Stoichiometric Effects on Nanostructures of Block- and Graft-Type Supramacromolecules via Acid−Base Complexation

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ABSTRACT: We report a systematic study on nanophase-separated structures from block- and graft-type supramacromolecules via acid−base complexation, where supramacromolecules are termed as supramolecules composed of a pair of macromolecules with complementary noncovalent bonding moieties. Block- or graft-type supramacromolecules were built up by blending component polymers, that is, sulfonic acid-terminated polystyrene (PS-SO_3H, M_n = 19 k) or polystyrene-block-poly(4-styrenesulfonic acid) (PS-P(SSO_3H), M_n =23k) with primary amine-terminated polyisoprene (PI-NH_2, M_n = 17 k). Self-assembled nanostructures of the blends were confirmed complementarily by transmission electron microscopy and small-angle X-ray scattering. At larger acid/base molar ratio, the blends show comparatively ordered nanophase-separated structures without macrophase-separated large PS domain. Morphological transition controlled by composition has occurred in the blends of PS-P(SSO_3H)/PI-NH_2 as ordinary block copolymers show, though the blends of PS-SO_3H/PI-NH_2 showed macrophase separation at excess ratio of PI-NH_2 to PS-SO_3H. The difference in composition dependence of morphology between two blend series is resulted from stoichiometric effects of sulfonic acid vs amine. Therefore, PS-P(SSO_3H) is more useful to build up various supramacromolecular complexes with PI-NH_2 than PS-SO_3H just by changing the molar ratios of component polymers, that is, multiple noncovalent bonding can be found more advantageous, resulting in conforming graft-type supramacromolecules, not a block-type supramacromolecule from PI-NH_2 and PS-SO_3H.

Introduction

Nanophase-separated structures of block copolymers have been extensively studied for four decades[1−7] because they have been expected to be a variety of highly functional materials. In addition, supramolecular concepts have attained increasing attention in macromolecular science, since one can design new supramolecular architectures with interesting morphologies or physical properties originated from noncovalent bonding.[7−17] On the basis of the interests in both polymer and supramolecular science, "supramacromolecular assembly" from a pair of different macromolecules with complementary noncovalent bonding moieties has been studied recently.[18−37] There are at least two types of experimental researches by using of supramacromolecular assembly. One is producing supramacromolecules by utilizing comparatively low association strength with a small number of hydrogen bonds to provide thermal-tunability.[11,28,31,33,38] The other is a study to create more stable supramacromolecular complexes with high association strength such as a large number of hydrogen bonds,[7,26,30] acid−base complexation,[18,19,21,22,27,32] and metal-to-ligand coordination.[13,14]

We have been investigating supramacromolecules to search thermal-tunability in mesoscopic structure formation in comparison with conventional self-assembly manner of block- and graft- polymers[33,39] and to observe more complex hirerachical structures beyond those of regular copolymers.[7,30] In those works, in principle, one set of noncovalent bonding moiety was attached on an end of each macromolecular building block to give a one-to-one complex, therefore, we could realize one-to-one complex via complementary noncovalent bonding only when we blend each building block stoichiometrically. Obviously, this limits wide-range utilization of the supramacromolecular concept. However, it could be widely useful if a variety of supramolecular connectivities is introduced, which gives one-to-*n* ($n > 1$) complexes in addition to usual one-to-one complex. Two different building blocks are required for this purpose. One carries on multiple moieties and the other has only one moiety. Ikkala and ten Brinke et al. employed a similar concept to have complexes via supramolecular assembly, that is, supramolecular comb copolymers composed of poly(4-vinylpyridine) and amphiphilic molecules, such as 3-pentadecylphenol and 4-nonadecylphenol, while they have not investigated 1-to-1 complexes in detail because of large molecular size difference.[9,40,41]

Here we present a building-up method of a variety of supramacromolecular complexes composed of a pair of macromolecules using the above concept. (Figure 1) Actually, stoichiometric effects on morphology of block- and graft-type supramacromolecules via acid−base complexation was studied and compared, just changing the blend ratio of macromolecular building blocks. The blends composed of polystyrene end-modified with sulfonic acid (PS-SO_3H), and polyisoprene end-modified with primary amine (PI-NH_2), were prepared to build up a block-type supramacromolecule. Furthermore, the blends composed of polystyrene-*b*-poly(4-styrenesulfonic acid) (PS-P(SSO_3H)) and PI-NH_2 were prepared to build up mainly graft-type[42−44] supramacromolecules. Sulfonic acid and amine[45] were known to form a one-to-one complex via acid−base complexation, which shows strong interaction power and hence leads to supramolecular formation.[46] In fact, there are several reports that these two moieties are very useful and functional units to build up one-to-one supramacromolecular complexes from different polymers, including pioneering work by Horrion et al. followed by the work of Russell et al. and so on.[18,19,21,22,27,32,47] In the present study, therefore, we examine the usefulness of these moieties for building up one-to-*n* complexes ($n > 1$) in addition to a one-to-one complex. Nanophase-separated structures resulted from supramacromolecules were discussed by changing molar ratio of building blocks, namely, mole ratio of acid versus base.

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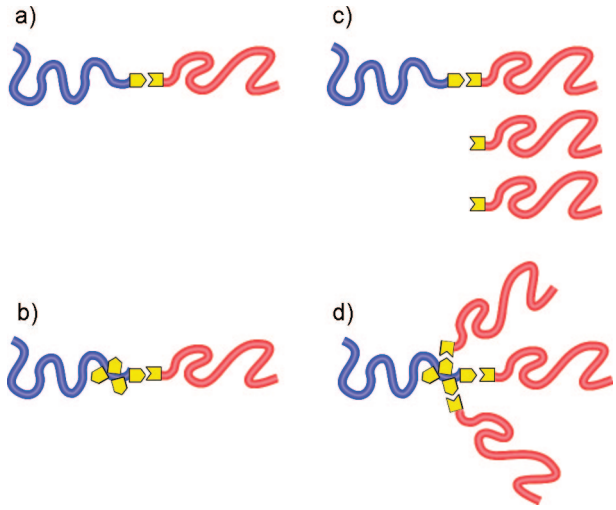
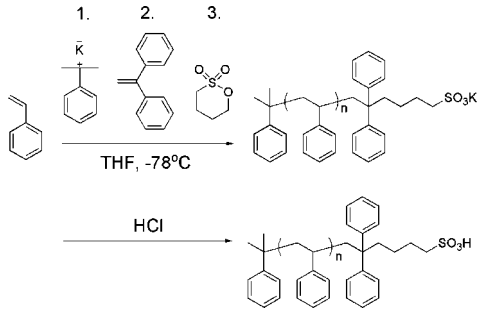


Figure 1. Schematic illustrations of block- and graft-type supramacromolecules: (a) A block-type supramacromolecule composed of a blue polymer with one noncovalent bonding moiety and a red polymer with one counterpart moiety; (b) A block-type supramacromolecule composed of a blue polymer with multiple moieties and a red polymer with one counterpart moiety. The former blend will show saturation at the excess molar amount of red polymer chain (c), while the latter will provide a graft-type supramacromolecule (d).

Scheme 1. Synthesis of Polystyrene End-Modified with Sulfonic Acid

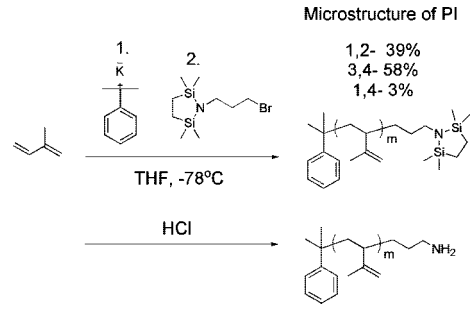


Experimental Section

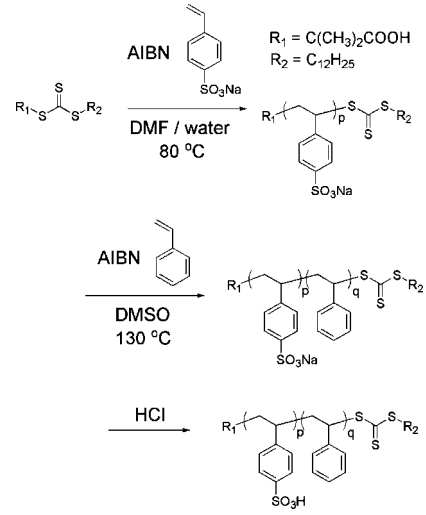
Materials. Styrene, isoprene, azobis-isobutyronitrile (AIBN), DMF, hydrochloric acid, and methanol were purchased from Kishida Regents Chemicals. 2,2,5,5-Tetramethyl-1-(3-bromopropyl)-1-aza-2,5-disilacyclopentane, 1,1-diphenylethylene, and 1,4-butane sulton were purchased from Aldrich, while *sec*-butyllithium solution, tetrahydrofuran (THF), sodium *p*-styrenesulfonate, and Solmix (A-7) were provided from Mitsuwa's pure chemical, Hayashi pure chemicals, TCI, and Japan Alcohol Trading Co. Ltd., respectively. Styrene, isoprene, 1,4-butane sulton, disilacyclopentane, 1,1-diphenylethylne, and THF for anionic polymerization were distilled before use as in the literature.[48] Styrene for RAFT polymerization was purified by passing through an aluminum oxide column. The others were used as received.

Synthesis of Polystyrene End-Modified with Sulfonic Acid. Polystyrene end-modified with sulfonic acid (abbreviated as PS-SO_3H) was synthesized as follows (Scheme 1).[49] Styrene was polymerized in THF at −78 °C at high vacuum by using cumyl potassium as an initiator via living anionic polymerization,[48] and then terminated with 1,1-diphyenylethylene. Subsequently, 1,4-butane sulton was added into THF solution with living polystyryl anions and the temperature of the solution was made back to RT gradually. After the color of living anions disappeared, this solution was precipitated into methanol three times to remove excess amount of 1,1-diphenylethylene and 1,4-butane sulton. To convert the end of $SO_3^-K^+$ to SO_3H, the THF solution of the obtained polymer was prepared, and hydrochloric acid was added to this solution.

Scheme 2. Synthesis of Polyisoprene End-Modified with Primary Amine



Scheme 3. Synthesis of Polystyrene-*b*-poly(4-styrenesulfonic acid)



The polymer was precipitated into methanol with a small amount of hydrochloric acid, and the obtained polymer was dried *in vacuo*. Reprecipitation procedure was repeated three times.

Synthesis of Polyisoprene End-Modified with Primary Amine. Polyisoprene end-modified with primary amine (abbreviated as PI-NH_2) was also synthesized at high vacuum by cumyl potassium via living anionic polymerization (Scheme 2).[50] Living polyisoprenyl anion was terminated with 2,2,5,5-tetramethyl-1-(3-bromopropyl)-1-aza-2,5-disilacyclopenetane, and the solution was precipitated into methanol multiple times to remove excess amount of the unreacted compounds. To convert 1-aza-2,5-disilacyclopentane unit on each chain end to NH_2, the THF solution of the obtained polymer was prepared, and hydrochloric acid was added to this solution. PI-NH_2 thus prepared was purified with multiple reprecipitations, and the obtained polymer was dried *in vacuo*.

Synthesis of Polystyrene-*b*-poly(4-styrenesulfonic acid). Polystyrene-*b*-poly(4-styrenesulfonic acid) (abbreviated as PS-P(SS-O_3H)) was synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerization (Scheme 3).[39,51−54] The monofunctional chain transfer agent (CTA), *S*-1-dodecyl-*S*′(α,α′-dimethyl-α″-acetic acid) trithiocarbonate, required for RAFT polymerization was prepared according to the literature.[52] Sodium *p*-styrenesulfonate as received (0.85 g, 4.1mmol) was polymerized in mixed solvent of DMF/water (2.4 mL/4.8 mL) at 80 °C for 5 h with AIBN (6.8 mg, 0.041mmol) and a CTA (0.10 g, 0.27 mmol). After the proper deactivation by cooling with dry ice methanol, poly(sodium *p*-styrenesulfonate) macro-CTA (abbreviated as P(SSO_3Na)) was purified with reprecipitation from a solution of DMF/water (1/2) into hexane/Solmix (3/1) three times. Then, styrene (2.64 g, 0.25mol) was polymerized in DMSO (6 mL) at 130 °C for 19 h with AIBN (3.4 mg, 0.02mmol) from the macro-CTA (0.24 g, 0.9mmol). After deactivation with dry ice methanol,

Table 1. Molecular Characteristics of all Component Polymers

sample	$M_n/10^4$	M_w/M_n [a]	F [b]
PS-SO_3H	1.9	1.03	1
PI-NH_2	1.7	1.06	1
PS-P(SSO_3H)	2.3[c]	1.09	13

[a] Polydispersity index measured by SEC using polystyrene standards. [b] The number of functionality determined by ^1H NMR, where decimal fractions were rounded off. [c] Calculated from degree of polymerization of P(SSO_3Na) and mole fraction of PS/P(SSO_3H) by ^1H NMR.

Table 2. Weight Ratios of Component Polymers and the Corresponding SO_3H/NH_2 Mole Ratios in the PS-SO_3H/PI-NH_2 Blends

code	$W_{PS\text{-}SO_3H}/W_{PI\text{-}NH_2}$ [a]	X_{SO_3H}/X_{NH_2} [b]
b-9/1	9/1	8.1/1
b-5/1	5/1	4.5/1
b-3/1	3/1	2.7/1
b-1/1	1/1	1/1.1
b-1/3	1/3	1/3.4
b-1/5	1/5	1/5.6
b-1/9	1/9	1/10

[a] Weight ratios of component polymers. [b] Mole ratios of sulfonic acid to amine calculated from molecular weights M_n and the number of functionality F of polymers in Table 1.

Table 3. Weight Ratios of Component Polymers and the Corresponding SO_3H/NH_2 Mole Ratios in the PS-P(SSO_3H)/PI-NH_2 Blends

code	$W_{PS\text{-}P(SSO_3H)}/W_{PI\text{-}NH_2}$ [a]	X_{SO_3H}/X_{NH_2} [b]
g-9/1	9/1	86/1
g-5/1	5/1	48/1
g-3/1	3/1	29/1
g-1/1	1/1	9.6/1
g-1/3	1/3	3.2/1
g-1/5	1/5	1.9/1
g-1/9	1/9	1.1/1

[a] Weight ratios of component polymers. [b] Mole ratios of sulfonic acid to amine calculated from molecular weights M_n and the number of functionality F of polymers in Table 1.

PS-P(SSO_3Na) was obtained and purified with reprecipitation of DMF solution into hexane/Solmix (10/1) three times. PS-P(SSO_3Na) was converted to PS-P(SSO_3H) by acidifying THF/ toluene mixture solution of PS-P(SSO_3Na), and PS-P(SSO_3H) was collected and dried *in vacuo*.

Characterization. Size exclusion chromatography (SEC) was performed to measure polydispersity of all samples by using DP-8020 dual pump combined with two or three TSK-GEL columns and RI-8022 reflectometer (Tosoh Corp.). The detailed conditions of each measurement were described in Supporting Information. 500 MHz ^1H NMR (Varian) was used to determine molecular weights of PI-NH_2 and P(SSO_3Na), and end-functionality of PS-SO_3H, PI-NH_2 by end-group determination method. [55] The mole ratio of PS/ P(SSO_3H) in the PS-P(SSO_3H) block copolymer was also measured by ^1H NMR, and the molecular weight of PS-P(SSO_3Na) was calculated from the degree of polymerization of P(SSO_3Na) and the mole ratio (see Supporting Information). Molecular characteristics of all samples used in this work were summarized in Table 1. Polydispersity indices (PDIs) for all component polymers are less than 1.1 and low enough for morphological observation,[48,56] as shown in Figure 2. Molecular weights of all the polymers are around 20 k. The end-functionality of PS-SO_3H, PI-NH_2 determined by ^1H NMR is 98 and 95%, respectively, which means the number of end-groups (sulfonic acid and primary amine) for these polymers are almost 1. It is revealed that PS-P(SSO_3H) has 13 sulfonic acid units by ^1H NMR.

Blend Samples and Morphological Observations. Blend samples were prepared from PS-SO_3H and PI-NH_2 or PS-P(SSO_3H) and PI-NH_2, leading to two series. Sample preparation is as follows: Each component polymer was dissolved in the mixed solvent of THF/toluene/water (66/33/1) and the films were cast from the blend solutions on Teflon petri dishes at RT for 1 day. THF and toluene

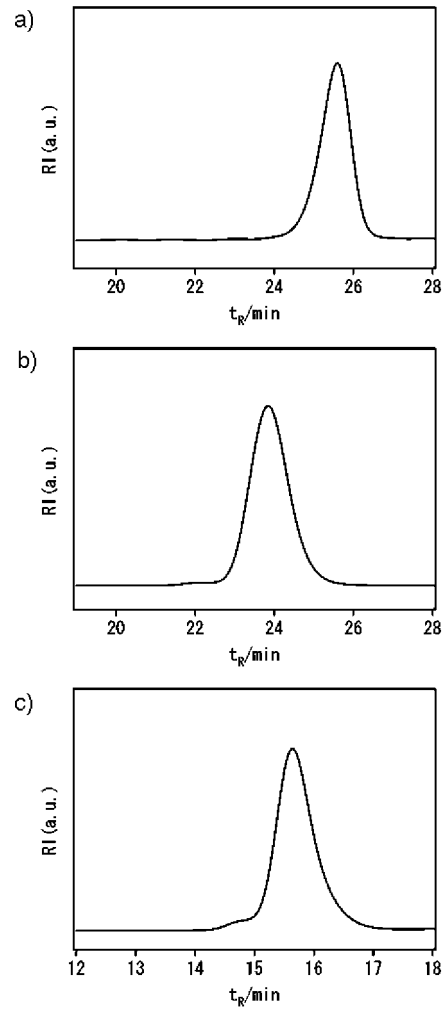


Figure 2. SEC chromatograms for all component polymers: (a) PS-SO_3H; (b) PI-NH_2; (c) PS-P(SSO_3H). The detailed experimental conditions were described in Supporting Information.

dissolve PS and PI components, while a small amount of water was added to enhance solubility of P(SSO_3H) component. The solvent-cast films were thermally annealed at 120 °C for 2 days. The number of the blends prepared for PS-SO_3H/PI-NH_2 is seven, and their blend ratios are 9/1, 5/1, 3/1, 1/1, 1/3, 1/5, and 1/9 by weight, respectively. The same blending manner was applied to the PS-P(SSO_3H)/PI-NH_2 series. The weight ratios of component polymers and mole ratios of sulfonic acid vs amine are listed in Tables 2 and 3 for both PS-SO_3H/PI-NH_2 and PS-P(SSO_3H)/PI-NH_2. Blend samples of PS-SO_3H/PI-NH_2 were named as b-x/y, where x/y means the PS-SO_3H/PI-NH_2 weight ratio. Blend samples of PS-P(SSO_3H)/PI-NH_2 were also named as g-x/y along the same line for b-x/y. To observe morphology of the blends in bulk, ultrathin sections were prepared from films and they were stained with osmium tetroxide. A transmission electron microscope (TEM) of Hitachi model H-800 was used under an acceleration voltage of 100 or 150 kV. Small-angle X-ray scattering (SAXS) experiments were also performed to observe the structures formed in the blend films. Two SAXS apparatuses were used in this study. One is installed in the beamline 15 A at Photon Factory in Tsukuba, Japan, while the other is Nano Viewer of Rigaku. Imaging plates were used to detect the scattered X-rays.

Results

TEM Observation. Figure 3 compares seven TEM images for the blends of PS-SO_3H/PI-NH_2 (see also Figures S7−S10). The content of PI-NH_2 increases from top left to bottom right where the scale bars for all images are 200 nm. The brighter

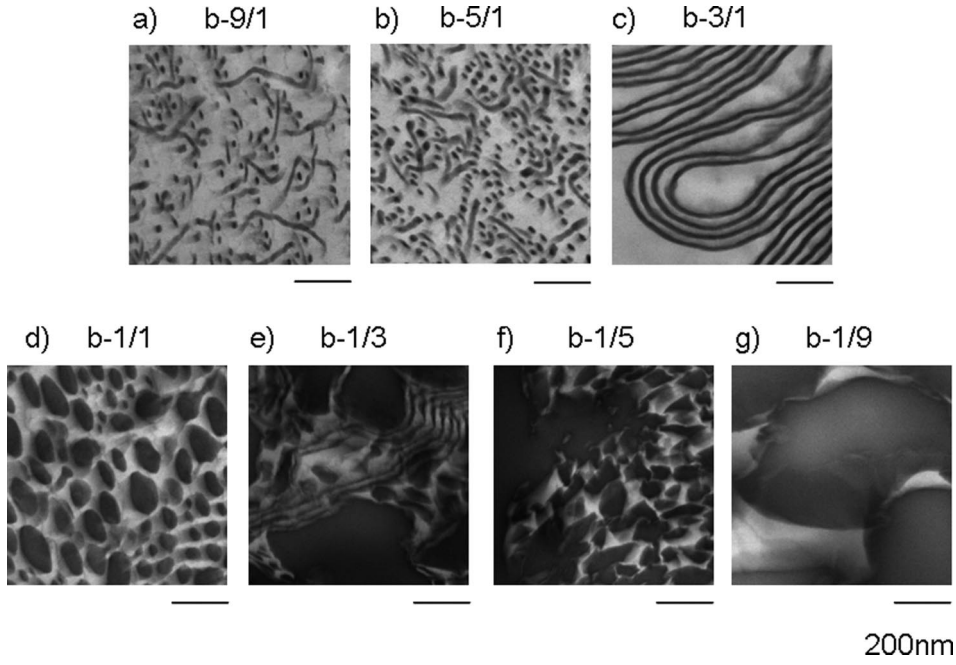


Figure 3. Typical TEM images of blends composed of PS-SO_3H and PI-NH_2: (a) b-9/1; (b) b-5/1; (c) b-3/1; (d) b-1/1; (e) b-1/3; (f) b-1/5; (g) b-1/9. The brighter phase is PS phase, while the darker phase shows PI phase.

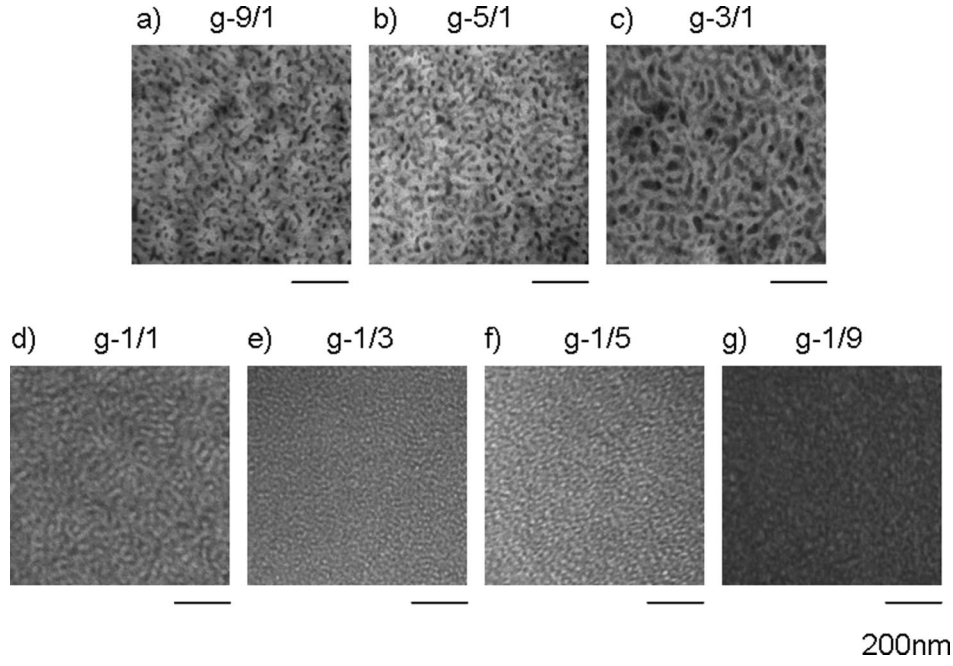


Figure 4. Typical TEM images for the blends composed of PS-P(SSO_3H)/PI-NH_2: (a) g-9/1; (b) g-5/1; (c) g-3/1; (d) g-1/1; (e) g-1/3; (f) g-1/5; (g) g-1/9.

phase expresses polystyrene phase, and the darker phase shows the polyisoprene one. Comparatively ordered nanophase-separated structures with the matrix of PS phase were observed at higher PS-SO_3H content, particularly asymmetric lamellar structure is evident at b-3/1. Note these samples are not block copolymers but actually homopolymer blends, nevertheless, they show nanophase-separated structures. On the other hand, if the mole fraction of amine is more than that of sulfonic acid in the blends, such as the case of b-1/1, b-1/3, b-1/5, and b-1/9, macrophase separation structure can be recognized, which includes PI large domains in PS matrix as immiscible homopolymer blends show.

Seven TEM images for the blends of PS-P(SSO_3H)/PI-NH_2 are displayed in Figure 4, where the content of PI-NH_2 increases from top left to bottom right. The samples, g-9/1 and g-5/1, show comparatively ordered nanophase-separated structures of PI domain in PS matrix over very wide range. The same type of structure can be recognized in Figure 4c for the sample of g-3/1 but the darker phase is richer in this figure than the images in Figure 4a,b. When the fraction of PI increases and PS/PI ratio reaches unity at g-1/1, the blend show alternating lamellar structure, although both ordering and orientation are poor. With further increasing PI fraction, the morphological transition takes place and we can see the isolated PS domain in PI matrix in Figure 4e−g for g-1/3, g-1/5, and g-1/9, respectively. After all, macrophase-separation has never been observed at any composition in the present experiments, and this is in contrast to the results for PS-SO_3H/PI-NH_2 blends.

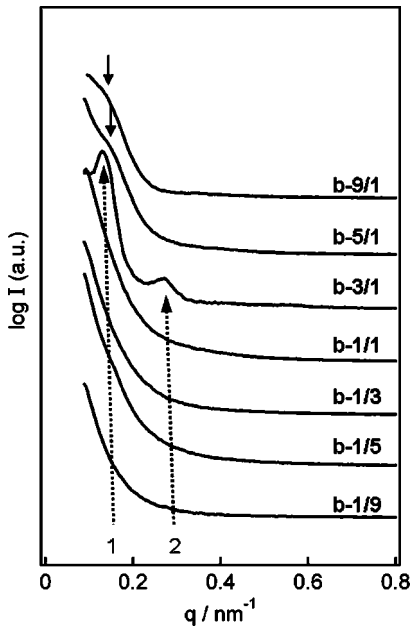


Figure 5. Comparison of SAXS diffraction patterns for the blends of PS-SO_3H/PI-NH_2. The profiles for b-9/1, b-5/1, b-3/1, b-1/1, b-1/3, b-1/5, and b-1/9 are displayed from top to bottom. Arrows are guide for the eyes.

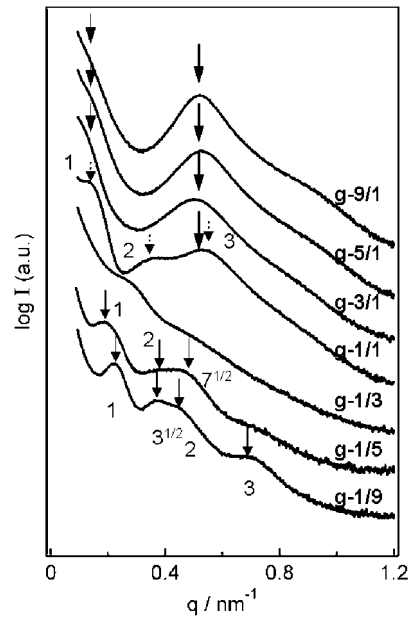


Figure 6. Comparison of SAXS diffraction patterns for the blends of PS-P(SSO_3H)/PI-NH_2. The profiles for g-9/1, g-5/1, g-3/1, g-1/1, g-1/3, g-1/5, and g-1/9 are displayed from top to bottom. Arrows are a guide for the eyes.

SAXS Measurements. SAXS intensities for all the blend samples were measured to confirm morphologies observed by TEM complementarily. Figure 5 displays SAXS profiles for PS-SO_3H/PI-NH_2 blends. Both b-9/1 and b-5/1 have a very broad and small scattering peak at approximately 0.14 nm^{-1}, in terms of $q(=4\pi \sin\theta/\lambda)$, where λ and 2θ are the wavelength of X-rays employed and scattering angle, respectively. These peaks might come from coarsely aligned nanostructures as were shown in TEM images of Figure 3. The profile of b-3/1 has two peaks at 0.13 and 0.26 nm^{-1}, which are reflecting lamellar structure with domain spacing of 48 nm ($D = q_1/2\pi$). There are no distinct peaks within the q range in the profiles of b-1/1, b-1/3, b-1/5, and b-1/9, indicating that the order of nanodomain arrangement is very poor and macrophase separation may occur.

On the other hand, Figure 6 displays the profiles of PS-P(SSO_3H)/PI-NH_2 blends. g-9/1, g-5/1, and g-3/1 have a very broad and small peak at approximately 0.15 nm^{-1} as was shown for b-9/1 and b-5/1, which might also come from coarsely aligned PI nanodomain in PS matrix with average distance of 42nm. There are one large and broad peak at approx 0.5 nm^{-1} on profiles of g-9/1, g-5/1, and g-3/1, which may be the correlation hole peaks for PS-P(SSO_3H) itself as shown in Supporting Information (see Figure S6). The profile for g-1/1 has integer number ordered peaks which reflect lamellar structure. However, the sample of g-1/3 has small scattering peaks, and they are difficult to assign, which might mean orientation of the nanostructure is quite poor as was shown in Figure 4e. At more extreme composition of g-1/5 and g-1/9, the profiles have several peaks at relative q values of 1, $3^{1/2}$, $4^{1/2}$, $7^{1/2}$, etc, which reflect hexagonally packed cylinders in matrix. Thus the SAXS data for these blends in Figure 6 are quite consistent with the structures observed in Figure 4a−g.

Discussion

We mainly discuss the difference in composition dependence of morphology between PS-SO_3H/PI-NH_2 blends and PS-P(SSO_3H)/PI-NH_2 ones. It is clear that supramacromolecules are formed in two blend systems, considering the facts that both TEM and SAXS show the strong evidence of nanophase-separated structures which have never been observed in blends of immiscible and nonassociating homopolymers. Sulfonic acid and amine are known to form a one-to-one complex via acid−base complexation, as is the present case, resulting in forming block-type or graft-type supramacromolecules composed of different polymers, that is, PS and PI, which are self-assembled into nanophase-separated structures in this work.

Composition dependence of morphology for the blends of PS-SO_3H/PI-NH_2 is shown directly in Figure 3 (see also Figures S7−S10), and they are summarized as follows. At PS-rich composition, the blends show isolated PI domain embedded in PS matrix. With decreasing the amount of PS-SO_3H, the regularity of the structure is getting higher up to b-3/1, where the blend shows comparatively clear but asymmetric PS-PI lamellar nanophase-separated structure with larger PS domain, its distance being at most 1 μm (see Figure S9). With further decreasing PS, the blends, such as b-1/1, b-1/3, b-1/5, and b-1/9, show macrophase separation composed of huge PI domain with large polydispersity.

Here, we pay attention to the asymmetry of structural formation of the first series, that is, PS-SO_3H/PI-NH_2. Acid−base stoichiometry between sulfonic acid and primary amine must be one of the key factors to determine morphology of the blends, but there are other factors. From Figure 3, it is evident this blend series does not show equal relationship, in another words, lamellar structure was not observed at b-1/1, it was recognized at b-3/1 instead. And three TEM images in the top row have some regularity in them, while four TEM images in the bottom row do not. It can be conceived that the efficiency of complex formation is not so high in evaporating solvents, so that the blends always include block-type supramacromolecule and component homopolymers in bulk more or less. In reality, when PS-SO_3H is rich at b-9/1, 5/1 and 3/1, block-type supramacromolecules self-assembled into periodic structure keep having PS homopolymer which behaves as so-called dry brush, and the phenomena have often been observed for block copolymer/homopolymer blends.[57] It is most evident at b-3/1, the image shows typical dry brush where block type supramacromolecules tend to form "vesicle" in the sea of PS homopolymer. The situation has been totally changed if we have a stoichiometric blend at b-1/1, which should include block-type supramacro-

molecules and equal amount of PS and PI homopolymers. It is clear that PI homopolymer phase-separated macroscopically and form micelle-like domain with irregular size,[58] which is obviously free from periodically nanophase-separated structure. This phenomenon is probably due to the aggregation formation of PI-NH_2 due to self-association of amine,[59] which induces the segregation of PI homopolymer easily from self-assembled regular structure.

Alternatively, the structures of the second series, that is, PS-P(SSO_3H)/PI-NH_2 keep regularity throughout the composition from g-9/1 to g-1/9, as shown in Figure 4, though the domain ordering is not so good. The most distinct difference between the first and second series is the acid/base ratio of SO_3H and NH_2 units. The ratio varies from 8/1 (sulfonic acid-rich) to 1/10 (amine-rich) for PS-SO_3H/PI-NH_2, while it varies from 86/1 for g-9/1 to 1/1 for g-1/9, since PS-P(SSO_3H) includes 13 SO_3H moieties. Note that the smallest ratio for the latter is unity for g-1/9. This means that all the excess mass of PI-NH_2 was associated with PS-P(SSO_3H) even at g-1/9. This might be the reason why PI was not segregated macroscopically even at excess mass amount of PI-NH_2 for the second series and the blends show comparatively homogeneous nanophase-separated structures which may be due to the formation of heterogeneous one-to-n ($n > 1$) supramacromolecular complexes, that is, graft-type supramacromolecules. If the acid/base ratio in the blend of PS-P(SSO_3H)/PI-NH_2 becomes smaller than unity, it would be possible to have macroscopic phase of PI.

Summary

In this paper, we carried out a systematic study on the formation of block- and graft-type supramacromolecules via acid−base complexation, where supramacromolecules are termed as supramolecules composed of a pair of macromolecules with complementary noncovalent bonding moieties. Block- or graft-type supramacromolecules were built up by components of sulfonic acid-terminated polystyrene (PS-SO_3H) or polystyrene-*b*-poly(4-styrenesulfonic acid) (PS-P(SSO_3H)) with primary amine-terminated polyisoprene (PI-NH_2) via acid−base complexation, and their nanophase-separated structures were confirmed by TEM and SAXS. At PS-rich composition for both series, the blends show comparatively ordered nanophase-separated structures without large PS macrophase-separated domain. However, the difference in morphological variation for two series is evident when the fraction of PI-NH_2 increased. That is, PI homopolymer was macroscopically segregated from self-assembled structure for the series of PS-SO_3H/PI-NH_2 at b-1/1, the phenomena was observed up to b-1/9. On the other hand, actually no macrophase separation was observed for the second series, that is, PS-P(SSO_3H)/PI-NH_2, even if the relative mass amount reaches 9 at g-1/9. The difference in composition dependence on morphology between two blend series is resulted from "stoichiometry" of acid versus base. This work also suggests that macromolecular building blocks with multiple noncovalent bonding moieties might be more useful than the blocks with single moiety to provide a variety of supramacromolecular complexes.

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Supporting Information Available: Details of characterization and morphological observations for component polymers and blends. This material is available free of charge via the Internet at http://pubs.acs.org.

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