Nanophase-Separated Structures of AB Block Copolymer/C Homopolymer Blends with Complementary Hydrogen-Bonding Interactions

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ABSTRACT: We report on the morphological variations of SP/H blends containing a poly(styrene-*block*−2-vinylpyridine) diblock copolymer (SP) ($M_w = 130$K) and poly(4-hydroxystyrene) (H) ($M_w = 14$K) with different blend compositions. The structures were observed by transmission electron microscopy (TEM) as well as by small-angle X-ray scattering (SAXS). The results were compared with those obtained from SP/P blends, where P denotes the poly(2-vinylpyridine) homopolymer. The neat SP diblock copolymer, with an S block volume fraction, ϕ_s, of 0.67, has a hexagonally packed cylindrical structure. As P (M_w of 6.6K) is added to the copolymer, morphology of the blend transits to a lamellar structure. Further addition of the homopolymer causes macrophase separation of P homopolymer chains. In contrast, macrophase separation of H homopolymer has never been observed in SP/H blends, even upon addition of large amounts of H. At first, it was noted that the unusual morphological transition from the cylindrical structure to the spherical structure occurs upon addition of H. Subsequently transitions to cylindrical, lamellar and, finally to inverse cylindrical structures occur with successive additions of H. This result is due to the miscibility of P and H via hydrogen-bonding interactions which appear to serve as the driving force for production of uniform nanophase-separated structures covering a wide composition range.

Introduction

It is well-known that block copolymers consisting of incompatible components form self-assembled structures. These are known as nanophase-separated structures in bulk.[1] The structures of various kinds of block polymers such as AB-,[1−3] ABA-,[3,4] ABC-,[3,5,6] and ABCD-[7]type linear block polymers have been investigated. The nanophase-separated structures of AB diblock copolymers have been extensively studied and it has been clarified that the morphology changes according to the volume fraction of the components of the copolymers. A typical morphological change is known to occur from a spherical structure to a lamellar structure through cylindrical and bicontinuous intermediate structures.

While it was well established that neat block copolymers adopt various structures depending on copolymer compositions, it has been found that blends of block copolymer with component homopolymers also undergo morphological transitions which are dependent upon the amount of homopolymer added. Hashimoto et al.[8]studied the effect of the molecular weight of the homopolymer on the ordered structures of the poly(styrene-*block*-isoprene) (SI)/polystyrene (S) blend system, and it was revealed that an S homopolymer with a molecular weight much smaller than that of the S block in the SI block copolymer is uniformly soluble in the S microdomain and that the morphological transition occurs upon addition of up to 5-fold of S homopolymer. For a higher content of homopolymer in the blend, macro-phase separation are required.[9] On the other hand, Torikai et al.[10] reported that lamellar domain spacing in poly(styrene-*block*-2-vinylpyridine) (SP)/P blend is dependent on the molecular weights of added homopolymers. Matsushita et al. reported on the structural effects induced by the manner of mixing on the same polymer system as measured by small angle neutron scattering method.[11]

In recent years, attention has also focused on the polymer blends with attractive intermolecular interactions between component polymers, though there were a few reports which have dealt with the influence of association on nanophase separated structures.[12−16] Among these investigations it was established that pyridine-containing polymers can form hydrogen-bonding associations by sharing valence electrons of nitrogen atoms with phenolic hydroxyl groups present in a different polymer chain.[15] From the viewpoint of supramolecular polymer chemistry, ten Brinke et al.[16] have studied hierarchical nanophase-separated structures in a (styrene-*block*-4-vinylpyridine) copolymer/octadecylphenol system which has hydrogen-bonding interactions. Furthermore, Asari et al.[17] have reported on the new hierarchical nanophase-separated structures exhibited by a poly(isoprene-*block*-2-vinylpyridine) (IP)/poly(styrene-*block*-4-hydroxystyrene) (SH) blend system which has hydrogen bonds.

The presence of interassociated hydrogen bonds in the blends is very important since it enhances miscibility, and as the result, gives highly complex structures[18,19] which significantly affects the properties of a given blend. Thus, investigation of morphological change in blends with intermolecular hydrogen bonds is a worthwhile effort which may lead to development of new miscible materials with highly functional properties. The objective of this work is to investigate the morphological behavior of the poly(styrene-*block*−2-vinylpyridine) block copolymer-(SP)/ poly(4-hydroxystyrene) (H) blend as a function of the blend ratio and, in comparison with the SP/P blend system.

Experimental Section

Preparation of Polymers. The SP diblock copolymer and the P homopolymer were prepared by anionic polymerizations in THF at −78 °C using cumyl-K as an initiator.[20] To obtain poly(4-hydroxystyrene) (H), first (4-*tert*-butoxy)styrene (tBOS) was prepared by an anionic polymerization in THF at −78 °C with sec-BuLi as an initiator. The *tert*-butyl group was successively hydrolyzed with HCl.[21] The molecular weights and the molecular

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Table 1. Molecular Characteristics of the SP Block Copolymer and the P and H Homopolymers

polymer	$10^{-3}M_w$[a]	M_w/M_n[b]	volume fraction[c] ϕ_s	ϕ_P
SP73	130	1.05	0.67	0.33
P	6.6	1.03		
H	14	1.03		

[a] Determined by light scattering. [b] Determined by SEC. [c] Determined by pyrolysis−gas chromatography.

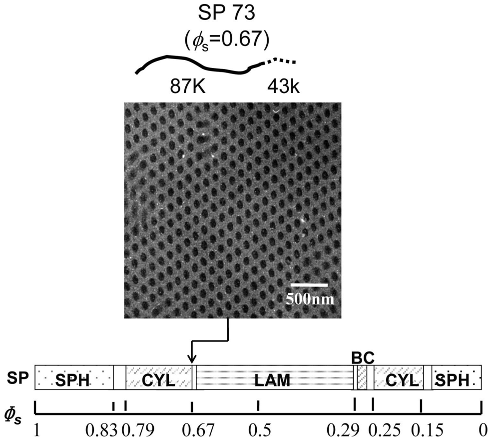

Figure 1. TEM micrograph of the SP73 block copolymer with styrene volume fraction, ϕ_s, of 0.6. The solid part of the chain at the top represents S block while the dotted one does P block. The diagram at the bottom shows the experimentally obtained morphological transition, where SPH, CYL, LAM, and BC denote spherical, cylindrical, lamellar, and bicontinuous structures.

weight distributions of polymer samples were measured by light scattering and size exclusion chromatography, respectively, in THF according to the previously reported procedure.[22] Molecular characteristics of the block copolymer and homopolymers thus obtained are listed in Table 1.

Preparation of the Blend. Two series of blends were prepared. The first blend contains samples SP and P (denoted SP/P), and the second consists SP and H (denoted SP/H). The composition in each series was designed to vary according to the weight fraction of polystyrene, w_s, from 0.3 to 0.6.

Blend sample films were obtained by solvent casting from THF solutions and annealed at temperatures above 150 °C for 5 days under vacuum. The samples were then cut into ultrathin sections of thicknesses of approximately 50 nm with an ultramicrotome (Ultracut UCT, Leica). The sections were stained with OsO_4 for 12 h at 70 °C and further stained with I_2 for 30 min. The nanophase-separated structures of the blends were observed using a transmission electron microscope (TEM), (Hitachi model H-800), under an acceleration voltage of 100 kV. Small angle X-ray scattering (SAXS) experiments were performed using the SAXS apparatus at the synchrotron radiation facility which is installed in beamline 15A at the Photon Factory in Tsukuba, Japan. The wavelength (λ) of the monochromated beam was 0.1508 nm. The scattering intensities were measured when the beam was irradiated on the cut and stacked film specimen along a direction parallel to the film surface.

Results and Discussion

Block Copolymer SP. Figure 1 is a transmission electron micrograph of the pure block copolymer designated SP73 which has a total weight-average molecular weight of 130K and a polystyrene volume fraction of 0.67. It is apparent from Figure 1 that SP73 possesses hexagonal cylinders of poly(2-vinylpyridine) packed in the polystyrene matrix. Since the sample was stained with osmium tetroxide, the darker phase represents block P, whereas the brighter phase represents block S. The diagram beneath the TEM micrograph represents the morphological change of the SP diblock copolymer with volume fraction of S, ϕ_S.[1] The TEM image observed in the present study is consistent with those studied previously.

Blends SP/P. The structures of SP/P blends are presented at the top of Figure 2. Parts b and c of Figure 2 prove that the addition of P homopolymer causes a morphological transition from the cylindrical structure observed for the neat SP73 (Figure 2a) to a lamellar structure. The homopolymer/ block polymer volume ratios in the P phase for these blends are 0.7 (Figure 2b) and 1.3 (Figure 2c), and the volume fractions of the polystyrene phase are 0.53 and 0.47, respectively. These results are consistent with the morphological behavior of the pure SP block copolymer as seen in the bottom diagram in Figure 1.

If additional homopolymer is added, a mixing problem arises, as can be seen in Figure 2, parts d and e, where the homopolymer/block polymer ratios are 2.3 and 4.1, respectively. Consequently, the polystyrene volume fractions are 0.38 and 0.28, respectively. These results indicate that the amount of P homopolymer miscible within the SP block copolymer is limited. This result is consistent with the observation reported in the previous study,[11] though the absolute molecular weight of the blended homopolymer is considerably low.

The morphologies of the SP/P blends were also analyzed by SAXS measurements. Figure 3 shows the SAXS intensity curves for SP/P blends, where the logarithm of intensity is plotted against the scattering vector $q = (4\pi \sin \theta)/\lambda$, and where 2θ is the scattering angle and λ is the X-ray wavelength. It is evident that the pure diblock copolymer SP73 exhibits a scattering profile characteristic of the hexagonally packed cylinders, for which the relative ratios of the q values of diffraction peaks to that of the first order peak are $1:3^{1/2}:4^{1/2}:7^{1/2}:9^{1/2}$ (see top of Figure 3).

The SAXS profile for a SP/P sample with $\phi_s = 0.53$ clearly shows the integer order peaks, which confirms the morphology as a lamellar structure. The SAXS profile of the blend of $\phi_s = 0.47$ exhibits a similar diffraction pattern with scattering maxima at scattering angles with ratios of 1, 3, and 5, that provide evidence of lamellar structure. Disappearance of even order peaks in this sample indicates that the true volume fraction, ϕ_s, equals almost 0.5. The SAXS profile for the sample with $\phi_s = 0.38$ also has integer order peaks, indicating an ordered, lamellar structure. However, relative to the profiles for 0.53 and 0.47, the peaks are broader and less intense. This effect may be due to dispersion of lamellar spacing or a very small grain size. The scattering curve (bottom) for the sample with ϕ_s of 0.28 shows more broad peaks, indicating that the dispersion tendency is more evident. Furthermore, as can be seen from Figure 3, when ϕ_s decreases by addition of P homopolymer, the peaks shift to lower scattering vectors. This indicates an increase in domain spacing and represents a result consistent with previous observations.[11]

Blends SP/H. The bottom section of Figure 2 indicates morphologies of SP/H blends. From these micrographs it is evident that all samples exhibit nanophase separated structures and no macrophase separation behavior was observed. The blend of SP/H with ϕ_s of 0.56 (f), where the H homopolymer/P block ratio equals 0.6, exhibits spherical microdomains of the H + P mixed phase in the S matrix, though the degree of orientation of spheres is poor. This abnormal morphology will be discussed in further detail below with respect to the volume fraction of polystyrene $\phi_s = 0.56$ where lamellar structure could be formed. Figure 2g, where the H homopolymer/P block ratio is 1.3, has a cylindrical structure. This sample is affected by the preparation conditions as shown in Figure 2f, while the micrograph of Figure 2h shows lamellar microdomain structure, where the H homopolymer/P block polymer ratio is 2.3. With further addition

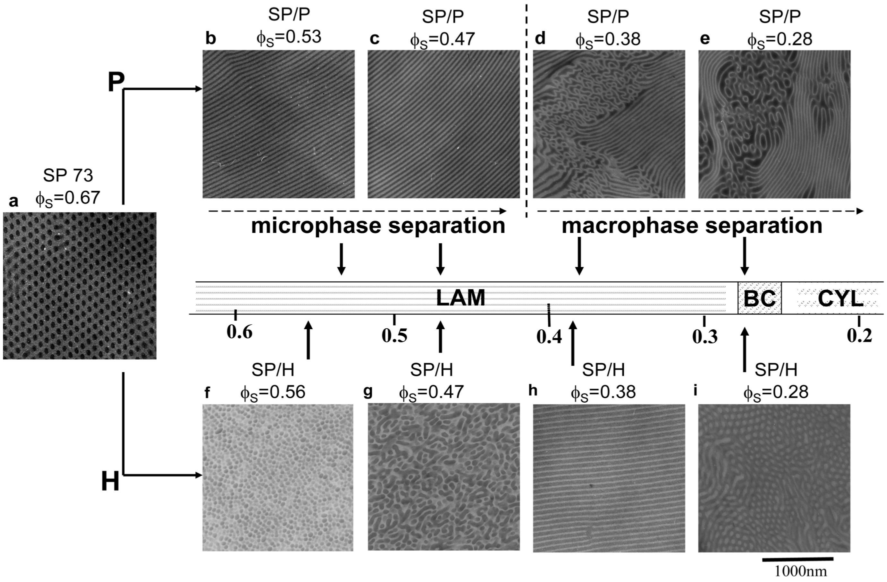

Figure 2. TEM micrographs showing different structures arose from mixing block copolymer SP 73 with homopolymers P and H. The intermediate phase diagram is shown by the partially enlarged diagram from bottom of Figure 1.

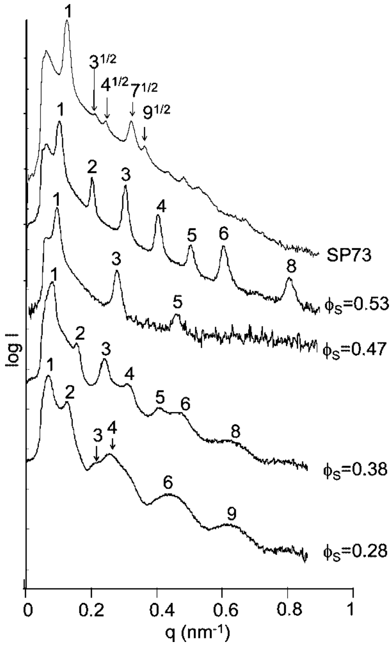

Figure 3. SAXS diffraction patterns of pure SP 73 block copolymer and SP/P blends with different volume fraction of polystyrene, ϕ_s.

of homopolymer, the blend SP/H with $\phi_s = 0.28$ Figure 2i, where the H homopolymer/P block ratio is 4.1, was found to exhibit cylindrical structure. This structure was also confirmed for the blend SP/H with $\phi_s = 0.20$, where the H homopolymer/P block ratio is 7.1.

Figure 4 shows the SAXS intensity curves for SP/H blends, in comparison with that of SP73 at the top. The blend with $\phi_s = 0.56$ has a very poor scattering curve, and no distinct peaks can be recognized. This is probably due to the lack of uniformity in sphere size, which essentially causes a random close packed sphere arrangement structure. The SP/H sample with $\phi_s = 0.47$ exhibits the scattering maxima at relative positions of $1{:}3^{1/2}{:}7^{1/2}$, which indicates cylindrical structure. The next SAXS profile for the SP/H blend ($\phi_s = 0.38$) shows integer order peaks up to the sixth order, which reflects lamellar structure. Upon further addition of H homopolymer, the SP/H blend with $\phi_s = 0.28$ shows a profile characteristic for cylindrical morphology, though the characteristic peaks are not quite evident in this scattering curve. Thus by comparing results obtained from TEM images (Figure 2) and SAXS scattering profiles (Figure 4), we can conclude that all of the TEM micrographs as well as the SAXS profiles for SP/H blends reveal only simple microdomain structures each without demonstrating macrophase separation phenomena. This is the most visible and fundamental difference for this SP/H system relative to the SP/P blend system. This is evidently due to interpolymer complex formation between poly(2-vinylpyridine) (P) and polyhydroxystyrene (H). In other words, P can form hydrogen-bonding interactions with the hydrogen of the hydroxyl group through sharing valence electrons of the pyridine nitrogen atoms.[12]Thus the formation of strong P−H interactions in SP/H blends provides a driving force leading to the miscibility of P and H into one homogeneous phase.

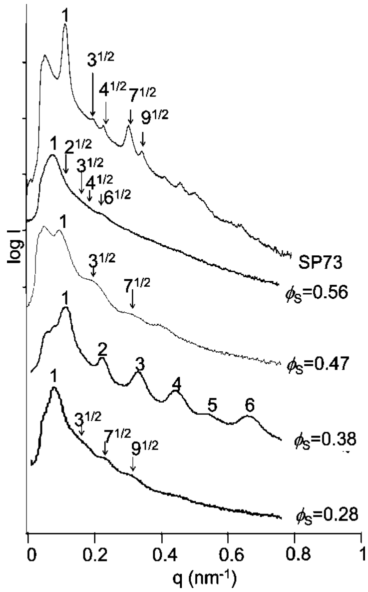

Figure 4. SAXS diffraction patterns of pure SP 73 block copolymer and SP/H blends with different volume fraction of polystyrene, ϕ_s.

The addition of an excess amount of H relative to the P block chain does not induce macrophase separation. Excess H chain can dissolve into the P/H mixed phase. This explains the fact that SP/H blends present uniform nanophase separated structures over a wide composition range. As emphasized above, this is primarily due to the presence of hydrogen bonds between P units in the block chains and the hydroxyl groups of homopolymer H.

Moreover, parts f and g of Figure 2 indicate another difference between SP/P and SP/H blends. While SP/P blends undergo a transition from a cylindrical structure to a lamellar structure upon addition of P homopolymer (a morphological change similar to that of a pure block copolymer), addition of homopolymer H to the SP block copolymer causes a reversal of this transition. This phenomenon can be understood by careful consideration of the solvent casting process. In the present case, samples were prepared by casting solvent from THF solutions, which is a common, good solvent for S, P, and H polymers. However in SP/H blends, it behaves as a selective solvent due to the strong interactions between P and H via hydrogen bonds.[23] As a matter of fact, THF is a nonsolvent for uniformly mixed P + H and a good solvent for S. Therefore the P+H complex shrinks and forms micelles in THF during the casting process. This memory remains until bulk and leads to the formation of a spherical structure instead of a lamellar structure, as seen in Figure 2f. It is possible that the further addition of H homopolymer to the system stabilizes the mixed phase in THF and produces the stable morphologies seen in Figure 2 parts g (cylindrical structure), h (lamellar structure), and i (inverse cylindrical structure) upon addition of H homopolymer.

Conclusion

From the results of this work, we conclude that the morphological changes that occur in SP/H blends are governed by strong interactions generated between P and H components during the solvent casting process and that formation of hydrogen bonds in the polymer blend dramatically induces the miscibility. Thus even excess amounts of poly(4-hydroxystyrene) can be added to the block copolymer SP without causing macrophase separation, which was clearly observed in the case of SP/P blends. Thus P block chains and H homopolymer chains can form one mixed phase, and the blend system presents various nanophase separated structures in a wide composition range. Therefore hydrogen bonds can play an essential role in determining the structure. This is expected to provide a simple and novel method for tuning block copolymer morphology.

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Supporting Information Available: Text describing studies on the behavior of SP/H blends in THF solution by multiangle laser light scattering and Figure S1, showing variation of R_g and N, the number of associated chains as a function of the ratio H/P. This material is available free of charge via the Internet at http://pubs.acs.org.

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