Notes

Bicontinuous Morphologies in Homologous Multiblock Copolymers and Their Homopolymer Blends

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Received May 18, 1998
Revised Manuscript Received August 17, 1998

Due to their ability to spontaneously order into nanometer-sized microstructures[1,2] and their versatility in a variety of established[3] and emerging[4,5] commercial applications, block copolymers remain the subject of intense research interest. The "classical" morphologies formed in AB diblock copolymers include alternating lamellae of A and B, A(B) cylinders arranged on a hexagonal lattice in a B(A) matrix, or dispersed A(B) spheres arranged on a body-centered cubic lattice in a B(A) matrix. Detailed studies of neat (unmodified) copolymers,[6−9] as well as their blends with either a parent homopolymer[10,11] or a second copolymer of differing composition,[12−14] have also demonstrated that cubic bicontinuous morphologies exist over relatively narrow composition windows between the lamellar and cylindrical microphases. Two such morphologies are the perforated lamellar (PL)[7] and gyroid (G)[8,9,13,14] microstructures. While the PL morphology has been found[15] to be a surprisingly long-lived metastable microstructure, the G morphology (exhibiting $Ia\bar{3}d$ symmetry) is believed to be thermodynamically stable on the basis of thermally reversible transition behavior and complementary theoretical analysis.[16−21]

This phase behavior has traditionally been explained as arising from competition between enthalpic considerations, which drive local separation of the mutually immiscible blocks, and entropic terms, which favor a well-mixed morphology in which the blocks exhibit random coil conformations. In the microphase-separated state, disparities in the preferred coil size of the A and B blocks generate spontaneous curvature at the A−B interface. This is opposed by the loss of entropy associated with stretching the A and B chains to fill their microdomains with a constant density of segments. Recent theoretical calculations indicate that both the average value of this stretching and the variation about this average in nonlamellar structures govern the phase behavior of the copolymer system. The latter contribution, referred[22] to as "packing frustration" in analogy with similar concepts in liquid crystal and surfactant systems,[23] dominates the stability of the bicontinuous morphologies.

In multiblock materials, another consideration that may affect mesophase stability is the degree to which the blocks of the copolymer are constrained. Linear multiblock copolymers, for instance, consist of at least one midblock that is tethered at both ends. Each midblock of such molecules may form either a loop (both ends locate at the same interface) or a bridge (each end locates at an adjacent interface). The presence of midblocks along the copolymer backbone affects the molecular conformations,[24−26] equilibrium microstructure,[27−29] mechanical properties,[27,30] and blending efficacy[30,31] of such copolymers. According to self-consistent field considerations, the G morphology is predicted[25] to develop as an equilibrium morphology in linear multiblock copolymers. Recent efforts by Laurer et al.[32] and Avgeropoulos et al.[33] have confirmed that the G morphology is stable in neat ABA triblock copolymers. It has also been observed[29] in *non*linear multiblock copolymers. In the present work, we investigate a homologous series of block copolymers of increasing architectural complexity—an AB diblock, an ABA triblock and an $(AB)_2$ tetrablock—as well as their blends with a parent homopolymer, using transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS).

Three block copolymers—a poly(styrene-*b*-isoprene) (SI) diblock, a poly(styrene-*b*-isoprene-*b*-styrene) (SIS) triblock, and a poly(styrene-*b*-isoprene-*b*-styrene-*b*-isoprene) $(SI)_2$ tetrablock—were synthesized via sequential living anionic polymerization in cyclohexane at 60 °C. The initiator in each case was *sec*-butyllithium. The composition (in terms of the styrene mass fraction, w_S) and number-average molecular weight ($\bar{M}_n$) of each copolymer were measured by ^{1}H NMR and GPC, respectively.[27] These values, as well as copolymer designations, are compiled in Table 1.[34] The molar mass of each styrene block in each copolymer was held constant at 15 000 g/mol. A homopolyisoprene (hPI) with $\bar{M}_n$ = 15 000, used in the production of copolymer/homopolymer blends, was also synthesized and characterized in similar fashion. All polydispersities were less than 1.09.

Blends of each copolymer with the hPI were prepared by dissolving predetermined masses of each component in 4% (w/v) toluene solutions, which were cast into Teflon molds following polymer dissolution. Upon slow solvent removal over the course of 3 weeks, films

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10.1021/ma9807872 CCC: $15.00

Table 1. Characteristics of the Block Copolymer/ Homopolymer Blends Examined in This Work[a]

copolymer	sample designation	Φ_S[b]	morphology
SI diblock ($w_S = 0.32$;[c] $\bar{M}_n = 47\ 000$;[d] $R = 0.47$)	SI28 (neat)	0.28	gyroid
	SI27	0.27	gyroid
SIS triblock ($w_S = 0.36$;[c] $\bar{M}_n = 83\ 000$;[d] $R = 0.28$)	SIS32 (neat)	0.32	gyroid
	SIS31	0.31	S-cylindrical
	SIS29	0.29	S-cylindrical
	SIS27	0.27	S-cylindrical
$(SI)_2$ tetrablock ($w_S = 0.38$;[c] $\bar{M}_n = 80\ 000$;[d] $R = 0.60$)	$(SI)_2$34 (neat)	0.34	lamellar
	$(SI)_2$33	0.33	lamellar
	$(SI)_2$31	0.31	bicontinuous
	$(SI)_2$29	0.29	S-cylindrical
	$(SI)_2$27	0.27	S-cylindrical

[a] *R* denotes the homopolymer−block molecular weight ratio (M_{hPI}/M_I), where $M_{hPI} = 15\ 000$. [b] Calculated using mass densities evaluated[36,37] at 100 °C. [c] Discerned from ^1H NMR. [d] Measured from GPC.

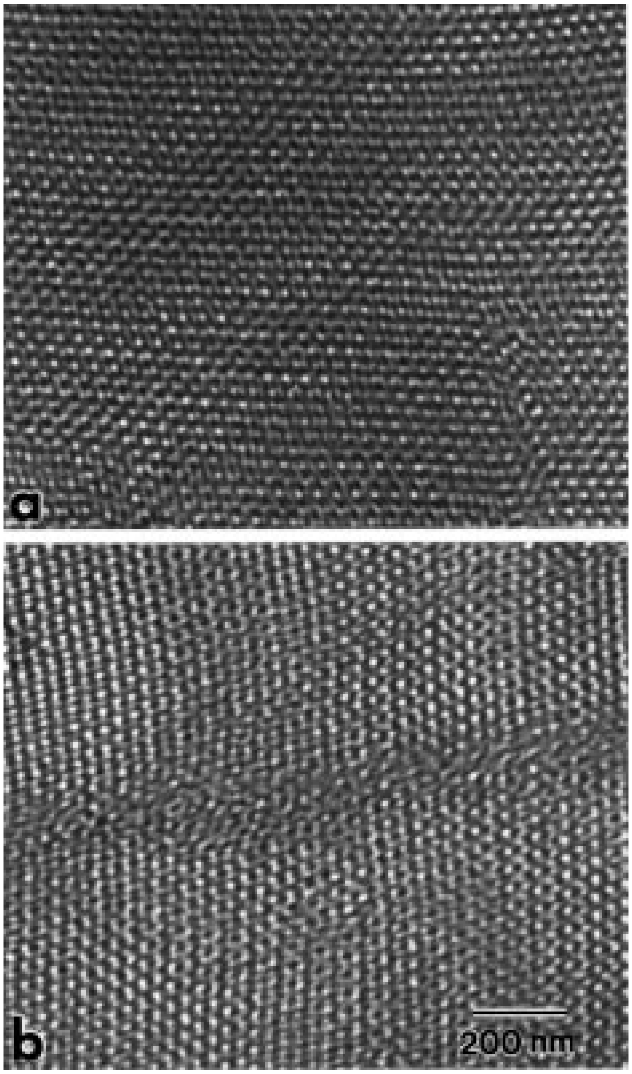

Figure 1. Transmission electron micrographs of (a) the neat SI28 diblock copolymer and (b) the SI27 blend. A bicontinuous morphology is apparent in both cases. In these images, as well as those presented throughout this work, the isoprene-rich microdomains appear electron opaque (dark) due to selective OsO_4 staining. Specimen designations are provided in Table 1.

measuring ca. 2 mm thick were dried at 90 °C for 4 h under vacuum to remove residual solvent and promote microstructural refinement. [According to thermal calorimetry, the upper (styrenic) glass transition temperature (T_g) of the neat copolymers ranged from 85 to 88 °C.] The films were cross-sectioned at −100 °C in a Reichert-Jung Ultracut-S cryoultramicrotome to produce electron-transparent specimens (suitable for TEM), which were subsequently stained with the vapor of 2% OsO_4(aq) for 90 min. Specimens for SAXS were uniformly cut from the bulk films and subjected to Cu Kα radiation from a Rigaku Ru-200BH rotating anode. The anode focal spot of the instrument,[35] which was equipped with Franks mirror optics and a CCD-based area detector, was foreshortened to 0.2 × 0.2 mm^2. Intensity versus scattering vector (q) patterns were generated by azimuthally integrating two-dimensional scattering patterns, corrected for detector response, along an arc ±15° from the horizontal axis.

Blend compositions are expressed in terms of the styrene volume fraction, Φ_S, which is discerned from the mass fraction of each blend in conjunction with the densities of polystyrene and polyisoprene measured at 100 °C (1.00 and 0.84 g/cm^3, respectively[36,37]). The compositions of the blends prepared during the course of this study, as well as their designations, are listed in Table 1. Micrographs obtained from the neat diblock copolymer (SI28) and its blend with hPI (SI27) are displayed in Figure 1. It is evident from these images that the morphology in each material can best be described as bicontinuous. Providing that sufficient long-range order exists, identification of the these morphologies is most reliably achieved through the use of SAXS.[9,32] Figure 2 shows SAXS profiles acquired from the SI27 blend and the neat SIS copolymer (SIS32) at ambient temperature. The markers identify the square of peak position ratios (moduli) expected for morphologies exhibiting cubic symmetry. Scattering peaks located at a spacing ratio of $\sqrt{3}$:$\sqrt{4}$ in each material are characteristic of the G morphology. Additional confirmation of the identity of the morphology in the SIS32 copolymer has been accomplished through the use of transmission electron microtomography.[13,32] For neat isoprene-rich SI diblock copolymers, the Φ_S range over which the G morphology has been observed[8] is 0.31−0.35. Our data suggest that the composition range over which this morphology is stable may be slightly broader than was previously realized.

Micrographs obtained from the three SIS32/hPI blends investigated here are presented in Figure 3 and indicate that addition of hPI to the SIS32 copolymer (presented in detail elsewhere[32]) results in disappearance of the G morphology and formation of a dispersed morphology of styrene-rich cylinders. Figure 3 shows an image of the SIS31 blend, which appears qualitatively similar to the SIS27 blend (data not shown). The ratio of the molar mass of an added parent homopolymer to that of the compatible block of a block copolymer (R) constitutes an important consideration in ensuring homopolymer solubility[30] and morphology development[10] in copolymer/homopolymer blends and should ideally be less than unity. In the SIS31, SIS29, and SIS27 blends, $R = 0.28$. Since, however, the midblocks must either bridge or loop, the mass of the isoprene midblock in the triblock copolymer is effectively halved, resulting in an *effective* R value of 0.56. Although the appearance of a cylindrical morphology in the SIS31 blend suggests that the G → C transition lies between 31 and 32 vol % styrene in the neat triblock, consistent with prior findings in SI diblock copolymers,[8] the stability of the G morphology may also be adversely affected by localization of the isoprene homopolymer in highly frustrated regions of

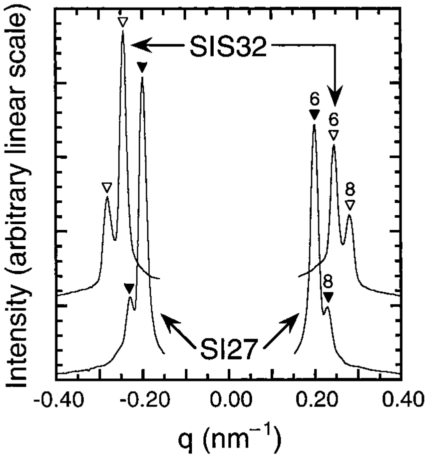

Figure 2. Small-angle X-ray scattering profiles obtained from the SI27 blend (Figure 1b) and the SIS32 copolymer. The squared peak position ratios (moduli) for the first two orders of the G morphology are shown as (▼) for the SI27 blend and (▽) for the SIS32 blend. In both cases, the scattering peaks exhibit a spacing ratio of $\sqrt{3}:\sqrt{4}$, which is consistent with the G morphology.[9]

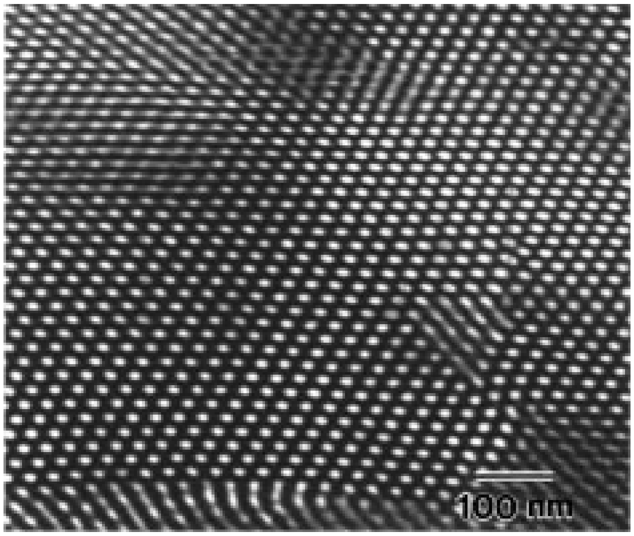

Figure 3. TEM micrograph of the SIS31 copolymer/hPI blend revealing the existence of dispersed styrene-rich cylinders in an isoprene matrix. This morphology persists from 31 to 27 vol % styrene. The neat SIS32 copolymer, characterized in detail elsewhere,[32] possesses the G morphology.

the majority component (polyisoprene) microdomain. Such localization is also predicted[38] to influence midblock conformations by reducing the fraction of bridged midblocks relative to looped midblocks in triblock copolymer/homopolymer blends.

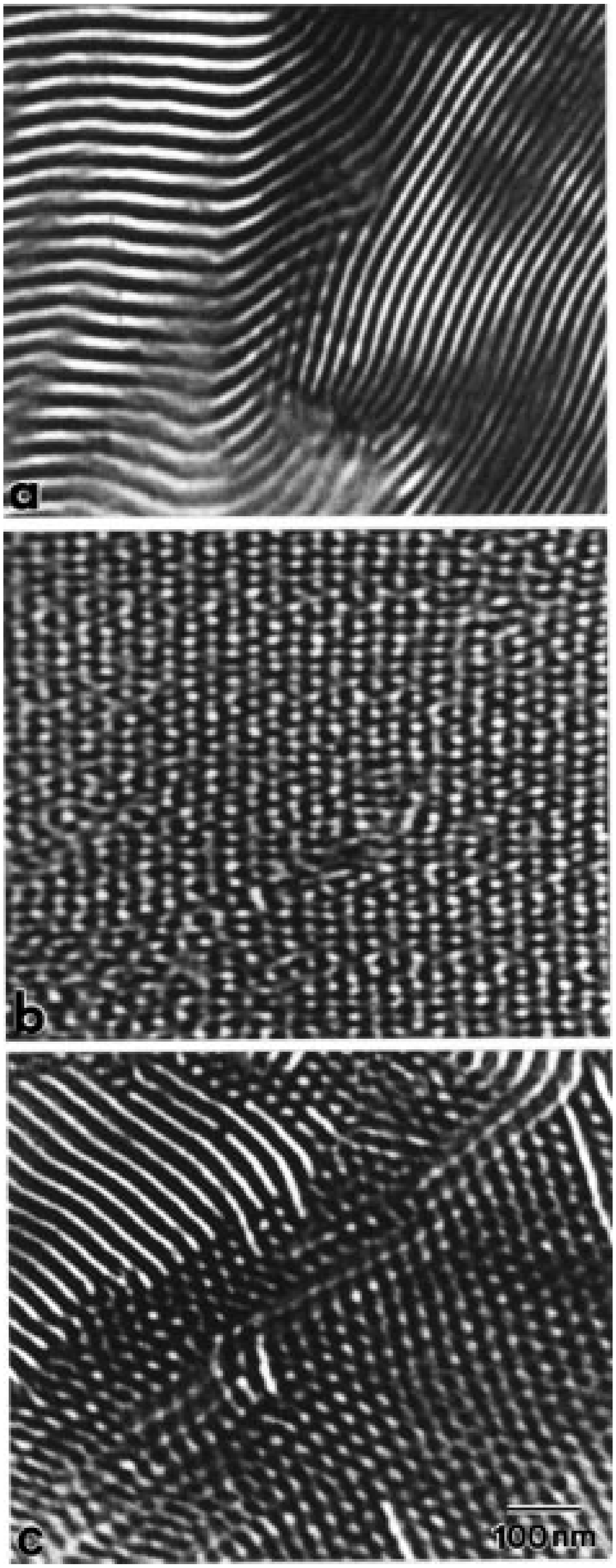

Figure 4. Series of TEM micrographs acquired from the (SI)$_2$34 tetrablock copolymer/hPI blends. An image of the neat (SI)$_2$34 copolymer is presented in (a) and shows that the copolymer exhibits the lamellar morphology. The (SI)$_2$31 blend, however, is seen in (b) to exhibit a bicontinuous morphology (which has not yet been conclusively identified due to insufficient long-range ordering). In (c), a poorly organized cylindrical morphology is evident in the (SI)$_2$29 blend.

In the (SI)$_2$34/hPI blends, this issue is complicated by the presence of an isoprene endblock (tail conformation) and an isoprene midblock (loop/bridge conformations) in the copolymer, for which the *effective* values of *R* are 0.60 and 1.20, respectively, due to the differences in block conformation discussed above. The (SI)$_2$34 tetrablock copolymer and the (SI)$_2$33 blend both exhibit the lamellar morphology, which is seen in the micrograph provided in Figure 4a. Upon further addition of hPI, a bicontinuous morphology appears, as in the (SI)$_2$31 blend shown in Figure 4b. Note that this corresponds to a composition virtually identical to that of the neat SIS32 triblock. Attempts to identify this morphology by SAXS are impeded by the presence of poorly resolved scattering maxima, indicating a lack of long-range order. This is possibly a result of each copolymer molecule possessing two endblocks and midblocks of equal molecular weight. Micrographs of the $(SI)_2 29$ and $(SI)_2 27$ blends, such as the one displayed in Figure 4c, reveal the existence of a poorly ordered cylindrical morphology. Thus, the bicontinuous morphology evident in Figure 4b appears to be stable over a very limited composition range. Morphological results obtained during the course of this study are summarized in Table 1.

According to these experimental observations, linear multiblock copolymers and their blends with a homopolymer are capable of microphase-ordering into bicontinuous morphologies, which have been identified as the G morphology in the diblock and triblock copolymer systems. Moreover, the composition range over which such morphologies are stable depends on the molecular architecture (diblock vs triblock vs tetrablock), suggesting that mesophase stability is sensitive to midblock conformation in linear multiblock copolymers.[39] Addition of matrix homopolymer serves to stabilize a bicontinuous morphology (such as the G) with respect to composition in diblock copolymers, but apparently not in multiblock copolymers. Since it is reasonable to assume that (i) the degree of packing frustration in the G morphology is comparable in diblock and multiblock systems and (ii) added homopolymer will localize first in highly frustrated regions of the unit cell to lower the system free energy,[40] an architecture-induced difference in mesophase stability may reflect different swelling properties of the tails, loops, and bridges present in multiblock materials. If this is the case, then the results presented here demonstrate that control over morphology in linear multiblock copolymers may not be as readily achieved through homopolymer blending as it is in diblock copolymers.

Acknowledgment. Support for this study was kindly provided by the Shell Development Co.

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MA9807872