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

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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.

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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 coalternating 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 $Pn\overline{3}m$ 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 $Ia\overline{3}d$ 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 (σ_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 σ_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 σ_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 8.3×10^4 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 ^1H 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 $+60°$ to $-60°$ in $2.5°$ increments on a computer-controlled Philips 430 electron microscope operated at 200 kV and equipped with a Thomson 1024×1024 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 contrast [22] 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 $Ia\bar{3}d$ space group [5]. Close examination of the nanostructure also reveals that the channel coordination is 3, which is consistent with the G morphology.
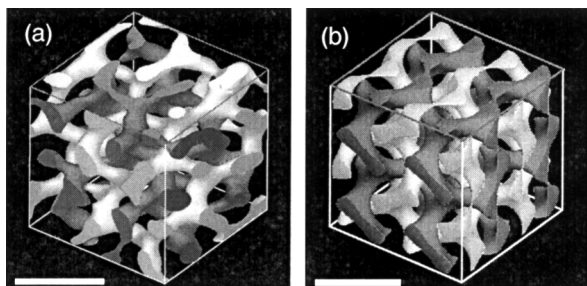

FIG. 1. Transmission electron microtomograph of the gyroid morphology in a SIS triblock copolymer (a), and the CT model based on Schoen's gyroid surface (b). The nonintersecting light and dark channels correspond to the minority microphase (S in the SIS copolymer), while the majority (I) microphase is transparent. The edge of each cube equals twice the periodic length, and the top cross-section identifies the (001) plane.

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

$$g(x, y, z) = \cos\frac{2\pi x}{L} \sin\frac{2\pi y}{L} + \cos\frac{2\pi y}{L} \sin\frac{2\pi z}{L}$$
$$+ \cos\frac{2\pi z}{L} \sin\frac{2\pi x}{L}, \qquad (1)$$

where L denotes the crystallographic unit cell edge of the gyroid. The periodic minimal surface, which divides space equally, is obtained by setting $g(x, y, z)$ equal to zero. 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 $K = \kappa_1 \cdot \kappa_2$ (κ_1 and κ_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 ($= \sum_i |A_\Delta^i|/N$), A_Δ^i is the area of the ith 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
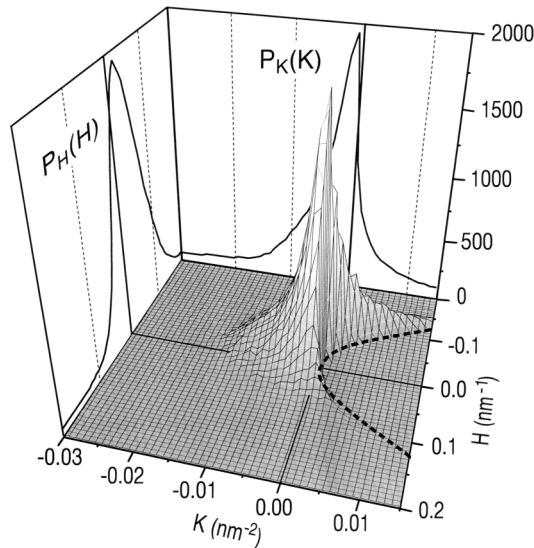
FIG. 2. Surface contour representation of the joint probability density, $P(H, K)$, measured for the G morphology of the SIS triblock copolymer. Marginal probability densities, $P_H(H)$ and $P_K(K)$, are also shown. The dashed parabolic curve represents $K = H^2$.

in the SIS triblock copolymer. Included in this figure are the probability densities of the mean and Gaussian curvatures—$P_H(H)$ and $P_K(K)$, respectively—calculated from $P(H, K)$:

$$P_H(H) \equiv \int P(H, K)\, dK \quad \text{and} \quad P_K(K) \equiv \int P(H, K)\, dH.$$
(2)

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 interface (77%) possesses $K < 0$, indicating that (i) the two principal curvatures (κ_1 and κ_2) have opposite signs, and (ii) most of the interface is hyperbolic. An important characteristic of $P(H, K)$ is that it satisfies the boundary condition $K \leq H^2$ (dashed line), which is required for κ_1 and κ_2 to be physically meaningful [19]. A qualitative conclusion that can be drawn from Fig. 2 is that, since H is not constant everywhere along the interface, the CMC representation does not accurately represent the G morphology. This point is addressed further below.

The interfacial curvature probability densities are displayed in Figs. 3(a) and 3(b) for the G morphology in the SIS copolymer and the CT model surface, respectively. To facilitate comparison, $P_H(H)$ and $P_K(K)$ have been scaled with respect to the interfacial area per unit volume (Σ) in the following fashion:

$$\tilde{P}(\tilde{H}, \tilde{K}) = P(H, K)\Sigma^3,$$
$$\tilde{P}_H(\tilde{H}) = P_H(H)\Sigma, \quad \tilde{P}_K(\tilde{K}) = P_K(K)\Sigma^2.$$
(3)

Here, $\tilde{H} = H\Sigma^{-1}$ and $\tilde{K} = K\Sigma^{-2}$, with $\Sigma = 0.070$ and 0.074 nm^{-1} for the SIS copolymer and CT model, respectively. Close examination of $\tilde{P}(\tilde{H}, \tilde{K})$ in Fig. 3(a) reveals

that a part of the scaled joint probability density for the SIS G morphology possesses $\tilde{H} < 0$ and $\tilde{K} > 0$, implying that the interface is an elliptic surface curved inward relative to the I microphase. Such interfacial concavity is not evident from $\tilde{P}(\tilde{H}, \tilde{K})$ derived from the CT model of the G morphology in Fig. 3(b), in which nearly all (just under 100%) of the measured points possess $\tilde{K} < 0$. Moreover, $\tilde{P}(\tilde{H}, \tilde{K})$ of the CT model exhibits two interesting characteristics. The first is that the measured data are distributed along $\tilde{H} = C_0\tilde{K}$, where the constant C_0 is related to the displacement used to construct the CT model in Fig. 1(b) from the Schoen G surface. Second, $\tilde{P}(\tilde{H}, \tilde{K})$ of the CT model exhibits two sharp maxima, in marked contrast to $\tilde{P}(\tilde{H}, \tilde{K})$ from the G morphology in the SIS copolymer, which possess a single broad maximum near $\tilde{K} = 0$. 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 σ_H provides a measure of packing frustration and nanostructural stability. Although predicted $\langle H \rangle$ and σ_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.

The unperturbed statistical end-to-end distance of the SIS triblock copolymer (R_0) is discerned from $R_0 = \sqrt{2l_S^2 N_S + l_I^2 N_I}$, where l_i and N_i ($i = S$ or I) denote the statistical segment length and block degree of polymerization, respectively. Since $l_S = 0.70$ nm and $l_I = 0.65$ nm, $R_0 \approx 22$ nm. The probability density measured for the G morphology in the SIS copolymer yields $\langle H \rangle = 0.034 \text{ nm}^{-1}$ and $\sigma_H = 0.042 \text{ nm}^{-1}$, 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 σ_H from the CT model of the G morphology are $0.86 R_0^{-1}$ and $0.51 R_0^{-1}$, respectively. According to 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, χN is a measure of the copolymer segregation power, wherein χ represents the Flory-Huggins interaction parameter and $N = 2N_S + N_I$. Since a microphase-ordered triblock copolymer can be envisaged as a diblock copolymer of half chain length, we treat the SIS copolymer examined here as its SI analog of molecular weight
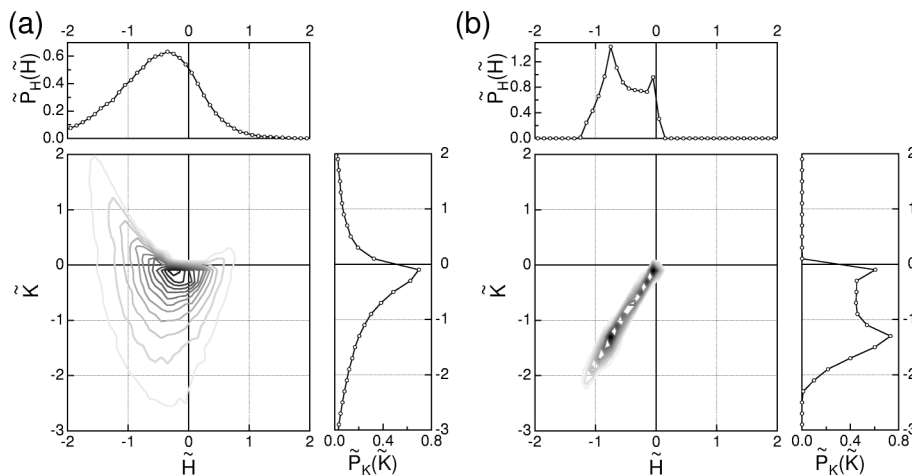
FIG. 3.   Contour map of the scaled joint probability density, $\tilde{P}(\tilde{H}, \tilde{K})$, and its marginal probability densities, $\tilde{P}_H(\tilde{H})$ and $\tilde{P}_K(\tilde{K})$, for (a) the G morphology of the SIS triblock copolymer and (b) the CT model of the G surface [Eq. (1)].

41 500, in which case χN 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 σ_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 χN (Matsen and Bates [11] predict that σ_H should increase with increasing χN). Further analysis of the factors influencing σ_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 (σ_H). According to recent SCFT predictions [10,11], σ_H is a measure of packing frustration and, hence, stability in complex nanostructures, in contrast to the CMC hypothesis (with $\sigma_H \approx 0$) [3]. Values of $\langle H \rangle$ and σ_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.

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