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Effect of Short Diblock Copolymers at Internal Interfaces of Large Diblock Copolymer Mesophases

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ABSTRACT: A model system of short polystyrene−polyisoprene diblock copolymers mixed with the corresponding strongly segregated long diblock copolymers is studied by small-angle X-ray scattering, electron microscopy, and self-consistent mean-field calculations of the ordered microphases. It is found that most of the small diblocks solubilize in the ordered domains, but a small amount segregates to the domain interfaces, in the manner of cosurfactants. Adding more short diblocks results in domain size shrinkage, consistent with a theoretical analysis of the changes in the interfacial energy and the chain stretching. The stability of the lamellar phase is discussed with respect to the structural fixed point in sections of the phase cube for diblock mixtures studied earlier. More complex systems, involving nonionic surfactants in solutions of water-soluble block copolymers, are expected to behave in the same way.

Introduction

Monodisperse diblock copolymer melts have long been the focus of much attention because of their rich phase behavior and useful material properties.[1] Recent experimental[2−4] and theoretical work[5−6] has turned to mixtures of diblock copolymers, with the goal of understanding the underlying principles of the observed complex phase behavior. However, there has been little work on mixtures of diblock copolymers where one of the components is so short as to remain in the disordered phase by itself and the other component is strongly segregated. Small amounts of the short diblocks added to the long diblocks are expected to act as internal interfacial surfactants[7] or as fillers in the ordered domains of the long diblocks, depending on their chemical composition and volume fraction. In this paper we study the addition of an almost symmetric short diblock of poly(styrene-*block*-isoprene) to an almost symmetric long diblock on the same material. The effect of adding increasing amounts of the short diblock is measured experimentally and calculated theoretically, and the evolution of the activity of the short diblocks from interfacial agents (at a few volume percent) to domain fillers (at ∼40 vol%) is noted.

The cosurfactant scheme of short diblocks interacting with and modifying the mesophases of the long diblocks is a simple but useful model for analyzing the changes in the enthalpy−entropy balance which exists for any self-assembling system of surfactants.[8] In particular, similar effects are expected in more complex systems, where solubilization of nonionic polymers in aqueous ordered liquid crystalline phases has been studied.[9]

Experimental Section

Sample Preparation. A series of monodisperse polystyrene−polyisoprene (PS/PI) diblock copolymers were synthesized using anionic polymerization techniques.[10] Cyclohexane (Pure grade) was purchased from Phillips Petroleum. *sec*-Butyllithium was obtained from Lithium Corp. of America (Lithco) as 1.4 M solutions and used without further purification. Styrene was purchased from Aldrich and purified by passing through an activated alumina column to remove inhibitors. Anionic polymerization grade isoprene was obtained from the Goodyear Corp. and used as received.

A fresh supply of cyclohexane was added to a clean reactor along with the desired amount of purified styrene. The reactor was heated to 60 °C and titrated by dropwise addition of *sec*-butyllithium. Once a persistent yellow color was achieved, the calculated amount of *sec*-butyllithium was charged to the reactor to give the desired molecular weight. A period of 30 min was allowed to elapse to permit complete conversion of the styrene, at which time a sample of the polystyrene first block was taken and the desired amount of isoprene was added. After an additional 90 min passed to allow for complete conversion of the isoprene, the reaction was terminated with degassed 2-propanol. The contents of the reactor were pumped out under pressure and precipitated into a slightly acidic methanol/2-propanol mixture. The precipitated mixture was stabilized with Irganox 1010, vacuum dried, and stored under refrigeration.

Copolymer characterization molecular weights and molecular weight distributions were determined by size exclusion chromatography with Ultrastyragel columns of 500, 1000, 10 000, and 100 000 porosities in tetrahydrofuran. Compositions were determined by ^{1}H-NMR analysis using a GE QE-300 NMR.

The physical characteristics of the polymers are given in Table 1, showing the molecular weight of each block, the volume fraction of polystyrene per diblock copolymer, *f*, and the polydispersity index.

The polymer samples were prepared in a manner to ensure an equilibrium structure as well as a uniform blend of the two constituent diblocks. The diblock copolymers were first dissolved in toluene, a nonselective solvent for both polystyrene and polyisoprene at ∼1 wt %. The solvent was evaporated under vacuum at room temperature until the solutions were ∼5 wt %. The solutions were then cast into films ∼0.5 mm in thickness in glass dishes for 10 days under vacuum at 40 °C until no changes in the sample mass were measured. Before

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Table 1. Physical Characteristics and Morphology of PS/PI Diblock Copolymers and Measured Domain Spacings, *d*, for Long Diblock Copolymer Mixtures with 2 and 5 vol % Short 1/1 Diblock Copolymers

	$M_w \times 10^{-3}$ (g/cm^3)					d (Å)		
sample	styrene	isoprene	$f = Z_{PS}/Z_{PI}$	M_w/M_n	morphology	melt	2 vol %	5 vol %
A	36	20	0.61	1.03	lamellar	338 ± 3	333 ± 5	325 ± 3
B	33	20	0.59	1.06	lamellar	325 ± 4	319 ± 3	312 ± 2
C	36	60	0.35	1.04	cylindrical	592 ± 10	592 ± 10	573 ± 10
D	36	78	0.29	1.05	cylindrical	624 ± 10	624 ± 10	611 ± 10
M	1	1	0.47	1.10	disordered			

the scattering experiments were performed, the samples were annealed under vacuum at 110 °C, above the polystyrene glass transition temperature, for 9 h.

Small-Angle X-ray Scattering. Small-angle X-ray scattering (SAXS) experiments were performed at the Stanford Synchrotron Radiation Laboratory (SSRL) on beam line 1−4. Details about the station can be found elsewhere.[11] The wavelength of the incident radiation was $\lambda = 1.493$ Å, and the scattered intensities were measured using a Reticon 1024 pixel linear photodiode array cooled to −80 °C. The X-ray beam was collimated using two sets of slits to reduce parasitic scattering. The sample to detector distance was set between 52 and 107 cm for a range of $q = (4\pi/\lambda)\sin(\theta/2)$, where θ is the scattering angle, between 0.005 and 0.18 Å^{-1}. The magnitudes of the scattering vector were calibrated using chicken tendon collagen (domain spacing, $d = 653$ Å). Typically, eight or nine peaks were observed and the q range was calibrated using the prominent sixth peak. We did not measure the absolute intensities, since they were not required in this study.

The ordered domains in the polymer samples were not oriented, and the resulting scattering patterns came from polycrystalline "powder" samples. The specific microphase domain structure was determined from the relative ratios of the peak positions in the scattering profiles. For example, the lamellar domains were characterized by peaks appearing in the ratio (1:2:3:4:...) and the hexagonally packed cylindrical domains had diffraction peaks at ratios of ($1{:}\sqrt{3}{:}\sqrt{4}{:}\sqrt{7}{:}\sqrt{9}{:}$ ...). By complementing the SAXS measurements with TEM observations, an unambiguous determination of the sample morphology was carried out.

The domain spacing, d, for a lamellar structure was determined by following Winey et al.[12] from linear regression on all observed diffraction peaks using the relations $d_n = C_1/n + C_2$, where n is the order of the diffraction peak and the domain spacing for each peak was determined from the magnitude of the scattering vector, $d_n = 2\pi/q_n$. The overall domain spacing is given by $d = C_1 + C_2$, where ideally $C_2 = 0$. We found that the domain spacing varied by less than 5 Å for multiple SAXS measurements on the same samples and C_2 was less than 2% of C_1.

For two of the diblock copolymers, higher order diffraction peaks were not distinct enough to accurately determine the domain spacing. We used the q value of the first diffraction peak to estimate the domain spacing. In general, accurate determination of the domain spacing cannot be made solely from the position of the first diffraction peak because an error in a single pixel results in larger errors in d, particularly at lower values of q; however, the data from these samples still provided good qualitative results.

Transmission Electron Microscopy. The diblock copolymer morphologies were examined using transmission electron microscopy (TEM) of ultrathin sections of the polymer samples. The observed sections were first stained in OsO_4 vapor for a short time and then embedded in an epoxy resin. The samples were first stained in order to see the polymer in the resin and also to monitor any diffusion of polymer into the epoxy matrix. No diffusion of the stained sample was observed. After hardening, the samples were sectioned into slices between 500 and 100 Å in thickness and floated onto poly(vinylformal)-coated electron microscope grids using a Reichert ultramicrotome with a diamond knife at room temperature. The sections were further stained in OsO_4 vapor for several hours. The OsO_4 vapor selectively stained the polyisoprene domains, which appeared dark on the electron micrographs, while the polystyrene domains appeared white. The sections were examined with a Philips 410 transmission electron microscope operating at 80 kV. The observed morphologies were consistent with the scattering measurements, indicating that no morphological changes took place during sample preparation.

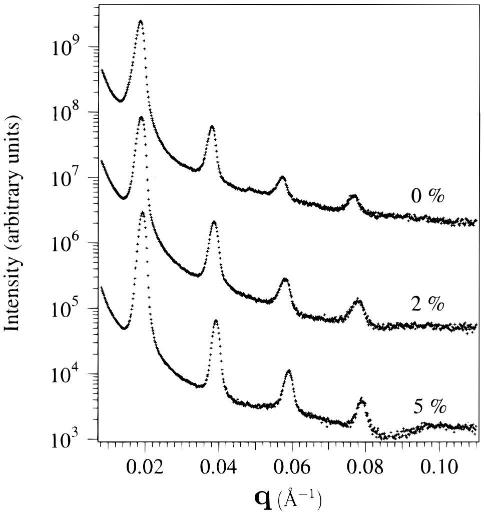

Figure 1. SAXS data for the addition of 2 and 5 vol % of short PS/PI 1/1 diblocks to sample A ($Z_L = 654$, $f_L = 0.61$, lamellar phase).

Results and Discussion

Pure Component Microstructure. Before examining the blended polymer systems, we characterized the bulk long diblock copolymer morphologies to provide a reference for any structural changes from the addition of the short diblock copolymer. The long diblock copolymers used in this study are in the strong segregation limit ($\chi N \gg 10$) and have morphologies characterized by sharp domain boundaries with polymer chains having highly stretched configurations. These diblocks exhibit two different morphologies, lamellas and hexagonally packed cylinders. Figure 1 shows a representative SAXS profile of the lamellar structure of sample A, and Figure 2 shows a representative transmission electron micrograph for the same system. The SAXS data from this diblock show four distinct scattering peaks with q values at ratios indicative of a lamellar structure with a domain repeat distance of 338 ± 3 Å. The TEM micrograph shows the sharp alternating dark and light bands characteristic of the lamellar structure seen in the scattering data. The polystyrene domains are larger than the polyisoprene domains; this feature is consistent with the volume fraction of polystyrene within this diblock ($f_L = 0.61$).

Small-Volume Fractions of Short Diblock. In this section, we study the structural changes that occur in diblock copolymer mixtures with the addition of small-volume fractions, 2 and 5 vol %, of the 1/1 diblock copolymer, sample M. The SAXS data for sample A with the addition of 2 and 5 vol % 1/1 diblock are shown

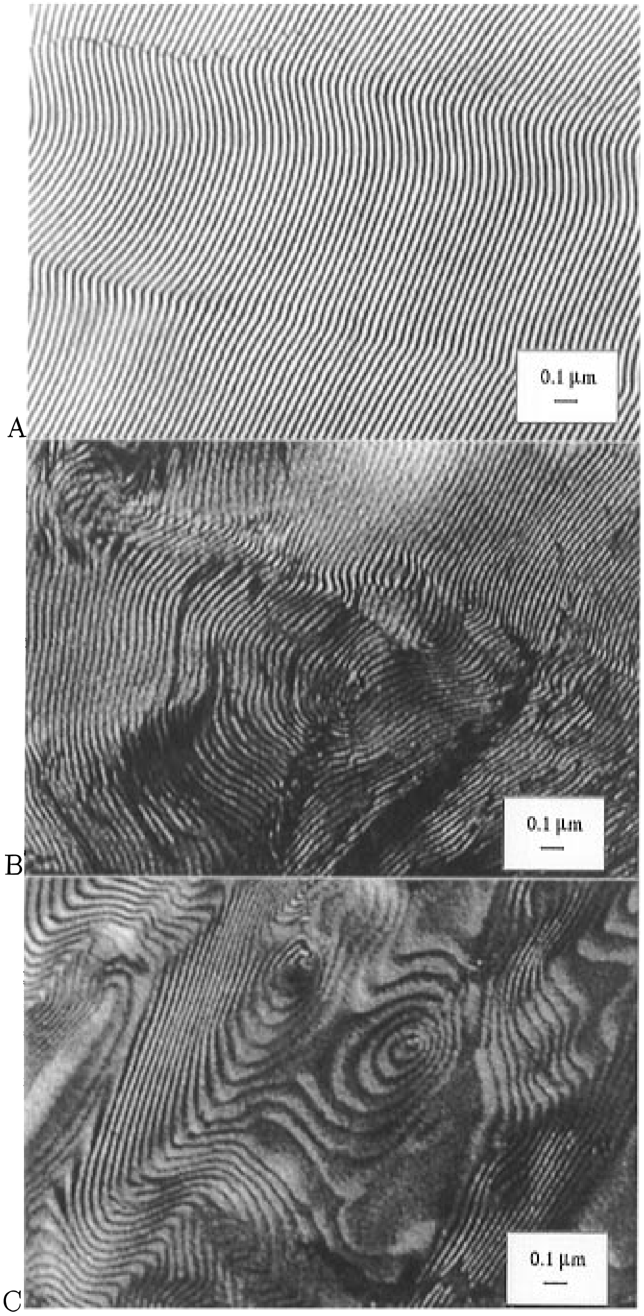

Figure 2. TEM pictures for sample A ($Z_L = 654$, $f_L = 0.61$, lamellar phase) with (a) 0, (b) 20, and (c) 30 vol% fractions of PS/PI 1/1 diblock copolymer.

in Figure 1. Each scattering profile has four sharp peaks indicative of a well-ordered lamellar morphology. With increasing amounts of the short diblock, the peak positions shift to higher values of *q*, corresponding to a decrease in the domain spacing. For each system studied here, the addition of the short diblock copolymer decreased the domain spacing without changing the microstructure. The measured domain spacings for each diblock copolymer system are shown in Table 1. Although it appears that the measured spacing in the large cylindrical systems does not change for 2 vol % of short diblock, decreases in the domain size are observed from the location of the more diffuse outer peaks at higher values of *q*. Even though the addition of short diblocks can shift the phase boundaries of the long diblock copolymer, we see no changes in the bulk morphology.

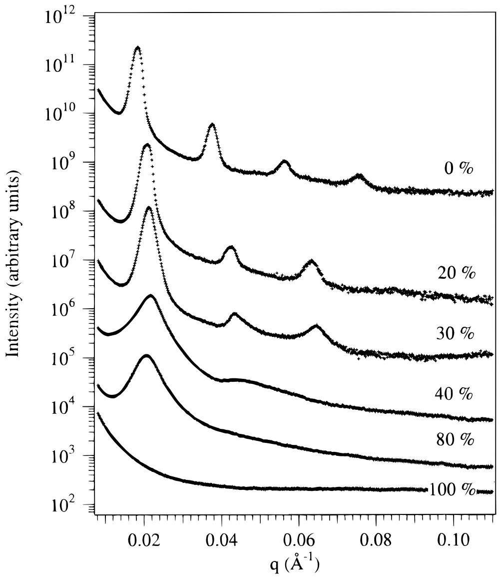

Figure 3. SAXS for mixtures of sample A ($Z_L = 654$, $f_L = 0.61$, lamellar phase) with volume fractions of 0, 20, 30, 40, 80, and 100 vol % PS/PI 1/1 diblock copolymer.

The decrease in the domain size with the added short diblock copolymer is a clear indication that at least some of the short diblocks have segregated to the domain interfaces. The location of the short diblock at the interfaces has two main effects on the free energy.[5] The location of the short diblocks at the domain interfaces reduces the interfacial tension due to the decrease in enthalpic mixing energy of the two diblocks. Also, if the domain spacing of the melt were to be maintained and some of the short blocks were located at the interface, the stretching free energy of the long diblock copolymers would increase because the polymers must retain a uniform density with fewer long diblocks per unit area. On the other hand, if most of the short diblocks are solubilized in the domains in order to increase the entropy of mixing and act as fillers, less stretching of the long diblocks is expected. When the total free energy is minimized with respect to the domain size, changes in both the enthalpic and stretching free energies will shift the equilibrium domain spacing. The magnitude of their effects is calculated in the theoretical section.

Larger Volume Fractions of Short Diblocks. The structure of diblock copolymer mixtures having a larger amount of short diblock copolymer are of interest because of the structural transition that occurs as the blend composition moves between the two composition limits of a disordered polymer melt and a strongly segregated ordered one. Few theoretical studies have examined these intermediate segregation regimes. We focused on polymer A having a bulk lamellar morphology and prepared samples with 20, 30, 40, 80, and 100 vol % of the short 1/1 PS/PI diblock copolymer in addition to the smaller volume fractions of the short block from the previous section. The SAXS data for this concentration series are shown in Figure 3. As expected, the scattering profile for the pure short diblock copolymer is featureless, characteristic of a uniformly disordered structure. A broad peak is expected from the dominant mode of the concentration fluctuations but is not observed in the *q* range of the experiment. The *q* value of the peak position can be calculated from the random phase approximation (RPA), and earlier studies have shown that the RPA approximation describes well the scattering data for other disordered diblock copolymer systems.[13] Using this theory, the maximum from the dominant mode of the concentration fluctuations for the short diblock is located at $q \approx 0.1$, at the edge of the q range accessed in this scattering configuration where the scattered intensity signal is weak. At the other composition limit, 0%, with only the long diblock copolymer, the lamellar structure is well-defined with four diffraction peaks.

As the volume fraction of the short diblock is increased, the gradual broadening and the loss of the fourth diffraction peak indicates a decrease in the long-range lamellar order. The lamellar order persists up to 30% of short diblocks but is not as well-defined as in the pure long diblock system. The position of the diffraction peaks also continues to shift to higher values of q for the 20% and the 30% short diblock mixtures, indicating a continued decrease in the domain spacing.

For the 40 and 80% blends, long-range lamellar order is lost and only one broad prominent scattering peak is resolved. These peaks are located close to the position of the first peak for the pure long diblock, suggesting that the observed structure is related to those observed in the 20 and 30% blends. The dominant peaks in the 40 and 80% mixtures are at higher q values than the first peak in the one for 30%, indicating that more of the short diblocks are located at the interfaces; however, the mixture with 80% short diblock has a very broad peak at a slightly lower q value than the 40% blend corresponding to an increase in the characteristic size of the order present in this sample relative to the 40% case. The small changes in the characteristic domain sizes at these higher concentrations suggest that a smaller fraction of the short diblocks moves to the interface than at lower short diblock concentrations. With less long-range order in the 40 and 80% samples than in the samples with smaller amounts of the short diblock, changes in the lamellar morphology may have occurred; however, the specific morphology of the 40 and 80% samples cannot be determined from the SAXS measurements alone.

The decrease in lamellar order with increasing amounts of the short diblock is also seen in several micrographs in Figure 2. Again, a well-developed lamellar morphology with larger polystyrene domains is seen in the pure long diblock system. For the 20 and 30% blends, the long-range lamellar order is diminished with decreases in the domain spacing as observed in the SAXS profiles. As more of the short diblock copolymer segregates to the interface, the reduction in both the interfacial energy and the strong chain stretching results in diminished order. The micrographs do not provide any structural details corresponding to the faint presence of a broad peak in the scattering profiles for the 20 and 30% samples. Unfortunately, due to the relatively low molecular weight of the short diblock, TEM pictures could not be obtained for the blends with greater than 30% of the short diblock because the resulting samples were not rigid enough to make the ultrathin sections needed for TEM. As a result, the bulk morphology of these systems is unknown at present.

We now compare our experimental results with data from Hashimoto et al.,[2] who examined another PS/PI diblock copolymer mixture involving different compositions of a binary blend with a disordered diblock and a lamellar diblock copolymer as part of a larger study of binary mixtures of larger diblocks; however, the disordered diblock in their study is several times larger than the ones used here. They observe some lamellar order with three diffraction peaks for 80 wt % of the shorter block. Additionally, they observe macrophase separation between the two polymer blocks even though weak segregation theories predict that there should not be any macrophase separation.[3] A broad scattering peak is correlated with the concentration fluctuations arising from disordered regions of the shorter diblock, which is phase separated from the ordered diblock copolymer domains. In contrast with their observations, we do not observe macrophase separation in the micrographs.

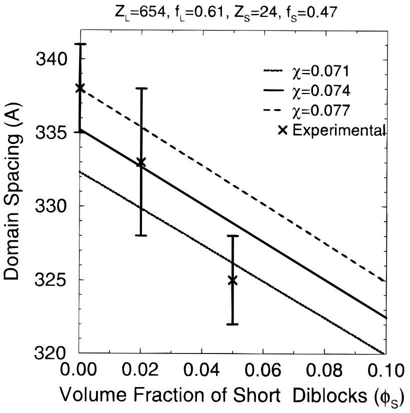

Figure 4. Calculated domain spacing for sample A ($Z_L = 654$, $f_L = 0.61$, lamellar phase) for different values of PS/PI χ parameter. The volume of $\chi = 0.074$ was chosen as the best fit to the data.

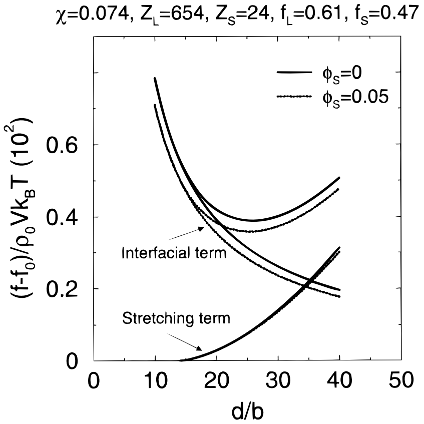

Figure 5. Calculated free energies for $\chi = 0.074$, $Z_L = 654$, $Z_S = 24$, $f_S = 0.47$, and $\phi = 0.05$. The solid lines are for the pure diblocks; dashed lines ($f_S = 0.47$) are with added short chains. The interfacial ($\propto d^{-1}$) and entropic ($\propto d^2$) free energy contributions are shown. The mixing free energy of the short diblocks is omitted in the figure. The domain spacing is scaled by the Kuhn's length b. For approximately symmetric short diblocks (cosurfactants) the domain spacing decreases as a consequence of the reduction of the interfacial term, and the cancellation of the reduction in the stretching free energy (due to the effect of the short diblocks as fillers) with the increase in the stretching free energy (due to the increased interfacial area of the long diblocks).

Theoretical Section

We have carried out mean-field calculations of the effect of small amounts of the short diblocks on the ordered lamellar domains. The results are shown in Figures 4−6. For the calculation the polymer densities were taken to be $\rho_{PS} = 1.053$ g/cm^3 and $\rho_{PI} = 0.913$ g/cm^3, and the average Kuhn length was $(b_{PS}b_{PI})^{1/2} = 0.65$ nm, where $b_{PS} = 0.71$ nm and $b_{PI} = 0.59$ nm.[3] Figure 4 shows the domain shrinkage with increasing volume fraction of short diblocks. The best fit for the χ

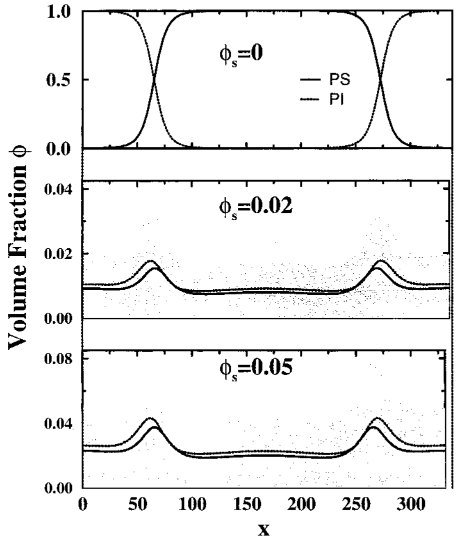

Figure 6. Calculated density profiles for long diblocks, sample A ($Z_L = 654$, $f_L = 0.61$, lamellar phase), with different amounts of short diblocks ($Z_S = 24$, $f_S = 0.47$) added. The χ volume for PS/PI is 0.074. The shaded area indicates the overall short diblock copolymer profile, and the dashed and solid lines correspond to the individual PI and PS profiles, respectively.

interaction parameter for PS/PI in this case is 0.074, in agreement with other values ranging from 0.074 to 0.1.[13]

As pointed out earlier, the decrease in the domain spacing may result from two effects. First, the segregation of some of the short diblocks to the PS and PI domain interface reduces the interfacial tension of the domain interface. Second, the localization of the short diblocks at the interface causes a spreading apart of the long diblocks, resulting in an increase in the interfacial area per long diblock. The smaller number of long diblocks per unit area must therefore stretch more to fill the middle of the domain. However, the large amount of small diblocks solubilized in the domains reduces the stretching of the long diblocks. The net result is little change in the stretching free energy for this particular case, as shown in Figure 5, which also shows the reduction in the interfacial free energy resulting from the effect of the short diblocks acting as internal surfactants at the domain interfaces. The reduction of the domain size in this case is primarily due to the internal surfactant effect.

Figure 6 shows the overall density profiles of the short diblocks in the ordered domains, as well as the individual block profiles. Remarkably, although only ~20% of the short diblocks segregate to the interface, this is enough to cause a shrinkage of the long period of the lamellar structure. Otherwise, the added short diblocks act as an almost nonselective solvent for the lamellar mesophase.

Figure 7 shows the changes in the different sections of the phase cube as more short diblocks are added to the system. The phase cube is a scheme for presenting the phase diagram for binary mixtures of two types of AB diblocks, with chemical compositions $f_1 = Z_{1A}/Z_1$, and $f_2 = Z_{2A}/Z_2$ as the x and y axes and the volume fraction of one of the components as the z axis.[6] This scheme is particularly useful for studying the global symmetries with respect to the chemical compositions and volume fractions of a system with a large number of variables. A previous theoretical study of weakly and strongly segregated regimes for binary mixtures of diblock copolymers focused on the points of invariance (structural fixed points) and on the structure–density profile diagrams of various phases.

In Figure 7 the experimental point, for $f_L = 0.61$ and $f_S = 0.47$, is shown by the black dot, and the structural fixed points, where the entropic and enthalpic changes to the free energy cancel,[6] are shown by the open circles. The experimental point is close to the structural fixed point on the righ-hand side of the diagram, and the lamellar order persists to high-volume fractions of the short diblock, as seen in the TEM pictures displayed in Figure 2. Samples C and D, having cylindrical symmetry, are very close to the structural fixed point on the left-hand side of the diagram and, consequently, do not show measurable changes in the domain sizes for extremely small amounts of added short diblocks (2%).

Conclusions

A model system of short and long PS/PI diblock copolymers has been studied experimentally and theoretically. The short diblocks were found to behave as cosurfactants in a surfactant system, in that they solubilized in the ordered domains formed by the large molecules, but also localized at the internal domain boundaries. The degree of localization and solubilization depends on the interaction parameter, chain lengths,

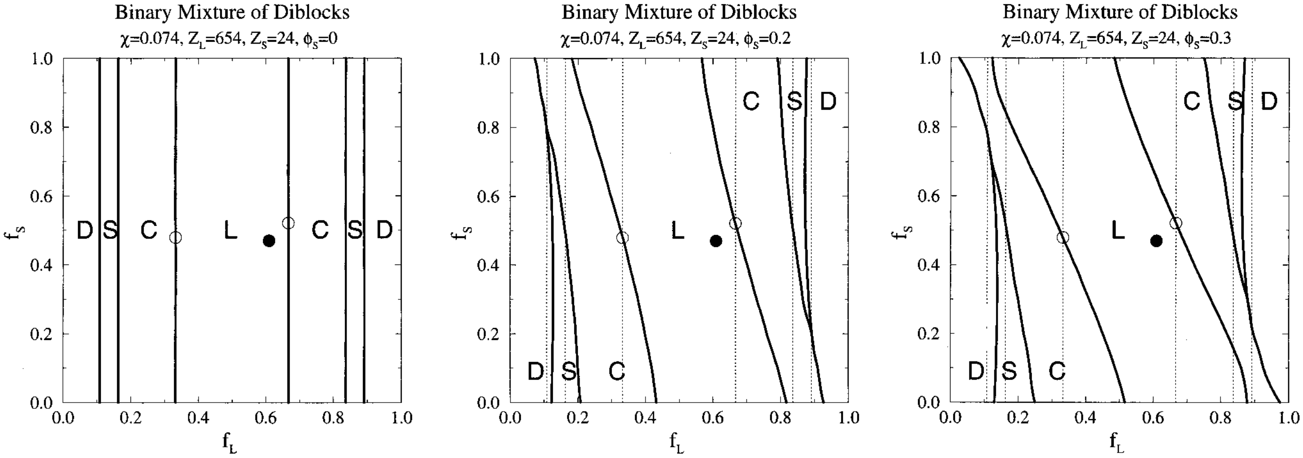

Figure 7. Phase diagrams for (a, left) 0, (to middle) 20, and (c, right) 30% volume fraction of short diblocks ($Z_S = 24$, $f_S = 0.47$) mixed into the ordered domains of the long diblocks ($Z_L = 654$, $f_L = 0.61$). The solid dot indicates the experimental point investigated in this paper, and the open circles indicate the structural fixed points in the phase diagrams. D refers to disordered; S, spherical; C, cylindrical, and L, lamellar.

and volume fractions. Small changes in these parameters, particularly for the cosurfactant, can be amplified through their effect on the overall morphology. In a sense, the approximately symmetric short diblocks act as a good solvent for both blocks of the large copolymers, except for the added feature of interfacial activity.

The experimental observations are in accord with the theoretical predictions, with respect to both the overall phase behavior and the interfacial effects. It is hoped that this study of a relatively simple system can serve as a guide for the analysis of more complex systems, such as mixtures of small nonionic surfactants with polymers in aqueous solutions.[9]

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