Self-Assembly in Mixtures of Block Copolymers: "Co-Surfactant Effects" on Morphology Control

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Summary: We found that competing long-range interactions of the two block chains in their binary mixtures give intriguing effects on ordered microdomain structures. One effect is a co-surfactant effect observed when the two blocks are mixed with their junctions on common interfaces, giving rise to such effects as (i) the two lamella-forming block copolymers give hexagonal cylinders and consequently to the increase of the interface curvatures, or (ii) a short symmetric block copolymer mixed with a large asymmetric block copolymer effectively decreases the interface curvatures, depending upon composition and molecular weight of the short block copolymer. The other effect is the one which causes two blocks macroscopically phase-separate into different ordered domains.

Keywords: block copolymer; cosurfacant effect; mixture of block copolymers

1. Introduction

It is extremely interesting for us to realize that just a single covalent bond between A and B polymers at their ends strongly alters the physics of the two component polymer systems. Without this covalent bond, polymer mixtures A and B can achieve macrophase separation with a single interface at thermal equilibrium. The important physical factor here is competing *short-range interactions* between A-B, B-B and A-B segments. On the other hand with this single covalent bond, A-B block copolymers can achieve microphase separation in which the bulk of the A-B is an assembly of numerous interfaces separating A and B microdomains with long range order and various space symmetries.

It is very important to realize that various nano-sized structural units in bulk block copolymers are created by *competing interactions* between the short-range interactions inherent in the mixture and the *long-range interactions* inherent in A-B which arises from the block connectivity of A and B blocks and from resulting packing effects of A and B block

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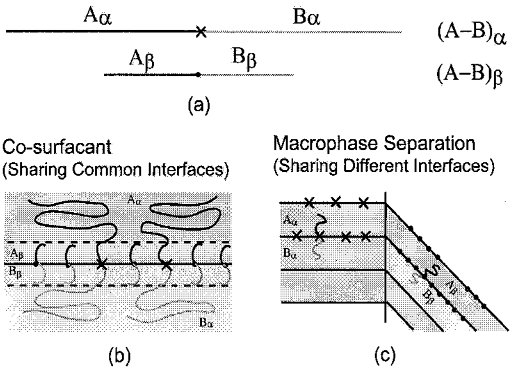

Figure 1. Effects of competing long-range interaction of two A-B diblock copolymers $(A\text{-}B)_\alpha$ and $(A\text{-}B)_\beta$ (or α and β) (part a) on morphology of mixtures of α and β, giving rise to co-surfactant effects (part b) and macrophase separation (part c).

chains in the respective microphases. The competing interactions yielded long-range-ordered nano-sized units with various symmetries such as body-centered cubic spheres, hexagonal cylinders, double gyroid networks, alternating lamellae, and so on [1].

What is new, when we mix two A-B block copolymers, designated hereafter $(A - B)_\alpha$ and $(A - B)_\beta$ or simply α and β (Figure 1a)? We have the same short-range interactions between A and B and its competition with the long-range interactions related to the block connectivity in both α and β. However the long-range interactions associated with two block copolymers α and β themselves now have to compete each other, which should give new delicate effects on the nano-sized patterns.

The *competing long-range interactions* can give two cases; one in which the two blocks α and β share common interfaces and act as *co-surfactants* (Figure 1b), and the other in which they share different interfaces, giving rise to macrophase separation in two different ordered phases α and β (Figure 1c). In our paper, we shall focus on the co-surfactant effects, but not on the macrophase separation which has been detailed to some extent elsewhere [2].

We shall discuss two types of co-surfactant effects. In the first case, the effect increases interface curvatures such as the case in which two lamella-forming block copolymers mix each other to give a single morphology of cylinder or bicontinuous domain [2]. In the second case, the effect decreases the interface curvatures, on the contrary to the above case. For example, the case in which A-cylinder and B-cylinder forming A-B block copolymers mix each other to form lamellae, or the case in which long asymmetric sphere-forming block copolymers $(A - B)_\alpha$ and short symmetric lamella-forming block copolymers $(A - B)_\beta$ mix each other to form cylinder, bicontinuous or lamellar morphology, depending on their composition.

Let us now review one of the previous results on mixtures of lamella-forming Poly(styrene)-

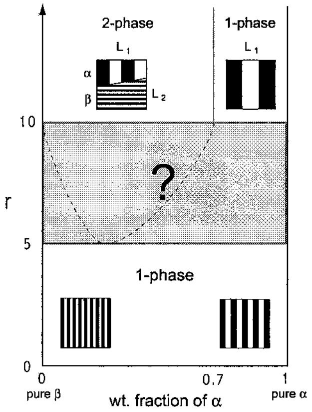

Figure 2. Phase diagram of binary mixtures of lamella-forming PS-PI block copolymers α and β in the parameter space of $r \equiv M_{n\alpha} / M_{n\beta}$, where $M_{n\alpha}$ and $M_{n\beta}$ are total number-average molecular weights of α and β, respectively, and composition of α.

block-poly(isoprene) (PS-PI) block copolymers (Figure 2)[2]. Here we define the ratio r as molecular weight of large $(\text{PS-PI})_\alpha$ block copolymer to that of small $(\text{PS-PI})_\beta$ block copolymer. We found that if $r < 5$, the two block copolymers α and β are miscible to form single lamellar morphology at all compositions. However when $r > 10$, they are not miscible for the mixtures with weight fraction of α less than 0.7, resulting in macrophase separation into large lamellae L_1 and small lamellae L_2 with interesting commensurating domain boundary structures at the macrointerface. Although some researchers were skeptical at that stage about our results on macrophase separation, Matsen[3] confirmed it. On the other hand when α is greater than 70 wt%, they mix each other. However at that time we were still lacking experimental results in the intermediate range of r. We can address a question on how the phase boundary for macrophase separation changes with composition in this range and also on what kind of co-surfacant effects we can anticipate in the miscible composition range.

2. Results and Discussion

2-1. Co-surfactant Effects Yielding Increasing Interface Curvatures

In order to unveil the above problems in the intermediate range of r in Figure 2, we used one large PS-PI block copolymer α with only slightly asymmetric composition and therefore forming lamella in ordered state, and four nearly symmetric short block copolymers, β_1 to

Table 1. Characteristics of PS-PI Diblock Copolymers.

code	M_n	M_w/M_n	$M_{n,PS} - M_{n,PI}$	f_{PS}	morphology	r
α	1.0×10^5	1.16	$5.0\times10^4 - 5.0\times10^4$	0.47	lamella	–
β_1	1.21×10^4	< 1.05	$6.3\times10^3 - 5.8\times10^3$	0.49	disorder	8.26
β_2	1.36×10^4	< 1.05	$7.1\times10^3 - 6.5\times10^3$	0.49	lamella	7.35
β_3	1.45×10^4	< 1.05	$7.0\times10^3 - 7.5\times10^3$	0.45	lamella	6.90
β_4	2.1×10^4	< 1.05	$9\times10^3 - 1.2\times10^4$	0.40	lamella	4.76

β_4, as shown in Table 1.[4] The copolymer β_1 is in disordered state, because of low molecular weight, but the ratio r is the largest, of course. The copolymers β_2 to β_4 have lamellae (thought their TEM are not shown here)[4] and the ratio decreases from 7.35 to 4.76. We prepared the film specimens of these blends α / β_i (i = 1 to 4), with varying compositions by casting their toluene solutions, where toluene is a neutrally good solvent for PS and PI.

Figure 3 shows a phase diagram in the intermatediate range of r in Figure 2 in the parameter space of r and composition of α. The phase diagram obtained at room temperature shows the region where macrophase separation occurs (the region indicated by 2-phase) and the region where only microphase separation occurs (the region indicated by 1-phase). So we could confirm again the macrophase separation for the mixtures of the lamella-forming block copolymers. The miscibility gap decreases with decreasing r, which is reasonable, because the macrophase separation should not occur in the limit of $r \rightarrow 1$.

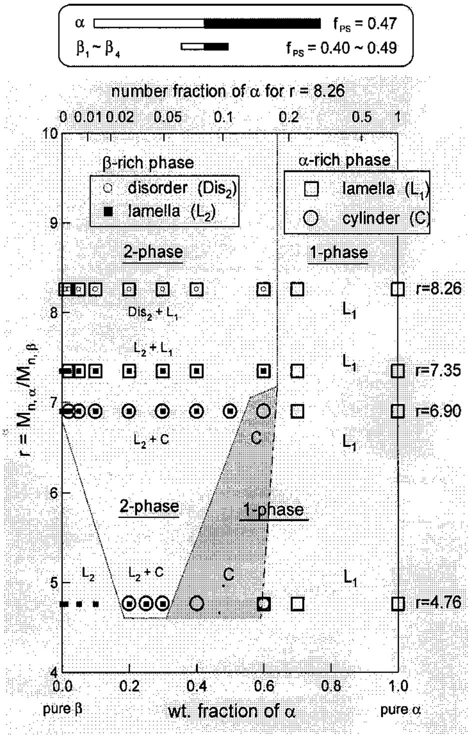

Figure 3. Phase diagram of binary mixtures of the lamella-forming PS-PI block copolymers α and β in the parameter space of r ($4.76 \leq r \leq 8.26$) and composition of α . the diagram contains four mixtures α/β_1, α/β_2, α/β_3 and α/β_4 (see Table 1).

To our big surprise we found the single phase region shown by the shaded area where cylinders are formed. Figure 4 shows some typical morphologies of the mixtures with r = 6.9. In this case we see macrophase separation into ordered cylinders C rich in α and ordered lamellae L_2 rich in β up to ca 55 wt% of the large block copolymer α, as typically shown in the mixture of α / β_3 = 20/80 (part a). Upon further increasing the composition of α, morphology turns into the ordered single phase of cylinders C and finally lamellae L_1, as shown, respectively, for the mixtures of α / β_3 = 60/40 (part b) and 70/30 (part c) . Thus we observe the lamella-to-cylinder order-order transition

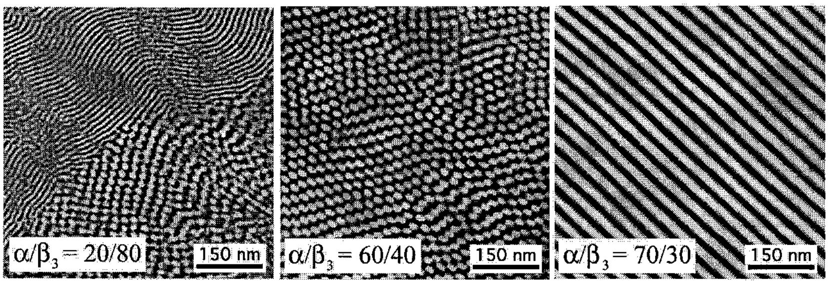

Figure 4. Transmission electron micrographs of α/β_3 with composition of (a) 20/80, (b) 60/40, and (c) 70/30. Part (a) shows macrophase separation between hex-cyl and lamellae.

with increasing composition α. In other words we found that lamella-forming block copolymers α and β mix each other to form the cylinder at this particular composition. Please note that this is a very unique cylinder having weight fraction of PS of 42 wt%. The composition range for the cylindrical morphology expands as r decreases (Figure 3).

The small-angle X-ray scattering profiles for the mixtures α/β_3 with various compositions were taken though they were shown elsewhere [4]. The results showed the following features. The neat large block copolymer α and short block copolymer β_3 themselves certainly showed the profiles typical to the ordered lamellar morphology. On the other hand the 60/40 mixtures showed the profile typical to hexagonal cylinder, consistent with the TEM results (Figure 4b). Moreover the 20/80 mixture showed the profile represented almost perfectly by a weighted sum of the profiles of the 60/40 mixture and the neat β_3, indicating that the macrophase separation into the cylinders of the 60/40 mixture and the neat β_3 lamellae.

How can we intuitively understand this intriguing lamella-to-cylinder transition? The neat short block copolymer, which is slightly asymmetric in composition, may tend to have the interface with an average mean and Gaussian curvatures inherent in the asymmetry of a single block copolymer chain, if packing interactions from other block copolymer chains are negligible, as schematically shown in Figure 5a. However many chain effects on packing do exist and do not allow the curved interface as shown in Figure 5b,because it creates density dip in the PI phase and excess density in the PS phase. As a consequence we have a flat interface for neat block copolymers having such a slightly asymmetric composition, and hence the lamellar morphology, as shown in Figure 5c. However when long symmetric block

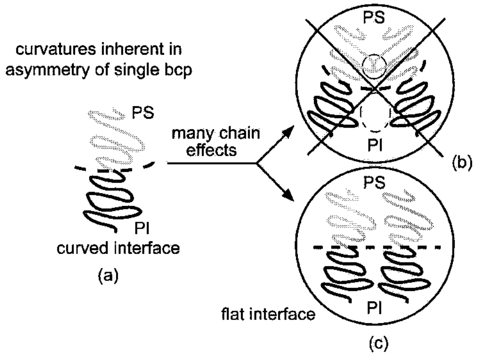

Figure 5. (a) Spontaneous curvature that a single slightly asymmetric block copolymer may take. However, neat slightly asymmetric block polymers cannot take its spontaneous curvature (b) but they rather take the flat interface (c).

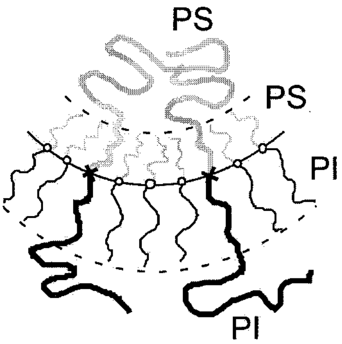

Figure 6. Cosurfactant effect demonstrating that a small amount of large block copolymers can allow to form the curved interface for the slightly asymmetric short block copolymer chains which by themselves form the flat interface.

copolymers are mixed as schematically shown in Figure 6, this packing constraint may be relaxed and the interface may tend to have the curvatures driven by the asymmetric block copolymer, even in the case where the asymmetry is very small. In this case the long block copolymers tend to fill the space unoccupied by the short slightly asymmetric block copolymers.

We found that the lamella-to-cylinder transition induced by mixing the lamella-forming block copolymers can be explained theoretically based on the strong segregation theory proposed by Birshtein et al [5]. For the short block copolymers β alone (Figures 7a and b), the lamella has free energy lower than the cylinder (Figure 7e at $\Phi_\alpha = 0$), because β is nearly symmetric . When we add the long block copolymer α, we assume that a subchain of α in the β-region takes the same conformation as the β chains, while the rest of α fill the space unoccupied by the β chains, satisfying incompressibility, as schematically shown in Figure 7c and 7d. Upon adding α, the free energy of lamella tends to monotonically increase but that of cylinder dramatically decreases first and then rapidly increases, as shown in Figure 7e. The initial drop of the free energy with Φ_α is due to relaxation of conformational penalty imposed on β-chains when they form cylinder and the subsequent rapid increase of free energy is again due to increasing conformational penalty imposed by increasing fraction of

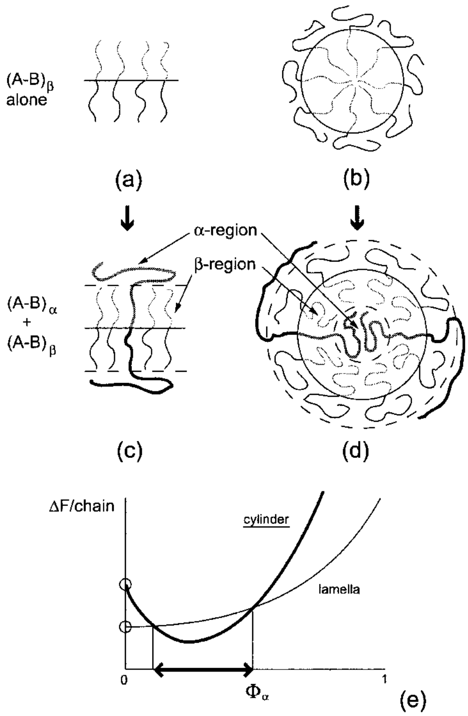

Figure 7. Schematic illustration of a theoretical interpretation of the co-surfactant effect based upon a strong segregation theory proposed by Birshtein and her coworkers. Φ_α is volume fraction of α.

nearly symmetric long A chains in the cylindrical morphology. Thus we can predict the cylinder being stabilized for a certain range of composition. Unfortunately the theory cannot predict the macrophase separation, simply because it apriori assumes that the mixtures form a single ordered phase.

Let us take a look more extensively at the theoretical predictions. First we consider the case where we keep total molecular weight M_t (=10^5) of a long symmetric block copolymer α and the ratio r (= 6.9) fixed, but we decrease $f_{B\beta}$, fraction of B block in the short block copolymer chain (from 0.43 to 0.37). The calculation of free energies of the cylinder and lamellar morphology as a function of n_α (mole fraction of α) indicates that making this B block chain short stabilizes the B cylinder, which is quite natural. However we can obtain the cylinder having total weight fraction of B (w_B) as large as 0.45. Let us consider the case of Figure 8 where we keep M_t and $f_{B\beta}$ of a short nearly symmetric block chain and the ratio r fixed, but we increases the length of long B block chains or increase $f_{B\alpha}$ as shown in the figure. Surprisingly upon increasing $f_{B\alpha}$, the B cylinder becomes more stable, though compositionally the system must favor lamellae, because w_B is as large as 0.5. Finally let us consider the case where we keep $f_{B\alpha}$ (= 0.5), $f_{B\beta}$(= 0.4), M_t (= 10^5) of α fixed but increasing the ratio r by decreasing M_t of the short block β. We found the larger the value r, more stable is the cylinder morphology. All these results demonstrate interesting co-surfactant effects.

2-2. Co-surfactant Effects Yielding Decreasing Interface Curvatures

Now let us discuss the co-surfactant effects which lower the interface curvatures. A typical

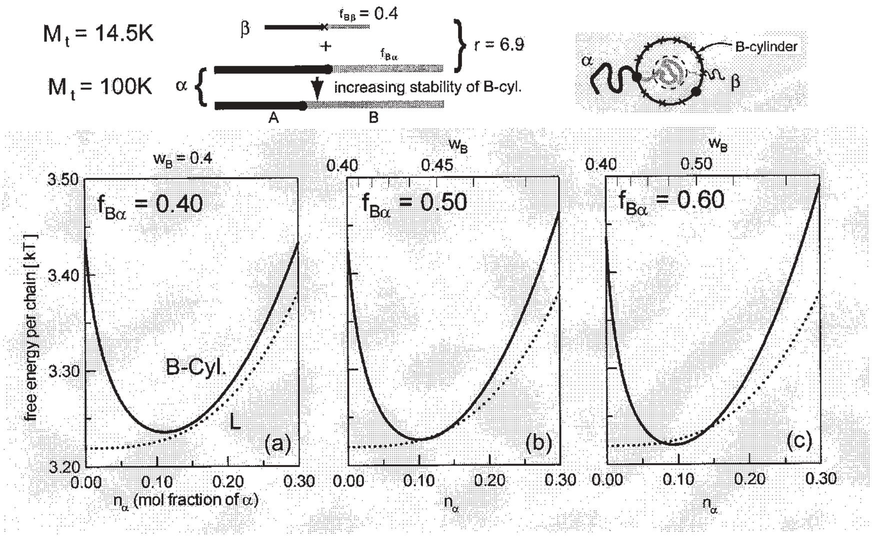

Figure 8. Co-surfacant effect showing the increased stability of the cylinder of B with increasing $f_{B\alpha}$.

example was reported by Koizumi et al.[6] : PS-cylinder- and PI- cylinder-forming PS-PI block copolymers mixed with 50/50 by weight formed lamellar morphology . This is intuitively clear, as the mixing of the two gives the PS/PI composition of the mixture close to 50/50.

We now consider a long asymmetric block copolymers α that form B spheres (as shown in Figure 9a), mixed with a short symmetric block copolymers β that form lamellae. When we replace some of the long chains α by the short chains β without changing the interface curvature, we will have a trouble of creating a density deficiency in A microphase (as shown in Figure 9b), this kind of matrix costs free-energy penalty. The mixture will then show such an interesting co-surfactant effect that gives rise to decreasing interface curvatures in order to satisfy the incompressibility, and hence the small fraction of the short symmetry blocks mixed to the system should transform its morphology from sphere to cylinder or lamella, as schematically shown in Figure 9c.

In order to check our intuition, we prepared a series of PS-PI block copolymers, as shown in Table 2 where *as* is a long asymmetric PS-PI and s_1 to s_3 short nearly symmetric PS-PI. We found all the mixtures as/s_1, as/s_2, and as/s_3 mix each other at all compositions.

Figure 10 shows a kind of phase diagram in the parameter space of r and total volume fraction of PS; ϕ_{PS}, in the mixtures [7]. It indicates the observed morphology for the three

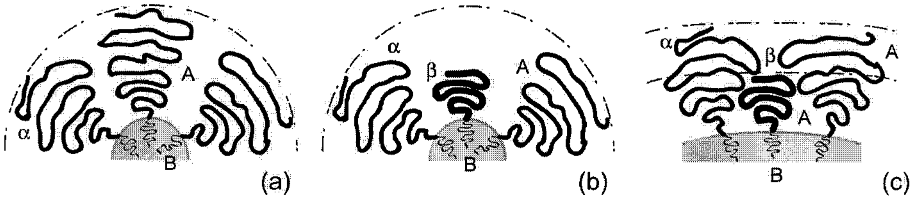

Figure 9. Cosurfactant effect found mixtures of a long asymmetric block copolymer and a short symmetric block copolymer, giving rise to a decreased interface curvature

mixtures of *as*/s_3, *as*/s_2 and *as*/s_1 having the different block length ratio *r*. On the top of the phase idagram, we show the morphological change with PS volume fraction for pure PS-PI. Interestingly enough, the short symmetry block copolymers stabilizes the lamella down to a very low value of ϕ_{PS}, lower than 0.33 for the pure diblocks (the criterion is shown by dashed line in the phase diagram). This trend depends on *r* and is enhanced by increasing *r*. In the case of *as*/s_3 the lamella is maintained down to $\phi_{\mathrm{PS}} \approx 0.24$ by adding only a small volume fraction of the short symmetric block copolymer of φ_{s} equal to 0.23. Upon further decrease ϕ_{PS} or φ_{s} the mixture has bicontinuous and cylinder morphology. For example at $\phi_{\mathrm{PS}} = 0.26$ (the criterion shown by the dotted line) we can obtain morphological change from lamella to bicontinuous and eventually to cylinder by decreasing *r* [7]. Thus we can decouple the composition ϕ_{PS} and morphology and, as a consequence, the mechanical properties as well. It should be noted that the co-surfactant effects affect not only the morphology of the microdomains as discussed here but also the domain size and interdomain distance as detailed elsewhere [8].

Table 2. Characteristics of the SI diblocks.

code	$\overline{M}_n \times 10^{-3}$ a)	*H. I.* b)	$\overline{M}_{n\,PS} - \overline{M}_{n\,PI} \times 10^{-3}$ c)	N_{PS}-N_{PI} d)	N e)	W_{PS} f)	f_{PS} g)
as	47.0	1.03	9.6 - 37.4	92-550	642	0.205	0.185
s_1	18.6	1.03	9.6 - 9.0	92-132	224	0.515	0.485
s_2	14.5	1.03	7.0 - 7.5	67-110	177	0.485	0.455
s_3	12.1	1.03	6.3 - 5.8	61-85	146	0.52	0.49

3. Conclusion

We found that the competing long-range interactions between two PS-PI block copolymers

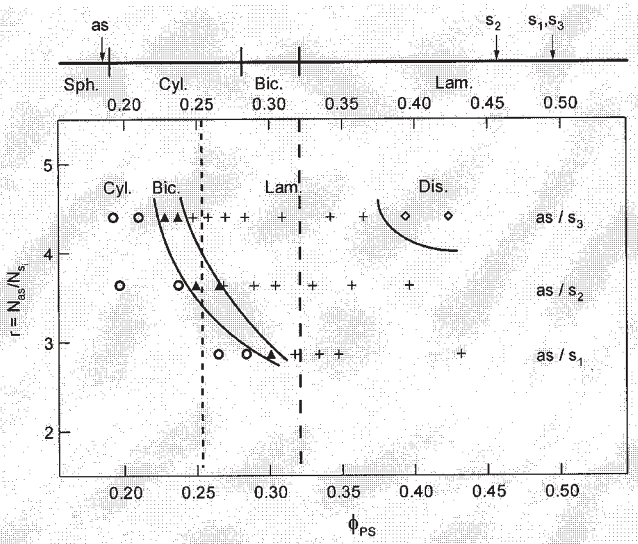

Figure 10. Phase diagram of the blends of the two block co-polymers *as*/*s*$_i$ (i= 1,2,3) in the parameter space of *r* and φ_{PS}.

give intriguing effects on ordered microdomain structures. One effect is the co-surfactant effect observed when the two block are mixed with their junctions on common interfaces, giving rise to such effects that effectively decrease or increase the interface curvatures and hence morphology of ordered microdomains. It should be noted that the effects were theoretically studied also by Nooland and his coworkers.[9] The other effect is the one which causes two blocks macrophase-separate into different ordered domains, as has been reported elsewhere. [2]

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