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ARTICLE

Effect of Homopolymer Molecular Weight on Nanophase-Separated Structures of AB Block Copolymer/C Homopolymer Blends with Hydrogen-Bonding Interactions

Katarzyna Dobrosielska,[†] Sou Wakao,[†] Jiro Suzuki,[‡] Kazutaka Noda,[†] Atsushi Takano,[†] and Yushu Matsushita*[,†]

[†]*Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan, and* [‡]*Computing Research Center, High Energy Accelerator Research Organization (KEK), 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan*

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ABSTRACT: We describe morphological variations in binary mixtures of a poly(styrene-*b*-2-vinylpyridine) diblock copolymer (SP) ($M_w = 151$K) and poly(4-hydroxystyrene)s ($M_w = 8$K, 14K, 52K) (H8, H14, H52) as a function of molecular weight of homopolymer H and as a function of blend ratio. Transmission electron microscopy reveals ordered nanophase-separated structures for all samples regardless of molecular weight and the amount of homopolymer added. As much as 28-fold homopolymer H52, which has a M_w higher than that of the P block, can be added to the SP block copolymer without inducing macrophase separation. This unusual miscibility is apparently due to the affinity of P for H via hydrogen-bonding interactions. Furthermore, at a constant volume fraction of polystyrene (ϕ_s of 0.48) and an H/P ratio of 3.2, a structural transition from hexagonally packed cylinders to lamellae occurs upon increasing the M_w of the homopolymer. The small-angle X-ray scattering (SAXS) data obtained for these blends show that the intercylinder distance increases as the M_w of homopolymer increases from 8K to 14K. This finding may imply that the low-M_w homopolymer (H8), which is distributed uniformly in the P microdomain, leads to an increase in the distance between block copolymer junction points, while chain localization of added H homopolymer may begin at SP/H14. Furthermore, the high-M_w homopolymer (H52) appears to be weakly segregated in the middle of the P domain. This constrains the homopolymer effect on the blocks chain conformation and on the distance between junction points and prevents the formation of the cylindrical structure when molecular weight of H increases. Thereby, the simple lamellar structure is maintained for SP/H52 blend at ϕ_s of 0.48. It should be noted that the SP/H52 blend forms an ordered lamellar structure even at a $M_w(\mathrm{H})/M_w(\mathrm{P})$ ratio of 1.5.

Introduction

Blends of a diblock copolymer which include a homopolymer identical to one of the blocks have been studied both theoretically[1−4] and experimentally.[5−15] It has been found that such blends undergo morphological transitions similar to those of the pure block copolymers,[5,6] which are dependent upon the amount of homopolymer added. The spatial distribution of the homopolymer depends upon the molecular weight of the homopolymer.[7,8] Homopolymers with low molar mass are known to be distributed uniformly within the corresponding domain. In contrast, if the molecular weight of the homopolymer is similar to that of the corresponding block, the homopolymer is confined at the center of the domain.[4,7,8] A homopolymer with a significantly higher molar mass causes macrophase separation.[9−12] Furthermore, the swelling of lamellar microdomains by addition of homopolymers has been clarified quantitatively.[13−15]

On the other hand, investigations on blends of a diblock copolymer with a homopolymer different from those of the block polymer components have revealed that the introduction of hydrogen-bonding interactions is a useful way to improve miscibility and to encourage self-assembly of molecules into well-defined periodic structures. Most of the studies on polymer blends with hydrogen-bonding interactions involve thermal and spectroscopic analyses of their miscibility.[16−19] Moreover, Coleman et al.[20,21] have determined the accessibility of the carbonyl functional groups on poly(alkyl methacrylate) (PAMA) blended with poly(2,3-dimethylbutadiene-*stat*-4-hydroxystyrene) copolymer, while Jong et al. have studied the effect of the PMMA tacticity on its miscibility with poly(styrene-*co*-4-hydroxystyrene) copolymer.[22]

We recently characterized the phase behavior of a poly(styrene-*block*-2-vinylpyridine) block copolymer (SP)/poly(4-hydroxystyrene) (H) blend, which has a lower homopolymer molecular weight than that of the P block. It was found that the excess H chain dissolves into the P/H mixed phase and causes the formation of uniform nanophase-separated structures over a wide composition range.[23] In the present work the effect of homopolymer molecular weight on the self-assembled structure is investigated with respect to polymer miscibility and other parameters which influence the morphological behavior of the SP/H blend system.

Experimental Methods

The poly(styrene-*b*-2-vinylpyridine) diblock copolymer (SP) used in this study was prepared by an anionic polymerization process according to a previously described procedure, which provides polymers with a narrow molecular weight distribution.[24]

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*Corresponding author: e-mail: yushu@apchem.nagoya-u.ac.jp; tel: +81-52-789-4604.

To obtain a poly(4-hydroxystyrene) (H), poly(4-*tert*-butoxystyrene) (tBOS) was synthesized by an anionic polymerization in THF at −78 °C with *sec*-BuLi as an initiator. The *tert*-butyl group was successively hydrolyzed with HCl.[25] Three H homopolymers with different molecular weights were prepared. All polymers were characterized by light scattering and size exclusion chromatography (SEC) in THF according to the previously reported procedure.[26] The molecular weights and the molecular weight distribution of polymers thus obtained are listed in Table 1.

Three blend series, i.e., SP/H8, SP/H14, and SP/H52, were prepared at different compositions, with a volume fraction of polystyrene (ϕ_s) varying from 0.1 to 0.7. The SP/H blend sample films were obtained by solvent casting from THF solutions. In some cases the samples were heated at temperatures of ∼150 °C for several days under vacuum, while the others were simply dried. We found that heating did not influence the state of the final structures. The samples were then cut into ultrathin sections with thicknesses of ∼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 TEM (Hitachi H-800; 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 for a specific geometry where the beam was irradiated on the cut and stacked film specimen along a direction parallel to the film surface.

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

			volume fraction[c]	
polymer	$10^{-3}M_w$[a]	M_w/M_n[b]	ϕ_s	ϕ_p
SP82	151	1.02	0.78	0.22
H8	8	1.03		
H14	14	1.03		
H52	52	1.05		

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

Results and Discussion

Figure 1 shows micrographs of SP/H8, SP/H14, and SP/H52 blends. The homopolymer content increases from left to right. Because of the contrast generated from OsO_4 staining, the brighter part represents the polystyrene phase and the darker part corresponds to the P/H mixed phase. The pure block copolymer with a volume fraction of polystyrene (ϕ_s) of 0.78 (coded as SP82) has a cylindrical structure, as can be recognized at the left edge in Figure 1. As the three homopolymers with different molecular weights, i.e., H8, H14, and H52, are added to SP82, the morphological transition from cylindrical structure to spherical, lamellar, and inverse cylindrical structures has occurred in all blend samples, as shown in Figure 1. The unusual morphological transition from the cylindrical structure (SP82 with ϕ_s of 0.78) to the spherical structures (samples with ϕ_s of 0.72 and 0.63) is due to the shrinkage of the P/H mixed phase in THF as discussed previously.[23] The most striking finding in the current experiments is that even the H52 homopolymer (52K), which has a molecular weight higher than that of P block (34K), does not induce macrophase separation in these blends at very high H/P ratios. In contrast, macrophase separation does occur in AB/B and AB/A blends. This miscibility is certainly due to hydrogen bonds formed between a proton on a hydroxy group of polyhydroxystyrene and a nitrogen atom on a pyridine ring. It is notable that the samples with $\phi_s = 0.11$ (the rightmost images in Figure 1) exhibit simple nanophase-separated structures, where the H homopolymer/P block weight ratio, 28, is extremely high. Therefore, in spite of the high molecular weight of H, as much as 28-fold of homopolymer (with respect to poly(2-vinylpyridine) block) can be added to the copolymer without inducing macrophase separation.

Different morphologies have been observed which are dependent on the M_w of the homopolymer for blends at constant ϕ_ss of 0.48 and 0.11, which correspond to constant H homopolymer/P block ratios of 3.2 and 28, respectively. The phase transition for

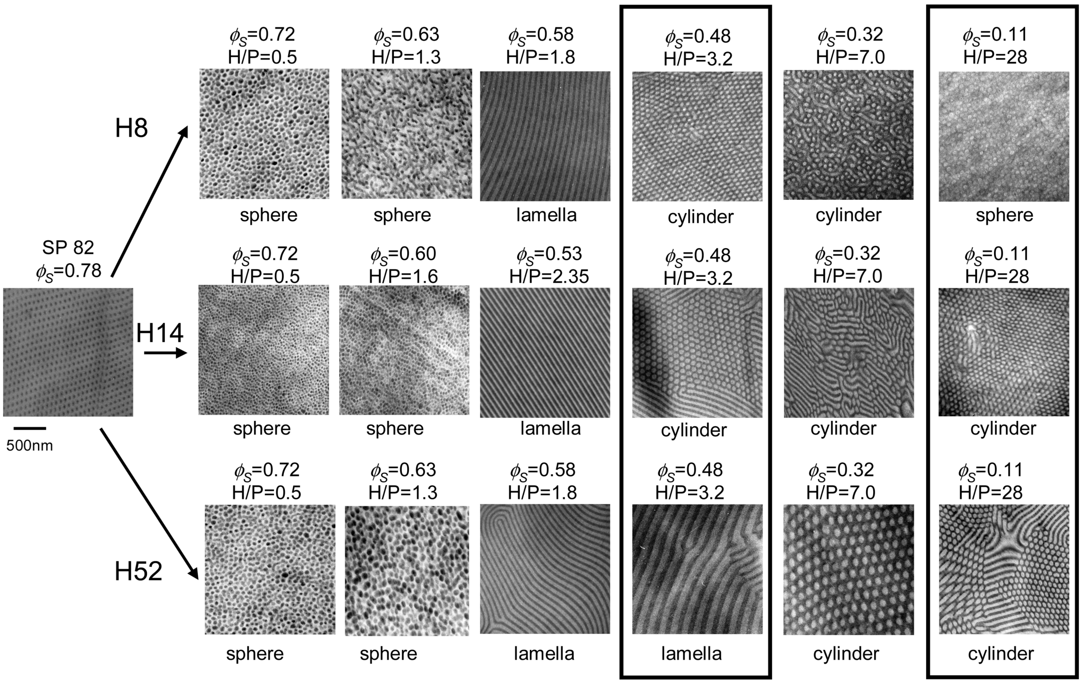

Figure 1. TEM micrographs showing nanophase-separated structures at different block copolymer SP82/H homopolymer mixing ratios for H8, H14, and H52. Samples showing different morphologies at constant ϕ_s and constant H/P ratio are highlighted in the frames. The scale bar of 500 nm refers to all micrographs.

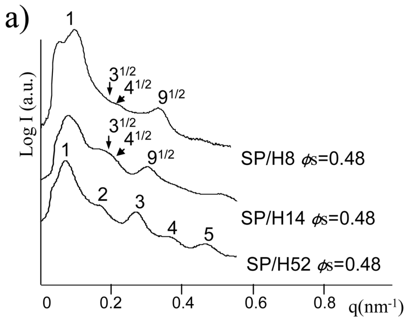

Figure 2. (a) SAXS diffraction patterns for three blends of SP82 with the H homopolymers of different M_w at constant ϕ_s of 0.48. (b) Assembly of hexagonally packed cylinders with intercylinder distance (*a*) and interdomain spacing (*D*).

the blends with $\phi_s = 0.48$ is highlighted in the left frame in Figure 1. Here, addition of low-M_w homopolymers, H8 and H14, to the block copolymer results in the formation of hexagonally packed cylinders of polystyrene in the P + H matrix (Figure 1, left frame, upper and middle micrographs). A spectacular feature appears with longer homopolymer chain lengths. In H52, the morphology transition to the lamellar structure occurs (Figure 1, left frame, bottom micrograph). A similar phenomenon was observed at a very high H/P ratio of 28 as shown in right frame in Figure 1, i.e., samples with ϕ_s of 0.11, where the transition from a spherical structure for the SP/H8 blend (top micrograph) to the cylindrical structures for blends, SP/H14 and SP/H52, was observed (middle and bottom micrographs). Hashimoto et al.[13] have observed similar structural changes in a poly(styrene-*block*-isoprene)/polystyrene blend system, upon increasing the M_w of the polystyrene homopolymer. However, the molecular weights of homopolymers covered within their work were equal to or less than the molecular weights of the polystyrene block chains. Essentially the same results were reported for the different polymer systems.[7,15] In contrast, SP/H blend systems studied here undergo morphological transitions with increasing M_w of added homopolymer up to a molecular weight ratio, M_H/M_P, of 1.5.

The morphology change for samples having a constant volume fraction of polystyrene can be rationalized in a quantitative manner using SAXS scattering profiles introduced in Figure 2a, where the logarithmic values of intensities are plotted against the scattering vector $q = (4\pi \sin \theta)/\lambda$, where 2θ and λ represent the scattering angle and the wavelength of X-ray, respectively. SAXS intensity curves for blends at constant ϕ_s of 0.48 indicate cylindrical structures for blends with lower molecular weight H homopolymers. The top and middle curves show characteristic peaks at q_1, $\surd 3q_1$, $\surd 4q_1$, and $\surd 9q_1$, while the SP/H52 blend exhibits scattering maxima at a relative scattering vector ratio of 1:2:3:4:5 as indicated by the bottom curve, which provides evidence of an alternating lamellar structure.

However, the peaks which were expected to appear at $\surd 7q_1$ are obviously missing in the curves for SP/H8 and SP/H14. The failure to observe these peaks was investigated by calculating scattering intensities as a function of the volume fraction of the minor component based on the structure factor for hexagonally packed cylindrical structures. The structure factor $F(\vec{q},\phi)$ can be generally expressed by eq 1

$$F(\vec{q},\phi) = \int_{\text{unit cell}} \rho(\vec{r},\phi) \exp(-i\vec{q}\cdot\vec{r})\, d\vec{r} \tag{1}$$

where $\vec{q}$ is the scattering vector, $\vec{r}$ is the position vector in the unit cell, and ρ is and the electron density distribution. A unit cell of two-dimensional hexagonally packed cylinders is spanned by the lattice vectors, **a** and **b**. They are defined as

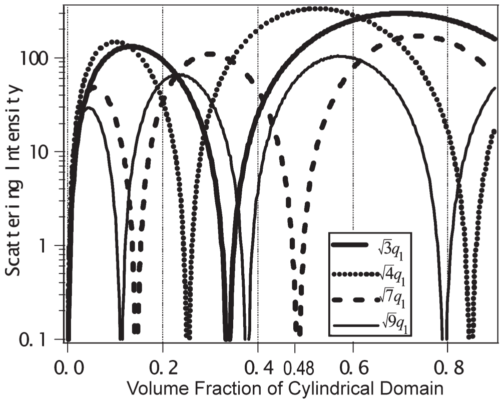

Figure 3. Calculated scattering intensities vs volume fraction of cylindrical domain, ϕ_s, for the given diffracted planes expressed by $(h^2 + hk + k^2)^{1/2}q$, with which $(hk0)$s are associated. The higher order maxima indicate different planes as follows: $\surd 3q_1$ corresponds to the (110) plane, $\surd 4q_1$ corresponds to (200) the plane, $\surd 7q_1$ corresponds to the (210) plane, and $\surd 9q_1$ corresponds to the (300) plane.

$$\begin{aligned} \mathbf{a} &= (1,0) \\ \mathbf{b} &= (1/2, \sqrt{3}/2) \end{aligned} \tag{2}$$

and their reciprocal vectors **a*** and **b*** are

$$\begin{aligned} \mathbf{a}^* &= (4\pi/\sqrt{3})(\sqrt{3}/2, -1/2) \\ \mathbf{b}^* &= (4\pi/\sqrt{3})(0,1) \end{aligned} \tag{3}$$

Using **a*** and **b***, $\vec{q}$ can be expressed as

$$\vec{q} = h\mathbf{a}^* + k\mathbf{b}^* \tag{4}$$

where h and k are the Miller indices. Since the phase-separated structure is composed of the two phases, S and P + H, $\rho(\vec{r},\phi)$ can be simply written as

$$\rho(\vec{r},\phi) = \begin{cases} 1 & \text{(S phase)} \\ 0 & \text{(P + H phase)} \end{cases} \tag{5}$$

Scattering intensity $I(\vec{q},\phi)$ can be related with $F(\vec{q},\phi)$ according to eq 6

$$I(\vec{q},\phi) = |F(\vec{q},\phi)|^2 \tag{6}$$

Numerical integrations for diffraction planes of cylindrical structure (110), (200), (210), and (300) were performed to obtain scattering intensities as a function of composition ϕ. The results are presented in Figure 3. Each curve has intensity minima at characteristic volume fractions and the curve for $\surd 7q_1$ (broken line) has a minimum at ϕ_s of ~0.48. This value is consistent with the one estimated for blends with an H/P ratio of 3.2 shown in Figure 1. The volume fraction of polystyrene in the blend samples was calculated based on the density of polystyrene ($\rho_S = 1.05$) and that of the P + H mixed phase ($\rho_{P+H} = 1.18$).[27] Importantly, the volume of P block and H homopolymer in the blend does not show additivity. This is unusual considering that the density of the mixed phase is larger than those of two polymers $\rho_P = 1.14$ and $\rho_H = 1.16$ but may be explained by the observation that the associated P and H polymers shrank due to formation of hydrogen bonds during the casting process.[23] This results in the formation of a high density phase in the final bulk samples.

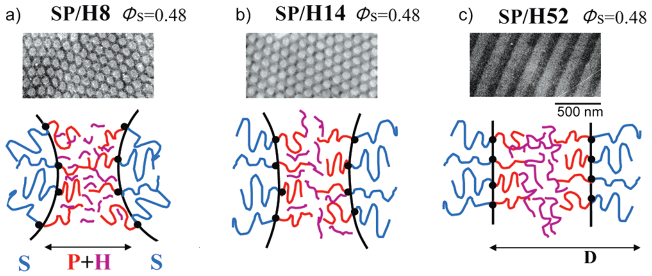

Figure 4. Possible distribution of homopolymer H chains (purple) within P domains (red) in SP/H blends at constant ϕ_s of 0.48 with a constant H/P ratio of 3.2. The dots along the interface indicate block copolymer junction points.

To explore the process of solubilization of the homopolymer in the blends, it is important to estimate the intercylinder distance. It is notable that the scattering peaks are shifted toward smaller q values with increasing M_w of homopolymer (Figure 2a). This indicates growth of domain spacing, D (Figure 2b), in the blends. D can be determined by the first-order peak position, q_1, using the formula $D = 2\pi/q_1$. For the SP/H8 sample, D is found to be 63.5 nm, while D equals 70 nm for SP/H14. The intercylinder distance, a (cf. Figure 2b), is related to D according to $D = (\sqrt{3}/2)a$,[28] and the average intercylinder distances for blends with H8 and H14 are calculated to be 73.3 and 80.8 nm, respectively. The evident growth of the intercylinder distance proves that homopolymers of higher molecular weight can be more effectively localized at the center of the mixed phase (as schematically shown in Figure 4) in accordance with previous observations.[7,8] Furthermore, the average radii of cylinders are measured from TEM images in Figure 1; the values are 23 and 30 nm for blends with H8 and H14, respectively. These values are consistent with the estimated values 26 and 29 nm, which can be evaluated from the relationship $R = (\sqrt{3}(1 - \phi_H)f/2\pi)^{0.5}$, where ϕ_H is the volume fraction of homopolymer H in the entire blend and f is volume fraction of S in SP block copolymer.[13] This result is natural because an increase in intercylinder distance effects an increase in the radius of the cylinder under the condition of the constant volume fraction and results in a decrease in the curvature of the cylindrical domain interface.

The distribution of the homopolymer in the lamellar microdomain for SP/H52 (ϕ_s = 0.58 and 0.48) can be examined by characterizing the lamellar domain spacing D (Figure 4c). If the homopolymer is segregated in the central regions of the mixed phase, D should increase consistently from its original value D_0 (lamellar domain spacing for pure SP block copolymer) as the fraction of the homopolymer increases. In contrast, the domain dimension differs only slightly from D_0 in the case of uniform distribution.[29,30] In the present case, the lamellar domain spacings (D) are 92.5 nm for SP/H52 with $\phi_s = 0.58$, 98.8 nm for SP/H52 with $\phi_s = 0.53$ (additional data), and 101.3 nm for SP/H52 with ϕ_s = 0.48. These values are much larger than the lamella domain spacing for the pure SP block copolymer which has similar molecular weight, $D_0 = 67.3$ nm.[14] The steady growth of lamellar domain size with addition of homopolymer may indicate localization of high-M_w homopolymer chains (H52) at the central part of the P domain which is known to occur in the case of a block copolymer and the corresponding homopolymer blend.

Thus, on the basis of the SAXS data, it can be interpreted that the morphology change for blends at constant ϕ_s is closely related to the distribution of homopolymer chains within P domains. As can be seen in Figure 4, the interfacial curvature between the S phase and the P + H phase decreases from left to right, as the chain length of the homopolymer increases (the homopolymer is represented by purple lines in Figure 4). As illustrated in Figure 4a, low molecular weight homopolymer (H8) can be distributed nearly uniformly in the P domain. This causes expansion of the poly(2-vinylpyridine) chains in both perpendicular and parallel directions with respect to the domain interface. Consequently, the distance of junction points is forced to be enlarged to distribute the segments on P chains uniformly. At the same time, the S block contracts to keep the segment density constant. Addition of 42 wt % of H8 and H14 to the block copolymer causes a large contraction of the S domain to reduce the conformational free energy of the S chains. As a result, polystyrene cylinders (represented by blue lines in Figure 4) are formed in the P (red lines in Figure 4) plus H matrix; i.e., the lower molecular weight homopolymer affects the interfacial structure formation directly. As the M_w of the homopolymer increases up to 14K, the structure remains cylindrical and the H chain remains soluble in the P block domain. However, the homopolymer chain might no longer be uniformly distributed in the P domain. This results in a smaller distance between S−P junction points as can be seen when Figure 4b is compared with Figure 4a. As the molecular weight of homopolymer increases, the longer chain (H52) can be weakly segregated in the middle region of the P phase. The chain conformation of the block and the distance between the copolymer junction points are less affected, and hence their contributions to the interfacial structure are less effective in comparison with the other two blends. Consequently, lamellar morphology is formed in the sample with ϕ_s of 0.48, as shown in Figure 4c. This result was expected due to the counterbalanced effects of homopolymer miscibility and the segregation phenomenon.

The phase transition for blends SP/H at constant ϕ_s of 0.11 (Figure 1, right frame) can be explained in the same way. Large amounts of low molecular weight homopolymer, H8, are easily and uniformly distributed in the P block domain. The solubilization affects the chain conformation and induces a morphology change to the spherical domains of polystyrene as the volume fraction, ϕ_s decreasing. In contrast, the blends SP/H14 and SP/H52 have cylindrical structures at ϕ_s of 0.11 because of nonuniform distribution of longer homopolymer chains in 2-vinylpyridine domains. Thus, the morphological transition behavior which depends upon the molecular weight of homopolymer added in block copolymer/homopolymer blends with hydrogen-bonding interactions is more evident than in the typical block copolymer and the corresponding homopolymer blends.

Conclusions

The effect of the M_w of the H homopolymer on the self-assembled structure formation of SP block copolymer/H homopolymer has been investigated. All blends exhibit well-ordered nanophase-separated structures regardless of both molecular weight and the amount of the homopoloymer added. The blends investigated in this work undergo a morphological transition upon addition of homopolymers up to an H/P ratio of as much as 28 with a M_H/M_P ratio of 1.5. Moreover, at constant ϕ_s and constant H homopolymer/P block ratio, a morphological transition from a cylindrical structure to a lamellar structure occurs for blends with ϕ_s of 0.48 as the M_w of the added homopolymer increases. Likewise, a morphological transition from a spherical to a cylindrical structure occurs for blends with ϕ_s of 0.11.

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Supporting Information Available: Section S1: bulk densities of the SP/H blends at different compositions are measured and the densities of the mixed P + H phase are calculated; section S2: intercylinder distance, the radius of cylinders, and junction point distance in the blends as a function of molecular weight of homopolymer are described in detail; section S3: composition dependence on lamellar domain spacing is discussed. This material is available free of charge via the Internet at http://pubs.acs.org.

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(27) Unpublished data. The densities of SP/H blends were measured by a pycnometer. The data were used to calculate the densities of the mixed P + H phases according to the simple equation $\rho_{P+H} = (1 - w_S)/[(1/\rho_{SP/H}) - (w_S/\rho_S)]$, where w_S is the weight fraction of polystyrene in the sample. The value of the avarage density was found to be $\rho_{P+H} = 1.18$ g/cm^3, where composition dependence is very weak. The volume fractions of polystyrene, ϕ_s, were calculated using the volumes of styrene (V_S) and P + H phase (V_{P+H}) according to the relationship $\phi_s = V_S/(V_S + V_{P+H})$. See Supporting Information.

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