Dependence of the OBDD Morphology on Diblock Copolymer Molecular Weight in Copolymer/Homopolymer Blends

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ABSTRACT: The ordered bicontinuous double-diamond (OBDD) morphology is known to depend strongly on the bulk composition of microphase-separated diblock copolymers and blends composed of a copolymer and a parent homopolymer. An additional factor that must be considered in blends is the homopolymer molecular weight relative to that of the corresponding block in the copolymer. In this work, transmission electron microscopy is employed to identify the morphologies which develop in a series of such blends, each composed of a symmetric poly(styrene-*b*-isoprene) (SI) diblock copolymer and a polystyrene homopolymer. The copolymers investigated here range in total molecular weight (M) from 20 000 to 180 000, and the corresponding homopolymers each possess a molecular weight equal to approximately $M/4$. While the OBDD morphology is generated in most of these blends, additional morphologies (e.g., lamellar catenoid, cylindrical, and disordered) are also observed and are found to depend on the magnitude of M. An experimental morphology diagram is presented for copolymer/homopolymer blends along the isopleth corresponding to a bulk composition of 66 vol % styrene.

Introduction

Factors responsible for producing the ordered bicontinuous double-diamond (OBDD) morphology in microphase-separated linear diblock and starblock copolymers have recently received considerable attention. This morphology, possessing a *Pn3m* space group, is the first to be reported in which both microphases appear to be bicontinuous and three-dimensionally periodic[1,2] and is a relatively new addition to the Molau[3] phase diagram of block copolymers. It has been observed with transmission electron microscopy (TEM) in strongly segregated poly(styrene-*b*-isoprene) (SI) starblock copolymers by Thomas and co-workers[4,5] and in neat SI diblock copolymers by Hasegawa et al.,[6] who refer to it as the *tetrapod* morphology. In both cases, however, the composition range over which the styrene-rich OBDD morphology occurs in these pure materials is relatively narrow, approximately 62–66 vol % styrene.

The geometrical properties of this morphology have fascinated experimentalists and theoreticians alike. Current efforts to elucidate the characteristics of OBDD microdomains and their interphase boundaries draw upon the wealth of structural data available in the field of small-molecule surfactants.[2] Thomas and co-workers[7] have been pioneers in this endeavor, modeling this and other related morphologies of constant mean curvature. Wang and Safran[8] have sought to predict the thermodynamic stability of the OBDD morphology, relative to the spherical, cylindrical, lamellar, and single-diamond morphologies, by considering the curvature elastic properties of neat diblock copolymers.

Difficulties arising from the narrow composition range required to generate the OBDD morphology in pure block copolymers have, however, hindered the study of this microstructure. Recent efforts by Winey et al.[9,10] focused on blends of an SI copolymer with homopolystyrene (hPS) as a simplified means of obtaining the OBDD morphology without such rigorous control over copolymer composition. Employing a single SI copolymer composed of 55 wt % styrene and possessing a nominal molecular weight of 49 000, they successfully demonstrated that the molecular weight of added polystyrene homopolymer (M_{hPS}) is another prime consideration in producing the OBDD morphology, as M_{hPS} must be less than M_S, the styrene block length of the copolymer. They report finding this microstructure in blends in which the ratios of M_{hPS} to M_S are approximately 0.2 and 0.5 only when the overall composition lies within the range 65–67 vol % styrene (in good agreement with that observed for neat block copolymers).

Separate studies focusing on the response of the diblock lamellar morphology to added polystyrene homopolymers of different molecular weights have revealed that hPS/S intradomain mixing is highly nonideal.[11,12] Evidence obtained with small-angle X-ray scattering (SAXS) indicates that an increase in M_{hPS} results in localization of the homopolymer near the center of swollen S-microdomains, whereas low molecular weight homopolymers are more evenly distributed over entire S-microdomain cores. This observed behavior has been explained in terms of homopolymer chain packing/penetration considerations which arise due to a positive entropy of mixing under athermal conditions.[13,14]

The objective of the present work is to probe the dependence of the styrene-rich OBDD morphology on the molecular weight of SI diblock copolymers in a series of copolymer/homopolymer (SI/hPS) blends. To maintain a relatively constant distribution of homopolymer within the styrene microdomains, the hPS in each blend satisfies the criterion that $0.2 \leq M_{hPs}/M_S \leq 0.7$, with many blends possessing $M_{hPS}/M_S \approx 0.5$.

Experimental Section

Materials. A series of neat poly(styrene-*b*-isoprene) diblock copolymers possessing 50 wt % styrene was synthesized via anionic polymerization in pure cyclohexane at 60 °C. The initiator employed was *sec*-butyllithium. The molecular weights of the resultant copolymers ranged from 20 000 to 180 000, as determined by gel permeation chromatography (GPC) with Waters ultrastyragel columns of 50-, 100-, 1000-, and 10000-nm porosities. Typical polydispersity indices were less than 1.04. Compositions were verified by ^{1}H NMR performed on a General Electric QE-300 spectrometer at 300 MHz. A series of polystyrene homopolymers of different molecular weights was also synthesized. Each of the diblock copolymers employed here is referred to as SI*M*, where M corresponds to $^1/_{1000}$ of the copolymer

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Table I
Molecular Characteristics of the SI Diblock Copolymers and hPS Homopolymers Employed in the Blends Investigated Here

designation	w_S[a]	$M_n \times 10^{-3}$ [b]	$M_S \times 10^{-3}$	N	T_g[c] (°C)	$\chi_{SI}N$[d]
SI20	0.50	20.0	10.0	243	82.5	28.0
SI30	0.50	30.0	15.0	365	87.7	40.9
SI40	0.50	40.0	20.0	486	90.5	53.8
SI49[e]	0.49	49.0	27.0	583	92.8	63.8
SI60	0.50	60.0	30.0	729	93.5	79.5
SI80	0.50	80.0	40.0	973	95.0	105
SI120	0.50	120.0	60.0	1459	96.6	157
SI180	0.50	180.0	90.0	2189	97.7	234
hPS3	1.00	3.0	3.0	29	58.1	
hPS7	1.00	6.5	6.5	63	75.3	
hPS10	1.00	9.5	9.5	91	81.8	
hPS15	1.00	15.0	15.0	144	87.7	
hPS20	1.00	20.0	20.0	192	90.5	
hPS30	1.00	30.0	30.0	288	93.5	
hPS42	1.00	42.0	42.0	404	95.3	
hPS45	1.00	45.0	45.0	433	95.6	

[a] Determined from ^{1}H NMR. [b] Obtained from GPC. [c] Calculated for polystyrene from eqs 2 and 3. [d] Evaluated[16] at the T_g of the styrene block. [e] Investigated by Winey et al. in refs 9 and 10.

molecular weight rounded to the nearest integral value. Likewise, all of the homopolymers are denoted hPS*M*. The designations and molecular characteristics of these materials are tabulated in Table I.

Sample Preparation. The molecular weight of hPS in each homopolymer/copolymer blend was selected so that it was approximately $0.5M_S$ for a given SI copolymer, unless otherwise specified. Films of the copolymers and powders of the homopolymers were combined in 5% (w/v) toluene solutions to yield blends composed of 66 vol % styrene, as determined from

$$\omega_{SI} = \frac{\rho_I(1-\Phi_S)}{(1-w_S)[\rho_I + \Phi_S(\rho_S - \rho_I)]} \qquad (1)$$

where ω_{SI} is the weight fraction of copolymer in the blend (=1 − ω_{hPS}), w_S is the weight fraction of styrene in the copolymer (=0.50 in this series), and Φ_S is the desired bulk volume fraction of styrene in the blend (=0.66). The mass densities of polystyrene and polyisoprene are given by ρ_S (1.05 g/cm^3) and ρ_I (0.90–0.91 g/cm^3), respectively. Solutions were cast in Teflon molds and permitted to dry slowly over the course of up to 3 weeks in a toluene-rich environment. After this time, the resultant films, measuring approximately 2–3 mm thick, were cycled between 50 and 70 °C for 1 day in air and then heated to 90–100 °C under low vacuum (ca. 10^{-3} Torr) to remove residual solvent. They were encapsulated in glass tubes and cycled between argon and a 10^{-5}-Torr vacuum three times. The asemblies were sealed with an argon atmosphere at just below ambient pressure and were subsequently heated to ca. 165 °C for 1 week and then allowed to cool slowly to ambient temperature. During this processing, there was little evidence of oxidative degradation, as indicated by color change.

Sections measuring about 70 nm thick for TEM were obtained by cryosectioning the films normal to the film surface at −100 °C with a Diatome 35° cryodiamond knife on a Reichert-Jung FC-4E cryoultramicrotome. The sections were cut from the center of the bulk films, to avoid complicating surface effects (such as segregation of low molecular weight components[15]). The unsaturated isoprene microdomains were preferentially stained for 90 min with OsO_4 vapor from a 2% aqueous solution at 25 °C. Micrographs were obtained with a Zeiss EM902 energy-filtered electron microscope operated at 80 keV and ΔE = 50 eV. The width of the energy slit was 30 eV.

Results and Discussion

All of the neat diblock copolymers synthesized here exhibit lamellar morphologies which remain ordered and nearly defect-free over relatively large areas (ca. several square micrometers). A pair of images obtained from the lowest (SI20, Figure 1a) and one of the highest (SI120, Figure 1b) molecular weight copolymers used in the blends is presented in Figure 1 to illustrate this point. Values of χ_{SI}, the Flory–Huggins interaction parameter between styrene and isoprene monomers, can be estimated[16] from $71.4T^{-1}$–0.0857 for each copolymer. The temperature above ambient at which χ_{SI} is evaluated is the glass transition temperature (T_g) of the styrene block, which is given by the Fox–Flory[17] equation when $N_S \geq 100$, where N_S is the degree of polymerization of the styrene block. For shorter blocks, Lu and Jiang[18] suggest the expression

$$T_g = \frac{2N_S T_g^{\infty}}{2N_S + C_\infty f(y)} \qquad (2)$$

where T_g^{∞} = 373 K, $C_\infty \approx 10.68$, and, assuming a wormlike chain, $f(y)$ is given by

$$f(y) = 1 - 3y + 6y^2 - 6y^3(1 - e^{-1/y}) \qquad (3)$$

Here, $y = C_\infty/[4N_S \sin^2(\theta/2)]$ for a vinyl polymer and θ is the angle formed by the C–C bonds along the backbone (=109.5°). Calculated values of the polystyrene T_g for each copolymer (neglecting interphase mixing) and each homopolymer, obtained from eqs 2 and 3, are in Table I.

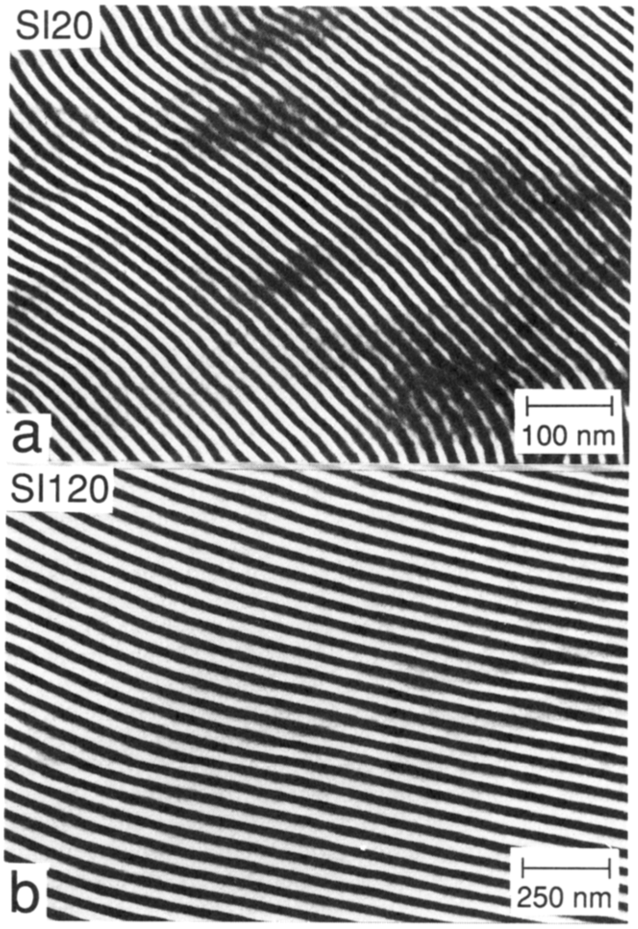

Figure 1. Transmission electron micrographs of low (a) and high (b) molecular weight SI diblock copolymers used in this study (SI20 and SI120, respectively). Well-ordered lamellar morphologies are observed in each, as well as in all of the other copolymers (not shown), thereby demonstrating that the copolymers employed in the blends are safely removed from the order–disorder transition (ODT) and the weak-segregation limit. In all of the micrographs presented here, the isoprene-rich microdomains are stained with OsO_4 to enhance contrast under the electron beam.

A measure of the chemical incompatibility exhibited by each copolymer is ascertained from $\chi_{SI}N$, where N is the total number of monomer units per copolymer. Values of N, along with estimates of $\chi_{SI}(T_g)N$, are also provided in

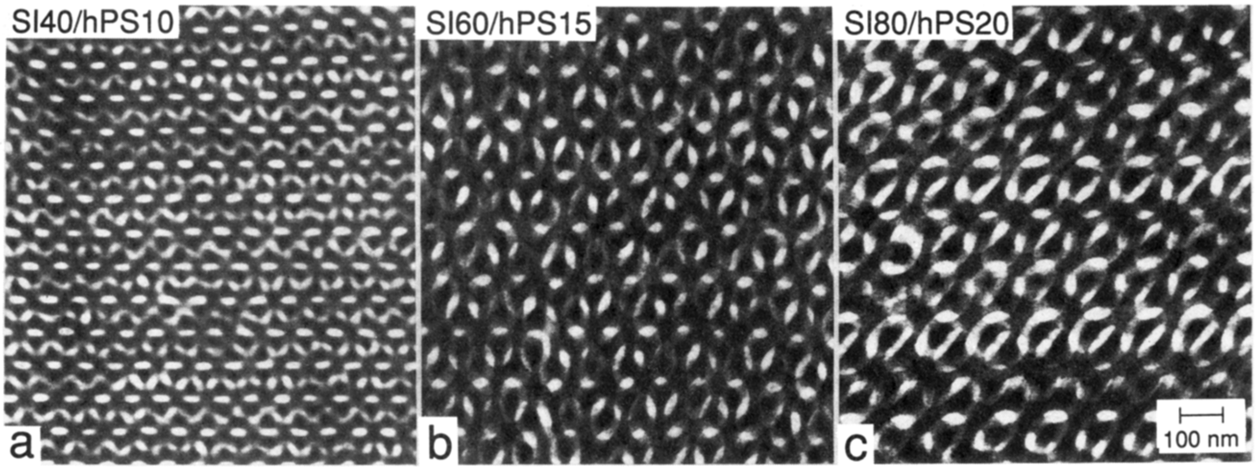

Figure 2. Energy-filtered images of the (a) SI40/hPS10, (b) SI60/hPS15, and (c) SI80/hPS20 blends, in which $\Phi_S = 0.66$ and $M_{hPS} \approx 0.5M_S$. In all three cases, the ordered bicontinuous double-diamond (OBDD) morphology is clearly evident.

Table I. According to the mean-field phase diagram predicted by Leibler,[19] all of these SI copolymers appear to be safely removed from the order–disorder transition (ODT), which occurs near $\chi_{SI}N \approx 10.5$ for symmetric copolymers of infinite N. Even when critical fluctuations[20] are considered (to account for copolymers of finite N), the materials investigated here are all expected to exhibit ordered lamellar morphologies. [According to the recent theoretical formalism developed by Melenkevitz and Muthukumar,[21] only SI120 and SI180 truly reside in the strong segregation limit ($\chi_{SI}N > 100$).] Also included in Table I are the characteristics of the copolymers used by Winey et al.[9,10] to produce the OBDD morphology in their blends ($T_g \approx 93$ °C and $\chi_{SI}N \approx 64$ from the above expressions). Their copolymer, here denoted SI49, comes very close in both chain length and composition to serving as an intermediate between SI40 and SI60.

If the added PS homopolymers are completely solubilized in the cores of the styrene lamellae (with negligible enthalpic interaction at the microdomain interphases), then the spatial distribution of hPS is expected to be comparable in each of the following blends. We begin with blends similar in composition and copolymer chain length to the one (SI49/hPS14) previously shown[9,10] to exhibit the OBDD morphology. Figure 2 is a set of micrographs obtained from the SI40/hPS10 (Figure 2a), SI60/hPS15 (Figure 2b), and SI80/hPS20 blends (Figure 2c), each clearly illustrating the OBDD morphology. As M increases, Figure 2 reveals that the size of the OBDD microdomains also increases. While Hasegawa et al.[6] have demonstrated that both the microdomain periodicity and channel radius of pure SI copolymers exhibiting the OBDD morphology scale reasonably well as $M^{2/3}$ in the strong segregation limit, no such scaling relationships are provided here due to the complicating factors discussed later. The set of micrographs provided in Figure 2 indicates that the OBDD morphology is produced in copolymer/homopolymer blends when $M_{hPS}/M_S \approx 0.5$ and the copolymer possesses an intermediate molecular weight (i.e., <100 000). Micrographs similar to the ones shown in Figure 2 are obtained when two diblock copolymers of identical molecular weights (80 000) but different compositions (50 and 85 wt % styrene) are blended together at a composition of about 61 vol % styrene.[22] It is of interest to note here that, upon annealing at 165 °C, the thick styrene-rich films possessing the OBDD morphology tend to exhibit a rough surface, as discerned by both light reflectance and surface replication.[22] These films, at the same bulk composition, are also more brittle than films possessing either lamellae or cylinders.

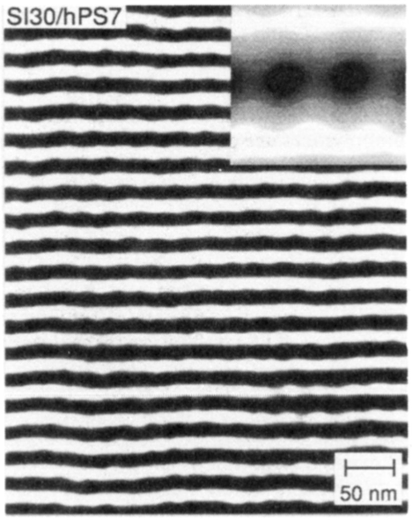

Figure 3. Electron micrograph of the low molecular weight SI30/hPS7 blend, displaying an interconnected lamellar morphology rather than the expected OBDD morphology. An enlarged image which has been processed is provided in the inset to facilitate scrutinization of the interconnecting catenoids. Note that this image is not the product of two orientations of superimposed lamellae.

The OBDD morphology is *not* observed in a SI30/hPS7 blend ($M_{hPS}/M_S \approx 0.43$) but is instead replaced by an interconnected lamellar morphology, as shown in Figure 3. The styrene-rich "lamellae" exhibit a relatively invariant optical density under the conditions presented here, while the stained isoprene microdomains appear to be divided by styrene-rich catenoids, which are more easily discernible in the processed[23] image presented in the inset of Figure 3. This morphology is not the product of two superimposed lamellar orientations, since the catenoids in the isoprene-rich lamellae appear to sit on a hexagonal lattice. Figure 3 does, however, resemble the lamellar catenoid morphology first identified by Thomas et al.[7] for a partially annealed diblock copolymer. Fourier transforms of these images reveal that the styrene lamellar microdomains and catenoids possess similar periodicities of approximately 28.6 and 29.3 nm, respectively. Recent theoretical efforts by Fredrickson[24] suggest that this morphology is metastable in the strong segregation limit, and Olvera de la Cruz et al.[25] predict that it is capable of developing only near the ODT. To the best of our knowledge, though, this is the first evidence that the lamellar catenoid morphology can be obtained in SI/hPS blends at near-equilibrium conditions.

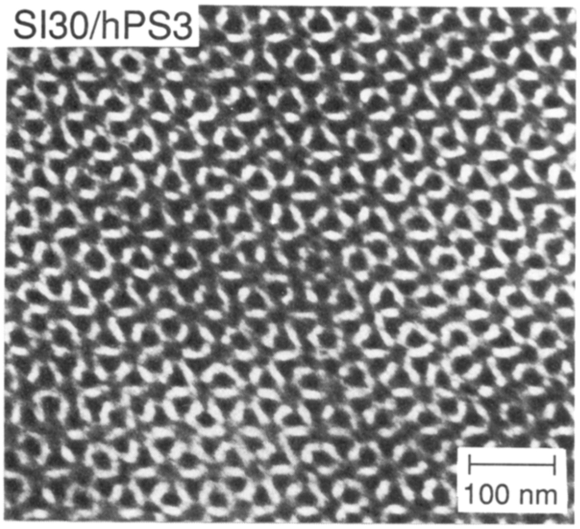

Figure 4. Micrograph of the OBDD morphology produced in the SI30/hPS3 blend and seen here along the [111] axis. Comparison of this image with the one shown in Figure 3 indicates that the resulting SI30/hPS blend morphology at $\Phi_S = 0.66$ is strongly dependent on M_{hPS}.

If SI30 is blended with hPS3, thereby reducing M_{hPS}/M_S to about 0.20, the OBDD morphology is again produced (see Figure 4). Comparison of Figures 3 and 4, which employ the same copolymer but homopolymers of different molecular weights, suggests that the equilibrium morphology is very sensitive to the spatial distribution of hPS, especially near the ODT. The OBDD morphology in Figure 4 possesses greater curvature than the lamellar catenoid microstructure seen in Figure 3. This trend is consistent with that reported[9,10] for blends composed of the SI49 copolymer, namely, addition of low molecular weight hPS to an SI copolymer results in a more uniform distribution of homopolymer within the styrene microdomain and generates morphologies of greater curvature.

The sensitivity of morphology near the ODT is illustrated further in Figure 5a, in which the SI20/hPS3 blend is depicted. The morphology seen in this micrograph does not exhibit evidence of long-range order, consisting of connected struts and micelles which measure up to 11 nm in diameter, and is reminiscent of the morphology previously reported[26] for an SIS triblock copolymer. For comparison, an SI10 copolymer is shown in Figure 5b. It possesses a value of $\chi_{SI}(T_g)N$ of approximately 15, which is lower than that corresponding to the ODT when critical fluctuations[20] are considered, and its disordered morphology appears to consist of both isoprene and styrene micelles. From Table I, $\chi_{SI}N$ for the SI20 copolymer is about 28 at 83 °C, which is expected to be reduced further upon addition of hPS. No value of $\chi_{SI}N$ for this blend is provided here, since Hashimoto et al.[27] have demonstrated that values of χ_{SI} representative of SI/hPS blends are complex functions of Φ_S and M_{hPS}/M_S. The apparent disorder seen in Figure 5a is presumed here to indicate that addition of hPS to SI20 at $\Phi_S = 0.66$ effectively prevents the formation of a periodic microstructure, at least before the styrenic components glassify.

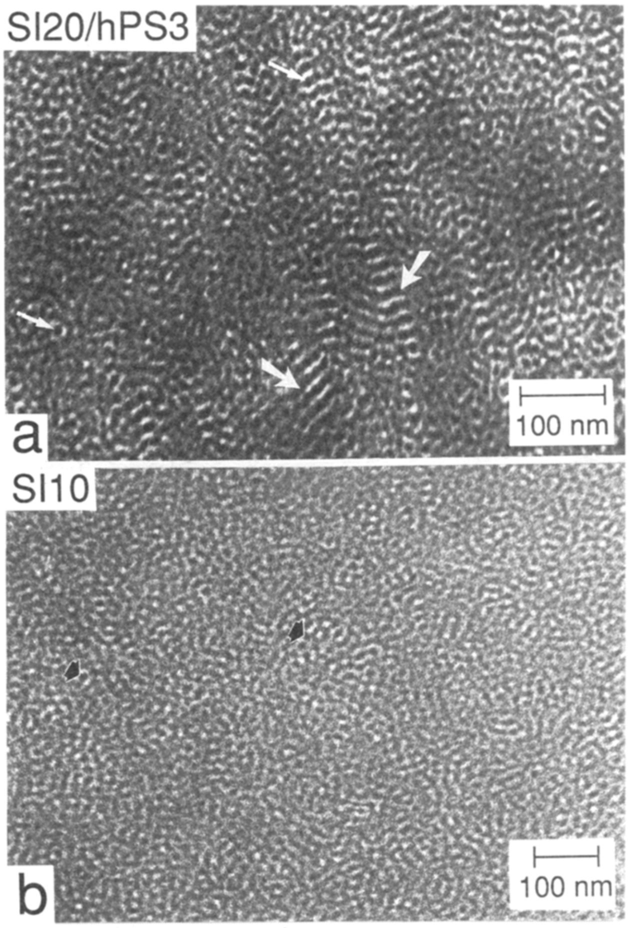

Figure 5. Energy-filtered image of SI20 blended with hPS3 (a). While the neat diblock copolymer is above the ODT ($\chi_{SI}N = 28.0$ from Table I) and possesses a lamellar morphology, addition of hPS results in a poorly defined morphology, which consists of struts, micelles (small arrows), and partially ordered regions (large arrows). A neat SI10 diblock copolymer with a value of $\chi_{SI}N$ just below that corresponding to the ODT is provided for comparison in (b). It possesses a morphology composed of coexisting styrene and isoprene micelles (arrowheads).

Attention is now drawn to the two high molecular weight copolymers investigated here, in which M_S assumes values of 60 000 and 90 000. Figure 6 is a pair of electron micrographs of the SI120/hPS30 blend, permitted to undergo solvent evaporation over the course of 3 weeks. In Figure 6a, the expected OBDD morphology is absent. In its place, a continuous matrix composed of styrene from both the homopolymer and copolymer is established, while the isoprene blocks assemble into discrete cylinders, few arranged on a clearly defined lattice. These cylinders measure approximately 97 nm in diameter. Figure 6b is also obtained from the SI120/hPS30 blend and reveals cylinders of isoprene connected to a region wherein the dispersion is replaced by a bicontinuous morphology reminiscent of the OBDD (Figure 2b). Regions such as the one shown in Figure 6b are, however, isolated and relatively uncommon in the blend.

Since previous studies by Winey et al.[9,10] indicate that cylindrical morphologies arise in homopolymer/copolymer blends when M_{hPS}/M_S is sufficiently low (≈ 0.10 in their study), SI120 has been blended with hPS42 to (i) increase M_{hPS}/M_S from 0.50 to 0.70 and (ii) decrease the interfacial curvature. The resulting morphology is again cylindrical (Figure 7) and is similar to that seen in Figure 6a. No evidence of a bicontinuous microstructure was present in this blend. The isoprene cylinders in Figure 7 measure approximately 105 nm in diameter (d) and possess a periodicity (D) of about 145 nm. If the interphase regions separating adjacent microphases are assumed to be negligible rather than finite,[28-30] Φ_S is estimated from $1 - \pi d^2/(4D^2 \sin 60°)$ for cylinders on a hexagonal lattice. The styrene content derived from this relationship is 0.52, which is significantly less than 0.66. Sections cut from different regions of the same bulk film exhibit the same morphology, thereby eliminating morphological variation induced by local composition fluctuations or surface effects. However, as seen in Figure 7, discrete pools of unsolubilized hPS are

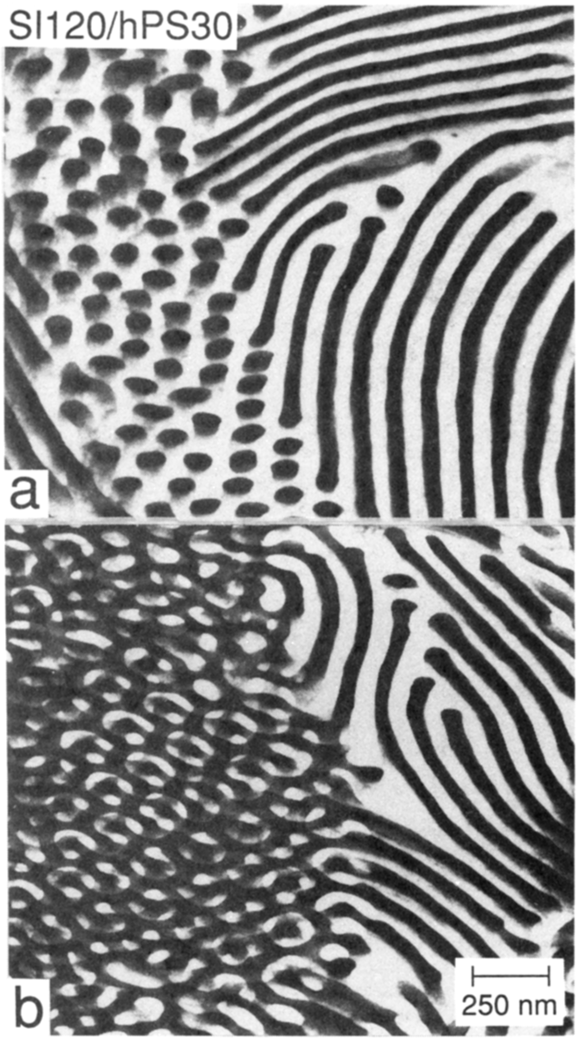

Figure 6. Pair of micrographs obtained from the SI120/hPS30 blend, permitted to undergo slow solvent evaporation alongside the blends shown in Figure 2. Isoprene cylinders dispersed in a continuous styrene matrix, presented in (a), are predominant. Isolated regions, such as the one shown in (b), consist of isoprene cylinders connected to a bicontinuous region which resembles the OBDD morphology seen in Figure 2b.

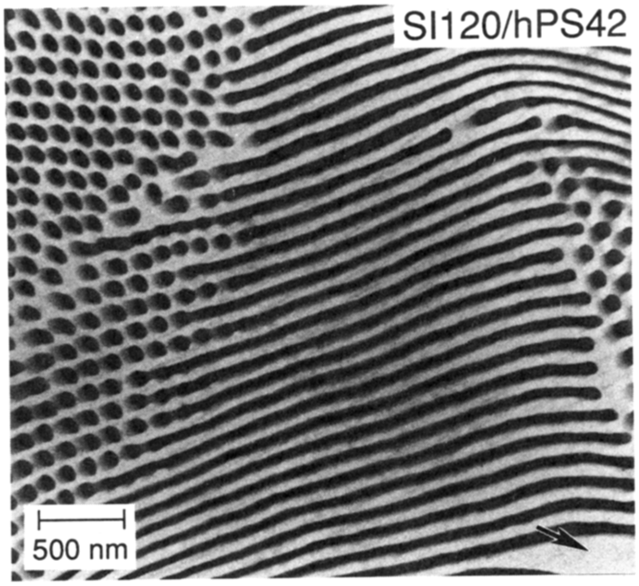

Figure 7. TEM micrograph of the SI120/hPS42 blend ($M_{hPS}/M_S \approx 0.70$), dried over the course of 3 days. The cylindrical morphology seen in Figure 6 for the SI120/hPS30 blend is again observed. Note that pools of styrene (arrow) are present among some of the isoprene cylinders.

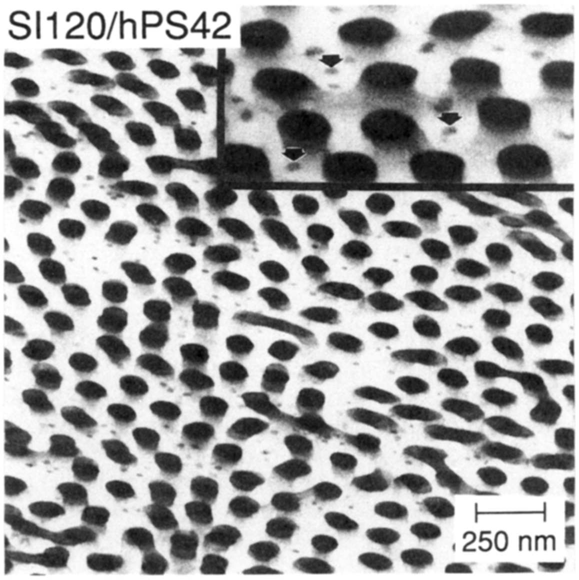

Figure 8. Image from the SI120/hPS42 blend after it had been allowed to dry for 3 weeks prior to annealing. The morphology appears as dispersed isoprene cylinders in a styrene matrix, with the cylinders exhibiting a variety of orientations. Upon close examination of the matrix, small isoprene-rich micelles are observed. The enlargement (1.9×) provided in the inset facilitates scrutinization of these micelles (arrowheads), which measure approximately 20 nm in diameter. The presence of these micelles suggests that a fraction of the isoprene blocks in the blend were immobilized during microphase separation and underwent self-assembly.

observed within the copolymer morphology and explain why Φ_S calculated for a hexagonally packed cylindrical morphology is significantly lower than 0.66.

While the rate of solvent evaporation can dramatically influence the morphology observed in copolymer/homopolymer binary blends,[31] the morphology shown in Figure 7, which corresponds to the SI120/hPS42 blend air-dried for 3 days, is not believed to represent an artifact induced by rapid solvent removal. Reproduction of this blend, after slow solvent evaporation over the course of 3 weeks, yields a very similar cylindrical morphology, shown in Figure 8. The microstructural dimensions measured from several micrographs analogous to the one presented in Figure 8 are comparable to those estimated from Figure 7 ($d \approx 100$ nm and $D \approx 135$ nm). Discrete hPS pools existing among the cylinders of the block copolymer are again seen and account for the low Φ_S (≈ 0.50) calculated for hexagonally packed isoprene cylinders.

A high-magnification image of the cross section of the cylinders in the SI120/hPS42 blend is displayed in the inset of Figure 8 and permits closer examination of stained micelles residing within the styrene matrix. These micelles have also been seen in longitudinal sections of the cylinders (not shown here), suggesting that they are spherical rather than cylindrical. They are found to measure approximately 20 nm in diameter and reside in the matrix near the midpoint separating adjacent cylindrical microdomains. The presence of such micelles throughout the bulk specimen indicates that (i) a fraction of the copolymer molecules was trapped within the styrene matrix during microphase separation and (ii) the thermodynamically incompatible isoprene blocks assembled into micelles to reduce the free energy of the system. A few similar micelles were observed in the slowly dried SI120/hPS30 blend (Figure 6a), but they were far less abundant than in the SI120/hPS42 blend shown in Figure 8.

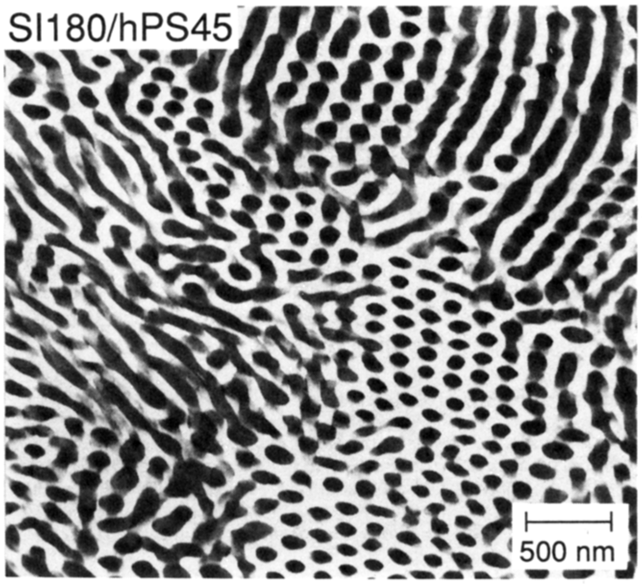

Figure 9. Electron micrograph of the blend containing the highest M copolymer (SI180) employed here and hPS45. Dispersed isoprene-rich cylinders, reminiscent of the ones seen in Figures 6–9 for SI120, are predominant. No bicontinuous structures were observed in this blend.

Micelles such as the ones seen in some of the SI120/hPS blends are not, however, observed in the cylindrical morphology of the SI180/hPS45 blend (Figure 9), also dried over the course of 3 weeks. The isoprene cylinders in this blend exhibit a variety of orientations and, assuming hexagonal packing, account for an average of 38 vol % of the isoprene in the blend, implying that $\Phi_S \approx 0.62$. No evidence of the OBDD morphology is found in this blend, but some of the cylinders on the left side of Figure 9 appear to constitute part of an interconnecting, possibly strutlike, microstructure.

While it is not inconceivable that an upper boundary on the OBDD morphology exists, the data of Hasegawa et al.[6] suggest that it does not, at least for neat diblock copolymers with molecular weights up to 207 000. The cylindrical morphologies exhibited by the SI120 and SI180 blends presented in Figures 6–9 are consequently presumed to be the result of diffusion-limiting chain entanglement induced by homopolymer localization. The appearance of micelles in the SI120/hPS42 blend, in particular, suggests that microphase separation in that system is incomplete when $M_{hPS} \approx 42\,000$. Hashimoto et al.[11] and Winey et al.[12] have investigated the extent of lamellar swelling upon addition of homopolymers of various molecular weights to diblock copolymers and conclude that high molecular weight homopolymers reside near the central plane of their preferred microdomain (to avoid contact with the chemically dissimilar moiety). In the case of athermal mixing, then, conformational entropy dictates the spatial distribution of homopolymer within the corresponding microdomain of the copolymer. Recent predictions obtained[14] from mean-field models of copolymer/homopolymer blends support this observed nonuniform mixing of hPS in S-microdomains. The possibility that some of the copolymer molecules in the SI120/hPS42 blend become entangled (to the point of being immobilized) with hPS42 during microphase separation and self-assemble into micelles is consistent with this picture. Note that the molecular weight of hPS42 in this blend is greater than the critical molecular weight of entanglement of hPS ($M_{hPS}^{\circ} \approx 36\,000$).[32]

The immediate ramification of this explanation, though, is that the morphologies seen in Figures 6–9 inherently reflect diffusion limitation during microphase separation and do not correspond to thermodynamic equilibrium. Complications arising from homopolymer entanglements can be potentially avoided by blending a high-*M* copolymer (SI120, for the sake of completeness in this study) with a homopolymer possessing M_{hPS} safely removed from M_{hPS}°. Figure 10 has been obtained from an SI120/hPS15 blend, for which $M_{hPS}/M_S = 0.25$. Under these conditions, the system is found to favor a bicontinuous morphology when $\Phi_S = 0.66$. The region displayed in Figure 10a is representative of the SI120/hPS15 blend and exhibits an OBDD microstructure. Isolated regions consisting of both the OBDD morphology and discrete isoprene cylinders are also observed in this blend, an example of which is presented in Figure 10b. This figure resembles Figure 6b obtained from the SI120/hPS30 blend. In contrast to the OBDD morphologies exhibited by previous blends (with intermediate-*M* copolymers), the one seen in this SI120/hPS15 blend possesses very small oriented grains, typically on the order of 10 periodicities or less. This observation suggests that long-range order is frustrated, presumably due to the molecular weight of the copolymer. Some of the bicontinuous and cylindrical microstructures seen in Figures 6b and 10a possess various orientations in projection and may, in part, be related to the "strut" or "mesh" morphologies recently reported by Hashimoto et al.[33]

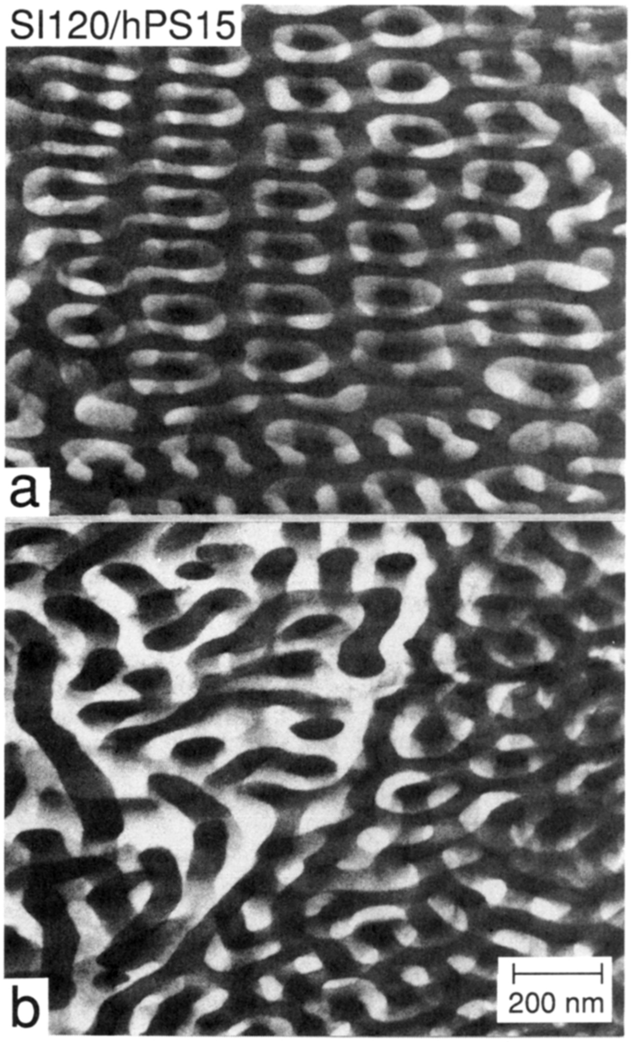

Figure 10. Morphology of SI120 blended with hPS15 at $\Phi_S \approx 0.66$. This blend consists principally of the OBDD morphology, which is shown in (a). As in Figures 6–8, some dispersed isoprene cylinders are also found (b). The micrographs presented here clearly illustrate that the morphologies in blends containing SI120 are dependent on the molecular weight of added hPS.

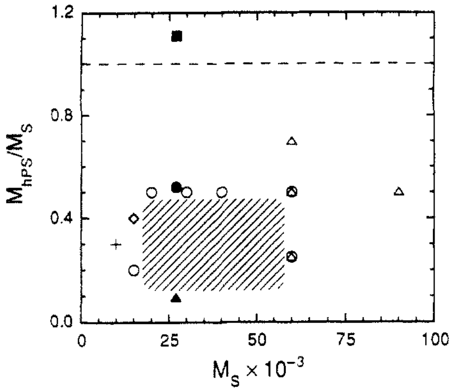

Figure 11. Experimental morphology diagram in which M_{hPS}/M_S is presented as a function of M_S ($\approx 0.5M$) when Φ_S is equal to 0.66 ± 0.01. Morphologies: disordered (+); lamellar catenoid (◇); OBDD (○); lamellar (□); cylindrical (△). Open symbols correspond to data from this work, whereas data depicted as solid symbols are obtained from refs 9 and 10. A dashed line is drawn at $M_{hPS}/M_S = 1.0$ as a reference, and the cross-hatched region represents the blend conditions that are likely to produce the OBDD morphology.

All of the data presented here, along with those provided earlier by Winey et al.,[9,10] have been compiled to illustrate graphically the dependence of the OBDD morphology on both M_S ($\approx 0.5M$) and M_{hPS}/M_S. These composition–morphology relationships are plotted in Figure 11, in which the homopolymer/copolymer blend conditions required to produce the OBDD morphology at $\Phi_S \approx 0.66$ are depicted. Unlike the diblock copolymer phase diagram derived from equilibrium thermodynamics,[19] Figure 11 is a morphology diagram based on experimental observations and implicitly reflects nonequilibrium factors (e.g., homopolymer localization) which contribute to the observed morphologies. In accord with the images displayed in Figure 2, the OBDD morphology is found to exist in blends containing intermediate-M copolymers and homopolymers of relatively low molecular weight ($M_{hPS} \leq 20\,000$). As the blend approaches the copolymer ODT, the value of M_{hPS}/M_S becomes crucial in morphology development, suggesting that additional morphologies (analogous to those found in small-molecule surfactant systems) may be accessible through judicious choice of M_{hPS}. Similar morphological variation is observed at high M_S, presumably due to the entanglement effects described earlier.

Conclusions

Transmission electron microscopy has been employed here to investigate the morphologies found in blends of several SI diblock copolymers with polystyrene homopolymers at 66 vol % styrene. To minimize differences arising from homopolymer/copolymer mixing and microdomain swelling, the molecular weight of added hPS in each blend is, in most cases, less than or equal to half the block weight of styrene in the copolymer. The OBDD morphology is observed in such blends when $30\,000 \leq M \leq 80\,000$. At the lower limit of this range, SI/hPS blends exhibit an interconnected lamellar morphology when $M_{hPS}/M_S \approx 0.43$ and the OBDD morphology when $M_{hPS}/M_S \approx 0.2$. A disordered morphology is produced if the molecular weight of the copolymer is reduced further to 20 000. At high molecular weights ($M \geq 120\,000$), resulting morphologies consist of isoprene cylinders dispersed in a continuous styrene matrix. Isoprene-rich micelles have been observed within the matrices of the SI120/hPS30 and SI120/hPS42 blends permitted to dry slowly and signify incomplete microphase separation, presumably due to homopolymer entanglement. When M_{hPS} is lowered in this blend so that $M_{hPS}/M_S \approx 0.25$, the influence of diffusion-limiting chain entanglement becomes less pronounced and the OBDD morphology is predominant. All of the data presented here have been compiled into an experimental morphology diagram for homopolymer/copolymer blends at 66 vol % styrene.

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References and Notes

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