Direct Measurement of Interfacial Curvature Distributions in a Bicontinuous Block Copolymer Morphology

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(Received 9 August 1999)

Self-consistent field theory predicts that the complex phase behavior of block copolymers does not originate solely from the interface seeking constant mean curvature as once thought, but instead reflects competing minimization of interfacial tension and packing frustration. To test this prediction, we directly measure interfacial curvature distributions from a 3D image reconstruction of the bicontinuous gyroid morphology. Results obtained here reveal that the gyroid interface is not constant mean curvature and confirm the importance of packing frustration in the stabilization of such complex nanostructures.

PACS numbers: 68.35.Ct, 42.30.Wb, 47.20.Hw, 83.70.Hq

Block copolymers exhibit periodic nanostructures due to immiscibility between the dissimilar (A and B) sequences [1]. Classical block copolymer nanostructures include spheres of A(B) on a body-centered cubic lattice in a B(A) matrix, cylinders of A(B) on a hexagonal lattice in a B(A) matrix, and coaligning lamellae. Of considerable recent interest are several complex (bicontinuous) nanostructures—the perforated lamellar (PL), gyroid (G), and double-diamond (D) morphologies [2–7]. These nanostructures may develop if the copolymer composition (f) falls within a narrow range between the cylindrical and lamellar morphologies, and can be difficult to distinguish experimentally. Block copolymer nanostructures once believed [2] to be D, exemplified by a Schwarz D surface with \( \text{Pn}_3\text{m} \) symmetry, have been reclassified [8] on the basis of their small-angle X-ray scattering (SAXS) signatures as G, which is represented by the Schoen G surface with \( \text{Ia}_3\text{d} \) symmetry. Identification of complex nanostructures by transmission electron microscopy (TEM) is often inconclusive, since they appear identical along several projection axes.

Complex nanostructures also develop in surfactant and lipid systems due to the formation of surfaces with constant mean curvature (CMC) that minimize contact between immiscible moieties [9]. Since block copolymer nanostructures share common topological features with those of other self-organized systems, the concept of CMC minimal surfaces has been used [3] to explain the stability of complex block copolymer nanostructures. On the basis of self-consistent field theory (SCFT), Matsen and Bates [10,11] have recently proposed that the area-averaged mean curvature (\( \langle H \rangle \)) governs the gross morphology (lamellar, bicontinuous, cylindrical, or spherical), whereas the standard deviation of the mean curvature distribution (\( \sigma_H \)) determines the delicate stability of the complex nanostructures (G, D, or PL). This additional consideration results from packing frustration [12] and implies that, while a surface strives toward CMC, the mean curvature cannot be constant everywhere along the interface since the microdomain-forming blocks must uniformly fill space in the most entropically favored manner. Thus far, neither \( \langle H \rangle \) nor \( \sigma_H \) has been measured experimentally despite their apparent importance.

Three-dimensional visualization of bicontinuous morphologies in block copolymer systems has been achieved [13–15] by transmission electron microtomography (TEMT). In this technique, TEM images are collected from a single specimen at incremental tilt angles over the maximum tilt-angle range permissible [16]. Following alignment, the images are reconstructed according to the filtered back-projection algorithm [17] to generate a 3D representation of nanostructural elements within the specimen. This technique affords the only real-space structural analysis of complex nanoscale morphologies without a priori symmetry or surface assumptions [18]. At larger length scales, laser scanning confocal microscopy (LSCM) can elucidate [19,20] the volumetric features of bicontinuous structures, such as those in polymer blends undergoing spinodal decomposition (SD). Application of numerical methods developed [20,21] to measure interfacial curvatures from 3D LSCM images of SD polymer blends to a TEMT reconstruction of the G morphology in the present work yields the first experimental measurements of interfacial curvature distributions, as well as \( \langle H \rangle \) and \( \sigma_H \), in a complex block copolymer nanostructure.

A polystyrene-block-polyisoprene-block-polystyrene (SIS) triblock copolymer was synthesized by living anionic polymerization. The number-average molecular weight and polydispersity index were \( 8.3 \times 10^3 \) and...
1.09, respectively. The styrene volume fraction $(f_S)$ was calculated to be 0.32 according to the measured mass fraction (36 wt% $S$ from $^1$H NMR) and mass densities reported for polystyrene (S) and polyisoprene (I). Specimens for TEMT were produced according to the protocol described [15] earlier. Forty-nine digital images were acquired at a resolution of $2.1$ nm/pixel and tilt angles ranging from $+60^\circ$ to $-60^\circ$ in $2.5^\circ$ increments on a computer-controlled Philips 430 electron microscope equipped with a Thomson $1024 \times 1024$ charge-coupled device (CCD) chip fiber-optically coupled to a single-crystal scintillator. Details of the image alignment and reconstruction algorithm are provided elsewhere [13,16,17]. Each 2D image in the 3D reconstruction was subjected to conventional image processing to enhance the signal-to-noise ratio and reduce noise, and then binarized using an appropriate threshold. The marching cubes algorithm (MCA) [23] modeled the interface as contiguous triangles.

Figure 1(a) shows the reconstructed 3D image of the nanostructure in the SIS triblock copolymer. Volumetric analysis of the reconstruction yields $f_S = 0.33$, in excellent agreement with the known composition of the copolymer ($f_S = 0.32$). This calculated composition is comparable to that deduced previously [15] ($f_S = 0.35$), although the measurement algorithm employed here is different from that used earlier. The light and dark channel networks evident in Fig. 1(a) both represent the $S$ microphase. They are shaded differently to demonstrate that the two $S$ channel networks do not intersect. For the sake of clarity in this figure, the $I$ microphase is transparent. A detailed crystallographic analysis of Fig. 1(a) reveals that the lattice constants of this nanostructure, identified [15] as G from two independent experimental observations, are $a = 78$ nm, $b = 71$ nm, and $c = 74$ nm. According to SAXS, this nanostructure exhibits a scattering peak at $\sqrt{4/3}$ relative to the first scattering maximum, which is characteristic of the I$a\overline{3}d$ space group [5]. Close examination of the nanostructure also reveals that the channel coordination is 3, which is consistent with the G morphology.

Displayed in Fig. 1(b) is a model bicontinuous morphology generated from the Schoen G surface. The trigonometric approximation used to generate this surface is given by

$$g(x, y, z) = \cos \frac{2\pi x}{L} \sin \frac{2\pi y}{L} + \cos \frac{2\pi y}{L} \sin \frac{2\pi z}{L} + \cos \frac{2\pi z}{L} \sin \frac{2\pi x}{L},$$

where $L$ denotes the crystallographic unit cell edge of the gyroid. The periodic minimal surface, which divides space equally, is obtained by setting $g(x, y, z) = 0$. To emulate the microphase-ordered nanostructure of the SIS copolymer with $f_S = 0.33$, a new model interface is formed by translating the interface obtained from Eq. (1) along its normals by an equal distance everywhere. Two parallel surfaces with opposite direction but the same displacement, selected so that the volume fraction of the swollen microphase is equal to 0.67, are consequently generated. The resultant morphology constitutes an approximate model of the hypothetical CMC interface and, following Hajduk et al. [5], serves as the constant thickness (CT) model. As in Fig. 1(a), the nonintersecting light and dark channels shown in Fig. 1(b) identify the minority microphase, with the majority microphase remaining transparent. The edges of the cubes presented in Figs. 1(a) and 1(b) represent a distance equal to $2L$, and the upper cross section of each image identifies the $(001)$ plane.

Interfacial curvature distributions are evaluated from Fig. 1 according to the sectioning and fitting method (SFM), which has been previously used [20] to calculate the interfacial curvature distributions of bicontinuous structures in polymer blends undergoing SD. Quantities characterizing the local geometry of a bicontinuous interface include the mean ($H$) and Gaussian ($K$) curvatures, where $H = (\kappa_1 + \kappa_2)/2$ and $K = \kappa_1 \cdot \kappa_2$ ($\kappa_1$ and $\kappa_2$ denote the principal curvatures at a given point on the interface). Since the SFM yields local interfacial curvatures at an arbitrary point on the interface, a joint probability density, $P(H, K)$, can be generated by sampling about 10% of the total number of surface points chosen at random. These points coincide with the vertices of the triangles from the MCA [23]. In this work, the number of points used to determine $P(H, K)$ is sufficiently large so that $P(H, K)$ is invariant with further sampling. The resultant joint probability density is normalized so that

$$\int \int P(H, K) \, dH \, dK = 1.$$ 

A crucial factor in determining $P(H, K)$ is surface roughness [21]. To ensure accurate curvature measurements, we define a surface roughness index (RI) as $\langle A_\Delta \rangle^{1/2}/(|\kappa_1| + |\kappa_2|)/2$, where $\langle A_\Delta \rangle$ represents the average triangle area ($= \sum_i |A_i^0|/N$), $A_i^0$ is the area of the $i$th triangle, and $N$ is the total number of triangles from the MCA. The value of RI computed for the TEMT data analyzed here is 0.12. If RI is less than 0.2 in the curvature distribution measurements, a 5% error is expected [20].

Figure 2 shows a surface contour representation of the $P(H, K)$ distribution measured from the G morphology.
In the present study, the curvature is arbitrarily chosen to
be positive if the center of the osculating circle resides
within the I microphase. According to Fig. 2, most of the
interfacial curvature probability densities are only available [11] for diblock copolymers (which differ from the present triblock copolymer in molecular architecture), it is worthwhile to compare the experimental interfacial curvature data obtained here with SCFT predictions.

The unperturbed statistical end-to-end distance of the SIS triblock copolymer \( R_0 \) is discerned from
\[ R_0 = \sqrt{2l_s N_S + l_l N_I}, \]
where \( l_s \) and \( l_l \) denote the statistical segment length and block degree of polymerization, respectively. Since \( l_s = 0.70 \) nm and \( l_l = 0.65 \) nm, \( R_0 = 22 \) nm. The probability density measured for the G morphology in the SIS copolymer yields \( \langle H \rangle = 0.034 \) nm\(^{-1}\) and \( \sigma_H = 0.042 \) nm\(^{-1}\), which can likewise be expressed as \( \langle H \rangle = 0.74 R_0^{-1} \) and \( \sigma_H = 0.91 R_0^{-1} \). Assuming that the unperturbed chain length \( R_0 \) remains constant, we find that \( \langle H \rangle \) and \( \sigma_H \) from the SCFT predictions [11] for an AB diblock copolymer with \( f_A = 0.34 \), \( \langle H \rangle = 0.70 R_0^{-1} \), and \( \sigma_H = 0.12 R_0^{-1} \) at \( \chi N = 20 \). Here, \( \chi \) is a measure of the copolymer segregation power, wherein \( \chi \) represents the Flory-Huggins interaction parameter and \( N = 2N_S + N_I \). It should be noted that the SCFT model exhibits two sharp maxima, in marked contrast to the G morphology in the SIS copolymer, which possess a single broad maximum near \( \bar{k} = 0 \). In this sense, the so-called G morphology in the SIS copolymer differs markedly from the mathematical G surface.

On the basis that interfacial tension constitutes the dominant factor for structure formation in microphase-ordered block copolymers, Thomas et al. [3] have proposed that the complex nanostructures formed in block copolymers correspond to area-minimizing surfaces. From extensive SCFT calculations, Matsen and Bates [10,11] find that an equally important, but thus far disregarded, factor in block copolymer nanostructure stability is packing frustration [12]. For the minority blocks of an ordered copolymer to fill space uniformly, the interface self-adjusts so that no blocks are excessively stretched. This entropic consideration causes the interface to deviate from CMC (with \( \sigma_H \approx 0 \)), in which case \( \sigma_H \) provides a measure of packing frustration and nanostructural stability. Although predicted \( \langle H \rangle \) and \( \sigma_H \) are only available [11] for diblock copolymers (which differ from the present triblock copolymer in molecular architecture), it is worthwhile to compare the experimental interfacial curvature data obtained here with SCFT predictions.

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FIG. 3. Contour map of the scaled joint probability density, \( \tilde{P}(\tilde{H}, \tilde{K}) \), and its marginal probability densities, \( \tilde{P}_{\tilde{H}}(\tilde{H}) \) and \( \tilde{P}_{\tilde{K}}(\tilde{K}) \), for (a) the G morphology of the SIS triblock copolymer and (b) the CT model of the G surface [Eq. (1)].

41 500, in which case \( \chi N \) is estimated [24] to be about 60. The value of \( \langle H \rangle \) derived from the probability densities in Fig. 3(a) for the G morphology in the SIS triblock is in reasonably good agreement with that predicted by SCFT, whereas the value of \( \sigma_H \) obtained here is higher than what is predicted. This discrepancy may reflect noise inherent in the TEMT reconstruction or, alternatively, the large difference in \( \chi N \) (Matsen and Bates [11] predict that \( \sigma_H \) should increase with increasing \( \chi N \)). Further analysis of the factors influencing \( \sigma_H \) is needed for more accurate comparison between experiment and theory.

Interfacial curvature distribution measurements of a bicontinuous block copolymer nanostructure have been performed on a 3D reconstruction generated by transmission electron microtomography. The joint probability density \( P(H, K) \) of the mean \( H \) and Gaussian \( K \) curvatures, experimentally measured for the first time in this class of nanostructured materials, demonstrates that the interface of the G morphology is principally hyperbolic with a non-negligible standard deviation in mean curvature (\( \sigma_H \)). According to recent SCFT predictions [10,11], \( \sigma_H \) is a measure of packing frustration and, hence, stability in complex nanostructures, in contrast to the CMC hypothesis (with \( \sigma_H = 0 \)) [3]. Values of \( \langle H \rangle \) and \( \sigma_H \) obtained here for the G morphology are consistent with predictions from SCFT and suggest that (i) the CMC model captures some, but not all, of the characteristics of complex morphologies in nanostructured block copolymers, and (ii) packing frustration cannot be disregarded in explaining the stability of such morphologies.

We thank J. H. Laurer and J. C. Fung for their contributions leading to this work. R. J. S. was partially supported by the U.S. Department of Energy (DE-AC03-76SF00098) through the National Center for Electron Microscopy, and D. A. A. was supported by the National Institutes of Health (GM31627) and the Howard Hughes Medical Institute. *Present address: Department of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Kyoto 606-8585, Japan.
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