Notes

A Reevaluation of Bicontinuous Cubic Phases in Starblock Copolymers

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Recently, a new equilibrium microstructure, a second bicontinuous cubic morphology similar in many respects to the ordered bicontinuous double diamond (OBDD) structure, has been identified in a weakly segregated polystyrene−polyisoprene (SI) diblock copolymer melt.[1,2] X-ray diffraction indicated that the new cubic phase was more consistent with a microstructure based on the Schoen G or "gyroid" minimal surface[3] than with an analogous model of the OBDD morphology based on the Schwarz D minimal surface.[4] This new cubic phase was therefore entitled the "gyroid*", with the "*" symbol serving to distinguish the block copolymer morphology from the G minimal surface.

Model microstructures of the OBDD and gyroid* morphologies were developed to determine the characteristics of the new cubic phase.[1,2,7] In these models, the majority component material (e.g., polyisoprene) is confined to lie within a constant distance from the underlying minimal surfaces (Schwarz D for OBDD, Schoen G for gyroid*). The resulting majority component phase has constant thickness (CT), and so the resulting structures are designated CT-D (for OBDD) and CT-G (for gyroid*). The minority component material (e.g., polystyrene) forms two distinct, interpenetrating networks of variable thickness which are embedded in the majority component phase. In both structures, both minority and majority component domains are continuous and periodic along the three principal directions of the cubic unit cell. The space group of the CT-G structure is $Ia3d$, while that of the CT-D structure is $Pn3m$. Analogues of the gyroid* and OBDD geometries are commonly observed in lipid−water dispersions.[5] In addition to the above references, the gyroid* has also been reported in shear-oriented, weakly segregated polystyrene−poly(2-vinylpyridine), poly(ethylene-*co*-propylene)−poly(ethylethylene), and polyethylene−poly(ethylethylene) melts.[6]

In spite of the difference in symmetry between the two cubic phases, computer simulations of electron microscopy images indicate that many projections of the gyroid* resemble the corresponding projections of the OBDD morphology.[1,7] For example, when viewed along the [111] direction, both structures produce a "wagon wheel" image depending on the thickness of the projection. Although the results show slight differences between the structures at the high resolution levels used in this simulations, it is unclear that these differences would be detectable at the resolutions typically obtained in electron micrographs of block copolymers. Micrographs of the material in which the gyroid* was first identified[1,2] display projections which resemble those predicted for the CT-D model,[1,7] as well as those predicted for a slightly different OBDD model possessing an interface of constant mean curvature.[8,9] Additional calculations[7] indicate that constant thickness models of an as yet unobserved bicontinuous morphology (space group $Im3m$) based on the Schwarz P surface[4] also generate projections with features which resemble those in experimental micrographs. In summary, differentiation of bicontinuous structures via TEM alone is expected to be extremely difficult.

Fortunately, scattering techniques, such as small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS), are sensitive to differences in space group symmetry. To simplify the discussion, we consider the case in which an unidentified cubic morphology possesses either $Pn3m$ (OBDD) or $Ia3d$ (gyroid*) space group symmetry. Generalization of this argument to include all of the 36 cubic space groups is straightforward and is, in fact, essential to avoid overlooking other candidate microstructures equally consistent with limited experimental data. Interested readers are referred to ref 1 for a detailed examination of this issue.

Since the (hkl) diffraction reflections produced by the $Ia3d$ space group are a subset of those permitted for the $Pn3m$ space group,[10] unambiguous elimination of the $Ia3d$ space group from consideration is indicated by the observation of a reflection which is not permitted for that symmetry, while unambiguous elimination of the $Pn3m$ space group is not possible *through diffraction methods alone*. The use of a monodomain of the diffracting morphology[7] simplifies the identification of the indices (hkl) for each observed reflection without altering this conclusion. However, since the $Pn3m$ space group also possesses a large number of additional diffraction reflections which are not permitted for the $Ia3d$ group, if a sufficiently large number of low-order reflections that are expected for $Pn3m$ are absent from the experimental data, it is reasonable to conclude that the diffracting material does not possess $Pn3m$ symmetry. This statement may be made more quantitative by comparing expected diffraction peak intensities calculated from the model CT-G and CT-D structures with values obtained from experimental data, as was done in the original analysis of gyroid* scattering data.[1]

By combining results produced by two or more techniques, it is possible to circumvent this difficulty. If the

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Table 1. Characteristics of the Starblock Copolymers

sample	no. of arms	M_w of S block (g mol^{-1})	S vol %	refs
SI 6/30/10	6	10 000	27	8, 11
SI 18/30/10	18	10 000	27	8, 12

unit cell dimensions are known, the radial positions in reciprocal space of the diffraction reflections produced by the *Ia*3*d* and *Pn*3*m* space groups differ sufficiently that the space group of the diffracting structure can be identified. Once an independent estimate of these dimensions has been obtained—through careful TEM, for example—this information can be compared with that obtained from diffraction data to eliminate one of the space groups from consideration.

As part of an investigation concerning experimentally detectable differences between the two cubic morphologies, we have reexamined two polystyrene–polyisoprene starblock copolymer films previously identified as possessing the OBDD morphology.[8,11,12] The characteristics of the polymers appear in Table 1; details of the sample synthesis and film preparation appear in the references cited for each material. Recent examination of both materials via size exclusion chromatography (SEC) with tetrahydrofuran as the solvent indicated that some branching (approximately 4 wt %) of the polyisoprene blocks had occurred in the 18-arm starblock during storage; no degradation was detected in the 6-arm material. SEC traces taken after annealing the 6-arm material showed only a very slight amount (less than 1 wt %) of branching, demonstrating that the annealing protocol employed did not produce significant degradation of this material. Although SEC of the annealed 18-arm starblock revealed branching of the polyisoprene component (25 wt %) as well as some fragmentation of the starblock (less than 4 wt %), diffraction taken after annealing differed from that recorded after removal from storage only in the widths of the highest order Bragg reflections, indicating that the observed degradation did not appreciably influence the sample morphology.

Figure 1 shows diffraction obtained from the 18-arm starblock at room temperature after 11 days of annealing at 120 °C; see refs 1 and 2 for methods. Four sharp reflections appear at position ratios of $\sqrt{3}$, $\sqrt{4}$, $\sqrt{10}$, and $\sqrt{11}$. Figure 2 shows diffraction obtained from SI 6/30/10 after annealing for 3 days at 120 °C, followed by slow cooling to room temperature and *in situ* examination at 120 °C. As in the case of the 18-arm starblock, four reflections are observed at position ratios of $\sqrt{3}$, $\sqrt{4}$, $\sqrt{10}$, and $\sqrt{11}$. Identical diffraction was recorded from both materials after dissolving a small quantity of each starblock in toluene, adding 1 wt % antioxidant, and preparing new specimens using the methods employed in the previous studies.[11]

Previous examination of the 18-arm starblock utilized a Kratky SAXS camera. The raw (smeared) data[13] exhibited only three peaks, at manually determined reciprocal space positions of q = 0.024, 0.027, and 0.045 Å^{-1} (all values are uncertain to within 0.001 Å^{-1}). Desmearing shifted the second Bragg reflection to a position of 0.028 Å^{-1} and produced an additional reflection at 0.032 Å^{-1}.[8,13] The absence of the latter reflection from the raw data suggests that it is an artifact of the desmearing process. As the *desmeared* reflections appeared at *approximate* spacing ratios of $\sqrt{2}$, $\sqrt{3}$, $\sqrt{4}$, and $\sqrt{6}$, the material was assigned the *Pn*3*m* cubic space group. However, this assignment of spacing ratios

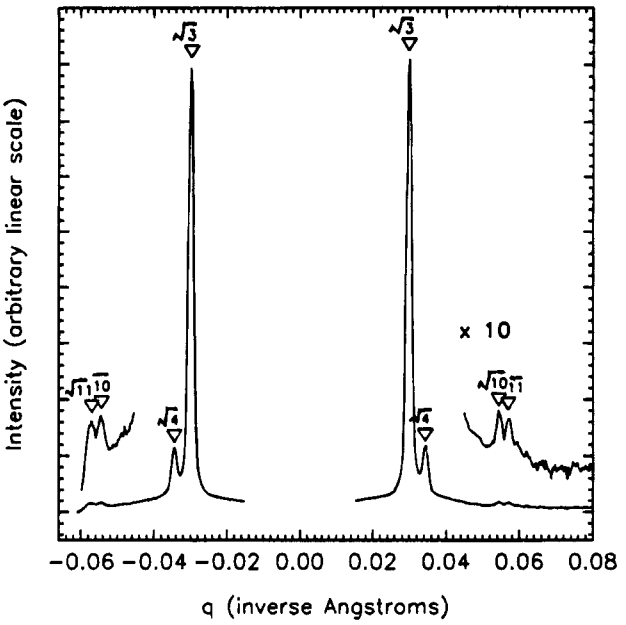

Figure 1. One-dimensional profile recorded from the 18-arm material after 11 days of annealing at 120 °C, followed by slow cooling to room temperature and subsequent examination at 20 °C. The plot shown was generated from the two-dimensional diffraction image by azimuthally averaging the scattered intensity over a fixed range of angles. Peak positions are indicated by inverted triangles. Four well-resolved peaks are visible, at spacing ratios of $\sqrt{3}$, $\sqrt{4}$, $\sqrt{10}$, and $\sqrt{11}$. The presence of the last two reflections indicates a cubic microstructure; the absence of the $\sqrt{2}$ reflection suggests that this material is not OBDD. Comparison of predicted peak intensities for model OBDD and gyroid* structures with the experimental data supports this conclusion. From the observed peak positions, the corresponding edge length for the gyroid* unit cell is 517 Å.

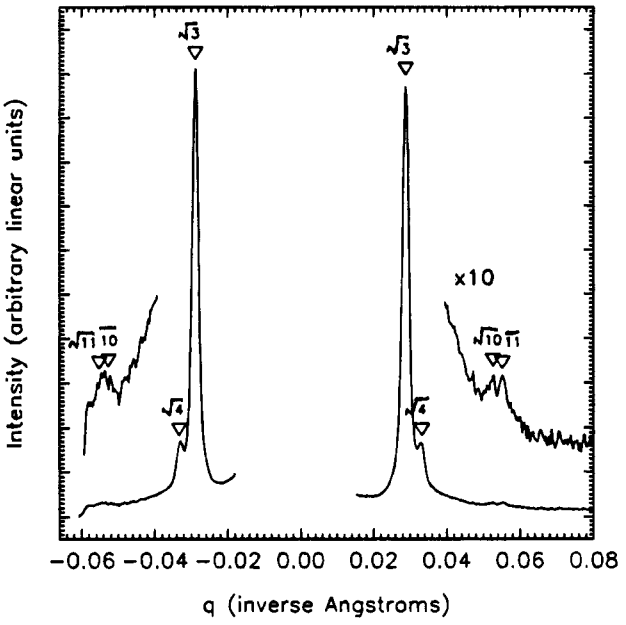

Figure 2. Scattering from the 6-arm starblock after 3 days of annealing at 120 °C, followed by slow cooling to room temperture and subsequent examination at 120 °C. As in Figure 1, four well-resolved peaks appear at spacing ratios of $\sqrt{3}$, $\sqrt{4}$, $\sqrt{10}$, and $\sqrt{11}$; arguments identical to those given for the 18-arm star indicate that this material possesses a gyroid* microstructure. The unit cell edge length for this cubic lattice is 540 Å at this temperature.

is not unique owing to the uncertainty present in the peak positions. The observed reflections (minus the

Table 2. Comparison of Predicted and Measured Peak Intensities for 27 vol % Minority Component

square of modulus[a]	corresponding reflections		predicted intensities[b]		measured intensities[c]	
	OBDD	gyroid*	OBDD	gyroid*	18-arm	6-arm
2	(110)	NA	3.180	NA[e]	NO[e]	NO
3	(111)	(211)	1.000[d]	1.000[d]	1.000[d]	1.000[d]
4	(200)	(220)	0.020	0.161	0.09 ± 0.02	0.13 ± 0.02
6	(211)	NA	<0.001	NA	NO	NO
7	NA	(321)	NA	<0.001	NO	NO
8	(220)	(400)	0.034	<0.001	NO	NO
9	(221)	NA	0.120	NA	NO	NO
10	(310)	(420)	0.042	0.008	0.009 ± 0.002	0.003 ± 0.001
11	(311)	(332)	0.011	0.029	0.011 ± 0.001	0.010 ± 0.005
12	(222)	(422)	0.006	0.016	NO	NO
13	NA	(431)	NA	0.018	NO	NO
14	(321)	NA	0.030	NA	NO	NO
15	NA	(521)	NA	0.001	NO	NO

[a] Modulus m is defined for reflection (hkl) as $h^2 + k^2 + l^2 = m^2$. Since all of the moduli for the observed reflections of the $Ia3d$ space group are divisible by $\sqrt{2}$, the experimentally observed reflections appear at the spacing ratios with respect to the position of the first order given in the table above. [b] Based on constant thickness models of the appropriate morphology developed from the D and G minimal surfaces. [c] For samples annealed at 120 °C as described in the text. [d] All intensities have been normalized by the intensity of the $\sqrt{3}$ reflection as this is the lowest diffraction order that appears in the experimental data. [e] NA = not allowed (predicted intensity < 10^{-19}), NO = not observed.

desmearing artifact) are also reasonably consistent with position ratios of $\sqrt{3}$, $\sqrt{4}$, and $\sqrt{10}$, a choice which agrees with the new scattering data presented here. Most probably, it is the improved X-ray apparatus (which does not require desmearing) and the greater degree of long-range order present in the newer samples which accounts for the identification of the correct peak spacing ratios and the detection of the $\sqrt{11}$ reflection in the new data.

As was discussed in the original identification of the gyroid* morphology,[1] reflections at reciprocal space position ratios of $\sqrt{3}$, $\sqrt{4}$, $\sqrt{10}$, and $\sqrt{11}$ are consistent with 12 of the 17 possible sets of permitted X-ray reflections for the cubic space groups (some of the 36 cubic space groups have identical sets of permitted reflections).[10] It is therefore impossible to *prove* that these starblock materials possess a particular cubic space group symmetry. However, most of these sets possess large numbers of additional reflections which are not observed. Although the absence of one or two reflections from experimental data may be produced by a minimum in the structure factor of the morphology at the appropriate location in reciprocal space, the absence of a large number of reflections strongly suggests that the diffracting structure does not possess the symmetry in question. The observed diffraction appears most consistent with the $Ia3d$ space group, whose first few reflections appear at position ratios of $\sqrt{3}$:$\sqrt{4}$:$\sqrt{7}$:$\sqrt{8}$:$\sqrt{10}$:$\sqrt{11}$: ....[15]

Peak intensities were determined from the experimental profiles by fitting the region about each peak to the sum of a parabolic background and a Gaussian line shape. After normalizing to the intensity of the $\sqrt{3}$ reflection, experimental intensities were compared to calculated values obtained from model CT-G and CT-D structures of the appropriate minority component volume fraction;[1] see Table 2. As the models are assumed to only approximate the actual experimental microstructure, differences between the measured and predicted intensities are expected and predicted to occur primarily in the weaker higher order reflections rather than in the stronger lower order ones. These differences reflect the degree to which the models agree with the experimental morphology at the spatial resolution characteristic of the corresponding Bragg reflection. It

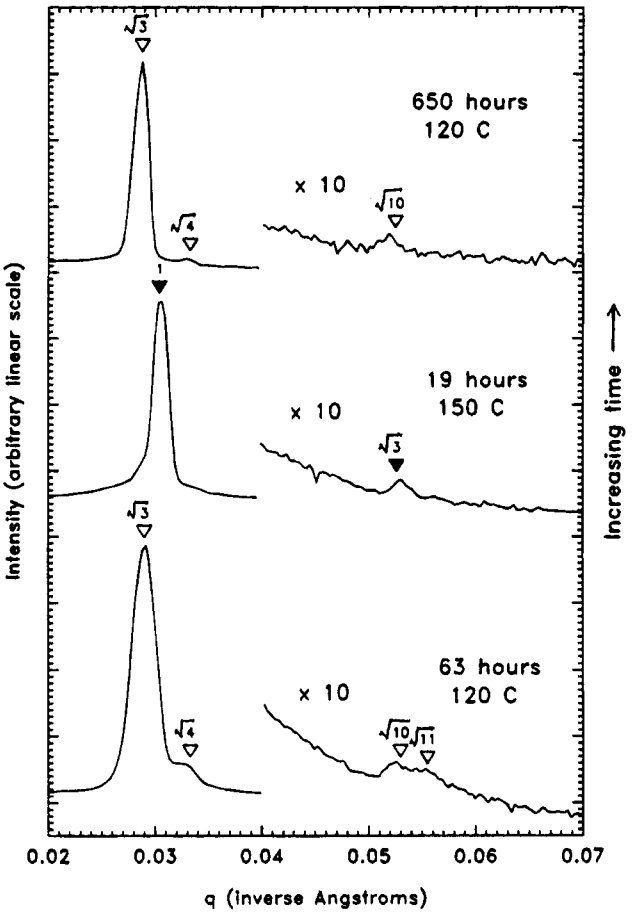

Figure 3. A thermoreversible transition from gyroid* to hexagonally packed cylinders in the 6-arm starblock system. Peak positions for the gyroid* morphology are indicated with hollow triangles; peak positions for the cylindrical phase are marked with filled triangles. After 63 h at 120 °C, diffraction produces two well-resolved peaks at spacing ratios of $\sqrt{3}$ and $\sqrt{4}$ and two poorly separated reflections at positions of $\sqrt{10}$ and $\sqrt{11}$. Heating the sample of 150 °C for 19.0 h induces the formation of the cylindrical morphology, as evidenced by the disappearance of the gyroid* signature and the appearance of new reflections at position ratios of 1 and $\sqrt{3}$. Subsequent annealing for 650 h at 120 °C returns the sample to the gyroid* morphology; the scattering profile shows two peaks at spacing ratios of $\sqrt{3}$ and $\sqrt{4}$.

is the general pattern of agreement between predicted and measured intensities (in which higher order reflections are deemphasized) which determines whether a model is accepted or rejected.

The experimental intensities agree reasonably well with the values predicted for the CT-G structure; the values of the $\sqrt{3}$, $\sqrt{4}$, and $\sqrt{10}$ reflections do not agree at all with values obtained for the model CT-D morphology. Also, the OBDD is expected to produce strong reflections at position ratios of $\sqrt{2}$, $\sqrt{8}$, and $\sqrt{9}$ which are not observed in the experimental data. We therefore conclude that, at 120 °C, the microstructure of this material is more consistent with the CT-G (gyroid*) morphology than with the CT-D (OBDD), contrary to earlier reports.[8,9,11,12] The revised structure of the 6-arm and 18-arm starblocks remains bicontinuous, but the two interwoven minority component networks are 3-coordinated rather than 4-coordinated.

After establishing the gyroid* morphology, subsequent annealing of the 6-arm material at a temperature of 150 °C causes a morphological transition to an array of hexagonally packed cylinders characterized by diffraction reflections at position ratios of 1, $\sqrt{3}$, and $\sqrt{7}$; see Figure 3. At this point, additional annealing at the original temperature of 120 °C produces the return of the gyroid* morphology, demonstrating that this microstructure is in equilibrium over a limited temperature range in the 6-arm starblock. Additional evidence in support of this claim comes from antioxidant-containing films which were first annealed for 30 min at 175 °C to produce the disordered phase and then immediately switched to a different vacuum oven for 30 min at a lower temperature to induce the formation of a microphase-separated morphology. After quenching in liquid nitrogen, samples were examined via SAXS at room temperature. Films quenched after annealing at 175 °C displayed a single broad scattering maximum characteristic of the disordered state, while samples quenched after subsequent annealing at 135 and 160 °C produced Bragg reflections at positions characteristic of the gyroid* and cylindrical morphologies, respectively. Unfortunately, analogous transformations were not observed in the 18-arm material, and so we are unable to say whether the gyroid* is a true equilibrium morphology in the that polymer or is merely a long-lived nonequilibrium state.

Since it is unlikely that any morphological transitions have taken place in these starblocks since their initial examination 10 years ago, it appears that the original identification of the OBDD morphology in these systems was incorrect. Based in part on these results, we believe it is possible that materials previously identified as OBDD may in fact possess microstructures more consistent with the gyroid* morphology. This conjecture is especially relevant for systems in which the OBDD was identified through electron microscopy alone.

The question then arises as to whether the OBDD morphology has been shown to exist in any block copolymer system. We are currently reevaluating samples previously identified as OBDD with the aim of identifying a polymer with that morphology, and we urge other investigators to consider a similar reexamination of their cubic phase materials.

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