The Ordered Bicontinuous Double-Diamond Morphology in Diblock Copolymer/Homopolymer Blends

Karen I. Winey[*,†]

Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003

Edwin L. Thomas

Materials Science and Engineering Department, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Lewis J. Fetters

Corporate Research, Exxon Research and Engineering Company, Annandale, New Jersey 08801

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ABSTRACT: The ordered bicontinuous double-diamond (OBDD) morphology was prepared in binary blends of poly(styrene-*b*-isoprene) or poly(styrene-*b*-butadiene) diblock copolymer (AB) and a homopolymer (hA). Previously reported observations of the OBDD morphology have been restricted to linear and star diblock copolymers. The ability to form the OBDD morphology was influenced by the homopolymer concentration, the homopolymer molecular weight, and the composition of the copolymer. The overall polystyrene (PS) volume fraction required for a polystyrene-rich OBDD morphology was approximately equivalent for the neat copolymers and the blend systems, namely, 64–67 vol % PS. If a diblock copolymer which forms the lamellar morphology was used in the blend, the homopolymer resides in the matrix region of the OBDD morphology. However, if a diblock copolymer with the cylindrical morphology was used to prepare the OBDD morphology in a blend, the homopolymer resides inside the channel regions. Attempts to prepare the OBDD blend morphology with homopolymer in the matrix region using a diblock copolymer with the cylindrical morphology failed; these blends underwent macrophase separation.

Introduction

The ordered bicontinuous double-diamond (OBDD) morphology is an intricate and elegant morphology recently shown to exist in linear and star diblock copolymers.[1-3] Both the minority and majority components of the OBDD structure are periodic and continuous in all three dimensions. This three-dimensional bicontinuity is not present in the other established morphologies found in block copolymer systems. The lamellar morphology in block copolymers is periodic in only one direction with both components continuous in only two directions, while the cylindrical morphology is periodic in two dimensions with only the majority component continuous in three directions. The spherical morphology is periodic in three dimensions, but only the majority component is continuous. The minority component of the OBDD morphology is divided into two interpenetrating networks or channels, each having diamond cubic symmetry. Both of the channels are separated from the majority component by an intermaterial dividing surface of approximately constant mean curvature. Constant mean curvature surfaces minimize the interfacial area given a volume fraction and a set of symmetry constraints. A color computer-generated image presented elsewhere will assist the reader in visualizing this microstructure.[3]

Researchers observe the OBDD morphology in narrow composition regimes. For example, the OBDD microstructure in linear poly(styrene-*b*-isoprene) diblock copolymers exists within the composition ranges of 28–33 vol % PS and 62–66 vol % PS.[2,4] Such narrow composition ranges require precise control of the copolymer synthesis in order to obtain the proper copolymer composition which results in a diblock copolymer with the OBDD morphology. This paper unveils a new method of producing the OBDD microstructure which eliminates this stringent synthetic requirement: binary blends of a diblock copolymer and a homopolymer.[5] In the absence of homopolymer, the copolymers used in the blends have either a lamellar or a cylindrical morphology which exists over wider composition regimes than the OBDD morphology and consequently is synthetically more accessible. The intrinsic domain structure of the neat diblock copolymers can be transformed to the OBDD morphology by blending the copolymer with a homopolymer. We present three molecular parameters which control the formation of the OBDD morphology in blends: the homopolymer concentration in the blend, the homopolymer molecular weight, and the initial morphology of the neat diblock copolymer.

The observed OBDD morphology in copolymer systems apparently minimizes the free energy with respect to the preferred interfacial curvature, the interfacial area and the chain conformations for a variety of systems: star diblock copolymers, linear diblock copolymers, and now diblock copolymer/homopolymer blends. A previous theoretical attempt to show that the free energy of the OBDD morphology is lower than that of spheres, cylinders, or lamellae over a range of compositions in star diblock copolymers was unsuccessful.[6] Wang and Safran have studied the equilibrium morphology in ternary blends of two homopolymers and a diblock copolymer in the absence of both interactions between and homopolymer penetration into the copolymer interfaces.[7,8] Their theory focuses on the elastic properties of the interfacial layer and does predict a stable OBDD morphology at certain compositions and molecular weights. However, the binary blends discussed here do not meet the criteria set forth by Wang

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[*] To whom correspondence should be addressed.

[†] Current address: AT&T Bell Laboratories, Murray Hill, NJ 07974.

Table I
Characteristics of the Poly(styrene-*b*-isoprene) and Poly(styrene-*b*-butadiene) Diblock Copolymers

diblock copolymer	M_n(PS block)/(g/mol)	wt % PS	morphology
SI27/22	26 600	55	lamellae
SI13/34	12 900	28	cylinders of PS
SI13/51	12 800	20	cylinders of PS
IS12/45	45 300	79	cylinders of PI
SB20/20	20 500	50	lamellae
SB10/23	10 200	30	cylinders of PS
SB23/10	22 200	71	cylinders of PB

and Safran. This paper attempts to assist the next generation of theoretical predictions concerning the OBDD morphology.

The OBDD morphology in polymeric systems also has potential industrial uses as an ordered microcomposite. Applications may arise from the fact that both components in the OBDD morphology are continuous, for example, separation devices, membranes, self-assembled composites, or a host of other possibilities. Further practical studies are now more likely due to the discovery of a more accessible route, that is, blending diblock copolymer and homopolymer, to form the intriguing OBDD morphology.

Experimental Methods

Materials. The anionic polymerization of poly(styrene-*b*-isoprene) and poly(styrene-*b*-butadiene) diblock copolymers was initiated with purified *sec*-butyllithium in a benzene/cyclohexane mixture (10/90 v/v) at 30 °C using high-vacuum techniques.[9] The polystyrene block (PS) was typically polymerized first, after which an aliquot was removed for characterization. A Waters 150C size-exclusion chromatograph (SEC) calibrated with polystyrene standards was used to determine the molecular weight and polydispersity index of the first block. The subsequent addition and polymerization of isoprene or butadiene monomers gave an approximate microstructure distribution of 70% cis-1,4, 24% trans-1,4, and 6% 3,4 addition for the polyisoprene (PI) block and 50% trans-1,4, 40% cis-1,4, and 10% 1,2 addition for the polybutadiene (PB) block. One diblock copolymer, IS12/45, was synthesized in the reverse order; first the PI block was polymerized and then the PS block; in this case the SEC was calibrated with polyisoprene standards. The molar composition and the polydispersity index of the complete diblock copolymers were measured with a 400-MHz ^{1}H NMR analysis and by SEC referenced to PS standards, respectively. The molecular weight of the second block to be polymerized and the PS weight percent were calculated from the molecular weight of the first block and the molar composition. The poly(styrene-*b*-isoprene) and poly(styrene-*b*-butadiene) diblock copolymers are identified as SI#/# (or IS#/#) and SB#/#, respectively, where the numbers refer to the block molecular weights given in kilograms per mole. Table I lists selected characteristics of the SI and SB diblock copolymers: the molecular weight of the PS block, the weight percent of PS, and the observed morphology. The polydispersity indices for the block polymerized first and the entire diblock copolymer are less than 1.05 in all cases. The SB diblock copolymers were used in previous studies.[10,11]

The homopolystyrenes (hPS) were purchased from Pressure Chemical Co. and characterized by SEC. The characteristics of the hPS, the number-average molecular weights and polydispersity indices (the latter in parentheses), follow: 2600 (1.11), 4000 (1.13), 5900 (1.08), 14 000 (1.02), 17 200 (1.04), and 30 100 g/mol (1.02). The homopolystyrenes are designated by their approximate molecular weight given in kilogram per mole followed by hPS: 2.6 hPS, 4 hPS, 6 hPS, 14 hPS, and 30 hPS. Prior to use the polystyrene homopolymers were treated at 160 °C under vacuum for 30 min to remove residual solvent, styrene monomer, dimers, and oligomers. During this procedure the material foamed. A homopolyisoprene, 13 hPI, was purchased from Goodyear Tire & Rubber Co., as sample CDS-I-3 with a reported microstructure distribution of 18% trans-1,4, 76% cis-1,4, and 6% 3,4 addition. The reported number-average molecular weight and polydispersity index of 13 hPI are 13 300 g/mol and 1.13, respectively, and agree with our SEC results referenced to PI standards. A homopolybutadiene, 7 hPB, was anionically polymerized in cyclohexane at 50 °C and has an approximate microstructure distribution of 57% trans-1,4, 34% cis-1,4, and 9% 1,2 addition. The number-average molecular weight and polydispersity index of 7 hPB were determined by SEC to be 6950 g/mol and 1.04, respectively. Sample 7 hPB is sample C-14 of an earlier paper.[12]

Blend Preparation. The protocol for blend preparation was designed to reproducibly prepare bulk binary blends at thermodynamic equilibrium by solvent casting and annealing.[13] Dilute polymer solutions (3 w/v %) in toluene were placed in treated glass casting dishes, and the solvent was allowed to slowly evaporate in 7–10 days at room temperature. The ~1-mm thick sample was dried (2 weeks at 40 °C) and annealed (1 week at 125 °C) in a vacuum oven. Blends are designated by the homopolymer concentration in the blend given in weight percent, the homopolymer, and the diblock copolymer: e.g. 30% 14 hPS and SI27/22.

Transmission Electron Microscopy. Blends were imaged with transmission electron microscopy (TEM) to identify the morphology. Thin sections (~500 Å) were cryomicrotomed from bulk samples and were stained with OsO_4 vapors.[13] The sections were examined in the bright-field mode using a JEOL 100CX transmission electron microscope at 100 kV.

Small-Angle X-ray Scattering. The lattice types and lattice parameters of selected binary blends were determined by small-angle X-ray scattering (SAXS) using Kratky slit collimation and a Braun one-dimensional position-sensitive detector. The experimental details were presented earlier.[13,14] Desmeared scattered intensities were obtained by Vonk's scheme using a computer program originally provided by Vonk and modified by previous workers at the University of Massachusetts (Amherst).[4,15,16] Well-resolved peaks result upon desmearing from which the interplanar spacings ($d_i = 1/s_i$) and order numbers (i) were obtained, where s_i is the magnitude of the scattering vector of the ith peak.

The direct TEM observations and the multiple interference peaks in the SAXS profiles combine to accurately determine the lattice types and the lattice parameters of the blends. Each lattice type exhibits a characteristic sequence of interplanar distances. The lamellar morphology, which is periodic in one dimension, has a single interplanar distance:

$$d_h(\text{lam}) = a_{\text{lam}}/h, \qquad h = 1, 2, 3, 4, ... \tag{1}$$

where h is the order of the reflection and a_{lam} is the lattice parameter of the lamellar unit cell, i.e. the lamellar domain spacing. The higher order reflections relative to the first reflection are given by d_h/d_1 or

$$d_h(\text{lam})/d_1(\text{lam}) = 1.00, 0.50, 0.33, 0.25, ... \tag{2}$$

A hexagonal lattice of cylinders is periodic in two dimensions and has the following spacings and characteristic spacing ratios:

$$d_{hk}(\text{hex}) = \frac{a_{\text{hex}}}{(4/3)^{1/2}(h^2 + hk + k^2)^{1/2}}, \qquad (hk) = 10, 11, 20, 21, 30, ... \tag{3}$$

$$d_{hk}(\text{hex})/d_{10}(\text{hex}) = 1.00, 0.58, 0.50, 0.38, 0.33, ... \tag{4}$$

where (hk) are the Miller indices and a_{hex} is the lattice parameter of the hexagonal lattice. The cubic lattice of the ordered bicontinuous double diamond has interplanar spacings given by

$$d_{hkl}(\text{OBDD}) = \frac{a_{\text{OBDD}}}{(h^2 + k^2 + l^2)^{1/2}}, \qquad (hkl) = 110, 111, 200, 211, 220, 221, ... \tag{5}$$

where (hkl) are the Miller indices of the *allowed* reflections of the *Pn*3*m* cubic space group and a_{OBDD} is the lattice parameter of the OBDD cubic lattice. The symmetry of the ordered bicontinuous double-diamond morphology is represented by the *Pn*3*m* space group.[3,6,17] The ratios of interplanar spacings relative

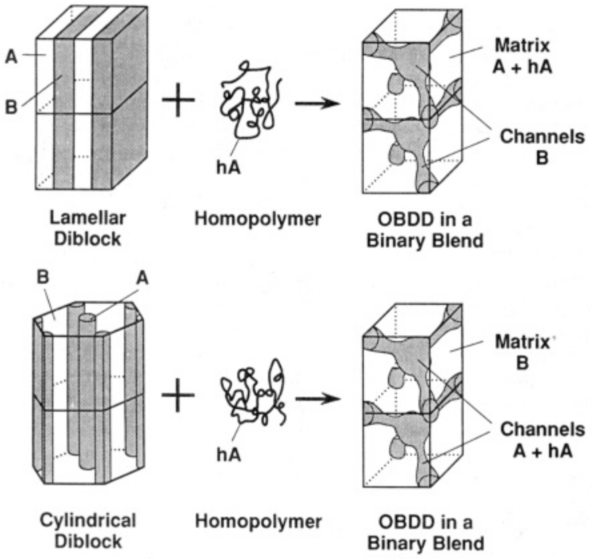

Figure 1. Schematic showing the preparation of the ordered bicontinuous double-diamond (OBDD) morphology from a diblock copolymer and a selective hompolymer: (top) lamellar diblock copolymer (AB) and homopolymer (hA) form the OBDD morphology with hA in the matrix; (bottom) cylindrical diblock copolymer and homopolymer in a type I blend form the OBDD morphology with hA in the channels of diamond symmetry.

to the first observed interference peak are

$$d_{hkl}(\text{OBDD})/d_{110}(\text{OBDD}) = 1.00, 0.82, 0.71, 0.58, 0.50, 0.47, \ldots \qquad (6)$$

These lattice types can be distinguished by their relative interplanar spacings given by eqs 2, 4, and 6. Once the lattice type was established by TEM and the relative planar spacings in SAXS, the Miller indices were assigned to each peak in the SAXS spectrum. All the observed peaks were included in calculating the lattice parameter by a linear regression method using the experimental interplanar spacings and the assigned Miller indices. For example, the linear expression for the cubic lattices is $d_{hkl}(\text{cubic}) = m(h^2 + k^2 + l^2)^{-1/2} + b$, where the y intercept (b) is ideally zero. In addition to the experimental values $(x,y) = ((h^2 + k^2 + l^2)^{-1/2}, d_{hkl}(\text{cubic}))$, the values (0,0) were used as a known limit. The resultant OBDD lattice parameter is given by $a_{\text{OBDD}} = d_{100} = m + b$, though the $Pn3m$ space group does not have an allowed (100) reflection. Equations 1, 3, and 5 and the lattice parameters are used to calculate the SAXS peak positions, which are indicated by the arrows in the desmeared SAXS patterns, $s'_{hkl} = 1/d'_{hkl}$. Good agreement was found between the observed and calculated peak positions.

Results

Ten binary blends are prepared which form the order bicontinuous double-diamond morphology. Figure 1 shows schematically the transformation of both a lamellar and a cylindrical diblock copolymer morphology into the OBDD blend morphology. The criteria for preparing the OBDD morphology with these two types of diblock copolymer will be presented separately.

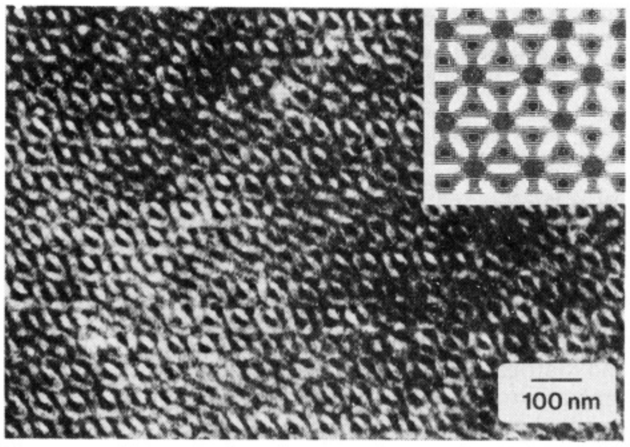

Figure 2. Transmission electron micrograph of the OBDD morphology ([111] projection) in a binary blend containing a lamellar diblock copolymer and homopolymer: 40% 17 hPS and SB20/20. Inset shows a computer simulated [111] or wagon wheel projection of the OBDD morphology.[3]

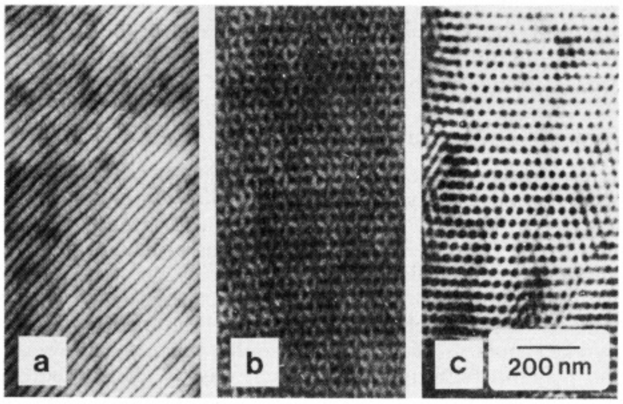

Figure 3. Transmission electron micrographs showing the homopolymer concentration dependence of the morphology in blends of 14 hPS and SI27/22: (a) 24%, lamellae; (b) 32%, the OBDD morphology; (c) 36%, cylinders on a hexagonal lattice.

Lamellar Diblock Copolymer and Homopolymer Blends. Figure 2 shows a blend of 40% 17 hPS and SB20/20, exhibiting the ordered bicontinuous double-diamond morphology. The homopolymer is fully solubilized in the diblock copolymer, as evidenced by the absence of separate domains of homopolymer appearing in the micrographs. Recall that SB20/20 is a lamellar diblock copolymer (Table I). The blend self-assembles from the initial homogeneous solution into the OBDD morphology rather than the lamellar morphology of the neat diblock copolymer (Figure 1, top). The homopolystyrene and the PS blocks of the copolymer mix together in the matrix region of the OBDD microstructure, while the PB blocks of the copolymer occupy the channels.

The [111] projection in Figure 2, also known as the "wagon wheel" projection, is the unique signature of the OBDD morphology since no other known morphology in block copolymer systems exhibits such a TEM projection. This projection of the OBDD morphology was previously confirmed by comparing a computer-simulated projection based on the Anderson constant mean curvature surface with 27 vol % PS, as shown in the inset of Figure 2, and a digitized TEM micrograph.[3,6,17,18] Small-angle X-ray scattering (SAXS) results also identify the OBDD morphology, as we will show later, by exhibiting the expected ratios of interplanar spacings given in eq 6. The long-range order in the binary blends is comparable to that of diblock copolymers as qualitatively evaluated by visual inspection of the electron micrographs and by the number and sharpness of the SAXS diffraction peaks.

The presence of the OBDD morphology in binary blends depends on the homopolymer concentration as shown in Figure 3. For example, blends containing 24, 32, and 36% 14 hPS with SI27/22 exhibit morphology changes upon increasing the homopolymer content from lamellae to the OBDD morphology to cylinders on a hexagonal lattice. Once again the absence of separate homopolymer domains indicates that the homopolymer is fully solubilized in the diblock copolymer. Additional homopolymer concentrations are given in Table II from 20 to 40% 14 hPS in SI27/22 in 2% intervals. (The biphasic regions observed

Table II
Homopolymer Concentration Series in Blends of 14 hPS and SI27/22

wt % hPS	morphology	Φ_{PS}/ %
20	lamellae	60
22	lamellae	61
24	lamellae	62
26	lamellae and cylinders	63
28	lamellae and cylinders	64
30	OBDD	65
32	OBDD	66
34	OBDD	67
36	cylinders	68
38	cylinders	69
40	cylinders	70

at 26 and 28% 14 hPS and SI27/22 will be discussed at the end of this section.) In this blend system of 14 hPS and SI27/22, the OBDD morphology is observed in the range of 30–34 wt % homopolymer.

The composition range for the OBDD morphology in blends of lamellar diblock copolymer and homopolymer is best described by the overall polystyrene volume fraction (Φ_{PS}). The quantity Φ_{PS} includes the polystyrene block and the homopolystyrene as calculated from the composition of the diblock copolymer, the homopolymer concentration in the blend, and the densities of the components with the assumptions of pure microdomains and narrow interfaces. Justification for this volumetric calculation of the overall PS volume fraction is discussed elsewhere.[13] Table II lists Φ_{PS} for the homopolymer concentration series in blends of 14 hPS and SI27/22 in which the OBDD morphology exists in the range of 65–67 vol % PS. The OBDD morphology also exists at the same overall polystyrene volume fraction, 66 vol % PS, in a *different* blend system, e.g. 17 hPS and SB20/20, as shown in Figure 2. The overall PS volume percent range for binary blends is comparable to that observed for the OBDD morphology in neat SI linear diblock copolymers, 62–66 vol % PS.[2,4]

Most interestingly, we find that at a fixed homopolymer concentration the morphology in the binary blends also depends on the molecular weight of the homopolymer. Blends with 30% homopolystyrene and SI27/22, which correspnds to Φ_{PS} = 65 vol % PS, exhibit *three* morphologies, depending on the homopolymer molecular weight, Figure 4. The blend with the lowest molecular weight, 2.6 kg/mol, exhibits cylinders on a hexagonal lattice, while the blends with intermediate molecular weights, 5.9 and 14.0 kg/mol, exhibit the OBDD morphology. For the blends with the highest molecular weight homopolymer, 30 hPS, the lamellae of the neat diblock copolymer swell but do not undergo a morphological transition.

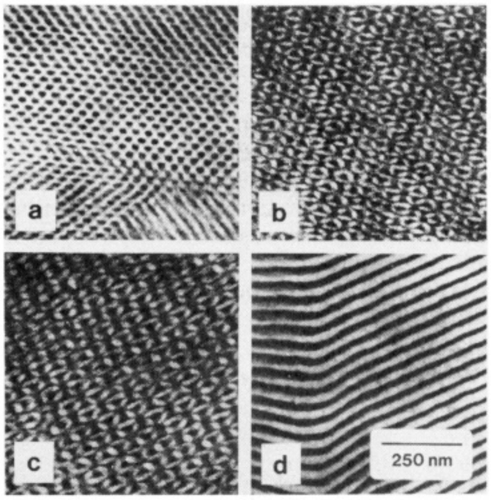

Figure 4. Transmission electron micrographs showing the homopolymer molecular weight dependence of the morphology in blends of 30% hPS and SI27/22: (a) 2.6 hPS, cylinders on a hexagonal lattice; (b) 6 hPS, the OBDD morphology; (c) 14 hPS, the OBDD morphology; (d) 30 hPS, lamellae.

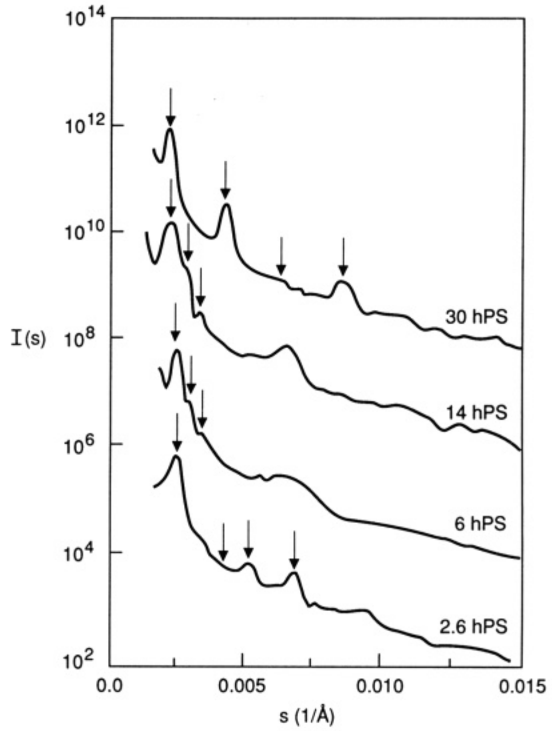

Figure 5. Desmeared small-angle X-ray scattering intensities as a function of the scattering vector for blends of 30% hPS with various homopolymer molecular weights and SI27/22: 2.6 hPS, cylinders on a hexagonal lattice; 6 hPS, the OBDD morphology; 14 hPS, the OBDD morphology; 30 hPS, lamellae. Arrows mark the allowed reflections. The intensity curves are offset vertically for legibility.

These blend morphologies are confirmed by the desmeared SAXS patterns, Figure 5. The lattice parameters to follow have an error of ±1%. The scattering pattern for 30% 2.6 hPS and SI27/22 indicates cylinders on a hexagonal lattice with a lattice parameter of 450 Å and the following *(hk)* reflections indicated by arrows: (10), (11), (20), and (21). In this particular case, the (11) reflection is suppressed because it coincides with a minimum in the form factor scattering for cylinders of radius 140 Å; the radius of the cylinders is determined volumetrically from the overall volume fraction of polystyrene in the blend and the lattice parameter. With the homopolymer 6 hPS or 14 hPS, the 30% hPS blend exhibits the OBDD morphology as indicated by (110), (111), and (200) reflections for a cubic lattice with double-diamond symmetry (space group *Pn*3*m*). The cubic lattice parameters are 585 and 630 Å for the blends with 30% 6 hPS and 14 hPS in SI27/22, respectively. The SAXS pattern for the blend 30% 30 hPS and SI27/22 indicates the ordered lamellar morphology with a period of 475 Å. The third-order peak is suppressed due to the coincidence of a form factor minimum.

The homopolymer molecular weight criterion for producing the OBDD morphology is generalized by introducing a reduced parameter, the relative homopolymer molecular weight. The relative homopolymer molecular weight is the ratio of the homopolymer molecular weight and the respective block molecular weight. More extensive work in binary blends shows the relative homopolymer molecular weight to be an important parameter.[14,19-21] The relative homopolymer molecular weight for the blend shown in Figure 2, 40% 17 hPS and SB20/20, is 0.84. Blends containing SI27/22, as shown in Figures 4 and 5, exhibit the OBDD morphology when the relative homopolymer molecular weight is approximately 0.15–1.0. Increasing or decreasing the relative homopolymer molecular weight outside of this range induces the lamellar and cylindrical morphologies, respectively. The morphologies in binary blends depend on the homopolymer molecular weight in contrast to the morphologies of SI or SB diblock copolymers of comparable molecular weights which are molecular weight independent.

Another apparent contrast between the case of binary blends and the neat copolymers is the absence of the OBDD morphology in blends having PS as the minority component. For example, in SI diblock copolymers the OBDD morphology exists in two PS volume percent ranges, 28–33 and 62–66 vol % PS. While we observe binary blends of lamellar diblock copolymer and homopolymer with the polystyrene-rich OBDD morphology, a polydiene-rich OBDD morphology has not yet been observed. Attempts to prepare a polydiene-rich morphology include blends of 14–34% 7 hPB and SB20/20 having an overall PS volume fraction range of 29–39 vol % PS; this composition range overlaps in part that of the polydiene-rich OBDD morphology observed in diblock copolymers. The relative homopolymer molecular weight of these blends is 0.34, which is within the acceptable range determined above. However, none of these blends exhibit a single-phase OBDD morphology via electron microscopy. The absence of a single-phase OBDD morphology in polydiene-rich blends is also observed in blends of cylindrical diblock copolymer and homopolymer.

In a two-component system, a first-order phase transition from one morphological phase (α) to another morphological phase (β) has an intermediate biphasic region containing both of the morphological phases ($\alpha + \beta$). In the binary blends of a diblock copolymer and a homopolymer that we have examined, the two-phase region is very narrow, not present at all, or if present does not contain the expected morphological phases. For example, the morphologies of the blends containing 14 hPS and SI27/22 given in Table II change from the OBDD morphology at 34% 14 hPS to the cylindrical morphology at 36% 14 hPS. If a biphasic region of OBDD and cylindrical morphologies does in fact exist, the homopolymer concentration range over which it exists is quite narrow (<2 wt % hPS).

This same blend system also gives the first of two examples showing unexpected types of biphasic regions. Blends of 26 or 28% 14 hPS and SI27/22 are biphasic, exhibiting both the lamellar and the cylindrical morphologies; however, the lamellar and the OBDD morphologies are expected, Table II. The coexistence of lamellae and cylinders is confirmed by both TEM and SAXS. Small-angle X-ray scattering from the blend 28% 14 hPS and SI27/22 indicates a lamellar lattice parameter of 445 Å and a hexagonal lattice parameter of 515 Å.

Another blend system, 7 hPB and SB20/20, does exhibit the coexistence of the OBDD morphology and lamellae at both 18% 7 hPB (37 vol % PS) and 22% 7 hPB (35 vol % PS), as determined by TEM, Figure 6. The OBDD morphology is shown in this micrograph in the "barber pole" projection having two-fold symmetry.[22,23] If the phase transitions between ordered morphologies in binary blends are first order, these biphasic blends containing the OBDD in the lamellar morphologies should be bounded by two single-phase blends, one of the OBDD morphology and the other of the lamellar morphology. However, both higher and lower homopolymer concentrations, 14% 7 hPB (39 vol % PS) and 26% 7 hPB (33 vol % PS), produce single morphology blends of lamellae. We currently have no explanation for these unexpected results concerning the biphasic regions.

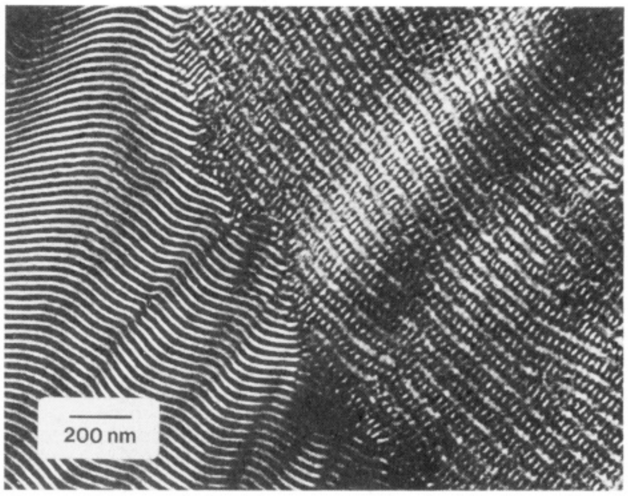

Figure 6. Transmission electron micrograph of the binary blend 22% 7 hPB and SB20/20 which exhibits the coexistence of lamellae (left) and the OBDD morphology (right).

Cylindrical Diblock Copolymers and Homopolymer Blends. The homopolymer (hA) used in binary blends with a cylindrical diblock copolymer (AB) must be selective for the minority component (A) so as to raise the overall composition of A. In general, the compositions for the ordered bicontinuous double-diamond morphology, as were determined for linear diblock copolymers, can be accessed by beginning with a cylindrical diblock copolymer and incorporating either a small amount (<20%) or a large amount (>50%) of homopolymer. For convenience we will refer to these blends as type I and type II, respectively. If the OBDD morphology is successfully formed, type I blends have homopolymer in the diamond channels, while type II blends have homopolymer in the matrix. We have successfully prepared the OBDD morphology in type I blends, but not in type II blends. A type I blend is illustrated in Figure 1, bottom.

The OBDD morphology exists in type I blends of SB23/10 with hPB and IS12/45 with hPI. Note that in both blend systems the minority component of the copolymer and the homopolymer are the same polydiene. The presence of small amounts of homopolydiene causes the typically cylinder-forming polydiene blocks of the copolymers to organize into the OBDD morphology. The homopolydiene is confined to the two interpenetrating networks with diamond symmetry. Blends of 2 or 4% 7 hPB and SB23/10 produce the OBDD morphology with overall PS compositions of 66 and 65 vol % PS, respectively. Since the presence of such a small amount of homopolymer is sufficient to cause the blend to self-assemble into a different morphology, researchers should be aware how sensitive the observed microstructure is to contaminants when investigating diblock copolymers near a volume fraction boundary between morphologies. Blends of 12, 14, or 16% 13 hPI and IS12/45 also produce the OBDD morphology with overall PS compositions of 66, 64, and 63 vol % PS, respectively. The relative homopolymer molecular weights are 0.78 for the SB23/10 with 7 hPB system and 1.07 for the IS12/45 and 13 hPI system.

The overall PS volume fractions and the relative homopolymer molecular weights for blends with the OBDD morphology are comparable for type I blends and the blends of lamellar diblock copolymer and homopolymer discussed previously.

Multiple attempts to prepare a polydiene-rich OBDD morphology in a type I blend have failed. Eight blends containing SI13/34 and hPS over a range of overall PS volume fractions (31–38 vol % PS) and a range of relative homopolymer molecular weights (0.31–1.09) do not exhibit the OBDD morphology. Similarly, four blends of SI13/51 and various hPS over a range of overall PS volume fractions (31–32 vol % PS) and the same range of relative homopolymer molecular weights (0.31–1.09) failed to form the desired morphology. These type I blends have overall PS compositions within the range for the polydiene-rich OBDD morphology in linear diblock copolymers and have relative homopolymer molecular weights within the suggested range. However, none of these twelve blends exhibit a single phase of the OBDD morphology but rather exhibit cylinders, macrophase separation, or biphasic separation. As in the blends of a lamellar diblock copolymer and a homopolymer, the OBDD morphology is only observed with polystyrene as the majority component in type I blends of a cylindrical diblock copolymer and a homopolymer. In both cases, we expect that a more thorough investigation will reveal the OBDD morphology in binary blends having PS as the minority component, possibly at compositions of less than 30 vol % PS.

Type II blends, which have a large amount of homopolymer blended with the minority component of the diblock copolymer, require an inverted morphology to form the OBDD morphology. The "inverted" morphology is a blend morphology in which the minority component of the diblock copolymer becomes the majority component of the blend. The blend and the diblock copolymer may or may not have the same type of domain morphology. Our every attempt to prepare an inverted OBDD morphology from type II blends fails: 54% 4 hPS and SI13/34, 54 or 60% 6 hPS and SI13/34, 58% 4 hPS and SI13/51, 58% 6 hPS and SI13/51, and 60% 17 hPS and SB10/23. These blends have an overall PS volume fraction range of 63–69 vol % PS and a relative homopolymer molecular weight range of 0.31–0.59; these values are appropriate for the OBDD morphology in other types of binary blends.

The cylindrical diblock copolymer does not form an inverted OBDD morphology when allowed to self-assemble in the presence of homopolymer. Rather, macrophase separation occurs when a large amount of homopolymer is present which is chemically identical to the minority component of the diblock copolymer, i.e. a type II blend. The homopolymer solubility limit is exceeded. Most of the macrophase separated type II blends exhibit domains of homopolystyrene and domains of lamellae. The presence of lamellae indicates that a portion of the homopolymer is incorporated into the diblock copolymer to induce a new morphology from the cylindrical morphology of the neat diblock copolymer. The absence of inverted morphologies will be discussed more fully in the Discussion section of this paper.

Discussion

In the case of linear or star diblock copolymers, all the microdomains contain solely block segments of the copolymer which are spatially constrained to the intermaterial dividing surface. Spatially ordered blends of diblock copolymer and homopolymer (AB/hA) contain microdomains with only block copolymers (B blocks) and microdomains with a combination of constrained block copolymers (A blocks) and unconstrained homopolymers (hA). We have shown that the homopolymer in these blends can be present in either the minority component (channels) or the majority component (matrix) of the OBDD blend morphology. This variety in the nature of the microdomains illustrates a tolerance on behalf of the OBDD morphology to the specific makeup of the microdomains. The overall polystyrene volume fraction is approximately the same in the binary blends, the linear diblock copolymers, and the star diblock copolymers exhibiting the OBDD morphology. Therefore, the free energy minimization of the OBDD morphology depends most strongly on the overall composition of the system. We however cannot ignore the singular homopolymer molecular weight dependence on the morphology at the fixed overall blend composition of 65 vol % PS. A forthcoming paper describes a variety of ordered blend morphologies in which the mean curvature and the area per junction of the intermaterial dividing surface increase generally with increasing homopolymer concentration and decreasing homopolymer molecular weight.[24]

The first-order phase transitions in AB/hA blends are rather abrupt between the highly ordered morphologies upon changing the homopolymer concentration. However, the two component blends do not exhibit the characteristic biphasic regions of a first-order phase transition. The observed absence of the predicted biphasic may be due to (1) the biphasic regions existing over smaller homopolymer concentration ranges than were investigated and/or (2) the free energy differences between the observed and predicted biphasic behavior being quite small making access to them during our careful sample preparation tenuous. The first explanation is a sufficient explanation in the absence of any observed two-phase region but does not address the observation of seemingly incorrect two-phase regions. Our explanations are currently incomplete and require further investigation into the specific nature of the phase transitions as a function of homopolymer concentration.

Finally, we will discuss the failure of type II blends to produce the inverted OBDD morphology. Moderate amounts of homopolymer can be added to a cylinder-forming diblock copolymer to form a lamellar morphology, which implies modest swelling of the minority block. At higher homopolymer concentrations, i.e. above the miscibility limit, self-assembly expels the homopolymer from the microstructure and forms a second phase containing approximately pure homopolymer. The binary blends of diblock copolymer and homopolymer exhibit macrophase separation rather than form an inverted morphology. For inverted morphologies to form, the minority block of the copolymer must swell to such an extent that its effective volume per chain is larger than that of the unswollen majority block of the copolymer. The effective volume per chain includes the volume of the minority block and the volume of homopolymer segments which mix with the block. Swelling is promoted by the favorable entropy of mixing between the minority blocks and the homopolymers, while the swelling is limited by the unfavorable chain stretching of the constrained blocks and the entropy loss for homopolymer near the interfaces. Similar free energy balances have been used to theoretically describe homopolymer mixing in the corona region of copolymer spherical micelles[25] and solvent swelling in gels.[26] Sadron and Gallot have reported inverted morphologies for a cylindrical diblock copolymer and solvents which are selective for the minority component of the diblock.[27]

These results indicate the solubility range for a selective small molecule solvent is greater than for a selective homopolymer, as expected.

Solubilization of a homopolymer (hA) in a diblock copolymer (AB) is severely limited when the minority component of the copolymer is component A. The assumption that macrophase separation occurs when the relative homopolymer molecular weight is greater than 1 is proven inadequate by the above blends. Homopolymer solubility depends on the composition of the copolymer as well as the relative homopolymer molecular weight.

Summary

This study establishes the presence of the ordered bicontinuous double-diamond morphology in binary blends of a diblock copolymer (AB) and a homopolymer (hA). The blend morphology is controlled by the overall composition of the blend, the morphology of the pure diblock copolymer, and the relative homopolymer molecular weight. The overall polystyrene volume fractions at which the OBDD microstructure is observed vary slightly between specific blend systems, but in general an OBDD morphology is observed between 64 and 67 vol % PS. The OBDD morphology in binary blends has homopolymer in the matrix when a lamellae-forming diblock copolymer is used or homopolymer in the diamond channels when a cylinder-forming diblock copolymer (type I blends) is used. Macrophase separation occurs when production of an inverted OBDD morphology with a cylindrical diblock copolymer and a large amount of homopolymer (type II blends) is attempted. The general requirements for forming the OBDD morphology in binary blends are as follows.

(1) The overall composition of the blend should equal the composition for the OBDD morphology in neat linear or star diblock copolymers.

(2) The diblock copolymer used in the binary blend can have either the lamellar or cylindrical morphology.

(3) The homopolymer molecular weight should be approximately equal to or less than the respective block molecular weight.

These blends of diblock copolymers and homopolymers exhibit long-range order comparable to that of the neat diblock copolymers. Our method of preparing the OBDD morphology in binary blends is significantly more accessible than synthesizing a block copolymer with the specific composition. An easier route to the OBDD morphology will allow more investigators to study this intriguing morphology.

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Registry No. (PS)(PI) (block copolymer), 105729-79-1; (PS)-(PB) (block copolymer), 106107-54-4; hPS, 9003-53-6; hPI, 9003-31-0; hPB, 9003-17-2.