

# Giant Thermal Tunability of the Lamellar Spacing in Block-Copolymer-Like Supramolecules Formed from Binary-End-Functionalized Polymer Blends\*\*

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In almost all fields of material science, the control of patterns and dimensions of nanometer-sized structures has been extensively pursued in recent years because of the strong potential for such materials to be incorporated into novel materials and devices. Self-assembly of block copolymers has been recognized as a promising strategy to fabricate functional nanostructured materials. In bulk or in concentrated solution, block copolymers form spatially periodic nanostructures; the best-known morphologies are lamellae, hexagonally arranged cylinders, spheres arranged on a body-centered cubic structure, and bicontinuous gyroids.<sup>[1–4]</sup> These nanostructures formed by block copolymers offer a number of potentially exciting applications in, e.g., magnetic-storage media,<sup>[5]</sup> silicon capacitors,<sup>[6]</sup> flash-memory devices,<sup>[7]</sup> nanoelectronics,<sup>[8]</sup> and photonic crystals.<sup>[9]</sup> Two factors in the fabrication of nanopatterns by block copolymers are technologically very important: one is the control of the form and size of the repeating structure that provides an elemental symmetry to the pattern, and the other is the achievability of perfect patterning over a very large area with a given symmetry. While several strategies have been proposed for the latter, such as those using graphoepitaxy,<sup>[10–12]</sup> electric fields,<sup>[13,14]</sup> shear fields,<sup>[15,16]</sup> temperature gradients,<sup>[17]</sup> solvent evaporation,<sup>[18,19]</sup> and chemically patterned substrates,<sup>[20–23]</sup> control of the form and size of the repeating structure has been pursued only by two basic conventional methods: changing the molecular weight or composition of block copolymers, or mixing of block copolymers with additional additives such as homopolymers.<sup>[24,25]</sup> In principle, changing the molecular weight or composition of block copolymers ideally can control the size and form of the resulting structure, but synthesis of such block copolymers is not easy and sometimes laborious. On the other hand, mixing of block copolymers with other polymers provides a relatively simple route; however, the controllability is usually hampered by undesirable macroscopic demixing between the constitu-

ents.<sup>[24–30]</sup> It has recently been demonstrated that noncovalent bonds can be used in constructing block-copolymer-like molecular complexes,<sup>[31–38]</sup> so-called supramolecules, that serve equally well as building units of nanostructures. Such noncovalent bonds include hydrogen bonding,<sup>[33–39]</sup> ionic interactions,<sup>[32]</sup> coordination complexation,<sup>[38]</sup> and charge-transfer interactions.<sup>[40]</sup> These supramolecular routes for block-copolymer-like architectures provide us not only with a new option for creating nanostructured materials but also with a fascinating means to design “smart” materials that respond to external stimuli or conditions.<sup>[41,42]</sup> Directing formation or cleavage of supramolecular complexes under a desired condition can thus be a basic strategy for developing materials with several tunable morphologies in the same material. Recently, we have theoretically demonstrated that, because of the thermally reversible nature of supramolecular bonds within block-copolymer-like molecular complexes, temperature variations can induce a drastic change in both form and size of the microphase structure.<sup>[43]</sup> Motivated by this theoretical prediction, in this paper we show an example of an immiscible binary polymer blend system in which the thermally reversible nature of the ionic bond between functional groups in dissimilar blend components induces a drastic swelling of the lamellar microphase (up to ~300%) upon heating. Thus, we demonstrate a very simple route to design a material in which the characteristic dimensions of the microphase are thermally tunable. Such an effective tunability of the microphase periodicity within the same material by means of the temperature has not been previously achieved.

As stated above, the present work has been motivated by our recent theoretical study that predicts morphological patterns of binary blends of end-functionalized polymers capable of producing block-copolymer-like supramolecules.<sup>[43]</sup> The morphology of such blends is basically governed by the competition between two types of interactions: the unfavorable interaction between dissimilar molecular species, and the specifically attractive interaction between two different functional groups attached to each of the chain ends of dissimilar polymers. In the theoretical model, this competition between the repulsive interaction between dissimilar polymers (for example, polymers of different kinds A and B) and the attractive bonding interaction between a pair of end-functionalized moieties within the A- and B-polymers is characterized by a molecular parameter  $\kappa = -f_b(N\chi k_B T)^{-1}$ , where  $f_b$  is the free-energy change associated with the formation of a noncovalent

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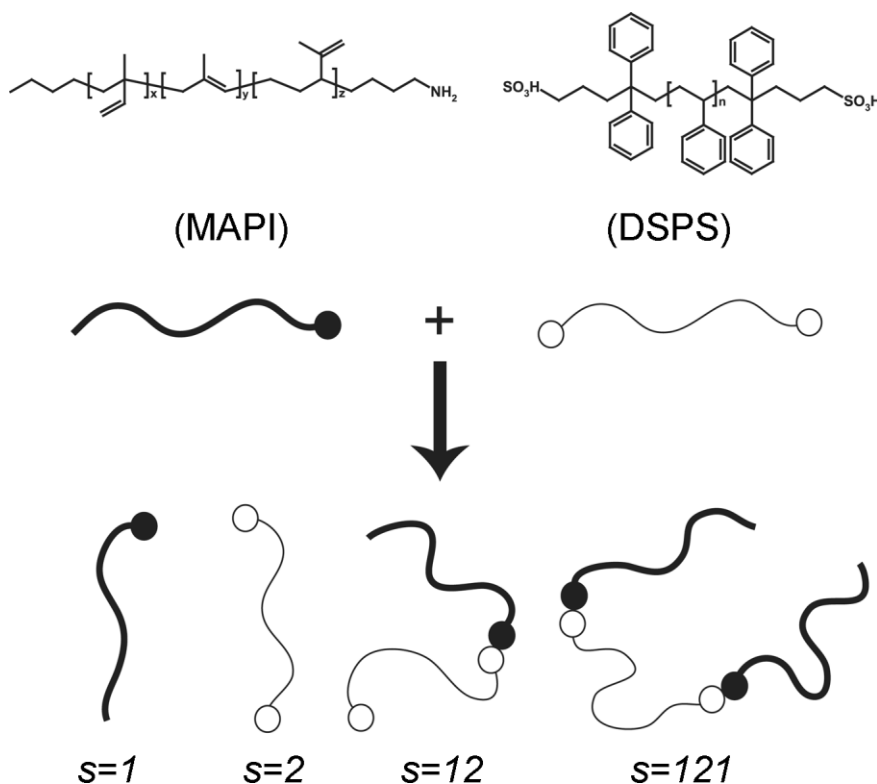
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bond,  $N$  is the degree of polymerization,  $\chi$  is the interaction parameter between the monomers of type A and B,  $k_B$  is the Boltzman constant, and  $T$  is the temperature. Depending on the magnitude of  $\kappa$ , three different scenarios are plausible: i) when  $\kappa \ll 1$ , the noncovalent bonding is too weak to prevent macroscopic demixing of the A- and B-chains; ii) when  $\kappa \gg 1$ , the bonding corresponds nearly to a permanent linkage; and iii) when  $\kappa \sim 1$ , the number of noncovalent bonds in the blend is drastically changed upon heating or cooling. The first two cases are in many ways trivial because the thermodynamic behavior of the system is nearly identical to the limiting cases of an A/B blend and an AB block copolymer. Our present interest is the third case, where the drastic change in the number of noncovalent bonds in the system upon heating or cooling may induce significant morphological variations.

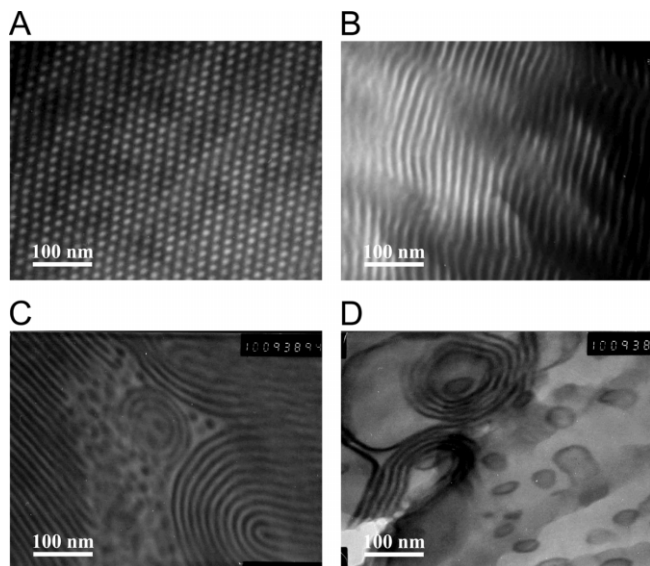
Our model system consists of a binary polymer blend of mono-end-aminated polyisoprene (MAPI) and di-end-sulfonated polystyrene (DSPS) in which the ionic interaction via proton transfer from the sulfonic acid group of DSPS to an amino group of MAPI is expected to yield a block-copolymer-like molecular complex. All polymers have been synthesized using living anionic polymerization, and the chain ends of the polymers were functionalized using standard methods. A pictorial representation of the blend system is given in Figure 1.

As shown schematically in Figure 1, the blend is expected to contain both diblock- and triblock-like complexes via 1:1 or 2:1 end associations between MAPI and DSPS chains. The relative amounts of diblock- and triblock-complexed species and remaining free chains can vary with the blend ratio and temperature. Figure 2 shows transmission electron microscopy (TEM) images of the morphologies of MAPI/DSPS blends with various blend ratios annealed at 110 °C, where the darker phase corresponds to the MAPI domains and the lighter phase to DSPS domains. The molecular weights of MAPI and DSPS are both 14.0 kg mol<sup>-1</sup>. Since the stoichiometric composition of this blend  $\phi_{st}$ , at which the number of amino groups is equal to the number sulfonic acid groups, is 67 wt.-% by MAPI content, it is expected that the complete 2:1 association between MAPI and DSPS chains at the stoichiometric condition leads to a blend that resembles a cylinder-forming polyisoprene-*block*-polystyrene-*block*-polyisoprene (ISI) triblock copolymer melt with 67 wt.-% polyisoprene. The TEM image of the blend sample at the stoichiometric composition annealed at 110 °C (Fig. 2A) shows hexagonally arrayed cylindrical DSPS microdomains embedded in a MAPI matrix, indicating that the ionic interaction between end groups at this temperature is strong enough to form triblock-copolymer-like supramolecules. As the composition deviates from the stoichiometric composition, the cylindrical morphology is transformed to a lamellar microphase (Fig. 2B) or to a phase where the lamellar and a disordered phase coexist (Figs. 2C,D). At these non-stoichiometric conditions with excess DSPS chains, the blend contains a number of unpaired sulfonated groups, which results in free DSPS chains or diblock-like supramolecules in which the DSPS chains are bonded at one end. The formation of the lamellar phase observed in the blend sample with 60 wt.-% MAPI (Fig. 2B) is possibly due to the presence of excess (unpaired) DSPS chains that enter the minor phase formed by ISI triblock-like supramolecules. At compositions far below  $\phi_{st}$ , where the blend contains a large amount of free DSPS chains, the free DSPS chains segregate from the supramolecules, leading to biphasic co-existence between a disordered phase with a large number of free DSPS chains and a supramolecule-rich lamellar phase. The theoretical calculation of a complete phase diagram for this blend and its more rigorous interpretation are reported in our previous paper.<sup>[43]</sup>



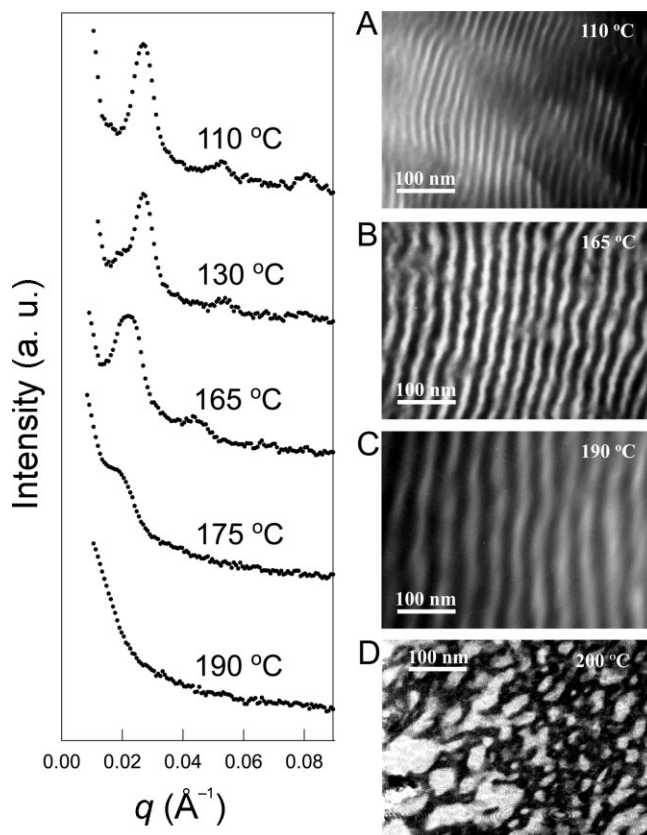
**Figure 1.** Schematic representation of four different free and complexed states possible in blends of MAPI and DSPS. The filled circles and the open circles represent, respectively, the aminated group and the sulfonated group, which can form an ionic bond via proton donation from a sulfonic acid to an amine. The states  $s=1$ ,  $s=2$ ,  $s=12$ , and  $s=121$  denote free MAPI, free DSPS, a diblock-like supramolecule, and a triblock-like supramolecule, respectively.

It is very interesting to examine the effect of heating on the lamellar spacing of the blend, since heating may induce a



**Figure 2.** TEM images of MAPI/DSPS blends with various blend ratios annealed at 110 °C: A) 70 wt.-% MAPI, B) 60 wt.-% MAPI, C) 40 wt.-% MAPI, D) 20 wt.-% MAPI. The stoichiometric composition for this blend is 67 wt.-% MAPI. Note that as the composition deviates from the stoichiometric composition the cylindrical morphology (A) is transformed to a lamellar microphase (B), and finally to co-existence between lamellar and disordered phases (C,D).

significant change in the composition of supramolecules. Figure 3 shows changes in TEM images and small-angle X-ray scattering (SAXS) patterns of the MAPI/DSPS blend with 60 wt.-% MAPI at various annealing temperatures. The TEM images of the blend sample annealed at 110–190 °C (Figs. 3A,B,C) show lamellar microphases, which indicates that the content of block-copolymer-like supramolecules in the blend is still large enough to form microphase-separated, ordered structures. The appearance of the correlation hole in the SAXS plots in the low-temperature regime confirms that the block-copolymer-like supramolecules are formed via the formation of ionic bonds between amino and sulfonic acid groups. The most notable feature in Figure 3 is the increase in interlamellar spacing ( $\lambda$ ) from  $\lambda \approx 20$  nm (Fig. 3A) to  $\lambda \approx 55$  nm (Fig. 3C) as the temperature increases. It is worth pointing out that such a strong temperature dependence of the lamellar spacing cannot be achieved in any covalently bonded block copolymer system. For block copolymer melts, the temperature dependence of the lamellar spacing ( $\lambda$ ) in the entire temperature regime is described by an expression of the scaling form  $\lambda \sim N^{1/2}(\chi N)^{\vartheta}$ , where  $\vartheta = 0$  in the weak segregation limit (WSL),  $\vartheta = 1/6$  in the strong segregation limit (SSL), and  $\vartheta = 0.22\text{--}0.45$  in the crossover regime between WSL and SSL.<sup>[44–47]</sup> Clearly, the spacing  $\lambda$  is independent of  $\chi$  in the WSL while it shows a very weak  $\chi$  dependence in the SSL and in the crossover regimes. According to the styrene–isoprene interaction parameter,  $\chi$ , obtained by Lodge et al.,<sup>[48]</sup> the  $\chi$  value at 110–190 °C ranges from 0.04 at 190 °C to 0.06 at 110 °C, and hence the degree of incompatibility ( $\chi N$ ) is roughly on the order of 12 to 18 for the corresponding diblock chain. (Here  $N$  represents



**Figure 3.** SAXS profile and TEM images for MAPI/DSPS blend with 60 wt.-% MAPI at various temperatures: A) 110 °C; B) 165 °C; C) 190 °C; D) 200 °C. Note that the interlamellar spacing increases as the temperature increases up to 190 °C, above which the blend eventually undergoes macroscopic demixing.

the total degree of polymerization of a block copolymer.) This suggests that the increase in lamellar spacing of covalently bonded styrene–*block*–isoprene block copolymers should be very small (less than 20 %) in the same temperature range ( $\chi = 0.04\text{--}0.06$ ), which is far smaller than the lamellar swelling shown in Figure 3. Besides, it should also be noted that the lamellar swelling in the present system occurs when the temperature is elevated (i.e., when  $\chi$  decreases), whereas the swelling should occur with increasing  $\chi$  in the covalently bonded block copolymer system. The drastic increase in interlamellar spacing by a relatively small change of  $\chi$  (or, equivalently, temperature) observed in the present system is attributed to a rapid increase in the number of free MAPI and DSPS chains that can swell the lamellar phase formed by block-copolymer-like supramolecules. The shift of the peak position toward smaller scattering vectors ( $q$ ) with increasing temperature also indicates that the content of block-like supramolecules decreases because of the breakage of ionic bonds linking the MAPI and the DSPS chains as the temperature is elevated; this in turn leads to the lamellar swelling. When the temperature is further elevated to 200 °C, the system eventually undergoes macroscopic demixing due to the marked decrease in number of supramolecular species, as can be seen in Figure 3D.

This temperature dependence of the number of supramolecular species and free chains can be estimated by the following theoretical approach, which will also provide us with additional information on the strength of an ionic interaction between amino and sulfonic acid groups. At this point, it may be necessary to clarify what we call the “supramolecular species”. In fact, due to the reversibility of ionic bonding, the system is in dynamic equilibrium, i.e., the supramolecular complex is continuously formed and broken. Nevertheless, on a macroscopic time scale, the number density of complex species does not fluctuate with time, which enables us to still identify free and complex species although all the individual molecules continuously change their identities (free or bonded). It has been shown from our previous theory that such a dynamic equilibrium between supramolecular species and free chains should satisfy<sup>[43]</sup>

$$\phi_1 = \Phi - \frac{\phi_{12}}{1+a} - \frac{2\phi_{121}}{2+a}, \quad \phi_2 = 1 - \Phi - \frac{\phi_{12}}{1+a} - \frac{\phi_{121}}{2+a}, \quad (1)$$

$$\phi_{12} = \frac{1+a}{N} e^{-\frac{f_b}{k_B T}} \phi_1 \phi_2, \quad \phi_{121} = \frac{2+a}{N^2} e^{-\frac{2f_b}{k_B T}} \phi_1^2 \phi_2$$

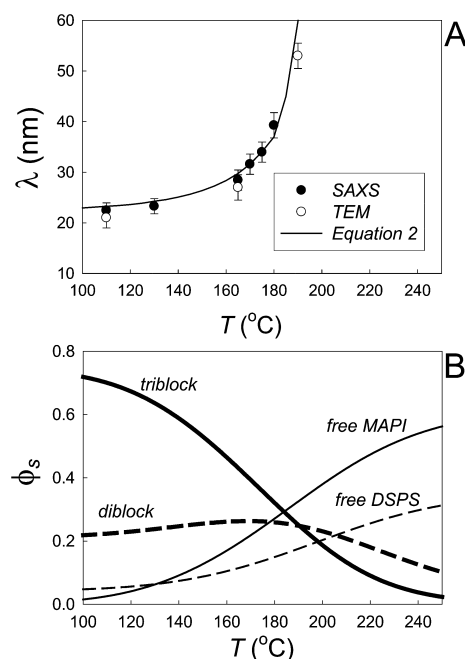
where  $\phi_1$ ,  $\phi_2$ ,  $\phi_{12}$ , and  $\phi_{121}$  are the volume fractions of free MAPI chain, DSPS chain, diblock-like complex, and triblock-like complex, respectively,  $\Phi$  is the total volume fraction of MAPI chains,  $N$  is the degree of polymerization of MAPI chains,  $a$  is the ratio of the molecular weights of DSPS chains to MAPI chains, and  $f_b$  is the free energy associated with the formation of a single ionic bond between an end-aminated group and an end-sulfonated group ( $\text{NH}_3^+ \cdots \text{SO}_3^-$ ). The free energy of bonding,  $f_b$ , can be further expressed by  $f_b = \varepsilon - Ts$ , where  $\varepsilon$  and  $s$  are the energy and the entropy associated with formation of a bond, respectively. The scattering function  $S(q)$  and the period of the microphase  $\lambda = 2\pi/q^*$  as a function of the volume fractions of free and complex species  $\{\phi_1, \phi_2, \phi_{12}, \phi_{121}\}$  can then be readily obtained by the random phase approximation (RPA)

$$S(q^*)^{-1} = \min_q \left[ \frac{\sum_{u,v} \bar{g}_{uv}(q)}{\|\bar{g}_{uv}(q)\|} - 2\chi \right], \quad (2)$$

$$\bar{g}_{uv} = \frac{\phi_1}{N} g_{uv}^{(1)} + \frac{\phi_2}{aN} g_{uv}^{(2)} + \frac{\phi_{12}}{(1+a)N} g_{uv}^{(12)} + \frac{\phi_{121}}{(2+a)N} g_{uv}^{(121)}$$

where  $g_{uv}^{(i)}$  is the density correlation function between monomers of type  $u$  and  $v$ , each of which can be either isoprene or styrene monomers belonging to supramolecular species (or free chains) of type  $i$ :  $i=1$  for free MAPI chains,  $i=2$  for free DSPS chains,  $i=12$  for diblock-like supramolecules, and  $i=121$  for triblock-like supramolecules. The density correlation functions are obtained using Gaussian chain statistics, and the temperature dependence of the isoprene–styrene interaction parameter  $\chi$  (based on the styrene segment volume)

is given as  $\chi = -0.0228 + 33/T$ , as obtained by Lodge et al.<sup>[48]</sup> Since the degree of incompatibility at 110–190 °C is not very large ( $2N\chi = 12\text{--}18$ ), the RPA approach is justified. Note that the only independently unknown variable in Equations 1,2 is the free energy of a single bonding  $f_b$ . This can be determined by fitting of the experimental  $\lambda$ – $T$  curve. The interlamellar spacing  $\lambda$  as a function of temperature,  $T$ , for MAPI/DSPS blends with 60 wt.-% MAPI is shown in Figure 4A, where filled circles and open circles represent values obtained from



**Figure 4.** A) The interlamellar spacing as a function of temperature for a MAPI/DSPS blend with 60 wt.-% MAPI. Filled circles and open circles represent values from SAXS and TEM measurements, respectively, and the solid line represents a theoretical fit based on Equation 2. B) The volume fraction of free species and block-copolymer-like supramolecular species  $\{\phi_1, \phi_2, \phi_{12}, \phi_{121}\}$  as a function of temperature for a MAPI/DSPS blend with 60 wt.-% MAPI.

SAXS and TEM measurements, respectively, and the solid line represents a theoretical fit based on Equations 1,2 with the two adjustable parameters  $\varepsilon$  and  $s$ . From the theoretical fit, we find that

$$\beta f_b = \beta(\varepsilon - Ts) = -8450/T + 13.9 \quad (3)$$

where  $\beta = (k_B T)^{-1}$ . Our estimation of the bonding energy ( $\varepsilon$ ) between  $\text{NH}_2$  and  $\text{SO}_3\text{H}$ , which roughly corresponds to 18 kcal mol<sup>-1</sup>, is in reasonably good agreement with the typical value of an ionic interaction. This further indicates that the parameter  $\kappa$ , which characterizes the competition between two opposing tendencies (supramolecular assembly versus macroscopic demixing between MAPI and DSPS chains) is in the range of 0.8–1.4 at  $T = 100\text{--}200$  °C. As stated above, this value of  $\kappa$  is a necessary condition for temperature sensitivity of a microphase period.

Using the theoretical fitting function of Equation 3, the temperature dependence of  $\{\phi_1, \phi_2, \phi_{12}, \phi_{121}\}$  can then be obtained from Equation 1, as shown in Figure 4B. At 100–150 °C, where the ionic interaction is relatively strong, the blend produces a large fraction of diblock- or triblock-copolymer-like supramolecules ( $\phi_{12} = 0.2\text{--}0.25$ ,  $\phi_{121} = 0.55\text{--}0.72$ ), which leads to the formation of a lamellar microphase, as seen in the TEM image at 110 °C (Fig. 3A). This supramolecule-rich composition is drastically altered by elevating the temperature. At 150–190 °C, the content of free MAPI and DSPS chains rapidly increases as the triblock-like supramolecules are converted to free MAPI and DSPS chains by breaking of ionic bonds at both ends of a DSPS chain. Thus, the lamellar phase becomes inflated by the presence of free MAPI and DSPS chains in the mid-plane of their respective lamellar domains. Also of interest is that the fraction of diblock-like supramolecules is nearly unchanged at 150–190 °C (or even slightly increased at 150–170 °C), whereas that of triblock-like supramolecules rapidly decreases. This suggests that the cleavage of diblock-like supramolecules is more or less balanced by the formation of diblock-like supramolecules created by the breaking of an ionic bond at one of two junctions in the triblock-like supramolecules. As a net result, the triblock-like supramolecule acts as a temperature-regulated reservoir that feeds free chains, while the diblock-like supramolecules are regarded as a secondary reservoir that keeps the supramolecules from completely cleaving. This stepwise cleavage of supramolecules allows a wide temperature regime of lamellar swelling (100–190 °C), as seen in Figures 3A–C. We expect that the design of a supramolecular system capable of forming a polydisperse supramolecular species, such as multiple-block copolymer-like supramolecules, would result in an even wider range in microphase dimensions.

This work demonstrates that the use of block-copolymer-like supramolecules can permit an efficient thermal tuning of the microphase periodicity owing to the reversibility between supramolecular assembly and disassembly. The preceding results based on a diblock- and triblock-like supramolecular system shows that the lamellar microphase swells upon heating to almost 300 % (20–55 nm), which cannot be achieved in any covalent-bonded block copolymer system of the same material. Conventionally, one can control the characteristic dimensions of a microphase either by varying the molecular weight of the block copolymer or by mixing the block copolymer with homopolymers. The former method is often hampered by a laborious and difficult synthesis, and the latter only allows the preparation of a limited range of microphase periods (typically less than 150 %), since the addition of a large amount of homopolymer usually leads to macrophase separation between block copolymer and homopolymer instead of a microphase.<sup>[24–30]</sup> Hence, the thermal control of microphase dimensions via supramolecular assembly and disassembly is advantageous since the control is in situ. Such a strong temperature sensitivity of the microphase period has never been achieved previously. One can envisage such a material in which the

characteristic dimensions of the microphase can be flexibly tuned for a variety of uses.

## Experimental

MAPI and DSPS were synthesized by anionic polymerization as described in the literature [49,50]. For synthesis of MAPI, living polyisoprene (PI) chains were reacted with an excess of aminating reagent, 2,2,5,5-tetramethyl-1-(3-chloropropyl)-1-aza-2,5-disilacyclopentane, and then the reaction product was precipitated at least three times by addition of an acid to remove the silyl protecting groups. For DSPS, styrene was polymerized using lithium naphthalate as an initiator, and then the living Li–polystyrene–Li chain was end-capped with 1,1-diphenylethylene. Subsequently, the sample was allowed to react with 1,3-propane sultone. The lithium sulfonate group was then transformed to the acid group by precipitating the polymer in methanol containing a small amount of HCl. Results of size-exclusion chromatography (SEC), thin-layer chromatography (TLC), and <sup>1</sup>H NMR showed that the number-average molecular weights of MAPI and DSPS were both 14.0 kg mol<sup>-1</sup> with a narrow molecular-weight distribution (polydispersity index < 1.1), and that 99 % of the polymers were properly end-functionalized.

The MAPI/DSPS blend samples were prepared by dissolving both MAPI and DSPS in toluene. The concentration of the initial solution was ca. 10 wt.-%. After complete dissolution, the solvent was slowly evaporated under vacuum at room temperature for a few weeks. For TEM and SAXS measurements, the blend samples were annealed at the desired temperature for five days, after which the samples were quenched in liquid nitrogen. This procedure froze the morphological structure developed at the annealed temperature.

SAXS patterns were obtained on a Nanostar small-angle X-ray scattering system. Measuring time for all samples was 1 h. Scattering patterns were averaged azimuthally to give the one-dimensional form of intensity  $I$  (arbitrary units) as a function of the magnitude of the scattering wave vector  $|q| = q = 4\pi\lambda^{-1}\sin(\theta/2)$ , where  $\lambda$  and  $\theta$  are the radiation wavelength ( $\lambda = 0.154$  nm) and scattering angle, respectively.

To obtain ultrathin sections for TEM, the blend samples were microtomed at –100 °C with a Leica Ultramicrotome low-temperature sectioning system using a diamond knife. The samples were collected on 400 mesh uncoated copper grids and then stained in osmium peroxide vapor for 7 h. Since the MAPI domain was preferentially stained by OsO<sub>4</sub>, it appeared dark under bright-field TEM. TEM was performed in the bright-field mode on a Philips Electron Optics CM-20 operated at 120 kV accelerating voltages.

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