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Creation of Hierarchical Nanophase-Separated Structures via Supramacromolecular Self-Assembly from Two Asymmetric Block Copolymers with Short Interacting Sequences Giving Hydrogen Bonding Interaction

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ABSTRACT: Polystyrene (S) having short poly(4-hydroxystyrene) (H) on one end (SH, $M_w = 71.4K$, $\phi_H = 0.04$) and polyisoprene (I) having short poly(2-vinylpyridine) (P) on one end (IP, $M_w = 57.6K$, $\phi_P = 0.04$) were mixed at various molar ratios, where H and P form a complex by hydrogen bonding interaction. The variation of phase-separated structures of solvent cast films depending on casting solvent and also on pH with heating time at elevated constant temperature were investigated by transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS). Asymmetric morphology for the H/P stoichiometric blend film obtained by casting from polar solvent can be easily transformed into symmetric nanophase-separated structure by the addition of nonpolar solvent. All samples cast from THF/toluene solutions reveal ordered nanophase-separated structures even though the contents of interacting H and P sequences are both merely 4%. The hierarchical three-phase lamellar structure from equimolar SH/IP blend is maintained even after 3 weeks of annealing at constant temperature because of the formation of a very strong one-to-one hydrogen bonded complex. It has been also found that the ordered cylindrical structures for nonstoichiometric blends have periodic three-phase morphologies and that their regular structures gradually disappear and finally reach macrophase separation as annealing time increases. Additionally, pH increase in equimolar blends causes macrophase separation in otherwise stable blends upon isothermal heating.

Introduction

Block copolymers have a fascinating feature to self-assemble into various ordered morphologies with nanometer length scales. Recently, as an alternative way to obtain nanophase-separated structures with one or more different length scales, the formation of block copolymer-like molecular complexes due to noncovalent bonding has attracted much attention.[1−4] Asari et al. have investigated the blend of poly(isoprene-*b*-2-vinylpyridine) (IP) and poly(styrene-b-4-hydroxystyrene) (SH), where S and I chains phase-separate spontaneously and H and P can form one miscible intermediate third phase through hydrogen bonding. As a result, periodic hierarchical structures possessing double periodicity have been found.[5,6] Hawker et al. have used a similar system of block copolymer blends to present supramolecular assembly from hydrogen bonding units with controlled phase separation, leading to the generation of nanoscale square patterns.[7] Furthermore, it has been found that the presence or absence of noncovalent bonding between polymers essentially affects the phase-separated structures, domain size, and miscibility.[8,9] The other polymeric systems that involve stable supramolecular complexes can be obtained when quadruple hydrogen bonding units serve as association end groups in high-molecular-weight polymers.[10,11] Moreover, recent review by Binder et al. summarized many other supramolecular systems with hydrogen bonds in the main and side chains.[12]

Consequently, the control of polymeric structures has become feasible by tailoring the strength of intermolecular forces between macromolecules. The most ubiquitous examples employ hydrogen bonds as the unique interactions, enabling tunability of material properties and architectures because of their inherent reversibility. The resultant hydrogen-bonded polymers are able to respond to external stimuli, for example, such as temperature, pressure, solvent, and so on, where the blends can be decomposed into parent polymers in a way that is not possible for traditional macromolecules. Recent reports show that temperature variations can induce a drastic change in both form and the size of the nanophase-separated structures in macromolecular complexes with comparatively low association strength.[13−15] Moreover, the temperature-dependent switching between nano- and macrophase separation was observed, where dynamic reversibility of hydrogen bond was maintained only up to the critical temperature, above which the system has undergone a macroscopic phase separation.[16,17] Binder et al. have studied nanophase−macrophase transition in macromolecules with multiple (≤6) hydrogen bonds as a function of temperature.[17] They confirmed that the critical temperature at which the bonds are broken and macrophase separation occurs is higher for complexes with stronger interactions. Lefevre et al. have studied the reorganization of hydrogen-bonded complexes of polystyrene-*block*-(4-vinylpyridine)/poly(acrylic acid) in solution by the addition of acidic or basic water.[18]

The control of formation or cleavage of supramacromolecular complexes can also be achieved by adjusting the strength of noncovalent bonding. The main parameter determining the strength of the interactions is the number of interacting moieties involved and their stoichiometry. The stoichiometric effects on nanostructures in supramolecules with ionic interaction have been investigated by Noro et al. for the blend samples with

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comparatively low molecular weight (36K), connected by a single ionic bond, where asymmetric morphology was observed probably due to acid (sulfonic acid)−base (amine) asymmetry.[19] Besides, an apparent solvent effect on the complexation was observed for solvent−cast films.[20,21] It has been demonstrated that the addition of proton-accepting solvent significantly lowers the hydrogen bond strength, leading to decomplexation in solutions[22,23] and to macrophase separation in bulk samples.[24,25] Additionally, nanophase−macrophase tunability was maintained by the introduction of a small molecule that served as an inhibitor for hydrogen bonding formation.[26]

Motivated by the above results, we conduct studies toward better understanding of the importance of the molar ratio of interacting units giving hydrogen bonding interactions in the polymer mixtures because the stoichiometry strongly influences polymer blend morphologies and phase behavior. The nanophase-separated structures obtained from hydrogen-bonded polymer complexes have an influence on solid-state properties, which are of utmost importance for the applicability of these materials. Therefore our goal is to check how the ordered structures can be maintained in the bulk state depending on stoichiometry. To do so, we investigate the effect of casting solvent, molar ratio of blended polymers, and pH of solutions on the resulting structures in a complex polymer system consisting of two extremely asymmetric block copolymers with short interacting sequences that can form hydrogen bonds.

Experimental Section

Materials. Table 1 lists molecular characteristics of the block copolymers used in this study, where SH indicates a polystyrene having short poly(4-hydroxystyrene) on one end, and IP refers to polyisoprene having short poly(2-vinylpyridine) on one end. SH and IP are referred to as asymmetric block copolymers because of very different chain lengths of their blocks (e.g., $M_w(S) = 68.8K$ and $M_w(H) = 2.5K$). Both polymers were synthesized via living anionic polymerizations according to the procedures described previously.[6] The polymers were characterized by multiangle laser light scattering in THF and by gel permeation chromatography (GPC) with THF as an eluent, and 2 wt % tetramethylethylenediamine was added to avoid absorption of P chain on a gel for IP. The compositions of the block copolymers were estimated from ^{1}H NMR spectra. From the data in Table 1, the numbers of interacting units in SH and IP are calculated to be 23 and 22, respectively.

Table 1. Molecular Characteristics of SH and IP Polymers

polymer	$10^{-3}\ M_w$[a]	M_w/M_n[b]	mole fraction[c]			
			ϕ_S	ϕ_H	ϕ_I	ϕ_P
SH	71.4	1.01	0.96	0.04		
IP	57.6	1.02			0.96	0.04

[a] Determined by MALLS. [b] Determined by GPC. [c] Calculated from ^{1}H NMR.

Blend Preparation. SH/IP blends with various molar ratios, 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, and 9:1, were prepared from the parent polymers. Sample films for morphological observation were obtained by solvent-casting method from 5 wt % THF or THF + toluene (1:1) solutions on the Teflon dishes. The films dried under vacuum at room temperature for one day (as-cast films) were used for investigation of solvent effects on phase behavior. For other samples, further thermal treatments were applied. To check the temperature effect on the phase behavior of SH/IP blends, the as-cast polymer films were put into the glass tube and sealed under vacuum. The glass tubes with the samples were heated at 150 °C for different times up to 3 weeks. After the glass tubes were taken out from the vacuum oven, they were immediately quenched in liquid nitrogen to preserve the structures characteristic for the melt state.

pH Change. A certain amount of potassium-*tert*-butoxide (K-*t*-B) was dissolved in 5 mL of methanol, and the solution was poured into 400 mL of THF and stirred for few hours. The concentration of the K-*t*-B was designed to maintain the condition within concentration range $5 \leq m \leq 20$, where m is the mol %, with respect to 2-vinylpyridine unit in the blend. The IP polymer was dissolved into K-*t*-B/MeOH/THF solution, whereas SH was into THF. After complete dissolution of polymers, the solutions were mixed at the SH/IP molar ratio of 5:5, and toluene was gradually added until the condition of THF/toluene 1:1 was reached. The cast samples were heated at 150 °C for different times up to 3 weeks.

Morphological Investigation. Thermally treated samples were cut into ultrathin sections with thicknesses of ~50 nm with an ultramicrotome (Ultracut UCT, Leica). Microtoming for blends with a higher fraction of IP polymer was conducted under cryocondition. 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, which is installed in the beamline 15A at the synchrotron radiation facility, 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.

Results and Discussion

Casting Solvent Effect on Phase Behavior. To check the solvent effect on the morphology of SH/IP blends, the sample films were prepared by solvent casting from the solutions of THF and those of the mixed solvent of THF + toluene (1:1). The structures for the as-cast films of SH/IP 5:5 blend are compared in Figure 1, where the bright phase represents polystyrene (S) and the darker phase indicates the polyisoprene (I) because the sample specimens were stained with OsO_4. In Figure 1a,b, the film obtained from a THF solution shows vesicle-type self-assembled asymmetric structures even though THF is a good solvent for all component polymers in the blend. This behavior might be due to the complex formation ability of two block copolymers in a polar solvent, THF, which prevents the formation of hydrogen bonding because the number of interacting groups in one polymer chain is not so large for both molecules ($N_P \approx N_H = 22$). Consequently, only a few molecules in the system are capable of interacting, and as a result, vesicles consisting of two bilayered block copolymers with H or P tails at the inner or outer surface are formed. As can be seen in Figure 1a,b, at least two regions, SH-rich region in (a) and IP-rich region in (b), can be formed to lower the total free energy of structure formation. Additional shots were also recognized, as can be seen in the Supporting Information (Figure S1). These results are in contrast with that for the blends SH/IP with longer H and P chains ($N_H = 100$, $N_P = 68$) cast from THF, which have exhibited well-ordered nanophase-separated structures.[6] Therefore, the resulting structure in THF-cast films is strongly dependent on the number of interacting groups attached on each one end of the main block chains.

Remarkable morphology change can be realized upon the addition of a typical inert solvent for hydrogen bonding toluene before casting the solvent. The resultant structure of the blend cast from THF + toluene (1:1) solution is shown in Figure 1c. The formation of regular lamellar morphology confirms efficient connectivity between long S and I chains with the aid of the mixed P + H phase, which is visible on the

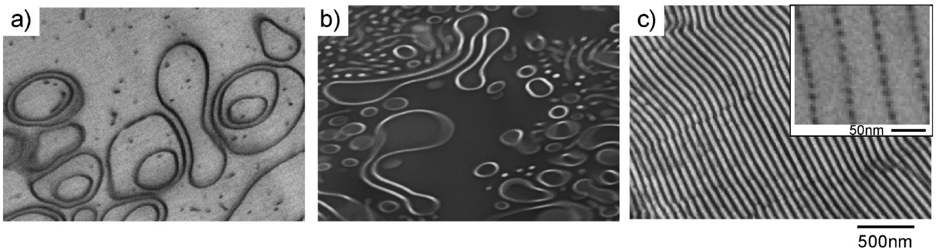


Figure 1. TEM images for SH/IP 5:5 blend cast from THF ((a) and (b)), whereas (c) is an image from a solution of the mixed solvent of THF + toluene (1:1). Sample specimens were stained with OsO_4. The inset in part c is a magnified image of c but stained with I_2.

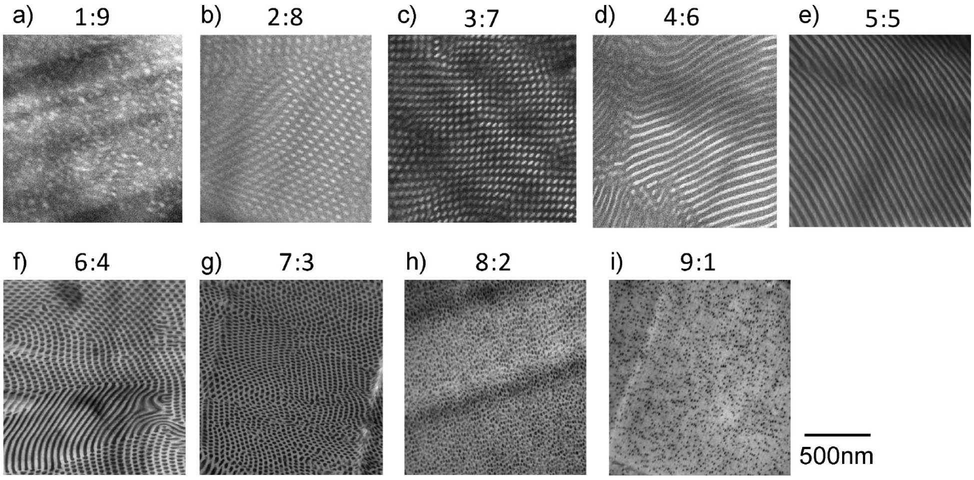


Figure 2. TEM micrographs showing microphase-separated structures at different SH/IP molar ratios (staining agent OsO_4).

inset in Figure 1c as a darker spherical domain periodically standing at the S/I interface. Therefore, the addition of a poor solvent for interacting chemical moieties induces the ability of self-assembly by hydrogen bonding.

The difference in the structures observed in Figure 1 indicates that hydrogen bonding interaction between poly(4-hydroxystyrene) and poly(2-vinylpyridine) as a part of these very asymmetric block copolymers can be easily tuned by choosing the casting solvent. Therefore, because it has been confirmed that THF/toluene (1:1) mixed solvent is adequate to realize the effective supramolecular complex formation, all other samples used in this study hereafter were prepared from THF/toluene (1:1) solutions.

Effect of the Blend Composition on Morphology. Figure 2 compares the microdomain morphologies of SH/IP blend films cast from THF + toluene solutions depending on their composition, where the relative fraction of SH increases from top left to bottom right. The composition of the blends is designed by the numbers, where the first digit refers to the mol fraction of SH polymer and the second digit indicates that of IP in the blend. Figure 2a shows a spherical structure of the sample consisting of 10 mol % SH. With increasing the amount of SH in the blend, hexagonally packed cylinders of S in I matrix have been formed (Figure 2b,c), followed by the appearance of regular lamellar morphology (Figure 2d,e) for the blends SH/IP 4:6 and 5:5. With further increase in SH component, the morphology has transformed into I cylinders (Figure 2f,g) and I spheres (Figure 2h,i).

The formation of these morphologies is due to the attractive interaction between H and P short sequences as well as repulsive force between S and I chains. Various ordered structures, frozen during solvent evaporation process, were observed over the whole examined composition range. It should be noted that the morphology transition shown in Figure 2 does not directly depend on chain length, as in pure block copolymer, but solely on the molar ratio of two polymers. This general trend in variation of the morphology with the blend composition resembles that observed for blends of AB block copolymer/A homopolymer;[27−29] however, if the structures of SH/IP polymer blends are analyzed in detail, it turns out that they are not as simple as those of AB/A blends. In short, the current system consists of four different polymeric chains but can be separated into three phases; that is, S and I domains are connected together with associative H and P segments that can result in the formation of one miscible phase due to hydrogen bonding interaction. The existence of the third phase can be recognized by selectively staining the mixed phase with I_2; one example was already shown in the inset of Figure 1c. Another example is displayed in Figure 3 for SH/IP 6:4 blend, in which the third phase can be conceived at the cylindrical S/I interface. This assembly is schematically shown in Figure 3b. Therefore, the third phase has been proven in Figures 1c and 3a for lamellar and cylindrical structures, respectively. It should be focused on the fact that there is no direct interface between S and I, and hence two polymers are connected by the H + P mixed phase, resulting in the formation of the hierarchical structure.

An additional advantage of the SH/IP blend system in comparison with conventional block copolymer systems is the ease of morphology design. That is, the block copolymer systems must require stringent molecular design including polymerization under control that allows defined structure formation. Tailored structure in SH/IP blends simply requires different blending ratio of the two asymmetric block copolymers without involving additional synthetic efforts. Therefore, the advantage of forming such self-assembled complexes lies mainly in overcoming a variety of synthetic

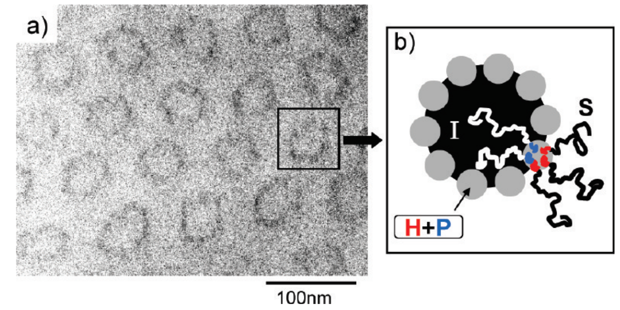


Figure 3. (a) Bright field TEM image of SH/IP 6:4 cast from THF + toluene solution stained with I_2. The image should be equivalent to the one in Figure 2f. (b) Schematic possible domain assembly and chain arrangement in the complex structure.

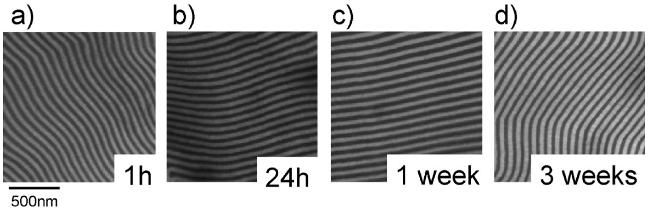


Figure 4. TEM micrographs of SH/IP 5:5 after thermal treatment at 150 °C for (a) 1 h, (b) 24 h, (c) 1 week, and (d) 3 weeks.

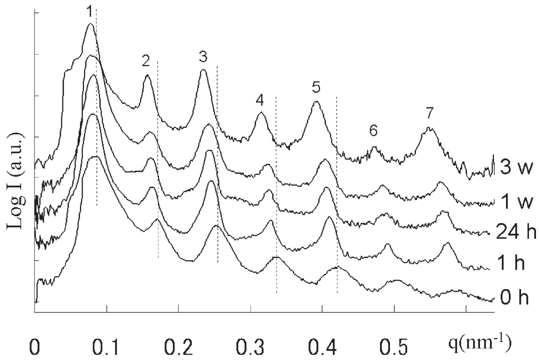


Figure 5. SAXS diffraction patterns of the SH/IP 5:5 blend before (0 h) and after thermal treatment for 1 h, 24 h, 1 week (1 w), and 3 weeks (3 w).

hurdles and at the same time allowing one to control easily morphologies and properties of the resultant materials.

Temperature-Dependent Morphology Change. For investigation of phase behavior under the thermal treatment, all samples were heated for a time period of 1 h, 4 h, 10 h, 24 h, 48 h, 4 days, 1 week, 2 weeks, and 3 weeks; however, for brevity, only representative samples of stoichiometric (SH/IP 5:5) and nonstoichiometric (SH/IP 7:3) blends were picked up and compared here.

Figure 4 compares the structures of the SH/IP 5:5 blend at each heating time under constant temperature of 150 °C. The morphology in all blends has not changed much upon heating in comparison with the result for as-cast sample shown in Figure 2 e. The lamellar structure remains undisturbed after long time heating, because of stoichiometric molar composition of P and H units in the blend. This result indicates that the one-to-one complex formed under this condition is very strong and stable even though the content of short blocks able to interact with each other in the blend is merely ~4% in volume.

Moreover, it was confirmed that heating has an effect on lamellar domain spacing, *D*. Figure 5 shows small-angle X-ray scattering curves for the SH/IP 5:5 blend after different annealing times, where the logarithmic values of intensities are plotted against the scattering vector $q = (4\pi \sin \theta)/\lambda$, where 2θ and λ are the scattering angle and the wavelength of X-ray, respectively. The integer order peaks confirm the ordered lamellar structures in all samples regardless of heating time. From Figure 5, it is also notable that peak positions shift toward smaller scattering vectors, *q*, as the annealing time increases. This indicates that the lamellar domain spacing grows from 70.8 nm for as-cast sample to 80.0 nm in the blend heated for 3 weeks. These values were obtained from the first maximum, q^*, using Bragg's low ($D = 2\pi/q^*$) and are in agreement with the domain spacing observed from TEM micrographs, that is, 71.4 nm for the as-cast sample and 80.2 nm for the 3 weeks annealed sample, respectively.

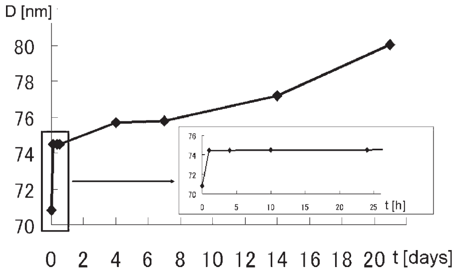


Figure 6. Variation of lamellar domain spacing, *D*, with annealing time, *t*, for SH/IP 5:5 blend.

This phenomenon can be analyzed and discussed in somewhat detail. Figure 6 shows domain expansion during heating in the SH/IP 5:5 sample. During the first hour of heating, *D* has increased up to 74.5 nm, and that size remains unchanged for 24 h. The similar jump in lamellar domain size after a few hours annealing has been observed in covalently bonded poly(styrene-*b*-isoprene) diblock copolymer;[30,31] in particular, the increased *D* value persisted constant after isothermal annealing periods ranging from 1 to 100 h.[31] However, it can be seen from Figure 6 that keeping the SH/IP blend for prolonged time at 150 °C has caused further increase in *D*, which reached expansion of another 11% after 3 weeks. In contrary to block copolymer systems, the *D* swelling after long time annealing in the present system is possible due to the dissociation of hydrogen bond upon heating. That is, the hydrogen bond association−dissociation equilibrium keeps shifting toward the dissociation side with annealing time, and resulting dissociated free block copolymer molecules can diffuse into the corresponding bulk phases after annealing long enough. These "free block copolymers" could behave like simple homopolymers, and they cause the expansion of the two lamellar phases, as shown in Figure 6 at the larger annealing time. However, that extent of increase in *D* is quite small compared with the drastic growth of domain spacing in other supramolecular systems upon temperature increase.[15,17] Huh et al. reported lamellar domain growth of almost 300% in end-functionalized polystyrene and polyisoprene connected with a single ionic bond, where the bond can be easily broken with temperature elevation, leading to a high number of free S and I chains by which the domain can be expanded. In contrast, for the present SH/IP 5:5 blend, the multiple hydrogen bonds from short H and P chains with 22-mers each are much stronger than a single ionic bond. Moreover, the heating temperature is constant, and long time annealing can shift hydrogen bonds equilibrium to dissociation side. A small amount of free SH and IP polymers formed in that way, diffuse away from the interface and

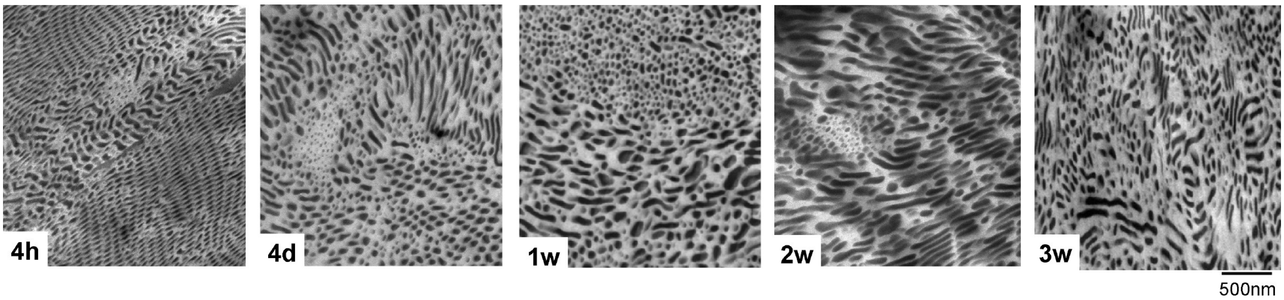


Figure 7. TEM images of the SH/IP 7:3 after thermal treatment at 150 °C for 4 h, 4 days (4d), 1 week (1w), 2 weeks (2w), and three weeks (3w).

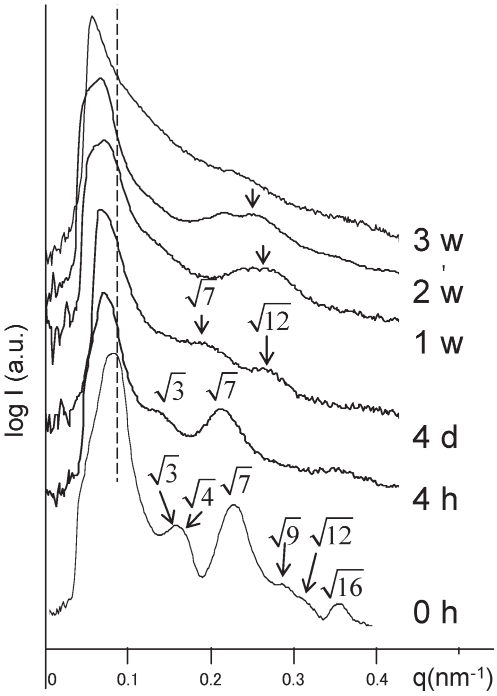


Figure 8. SAXS diffraction patterns of the SH/IP 7:3 blend before (0 h) and after thermal treatment for 4 h (4 h), 4 days (4d), and 1, 2, and 3 weeks.

possibly dissolve in the corresponding domains and contribute to a small increase in domain spacing, but macrophase separation has never taken place.

In contrast with the 5:5 mixture, when blends of nonstoichiometric molar composition were exposed to thermal treatment, distinct structural changes have been observed. As an example, Figure 7 compares morphologies of the SH/IP 7:3 blend developed during isothermal heating for time periods ranging from 1 h to 3 weeks. The hexagonally packed cylinders for the as-cast sample (Figure 2 g) become disordered with annealing time. After exposure to 150 °C for more than 1 week, distinct cylinder deformation leads to global disorder in the structure and finally reaches macrophase separation.

This significant structure disorder after long annealing times was also confirmed by SAXS measurements. Figure 8 shows SAXS diffractions obtained for SH/IP 7:3 for as-cast blend (0 h) and after isothermal heating at 150 °C for time periods varying from 4 h to 3 weeks. The profile of the solution-cast sample (0 h) exhibits the scattering peaks at relative positions of $1{:}3^{1/2}{:}4^{1/2}{:}7^{1/2}$, and so on, which indicates well-ordered cylinders packed in a hexagonal lattice (refer to Figure 2 g). The sample heated for 4 h still has a scattering profile characteristic of cylindrical morphology; however, relative to the "0h" curve, the peaks are broader and less intense. Upon further heating, profiles 4d, 1w, and 2w present broad maxima that may arise because the dispersion of cylindrical spacing and domain ordering in the samples becomes poor (refer to Figure 7, 1w and 2w). Finally, at extreme long annealing time (3w), almost no distinct peaks can be identified, indicating that the order of microdomain arrangement is very poor and macrophase separation may occur. Therefore, the SAXS data in Figure 8 are quite consistent with the structures observed in Figure 7.

Table 2. Molar Ratio of Hydroxyl/Pyridine Units and the Fraction of Non-Hydrogen Bonded Hydroxyl Groups in the Blends

blend	molar ratio of −OH groups to pyridine units	fraction of non-hydrogen bonded −OH groups[a]
SH/IP 3:7	1:2.3	
SH/IP 5:5	1:1	0
SH/IP 6:4	1.5:1	0.33
SH/IP 7:3	2.3:1	0.57

[a] Estimated from mole fraction of H and P in the blend assuming H−P one-to-one complex formation according to $(f_{\mathrm{mol(H)}} - f_{\mathrm{mol(P)}})/f_{\mathrm{mol(H)}}$.

In general, annealing of block copolymer gives energetically stable equilibrium structures. In the present macromolecular complex system, however, thermal treatment finally leads to the disordered state because of hydrogen bonds breakage as well as localization of the excess amount of free chain. To explain this phenomenon, attention will be paid to the asymmetry of SH/IP 7:3 blend, where the stoichiometry between the hydroxyl group and the pyridine unit is the key factor that determines the phase behavior in the blends upon heating.

In the as-cast film of the nonstoichiometric blend, SH/IP 7:3, all nitrogen atoms can form a hydrogen bond with hydroxyl groups, whereas there remains more than 50% of non-hydrogen bonded −OH groups (Table 2), and these free SH chains can be dissolved in the S domain at the initial nonequilibrium state. The situation is different in the equimolar SH/IP 5:5 blend having the same number of hydroxyl and pyridine units that form a one-to-one complex,[32] as confirmed by FTIR analyses (Figure S2 in the Supporting Information).

When these blends are exposed to high temperature for a long time, an excess number of free SH chains can be first localized at the center of S domain in the ordered structure of supramacromolecules[33] and eventually segregated from the ordered phase. Moreover, this tendency could be enhanced with annealing time because a part of the hydrogen bonds gradually dissociates. The swelling of the domain with annealing time for the SH/IP 7:3 can be noticed in Figure 8, where the shift of the principal peaks to lower q values indicates an increase in domain spacing.

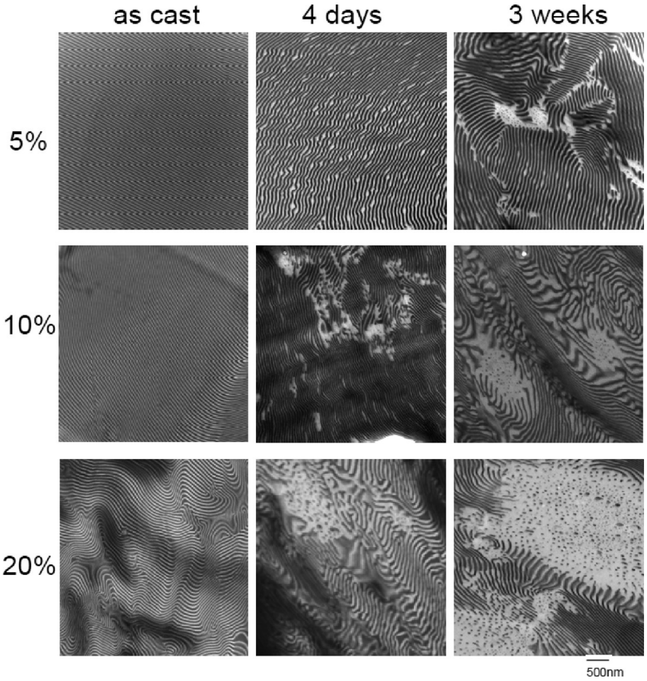
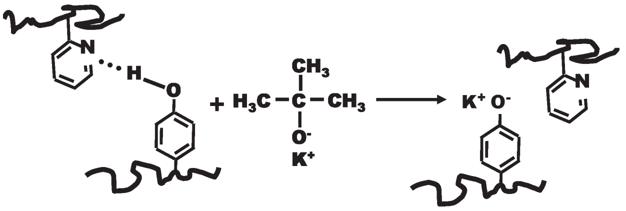


Figure 9. TEM micrographs of SH/IP 5:5 blends containing 5, 10, and 20% K-*tert*-butoxide cast from THF/toluene solutions and annealed at 150 °C for 4 days and 3 weeks.

Scheme 1. Polymer Complex Breakage under the Addition of K-*t*-butoxide



In contrast, the equimolar SH/IP 5:5 blend has no free SH polymer under the as-cast condition (all −OH groups are involved in hydrogen bonds formation), so even though there is a cleavage of hydrogen bonds upon heating, a tiny number of the dissociated free SH chains can dissolve into the S domain. Therefore, on the basis of TEM and SAXS data, distortion of the initial ordered structures in nonstoichiometric SH/IP blends upon isothermal annealing can be interpreted not only by excess of free chains (molar asymmetry of the blend) but also by dissociated additional free chains, whereas such behavior has never been observed in stoichiometric blend with equimolar proton donors and proton acceptors.

Phase Behavior upon pH Change. To investigate the effect of pH of cast solutions for bulk films on the phase behavior in the SH/IP blends and thus on hydrogen bonding interaction, the most thermally stable sample, that is, SH/IP 5:5 has been chosen. The advanced experiments were conducted by adding NaOH to polymer solutions (details of the experiments in the Supporting Information). According to the test experiments, polymer complex of H and P homopolymers precipitated only when the amount of the base in the solutions was < 15% with respect to poly(2-vinylpryridine). (See Table S2 in the Supporting Information.) On the basis of this result, the bulk samples of SH/IP 5:5 containing 20, 10, and 5% potassium-*tert*-butoxide (K-*t*-B) with respect to the P block were prepared. (K-*t*-B was used as a base because NaOH is not soluble in THF nor toluene). Figure 9 shows phase-separated structures in these samples before and after thermal treatment. It is evident that samples containing K-*t*-B show disorder in nanophase-separation after long time annealing unlike pure SH/IP 5:5 in Figure 4. Comparing the TEM micrographs for blends with different amounts of K-*t*-B and annealing time, it is evident that the higher concentration of K-*t*-B, the larger the degree of disorder, and this tendency is getting clearer with increasing annealing time. These results confirm that the base can deprotonate hydroxyl groups at high temperature and thus hinder hydrogen bond formation between H and P chains, as depicted in Scheme 1.

As can be seen in Figure 9 (also Figure S5 in the Supporting Information), the macrophase separation is only local and coexists with lamellar morphology, indicating that hydrogen bonds are only partially broken, and moreover, the stronger the alkalic environment in the blend, the more the extent of macrophase separation.

In summary, bulk structures of blends of two extremely asymmetric block copolymers, SH/IP, where end-capped short block chains, H and P, can form hydrogen bonding have been investigated at various compositions after casting from solutions of a polar, common good solvent, THF and THF/toluene mixed solvent, as well as with and without base addition. Thanks to the nature of the interaction, various ordered structures have been observed. It was found that equimolar blend forms a hierarchical three-phase lamellar structure that is very stable against heating, whereas structures of asymmetric mixtures are more sensitive to the temperature, and disorder of nanophase-separated structure or macrophase separation phenomena were eventually observed after isothermal heating for prolonged time. Moreover, the controlled addition of an organic base to equimolar blends affects the structure degradation, where the size of the macrophase-separated phase depends on the annealing time and the amount of the base in the blends. Therefore, by manipulating these external conditions, one can maintain and optimize the extent of intermolecular hydrogen bonding interaction and hence the scale of phase separation in the polymer blends.

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Supporting Information Available: The wide-range TEM images of selected samples, FTIR analysis, and description of pH change experiments for P/H blends in solution. This material is available free of charge via the Internet at http://pubs.acs.org.

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