = 0$ is defined as horizontal, parallel

to the z axis in Fig. 1a and the y axis in Fig. 1b. See the inset in Fig. 2 for a schematic defining μ . In order to compare data from different measurements we normalized the data with the formulas,

$$\bar{I}_{\text{int, through}}(\mu) = \frac{I_{\text{int, through}}(\mu)}{\int_0^{2\pi} I_{\text{int, through}}(\mu) d\mu} \times \frac{\ln(t_{\text{edge}})}{\ln(t_{\text{through}})} \quad (2)$$

and

$$\bar{I}_{\text{int, edge}}(\mu) = \frac{I_{\text{int, edge}}(\mu)}{\int_0^{2\pi} I_{\text{int, through}}(\mu) d\mu} \times \frac{\ln(t_{\text{edge}})}{\ln(t_{\text{edge}})} \quad (3)$$

where $\bar{I}_{\text{int, through}}(\mu)$ and $\bar{I}_{\text{int, edge}}(\mu)$ are the normalized data for $I_{\text{int, through}}(\mu)$ and $I_{\text{int, edge}}(\mu)$ for the through and edge views, respectively. t_{edge} and t_{through} are the measured values of the X-ray transmission, and the ratio of their logarithms is used to correct for differences in the scattering volume between the edge and through views. Normalized intensity data $\bar{I}_{\text{int, through}}(\mu)$ and $\bar{I}_{\text{int, edge}}(\mu)$ are presented in the following figures.

Figure 2 shows the \bar{I}_{int} as a function of the azimuthal angle taken from the data in Figs. 1a and b. From this plot, we can clearly see that the orientation is predominantly perpendicular, with peaks at azimuthal angles of 0 and 180° in the through view; that is, the lamellar normals are along the

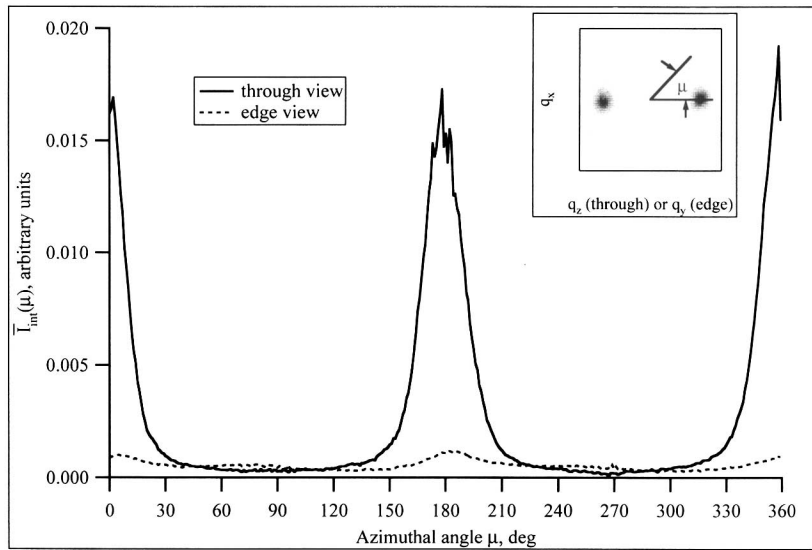


Fig. 2. Azimuthal angle dependence of the first-order maximum from a shear-oriented sample, $\gamma_0 = 1.50$.

vorticity (neutral) direction. In addition, there is evidence for weak parallel orientation, shown by peaks at 0 and 180° for the edge view (lamellar normals parallel to the gradient direction). Finally, there is some slight evidence of transverse alignment in the edge view as evidenced by very weak peaks around 90 and 270° (lamellar normals along the flow direction). For a magnified view of the edge-view data of all three samples, see Fig. 4.

In Fig. 3, we show the azimuthal angle dependence of the scattered intensity for three samples sheared under the same conditions (1.5 h, 153°C, 0.1 Hz), but with strain amplitudes of 1.50 (also shown in Fig. 2), 0.96, and 0.70. Here, we see that there is again predominantly perpendicular alignment due to peaks at 0 and 180° in the through view, with weak parallel alignment (0 and 180° in the edge view), and some small evidence of transverse alignment (90 and 270° in the edge view) in the edge view of these samples. The edge-view data are shown on an expanded scale in Fig. 4. In all the samples described here, we only see transverse alignment in the edge view, though, in principle, we should see it in the through-view measurements as well. We suspect that due to the strong perpendicular alignment dominating the scattering in the through view, the transverse alignment cannot be clearly discerned. More detailed X-ray experiments, necessary to check this point, are currently underway.

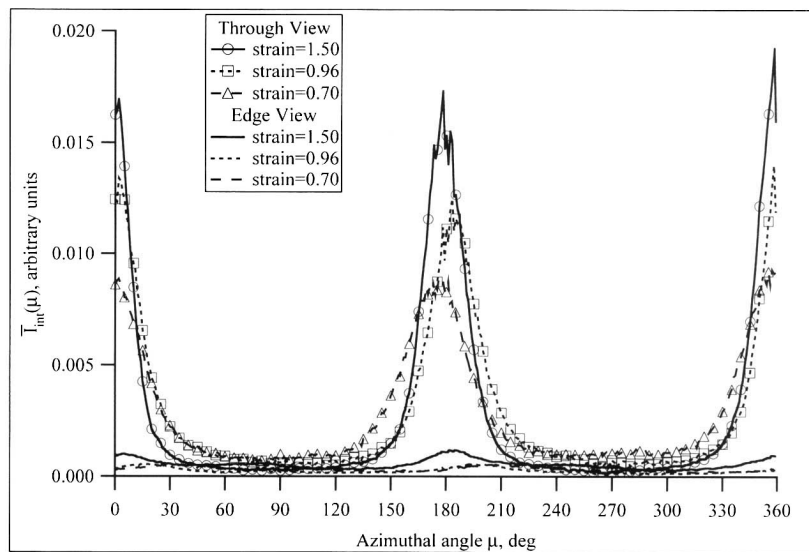


Fig. 3. Azimuthal angle dependence of the first-order maximum from shear-oriented samples at various strains. Different symbols are used to indicate data for different values of γ_0 .

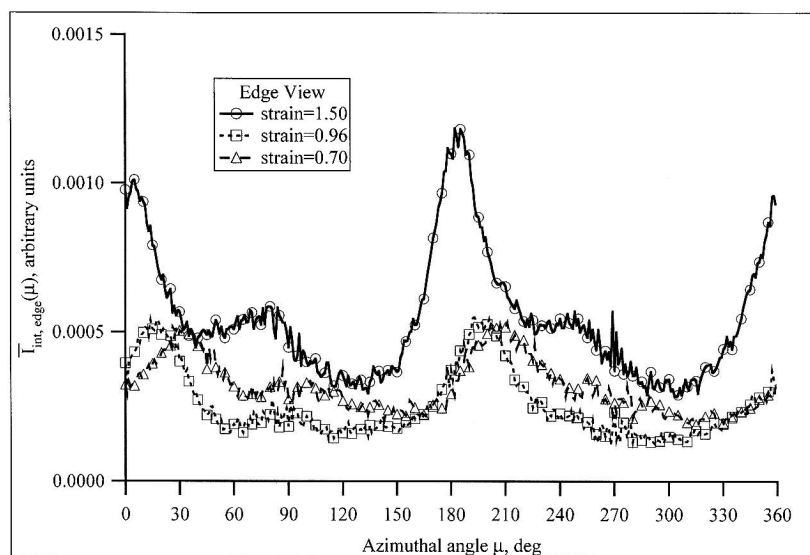


Fig. 4. Comparison of azimuthal angle dependence of the first-order maxima, edge views. Different symbols are used to indicate data for different values of γ_0 .

The predominantly perpendicular alignment mixed with some parallel alignment is consistent with results measured by birefringence from shear on other SI diblocks at temperatures close to the ODT temperature [9, 10]. In the case of the measurements presented here, the shearing temperature is close to the ODT temperature ($T/T_{\text{ODT}} = 0.96$). The frequency is also low, below the critical frequency observed by Gupta et al. [7] for a similar SI diblock, again suggesting perpendicular alignment dominates. It also has been shown previously by birefringence measurements that the transverse alignment is suppressed first, followed by suppression of parallel alignment during the shear alignment of SI diblocks to the perpendicularly aligned condition [5]. Here, we observe that the intermediate alignments are suppressed most, that is, alignments that are neither parallel, nor perpendicular, nor transverse, closely followed by the transverse alignment and, finally, by the parallel alignment, suggesting agreement with the *in situ* birefringence measurements [5]. By using X-ray scattering, we are able to discern more details concerning the alignment than is possible with birefringence measurements.

One interesting observation is the presence of weak transverse alignment. However, this is not unprecedented. Gupta et al. [12] observed the predominance of transverse orientation at the expense of perpendicular orientation during evolution of parallel lamellar orientation. Furthermore,

Okamoto et al. [8] observed biaxial parallel and transverse orientation after shear of an SEP sample in the strong segregation limit. Here, we observe transverse orientation during the evolution of perpendicular orientation. We also note, in all cases presented here, that the transverse orientation is quite weak compared to perpendicular or parallel orientation.

From Fig. 4, the edge-view data, no clear trend is apparent, probably due to the relatively weak scattering from the sample in this orientation. This point is worth future study. However, from Fig. 3, we see qualitatively that increased strain increases the sharpness of the perpendicular orientation distribution of these diblocks.

In order to compare quantitatively the sharpness of the perpendicular orientation, we fit the through-view data in Fig. 3 with a Gaussian function and obtained the square of the peak half-width at half-height as a measure of sharpness. These results are plotted in Fig. 5. We see that increased strain amplitude at constant duration leads to a sharper orientation as indicated by the decreasing value of the peak half-width at half-height with increasing shear strain amplitude.

In these samples, there is no reason to believe that these results are terminal. That is, we expect that longer shearing times would lead to more perfectly aligned samples. However, these results do capture the alignment

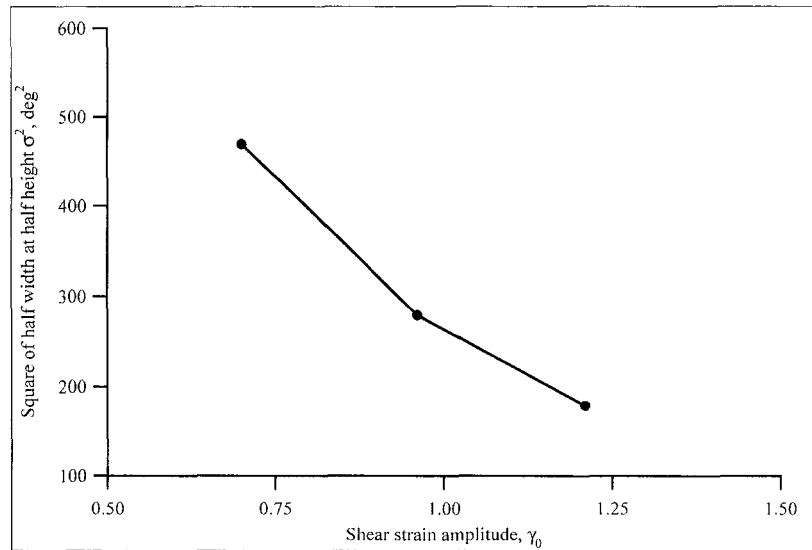


Fig. 5. Width of perpendicular orientation peaks in $\bar{I}_{\text{int, through}}(\mu)$ as a function of shear strain amplitude γ_0 at a constant shear duration, temperature, and frequency.

of these samples at intermediate shear duration and show that (a) large-strain oscillatory shear of this diblock at 153°C leads to a perpendicular alignment; (b) shear leads to alignment in all principal directions, at the expense of intermediate orientations, however, parallel and transverse alignment is much weaker than perpendicular alignment; and (c) a higher strain amplitude at constant time leads to a stronger perpendicular alignment.

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