In Situ SAXS Studies of Shear Alignment Processes in a Lamellar Diblock Copolymer

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Introduction

Block copolymers (BCPs) are intriguing synthetic materials that self-assemble into a variety of microscopically ordered phases owing to incompatibility between the polymer constituents. Many of the applications envisioned for these nanostructured materials would benefit from the ability to induce macroscopic alignment of the ordered fluid structure. For many years, it has been appreciated that shear flow can provide an effective and efficient means for promoting alignment in ordered BCP phases [1]. A variety of experimental methods have been used to probe the dynamics of such shear alignment processes, including flow birefringence, *in situ* and *ex situ* x-ray and neutron scattering, and *ex situ* transmission electron tomography (TEM). Birefringence provides excellent time resolution but only a coarse picture of the structural evolution. Conversely, TEM provides exquisite detail on the microscopic structure but is restricted to off-line measurements. *In situ* scattering methods offer a favorable middle ground in that they provide greater structural detail than birefringence but may be performed on-line during the shear flow. Between x-ray and neutron methods, high-intensity synchrotron sources provide opportunities to study the transient dynamics of alignment processes. This is the focus of the present report.

Materials and Methods

We studied a symmetric poly(styrene-b-isoprene) diblock copolymer with M = 20,850 and f_{PS} = 0.49. Its order disorder transition (ODT) temperature is 170°C. The sample was first heated above its ODT, then cooled into the lamellar phase to the test temperature of 115°C. This leads to an ordered lamellar structure but in a polycrystalline state with no net preferred orientation. The lamellar d-spacing of this sample is 17.5 nm.

X-ray scattering experiments were performed in a novel annular cone and plate shear cell that allows the fluid structure to be probed in the flow-gradient (1-2) plane. Details on construction of the shear cell are available in Ref. 2. Experiments were performed on APS beamline 5-ID-D by using 17-keV undulator radiation. A MarCCD detector was used to collect 2-D small-angle x-ray scattering (SAXS) patterns; the sample-to-detector distance was 3.8 m. A vacuum chamber was placed between the shear cell and detector to reduce air scatter.

Results

Figure 1 presents representative SAXS patterns observed during shear flow inception at a rate of 0.03 s^{-1}. Shear flow is from right to left in these patterns. Initially, the random grain structure leads to an isotropic ring of scattered intensity. After flow inception, peaks of intensity build in the second and fourth quadrants. These peaks subsequently intensify and rotate toward the velocity gradient (vertical direction). We attribute the peak development and rotation to "grain rotation," a simple mechanism postulated to play a significant role in lamellar BCP orientational dynamics [3].

To extract quantitative metrics of the degree of orientation induced by shear, an azimuthal intensity scan $I(\theta)$ is extracted from the data. The azimuthal angle θ is measured from the flow direction toward the velocity gradient direction. This intensity scan is normalized by the initial uniform intensity value so that its normalized initial value is unity. Next a second moment tensor of the dimensionless scattering vector **q** is constructed:

$$\langle \mathbf{qq} \rangle = \begin{bmatrix} \langle \cos^2\theta \rangle & \langle \sin\theta\cos\theta \rangle \\ \langle \sin\theta\cos\theta \rangle & \langle \sin^2\theta \rangle \end{bmatrix}, \qquad (1)$$

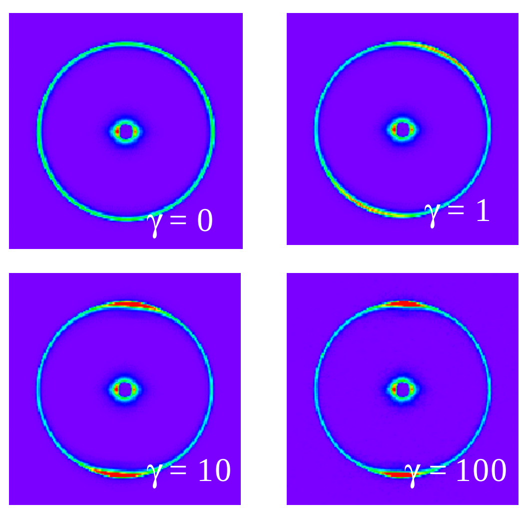

FIG. 1. Two-dimensional SAXS patterns collected in the 1-2 plane during shear flow inception at a shear rate of 0.03 1/s. Flow is from right to left.

where the 11-component, for instance, is computed according to:

$$\left\langle \cos^2 \theta \right\rangle = \frac{\int_0^\pi \cos^2 \theta I(\theta,\gamma) d\theta}{\int_0^\pi I_0(\theta) d\theta} . \qquad (2)$$

Defined in this way, the diagonal components of <**qq**> equal one-half for the random initial orientation, while the off-diagonal components initially equal zero.

Figure 2 presents the components of the second moment tensor as a function of applied shear strain for the inception experiment whose SAXS patterns are documented in Fig. 1. As expected, the 11- and 22-components initially equal one another (with a value of one-half), and the off-diagonal (12) component equals zero. During inception, the 22-component grows, and the 11-component decreases. The 12-component also rises, then falls. These trends reflect the evolution of scattered intensity in the 1-2 plane SAXS patterns.

Solid lines in Fig. 2 represent the predictions of a simple grain rotation model advanced by Polis and coworkers to describe orientational dynamics of lamellar structures within the 1-2 plane in shear flow [3]. The model postulates that (1) grains with normals lying in the 1-2 plane are conserved and (2) the rotation of an individual grain follows a very simple rate law, that of the affine rotation of an inextensible line segment. Starting with an initially random distribution of grain orientation, this model may be readily solved to give an expression for the azimuthal intensity distribution *I(q)* as a function of applied strain, and, through Eq. (1), for the second moment tensor components:

$$\left\langle q_1 q_1 \right\rangle = \frac{2}{4+\gamma^2} , \qquad (3)$$

$$\left\langle q_2 q_2 \right\rangle = \frac{2+\gamma^2}{4+\gamma^2} , \qquad (4)$$

$$\left\langle q_1 q_2 \right\rangle = \frac{-\gamma}{4+\gamma^2} . \qquad (5)$$

Predictions of Eqs. (3)–(5) are shown as the solid lines in Fig. 2.

Discussion

The grain rotation model captures some of the qualitative characteristics of orientation development upon inception of shear flow, but there are significant quantitative differences. Most notable is the failure of the measured 11-component of the second moment tensor to drop to zero as the rotation model predicts. This is also

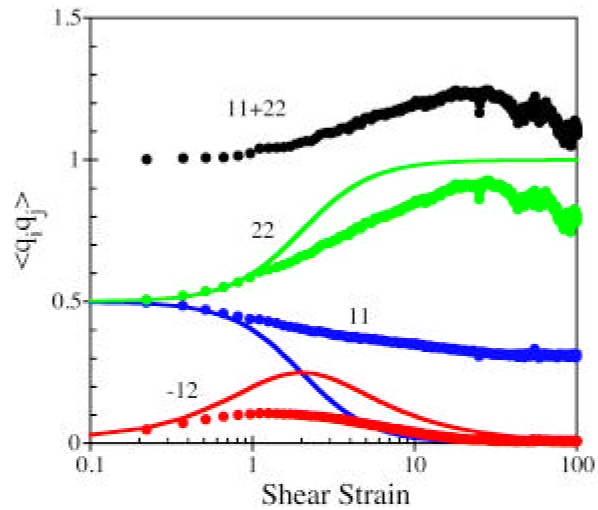

*FIG. 2. Components of the second moment tensor <**qq**> extracted from SAXS data.*

manifested in the SAXS patterns in Fig. 1, in which a persistent isotropic ring is superimposed on the anisotropic pattern. Independent measurements in the 1-3 plane by using a rotating disk shear cell (not shown) suggest that there might be an artifact of end-effects in the 1-2 plane measurements, by which the beam passes through material that is not significantly sheared and hence remains in the isotropic configuration. If a constant isotropic background were subtracted from these data and the results were re-normalized, this would lead to improvements in agreement with model predictions for both the 11- and 12-components.

Another way to look at this is to consider the average orientation angle, computed from the second moment tensor components according to:

$$\chi = \frac{1}{2} \tan^{-1} \left(\frac{2\left\langle q_1 q_2 \right\rangle}{\left\langle q_1 q_1 \right\rangle - \left\langle q_2 q_2 \right\rangle} \right) . \qquad (6)$$

The orientation angle would not be affected by any isotropic background. When the grain rotation predictions [Eqs. (3)–(5)] are inserted into Eq. (6), the following expression results:

$$\chi = \frac{1}{2} \tan^{-1} \left(\frac{2}{\gamma} \right) . \qquad (7)$$

Figure 3 presents comparisons of this model prediction to experimental data. It is found that the grain rotation model does a good job in predicting the overall geometry of the orientation development, as characterized by the orientation angle.

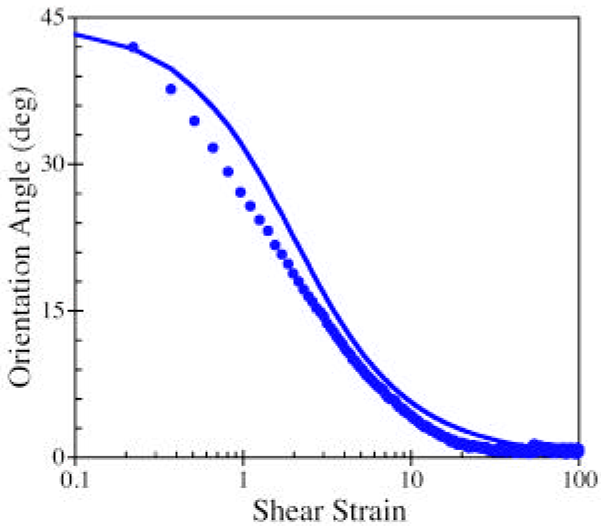

FIG. 3. Average orientation angle extracted from SAXS data during shear flow inception at 0.03 1/s. Line indicates predictions of grain rotation model (Eq. 7).

Another discrepancy in Fig. 2 concerns the total scattered intensity within the 1-2 plane. The grain rotation model postulates that the number of lamellar grains with normals lying within the 1-2 plane is conserved. If this is true, then the sum of the diagonal elements of <**qq**> should remain constant and equal to unity throughout the course of the experiment. Instead, the data show that the total intensity first increases, indicating an increased number of grains lying within the 1-2 plane, but then at longer times, the total intensity decreases (a trend that continues with prolonged shearing over longer times than represented in Fig. 2). Changes in the 1-2 plane SAXS patterns continue to occur even after more than 1000 shear strain units are applied, indicating that “steady state” orientation might be a concept that is difficult to apply in these materials.

Acknowledgments

We acknowledge the donors of the American Chemical Society-Petroleum Research Fund for financial support. This research was carried out at Dow-Northwestern-DuPont Collaborative Access Team (DND-CAT) sector, which is supported by E. I. DuPont de Nemours & Co., The Dow Chemical Co., the National Science Foundation through Grant No. DMR-9304725, and the State of Illinois through the U.S. Department of Commerce and Illinois Board of Higher Education Grant No. IBHE-HECA-NWU-96. Use of the APS was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-102-ENG-38.

References

[1] G. H. Fredrickson and F. S. Bates, Ann. Rev. Mater. Sci. **26**, 501 (1996).
[2] F. E. Caputo and W. R. Burghardt, Macromol. **34**, 6684-6694 (2001).
[3] D. L. Polis, S. D. Smith, N. J. Terrill, A. J. Ryan, D. C. Morse, and K. I. Winey, Macromolecules **32**, 4668-4676 (1999).