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Competing Short-Range and Long-Range Interactions in Block Copolymers: A Role of Connectivity in Polymer Science

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Summary: We explored a role of connectivity in polymer science by using two model systems: mixtures of two lamella-forming block copolymers with short and long chain lengths and triblock terpolymers of polyisoprene-*block*-polystyrene-*block*-poly(vinyl methyl ether). These two systems commonly have enriched competitions or interplays of short-range segmental interactions and long-range interactions arising from connectivity between block chains and their packing in the respective domains. The enriched interplays were found to give an intriguing cosurfactant effect for the block copolymer mixtures and interesting two-step microphase transitions for the triblcock terpolymers.

Kerwords: cosurfactant effects, microphase transition, mixtures of block copolymers, polyisoprene-*block*-polystyrene-*block*-poly(vinyl methyl ether), triblock terpolymers

Introduction

We would like to discuss "Short-range and Long-range Interactions" which can compete each other and which are important in self-assembly in block copolymer systems. For this purpose we select two model systems: a mixture of lamella-forming polystyrene-*block*-polyisoprene having a large difference in molecular weights. By presenting the experimental studies of these two systems, we hope we can highlight a role of connectivity in polymer sciene.

It is extremely interesting for us to realize that just a single covalent bond between one end of A and that of B polymers strongly alter the physics of these two-component polymer systems, i.e., mixtures of A and B denoted hereafter A/B and diblock copolymers designated hereafter A-B. Without this covalent bond, polymer mixtures A/B can achieve macrophase separation with a single interface at thermal equilibri-um. The important physics here is competing short-range

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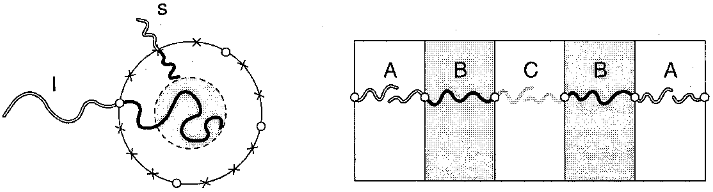
interactions between A-A, B-B and A-B segm-ents. On the other hand with this single covalent bond, A-B block copolymers can achieve microphase separation in which the bulk block copolymer is an assembly of monolayers of A and B blocks separated across the interface and is considered to be nothing other than interfaces themselves, if the monolayers are considered to be a part of the interface. It is very important to realize that the unique microphase-separated structure in neat block copolymers is created by an interplay of the short-range interactions inherent in the mixture and the long-range interactions arising from the block connectivity and the resulting packing effects of A and B in the respective microphases. The long-range interactions involve conformational entropy of block chains which is inherent and very important in polymer science. The interplay of these two interactions yields such long-range-ordered domain structures with various symmetries comprised of the nano-sized structural units,[1-3] such as spheres in body-centered and face-centered cubic lattice,[4] hexagonal cylinder, double gyroid network with $Ia\bar{3}d$ space group symmetry[5,6] and alternating lamellae for diblock copoymer melts.



(a) $(A\text{-}B)_l/(A\text{-}B)_s$ (b) A-B-C

Fig. 1. Schematic representation of the model systems used in this study. (a): mixtures of long and short block copolymers, (b): A-B-C triblock terpolymers.

We should further note the fact that there is enrichment of competitions and interplays in the short-range and long-range interactions for such systems as, for example, (a) mixtures of long and short block copolymers, and (b) A-B-C triblock terpolymers. In the mixtures of long and short block copolymers, designated respectively as l and s, as shown in Figure 1(a) with either identical or different block composition, the short-range interactions are the same as those in neat block copolymers but the long-range interactions between l and s will compete each other.

Furthermore, the short- and long-range interactions interplay each other. In the A-B-C triblock terpolymers, we have three kinds of competing short-range interactions between two different block sequences; A•B, B•C and C•A and long-range interactions due to A-B and B-C connectivity. The short- and long-range interactions interplay each other. We should note that these interplays and competitions are fundamental elements in polymer science and enrich varieties in nano-sized domain structures.

A Cosurfact Effect in a Mixture of Block Copolymers

Now let us discuss the self-assembly of mixtures of block copolymers. As we discussed already, we have the same short-range interactions between A and B as in neat A-B block copolymers. However, the long-range interactions of the block copolymers now have to compete each other, which should give new "delicate effects" on nano-sized patterns. The competing long-range interactions can give two cases: (a) one in which the junctions of two blocks share common interfaces and act as co-surfactants as shown in Figure 1(a), and (b) the other in which they share different interfaces, giving rise to macrophase separation into two different ordered phases. The macrophase separation between the two block copolymers having the same block compositions was experimentally discovered by Hashimoto and coworkers[7] and theoretically predicted by Matsen.[8]

Let us now demonstrate one intriguing example among various cosurfactant effects we encountered. We consider a mixture of lamellar forming polyisoprene-*block*-polystyrene (designated hereafter as PI-PS) block copolymers, one having total number-averaged molecular weight M_n of $100x10^3$ and polystyrene (PS) volume fraction of 0.47 (Figure 2(a)) and the other having total M_n of $14.5x10^3$ and PS volume fraction of 0.46 (Figure 2(c)). Surprisingly enough the 60/40 mixture in weight of the large/small molecular weight block copolymers shows up cylindrical domains as shown in Figure 2(b). The results are reproducible and confirmed also by SAXS. Please note that this cylinder is unique, because it has total weight fraction of cylinders as high as about 50%.

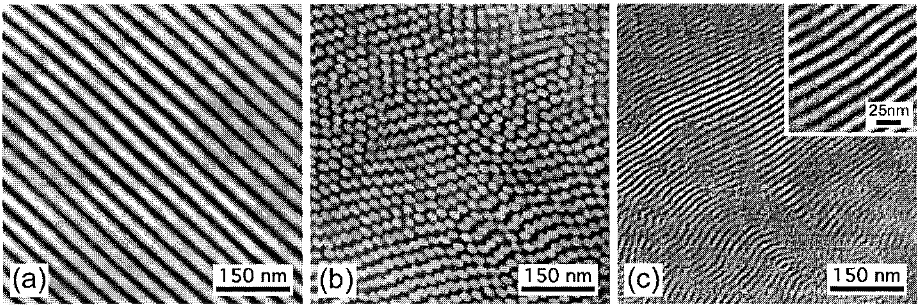


Fig. 2. TEM micrographs of neat PS-PI diblock copolymers: (a) PS(47K)-PI(53K), f_{PS}=0.47, (c) PS(7.7K)-PI(6.8K), f_{PS}=0.46, and its polymer blend: (b) (a)/(c) = 60/40 (wt%)blend.

Why can mixing the two blocks of nearly the same PS volume fraction give the cylinder? One important hint is that as far as the number of molecules is concerned, the small molecular weight block copolymer is a major component, occupying 72 mol% and the large molecular weight block copolymer is a minor component, occupying only 18 mol%. Thus we can interpret our result in such a way that the minority long block copolymer changed the curvature of the majority phase from lamellae to cylinder, due to the competing long-range interactions.

How can we intuitively understand this intriguing lamella-to-cylinder transition upon the mixing of the two blocks? The neat short block copolymer, which is the majority component and which is slightly asymmetric in volume of PS and PI blocks, may want to have the curved interface with a spontaneous curvature such as shown in Figure 3(a), if packing interactions from other block copolymer chains are negligible. However, in the real world, many-chain effects on packing do exist and do not allow the spontaneously curved interface as shown in part a, 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 the neat short block copolymers with such a composition as PS volume fraction of 0.46, and hence the lamellar morphology as shown in Figure 3(b). However, when the long nearly symmetric block copolymers are mixed by a small amount, this packing constraint encountered in the neat block copolymer may be relaxed and the interface may tend to have the spontaneous curvature driven by the slightly asymmetric short block copolymer as shown in Figure 3(c), 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, therefore stabilizing the curved interface driven by the cosurfactant effect and the competing long range interactions of l and s. We found 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 Brishtein and her coworkers.[9-10]

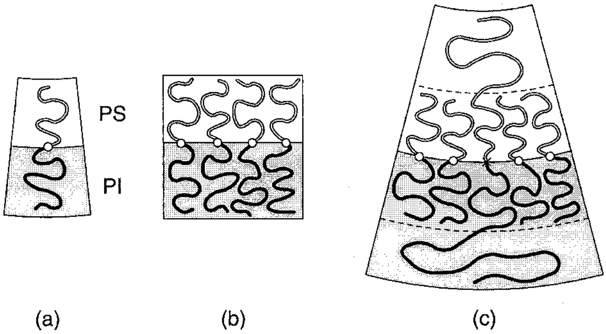


Fig. 3. Schematic illustrations of (a) a slightly asymmetric diblock copolymer molecule with the spontaneous curvature, (b) aggregation of the slightly asymmetric short diblock copolymers with a flat interface, (c) mixture of a large amount of slightly asymmetric short block copolymers and a small amount of long nearly symmetric block copolymers with the spontaneous curvature.

Phase Transitions in Triblock Terpolymers

Let us now move to the second topic of self-assembly of A-B-C triblock terpolymers. In A-B-C triblock terpolymers we have competing long-range interactions due to A-B and B-C connectivities as well as competing short-range interactions between A•B, B•C and C•A. Moreover, these long-range and short-range interactions interplay each other. The enriched competitions and interplays create rich variations of the ordered structures as illustrated in Figure 1 of our previous report.[11] Some of them have been actually found.[12-13] So far, however, most of the reported works have been directed toward finding various ordered structures developed by changing compositions or components of A-B-C. However, little works have been devoted to ordering process of these structures and phase transitions among various ordered structures.

If we can induce order-disorder transition and order-order transitions to the systems at will, we can attain a very rich morphology control. We like to present one of our recent studies along this line, concerning phase transitions with temperature for a given triblock terpolymer.

The triblock terpolymer we shall discuss here is polyisoprene-*block*-poly(deuterated styrene)-*block*-poly(vinyl methyl ether) (PI-DPS-PVME) having rather small block molecular weights of 14K, 3K and 3K for PI, poly(deuterated styrene) (DPS) and poly(vinyl methyl ether) (PVME) blocks, respectively. These blocks have interesting competing short-range interactions: (a) The interactions between PI and DPS and those between PI and PVME decrease with temperature so that they tend to go from the 2-phase to the 1-phase state with temperature; (b) On the contrary, the interactions between DPS and PVME increase with temperature so that they tend to go from the 1-phase to the 2-phase state with temperature. These interesting short-range interactions interplay with the long-range interactions coming from the PI-DPS connectivity and the DPS-PVME connectivity, which is anticipated to create interesting phase transitions with temperature.

Figure 4 shows morphology of the as-cast film at room temperature observed by transmission electron microscopy on the ultra thin sections stained with OsO_4. In part (a) we see a two-phase morphology composed of PI matrix stained dark by OsO_4 and unstained bright cylinders composed of DPS and PVME. At this stage we do not know whether or not DPS and PVME microphase-separate. Thus we further stained with aqueous phosphotungstic acid (PTA) which should selectively stain the PVME phase but not DPS phase. We observed no change with the PTA staining as shown in part (b). Therefore, we conclude that DPS and PVME are mixed together to form the cylinders hexagonally-packed in the PI matrix.

In the results shown in Figure 4(c), we exposed the ultrathin section stained with OsO_4 to water for 1 hour and then stained with PTA. We observe core-shell cylinders in which the unstained bright shell are PS phase and the stained dark cores are PVME. This result demonstrates the solvent (water)-induced microphase transition inside the nanocylinders in which PVME brushes are emanating from the vitrified DPS shells and swollen with water. Evaporation of water would create a channel of hole inside each PVME core. This nano-sized channel structure would be interesting for practical applications such as for membrane reactors, selective permeations, and so on.

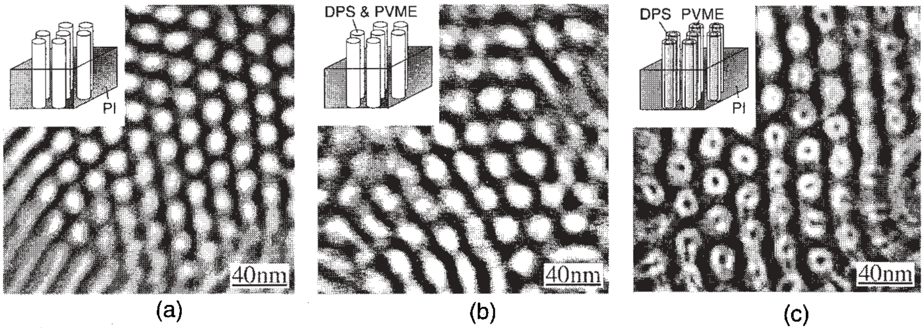


Fig. 4. TEM micrographs of as-cast PI-DPS-PVME film: (a) is the ultrathin section stained by OsO_4, (b) and (c) are the ultrathin sections first stained with OsO_4 and then PTA, the difference between (b) and (c) exists in the time exposed to purified water before staining with PTA: (b) 0 min. and (c) 60 min. The insertions are the model structures corresponding to each TEM micrograph.

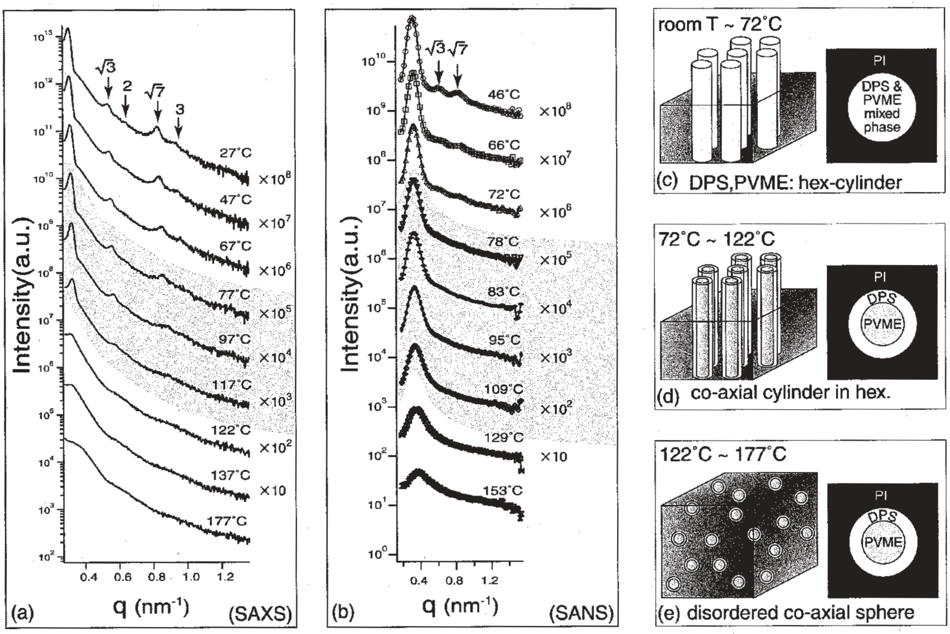


Fig. 5. In-situ SAXS (a) and SANS profiles (b) obtained at various temperatures and schematic models of microdomain structures in the temperature ranges between room temperature and 72°C (c), between 72 and 122°C (d), and between 122 and 177°C (e).

In order to explore such morphological change or phase transition *in-situ* at elevated temperatures, we should use scattering methods by which we can distinguish phases composed of these 3 components. For this purpose we used a combined small-angle neutron scattering (SANS) and small-angle X-ray scattering (SAXS). In SANS the scattering contrast of PI and PVME are almost same ($2.69\text{x}10^9$ and $3.5\text{x}10^9$ cm/cm^3, respectively) and about 1/20 of DPS ($6.49\text{x}10^{10}$ cm/cm^3) so that only DPS is highlighted against others. On the contrary in SAXS, the contrast between DPS and PVME are identical ($3.41\text{x}10^{23}$ and $3.42\text{x}10^{23}$ electrons/cm^3, respectively), so that only PI is highlighted against others.

Figure 5 shows the SAXS (a) and SANS profiles (b) obtained in-situ at various temperatures and plotted with a logarithmic intensity scale and a linear scale for scattering vector q. At room temperature both the SAXS and SANS profiles show scattering peak at $1:\sqrt{3}:2:\sqrt{7}:3$ relative to the 1st-order peak position, suggesting hexagonally packed cylinders. This result is consistent with TEM observation of the two-phase cylindrical structure where DPS and PVME are mixed as shown in part (c): (a) With SAXS, DPS and PVME cannot be distinguished, so that the morphology looks the 2-phase structure with hexagonally packed cylinders is observed anyway; (b) With SANS, a high contrast of DPS with respect to PI is uniformly diluted with a low contrast of PVME, so that the observed morphology is again the 2-phase cylinder.

Upon raising temperature, the SANS profiles undergo a big change above 72°C in such a way that the scattering peaks become weak and broad, whereas the SAXS profiles show almost no change. Let us call this as *Transition 1*. Upon further raising temperature, the SAXS profiles now show a big change above 122°C in such a way that the peaks become weak and broad, whereas the SANS profiles show little change. Let us call this as *Transition2*. The SAXS and SANS profiles between *Transition 1* and *Transition 2* are distinguished from those below *Transition 1* and above *Transition 2* by shading in part (a) and (b) of Figure 5.

Based upon these results we can draw the following two conclusions. Conclusion 1: We obtain the two-step phase transition with temperature. In *Transition 1* at the low temperature, the phase transition occurs within the cylinders so that DPS and PVME respectively microphase-separate into shells and cores of the cylinders as shown in part (d). Note that this transition is obviously expected to cause a big change in SANS but no change in SAXS, as indeed observed in parts (b) and (a) above 72°C, respectively. In *Transition 2* at the high temperature, the core-shell cylinders transforme into core-shell spheres with liquid-like short-range order as shown in part (e), the detailed analysis of which will be reported elsewhere.[14] This transition causes a big change in SAXS. This transition may also cause a change in SANS. However the cylindrical shells may be thermally fluctuating and, therefore, give only a weak and broad SANS peak after the low-temperature *Transition 1*. Then no further drastic change upon this change of the structure is expected at higher temperature (*Transition 2*). We should note here that the low temperature transition occurs at the very low temperature of 72°C. If we have a DPS-PVME diblock copolymer with each block having M_n of 3K, respectively, it would microphase-separate only at much higher temperature, higher than at least 200°C.[15] Thus tethering one-end (DPS end in this case) of DPS-PVME block at the interface of PI microdomains enhances microphase separation between DPS and PVME. Note also that the microphase separation of PI and DPS is stable up to high temperature as high as 177°C. If we have PI-DPS diblock copolymer having M_n of PI and DPS of 14K and 3K, respectively, PI and DPS blocks will be demixed to form a disordered state at much lower temperature. Therefore, we can conclude that the tethering one end of DPS in PI-DPS at the interface of PVME microdomains again enhances the microphase separation between PI and DPS.

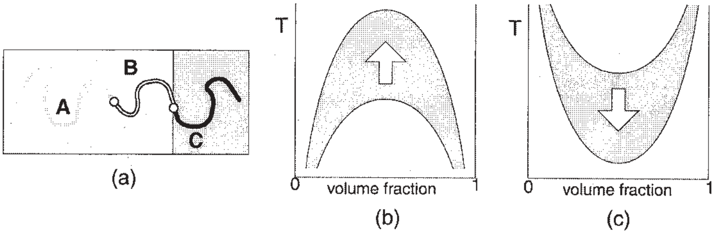


Fig. 6. Promoted microphase transition of A-B block chain in A-B-C triblock terpolymer with one end of B tethered on the interface of microdomains of C blocks (a). Part (b) and (c) show the cases where A-B has UCST-type interactions and LCST-type interactions, respectively.

Those tethering effects on the microphase separation as discussed above are the second conclusion of our studies and are summarized in Figure 6. The tethering one end of diblock copolymers as shown in part (a) where A-B diblock in A-B-C triblock terpolymer is tethered on the interface of C microdomains promotes microphase separation between A and B, raising UCST if A-B has UCST-type phase diagram or lowering LCST if B-C has LCST-type phase diagram as shown by the shaded regions in parts (b) and (c), respectively.

Concluding Remarks

We discussed the enriched short-range and long-range interactions in (1) mixtures of block copolymers having long and short chain lengths and (2) PI-DPS-PVME triblock terpolymers. In the mixture we elucidated an interesting cosurfactant effect originating from competing long-range interactions between the long and short block chains: The two lamella forming block copolymers mixed together to form special cylinders with a large PS volume fraction, as demonstrated by Figure 2 and interpreted by Figure 3. We note that the elastic free energy of block copolymer chains plays an important role here.

In the triblock terpolymer, we found interesting two-step phase transitions with temperature as summarized in Figure 5, and the enhanced microphase separation for the triblock terpolymer, as summarized in Figure 6. Thus even triblock terpolymers with a very small molecular weight undergo microphase separation.

We hope we could elucidate a role of connectivity in polymer science by using the two model systems as discussed above. Specifically the block connectivity plays an important role on molecular assembly of block copolymers through interplays and competitions of the short-range interactions and the long-range interactions discussed in this paper. The role of sequence distributions of different monomer units on molecular assembly and their static and dynamical properties and functions is one of the most important and fundamental problems in polymer science.

[1] M. Matsuo, T. Ueno, H. Horino, S. Chujyo, H. Asai, *Polymer*, **1968**, *9*, 425; T. Inoue, T. Soen, T. Hashimoto, and H. Kawai, *Macromolecules*, **1970**, *3*, 87

[2] H. Hasegawa, H. Tanaka, K. Yamasaki, T. Hashimoto, *Maromolecules*, **1987**, *20*, 1651

[3] M. W. Matsen, F. S. Bates, *Macromolecules*, **1996**, *29*, 1091

[4] Y.-Y. Huang, H.-L. Chen, T. Hashimoto, Macromolecules, in press and a paper in preparation.

[5] D. A. Hajduk, P. E. Harper, S.M. Grüner, C. C. Honeker, G. Kim, E.L. Thomas, *Macromolecules*, **1994**, *27*, 4063

[6] M. F. Schulty, F. S. Bates, K. Almdal, K. Martensen, *Phys. Rev. Lett.*, **1994**, *73*, 86

[7] T. Hashimoto, S. Koizumi, H. Hasegawa, *Macromolecules*, **1994**, *27*, 1562

[8] M. W. Matsen, *J. Chem. Phys.* **1995**, *103*, 3268

[9] D. Yamaguchi, T. Hashimoto, *Macromolecules*, **2001**, *34*, 6495

[10] Ju. V. Lyatskaya, E. B. Zhulina, T. M. Birshtein, *Polymer,* **1992**, *33*, 343

[11] K. Yamauchi, H. Hasegawa, T. Hashimoto, N. Köhler, K. Knoll, *Polymer,* **2002**, *43*, 3563

[12] Y. Mogi, K. Mori, Y. Matsushita, I. Noda, *Macromolecules*, **1992**, *25*, 5412

[13] R. Stadler, C. Auschra, J. Beckmann, U. Krappe, I. Voigt-Martin, L. Leibler, *Macromolecules,* **1995**, *28*, 3080

[14] K. Yamauchi, H. Hasegawa, T. Hashimoto, in preparation.

[15] T. Hashimoto, H. Hasegawa, T. Hashimoto, H. Katayama, M. Kamigaito, M. Sawamoto, M. Imai, *Macromolecules,* **1997**, *30*, 6819.