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Phase Transition in End-Functionalized Polystyrene-*block*-polyisoprene-*block*-polystyrene Copolymers

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ABSTRACT: Phase transition in polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS triblock) copolymers end-capped with carboxylic acid group (−COOH) or sodium carboxylate group (−COONa) was investigated using oscillatory shear rheometry and transmission electron microscopy (TEM). For the study, three SIS triblock copolymers having almost an equal block length ratio, but varying molecular weights, were synthesized via sequential anionic polymerization. The number-average molecular weights of the three block copolymers synthesized were 1.8×10^4 g/mol (SIS1), 2.3×10^4 g/mol (SIS2), and 3.4×10^4 g/mol (SIS3). It was found that both SIS1 and SIS2 were homogeneous block copolymers, while SIS3 had lamellar microdomains, and it had an order−disorder transition temperature (T_{ODT}) of 180 °C. Each of the triblock copolymers was end-capped with a −COOH group to obtain SIS−COOH using high-purity, gaseous carbon dioxide. Subsequently, part of the SIS−COOH was neutralized with sodium hydroxide to obtain SIS−COONa. It was found that SIS1−COOH, SIS1−COONa, and SIS2−COOH remained homogeneous, while SIS2−COONa microphase-separated into a lamella-forming triblock copolymer, as determined from TEM, which has a T_{ODT} of 123 °C as determined from oscillatory shear rheometry. The T_{ODT} of lamella-forming SIS3 was found to increase from 180 to 182 °C after it was end-capped with a −COOH group and to 228 °C after it was end-capped with a −COONa group. Cloud point measurements show that (i) the upper critical solution temperature (UCST) of the mixtures composed of polyisoprene (PI) and polystyrene (PS) end-capped with a −COONa group, PI/(PS−COONa) mixtures, is much higher than that of the mixtures composed of PI and PS end-capped with a −COOH group, PI/(PS−COOH) mixtures, and PI/PS mixtures, and (ii) the UCST of PI/(PS−COOH) mixtures is only slightly higher than that of PI/PS mixtures. It is concluded that the formation of lamellar microdomains in SIS2−COONa from homogeneous SIS2 after it was end-capped with a −COONa group and a very high T_{ODT} observed for SIS3−COONa are attributable to strong ionic associations and significantly increased repulsive segment−segment interactions between the PI and PS−COONa phases in the block copolymers.

1. Background

During the past three decades the synthesis, structure, properties, and applications of ion-containing polymers have been reported extensively in the literature.[1−4] Roughly, one can divide the ion-containing polymers into four categories: (i) ion-containing homopolymers with randomly functionalized species[5−9] or ion-containing random copolymers with functionalized species selectively on one of the components,[10−17] (ii) end-functionalized homopolymers,[18−21] (iii) ion-containing block copolymer with randomly functionalized species,[22−30] and (iv) end-functionalized block copolymers.[31] Today it is well established that the common feature in all ion-containing polymers is the formation of ionic associations giving rise to clusters or aggregates, which in turn affect greatly their rheological behavior in the solution and bulk states. Among the studies cited above, the least investigated is end-functionalized block copolymer. To the best of our knowledge, there appears to exist only one study[31] reporting on the solution properties of end-functionalized polystyrene-*block*-polyisoprene (SI diblock) and polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS triblock) copolymers, in which dipolar sulfobetaine group was attached onto one end of the diblock copolymer or onto both ends of the triblock copolymer. However, little has been reported on phase transition in end-functionalized ABA-type triblock copolymers.

In this study, we synthesized, via sequential anionic polymerization, SIS triblock copolymers with varying molecular weights, which were later end-functionalized with carboxylic acid or sodium carboxylate. We then investigated their phase transitions using oscillatory shear rheometry and transmission electron microscopy (TEM). To facilitate our discussion later in this paper, below we summarize briefly the highlights of two previous studies that are closely related to our study.

Fetters et al.[20] investigated the viscoelastic behavior, in the molten state, of polyisoprene (PI) end-capped with carboxylic acid, sodium carboxylate, amine, or zwitterion and then compared it with the viscoelastic behavior of nonfunctionalized counterparts. They observed that the sodium carboxylate series had long-lived spherical clusters in the melt, while the polymers end-capped with carboxylic acid were only weakly associated. They compared the zero-shear viscosity of PI end-capped with carboxylic acid group (−COOH), $\eta_{0,\mathrm{COOH}}$, with that of PI end-capped with sodium carboxylate group (−COONa), $\eta_{0,\mathrm{COONa}}$. They found that the ratio $\eta_{0,\mathrm{COOH}}/\eta_{0,\mathrm{H}}$, with $\eta_{0,\mathrm{H}}$ being the zero-shear viscosity of the nonfunctionalized counterpart, varied from 1.1 to 1.8, whereas the ratio $\eta_{0,\mathrm{COONa}}/\eta_{0,\mathrm{H}}$ varied from 11 to 22, depending upon the molecular weight. They attributed the significantly increased $\eta_{0,\mathrm{COONa}}$ to the ionic associations of end groups forming noninteracting spherical clusters.

Using small-angle X-ray scattering and isochronal dynamic temperature sweep experiments, Mani et al.[28] investigated microstructure and order−disorder transition (ODT) in ionomers that were obtained by lightly sulfonating (from 1 to 17 mol % of the styrene repeat units) polystyrene (PS) blocks of diblock and triblock

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copolymers of PS and poly(ethylene-*alt*-propylene) (PEP). They observed that (i) sulfonation of a PS-*block*-PEP copolymer ionomer containing ca. 20 wt % PS block resulted in a transition of the microdomain structure from hexagonally packed cylinders to lamellae, (ii) the ODT temperature (T_{ODT}) of the block copolymer ionomers was much higher than that of the nonfunctionalized counterpart, and (iii) the T_{ODT} of the block copolymer ionomers increased as the degree of functionalization increased.

The end-functionalized SIS triblock copolymers investigated in the present study have a common feature with the end-functionalized homopolymer PIs investigated by Fetter et al.[20] in that both polymer systems are functionalized only at the end of a polymer chain. However, there are significant differences between the two polymer systems. In the SIS triblock copolymers investigated in the present study both ends were functionalized, while only one end was functionalized in the homopolymer PIs investigated by Fetter et al. More importantly, the SIS triblock copolymers employed in our study provided an opportunity to investigate ODT as affected by end-functionalization. There is a similarity between the present study and the study of Mani et al.[28] in that both studies dealt with ion-containing block copolymers. However, there is also a very significant difference between the two studies in that our study dealt with the end-functionalized ABA-type triblock copolymers, while the study of Mani et al. dealt with an AB-type diblock copolymer functionalized randomly over the entire chain of one of the two blocks and an ABA-type triblock copolymer functionalized randomly over the entire chain of both end blocks. The differences in the numbers and positions of the functionalized groups in a given block copolymer may affect the extent of phase transition in the block copolymer.

In this study we have made a very interesting observation for an SIS triblock copolymer end-capped with sodium carboxylate group (−COONa). Specifically, we were able to induce microphase separation from a homogeneous SIS triblock copolymer by end-capping with a −COONa group, as determined from oscillatory shear rheometry and TEM. This paper is organized as follows. First we will present linear dynamic viscoelastic properties of two homogeneous SIS triblock copolymers before and after they were end-capped with a −COOH group or a −COONa group. Then we will present a TEM image, showing that lamellar microdomains were induced after a homogeneous SIS triblock copolymer was end-capped with a −COONa group. Also, we will present binodal curves, obtained from cloud point measurements, for binary mixtures of homopolymer PI and homopolymer PS (end-capped with a −COOH group or a −COONa group). Finally, we will explain the results of linear dynamic viscoelastic measurements and phase transition in the end-functionalized SIS triblock copolymers prepared in this study.

2. Experimental Section

Synthesis of Polymers and Characterization. We synthesized, via sequential anionic polymerization, three nearly symmetric SIS triblock copolymers with different molecular weights.

For this, we first prepared difunctional initiator by purifying a precursor, 1,3-bis(phenylethenyl)benzene (PEB) (yellowish liquid), which was obtained from Dow Chemical Co. The following procedures were used to purify PEB. The crude, viscous PEB was dissolved in *n*-hexane. Initially the PEB/*n*-hexane solution exhibited two spots in thin-layer chromatography (TLC), indicating the presence of impurities. Impurities were removed by passing repeatedly the PEB/*n*-hexane solution through the chromatographic column packed with activated silica gel (230−400 mesh) (Selecto Scientific) until only one spot in TLC was detected. The purified PEB/*n*-hexane solution was distilled under a high vacuum. The distilled residue, purified PEB, was a highly viscous, colorless liquid. Dilithium initiator (DLI) was prepared by reacting 2 mol of *sec*-BuLi with 1 mol of PEB in cyclohexane using the following procedures. The purified PEB was weighed into a round flask with a sidearm that had been purged with argon gas, and cyclohexane was vacuum-distilled from a storage flask containing purified cyclohexane. The solution was heated, while stirring, to 60 °C. Upon addition of *sec*-BuLi solution in cyclohexane to a flask using a syringe, the colorless solution became dark red in a few seconds. The addition reaction continued for 2 h at 60 °C. The DLI thus obtained was analyzed, via proton nuclear magnetic resonance (^{1}H NMR) spectroscopy, to confirm the molecular structure and completeness of the addition reaction. Cyclohexane and isoprene were vacuum-distilled. Pentamethyldiethylenetriamine (PMDETA) (Aldrich) needed to obtain narrow molecular weight PI was purified by vacuum distillation in the presence of calcium hydride. A mixture consisting of 2 mol of PMDETA and 1 mol of *sec*-BuLi in DLI was added to the reactor using a syringe. The reactor was then purged with argon gas and heated, while stirring, to 55 °C using a water bath. When the temperature of the water bath reached about 55 °C, DLI was added to first polymerize the isoprene monomer. About 2 h after the addition of DLI, styrene monomer was added to the reactor. After the copolymerization of isoprene and styrene monomers for 1.5 h, a small amount of degassed methanol was added to terminate the living polymers, at which point the color of the solution changed from yellowish red to colorless. Then the reactor temperature was lowered to room temperature, and the solution was precipitated by addition of an excess amount of methanol. The precipitated polymer was filtered and dried at room temperature for 3 days in a fume hood and then at 60 °C for 12 h in a vacuum oven.

Membrane osmometry (Jupiter Instrument) was used to determine the number-average molecular weight (M_n) and gel permeation chromatography (GPC) (Waters) to determine the polydispersity index (M_w/M_n) of each block copolymer synthesized. Block copolymer composition was determined using ^{1}H NMR spectroscopy. Table 1 gives a summary of sample codes and the molecular characteristics of the block copolymers synthesized in this study.

Carbonation and Neutralization of SIS Triblock Copolymers. Each of the three SIS triblock copolymers synthesized was subjected to carbonation to end-cap the PS end blocks with carboxylic acid group by introducing high-purity, gaseous carbon dioxide (CO_2). Carbonation of an SIS triblock copolymer was carried out using the following procedures. After polymerization, a vacuum line was attached to the reactor containing the solution of polymeric anions and polar solvent (PMDETA), which was then purged by CO_2 gas. Then CO_2 gas at a constant pressure of 0.103 MPa (15 psig) was passed through the vacuum line into the reactor, after which the CO_2 gas reacted with the polymeric organolithium compound in the solution without stirring. As the reaction progressed, gradual discoloration of the red “living” anionic solution containing poly(styryl−isoprene−styryl)lithium was observed. The solution became colorless after about 12 h, at which point the reactor was opened to atmospheric air. Immediately after that, about 1 mL of hydrochloric acid/methanol mixture (1/9 v/v) was added dropwise into the polymer solution, and the mixture was stirred for 12 h to hydrolyze the polymeric lithium carboxylate salt, yielding SIS triblock copolymer end-capped with −COOH group. To remove the residual hydrochloric acid, distilled water was added to the reactor. The resulting oily phase was collected, and it was added dropwise into methanol, precipitating the end-functionalized SIS triblock copolymer. The precipitated polymer, SIS−COOH, was filtered and dried in a vacuum oven. The concen-

Table 1. Molecular Characteristics of Neat and End-Functionalized SIS Triblock Copolymers Synthesized in This Study

sample code	end group	$M_n{}^a$ (g/mol)	$M_w/M_n{}^b$	$w_{PS}{}^c$	$T_{g,PS}{}^d$ (°C)	$T_{g,PI}{}^d$ (°C)	TODT (°C)	functionality (%)^e (COOH or COONa)
SIS1	H	1.8×10^4	1.08	0.47	46	−17	disordered	
	COOH				56	−17	disordered	98
	COONa				57	−15	disordered	100
SIS2	H	2.3×10^4	1.09	0.44	67	−4	disordered	
	COOH				77	−2	disordered	97
	COONa				78	−3	123	100
SIS3	H	3.4×10^4	1.09	0.44	75	−6	180	
	COOH				79	−5	182	99
	COONa				80	−5	228	100

[a] Determined from membrane osmometry. [b] Determined from GPC. [c] Determined from ^{1}H NMR spectroscopy. [d] Determined from differential scanning calorimetry. [e] Determined by titrating a polymer solution in toluene with 0.01 M KOH in methanol to the phenolphthalein end point.

tration of carboxyl chain ends in SIS−COOH was determined by titrating a polymer solution in toluene with 0.01 M potassium hydroxide (KOH) in methanol to the phenolphthalein end point.[32] The efficiency of carbonation was found to be over 97%. Subsequently, the triblock copolymer SIS−COOH was neutralized to obtain SIS−COONa by adding an excess amount of sodium hydroxide (NaOH)/methanol mixture, while vigorously stirring, into a solution in which an SIS−COOH was dissolved in toluene. After the completion of neutralization, a triblock copolymer, end-capped SIS−COONa, was precipitated with methanol. The precipitated polymer was washed thoroughly to remove excess NaOH and then dried in a vacuum oven. The concentration of sodium carboxylate chain ends in an SIS−COONa was determined by titrating a polymer solution in toluene with phenolphthalein. Upon addition of phenolphthalein, the colorless polymer solution became red in a few seconds.

Sample Preparation. Samples for oscillatory shear rheometry and transmission electron microscopy (TEM) were prepared by first dissolving a predetermined amount of block copolymer in toluene (10 wt % in solution) in the presence of 0.1 wt % antioxidant (Irganox 1010, Ciba-Geigy Group) and then slowly evaporating the solvent. The evaporation of solvent was carried out initially in a fume hood slowly at room temperature for 1 week and then in a vacuum oven at 40 °C for 3 days. The last trace of solvent was removed by drying the samples in a vacuum oven at an elevated temperature by gradually raising the oven temperature about 20 °C above the glass transition temperature of each block copolymer. Table 1 gives a summary of the glass transition temperatures, $T_{g,PS}$ and $T_{g,PI}$, of polystyrene and polyisoprene blocks, respectively, in each block copolymer. The drying of the samples was continued until there was no further change in weight, and then the specimens were stored in a refrigerator. Prior to oscillatory shear rheometry or TEM, the solvent-cast samples were thermally treated under predetermined conditions.

Oscillatory Shear Rheometry. An Advanced Rheometric Expansion System (ARES, Rheometric Scientific) was used in the oscillatory mode with parallel plate fixtures (25 mm diameter). Dynamic frequency sweep experiments were conducted; i.e., the dynamic storage modulus (G') and dynamic loss modulus (G'') were measured as functions of angular frequency (ω) ranging from 0.01 to 100 rad/s at various temperatures during heating. The temperature increment in the frequency sweep experiment varied from 3 to 10 °C, and the specimen was kept at a constant temperature for 30−40 min before rheological measurements actually began. Data acquisition was accomplished with the aid of a microcomputer interfaced with the rheometer. The temperature control was satisfactory to within ±1 °C. A fixed strain of 0.04 was used, which ensured us that our rheological measurements were well within the linear viscoelastic range for the materials investigated. Dynamic temperature sweep experiments under isochronal conditions were also conducted; i.e., G' and G'' were measured at $\omega = 0.1$ rad/s during heating. All experiments were conducted under a nitrogen atmosphere to preclude oxidative degradation of the samples.

Transmission Electron Microscopy (TEM). TEM was conducted to investigate the microdomain structures of SIS2 and SIS3 before and after they were end-capped with −COONa group. The ultrathin sectioning was performed by cryoultramicrotomy at −100 °C using a diamond knife, which was below the glass transition temperature ($T_g = -68$ °C) of PI to attain the rigidity of the specimen, using a Reichert Ultracut S low-temperature sectioning system. A transmission electron microscope (JEM1200EX II, JEOL) operated at 120 kV was used to record the morphology of the specimens stained with osmium tetroxide vapor.

Cloud Point Measurement. To investigate the extent to which the segment−segment interactions between the PI and PS phases in an SIS triblock copolymer were affected by end-functionalization of the PS block with −COOH group or −COONa group, in this study we conducted cloud point measurements using laser light scattering. For this, we employed a polyisoprene (PI6) with $M_n = 6100$ g/mol and $M_w/M_n = 1.05$ and a polystyrene (PS2) with $M_n = 2200$ g/mol and $M_w/M_n = 1.05$. PI6 and PS2 were synthesized in conjunction with our previous study.[33] In this study, PS2 was end-functionalized with a −COOH group to obtain PS2−COOH using high-purity, gaseous CO_2, and part of PS2−COOH was neutralized with NaOH to obtain PS2−COONa. Cloud points of PI6/PS2, PI6/(PS2−COOH), and PI6/(PS2−COONa) mixtures were measured on thin films, which were prepared by dissolving predetermined amounts of the constituent components in toluene (ca. 10 wt % solution). A few drops of this solution were placed on a glass slide and then dried. The solvent was evaporated slowly at room temperature first in fume hood and then in a vacuum oven at elevated temperature. The cloud point of a specimen was determined using laser light scattering. Specifically, a glass slide containing a blend specimen was placed on the hot stage of the sample holder equipped with a programmable temperature controller. A low-power He−Ne laser (wavelength of 635 nm) was used as the light source, and a photodiode was used as the detector. A specimen was first heated to a temperature slightly (ca. 20 °C) above the cloud point (i.e., in the isotropic region) followed by slow cooling into the two-phase region where a change in light intensity was noticeable, and then the specimen was heated again at a preset rate (0.5−5 °C/min), during which information on both temperature and the intensity of scattered light was recorded. For each composition of a particular blend system, cloud point measurements were repeated 3−5 times until data were reproducible, and a fresh specimen was used for each experimental run. For a given blend system, nine compositions from 10/90 to 90/10 blend ratios were used for cloud point measurements. A plot of the intensity of scattered light vs temperature during heating was prepared, from which a binodal curve was constructed, the results of which are presented below.

3. Results and Discussion

Figure 1 gives log G' vs log G'' plots for (a) SIS1, (b) SIS1−COOH, and (c) SIS1−COONa at various temperatures. Figure 1 is divided into three panels to avoid

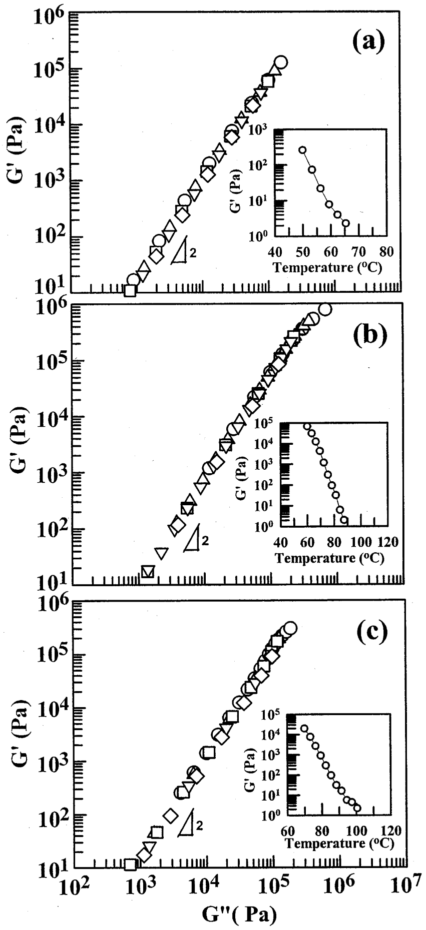

Figure 1. Plots of log G' vs log G'' for: (a) SIS1 at (○) 60, (△) 63, (□) 66, (▽) 69, and (◇) 72 °C; (b) SIS1−COOH at (○) 70, (△) 75, (□) 80, (▽) 85, and (◇) 90 °C; (c) SIS1−COONa at (○) 80, (▽) 85, (□) 90, (▽) 95, and (◇) 100 °C. The inset on the lower right-hand side of each panel describes the dependence of G' on temperature during the isochronal dynamic temperature sweep experiment at $\omega = 0.1$ rad/s in the heating cycle. The specimens were annealed at 80 °C for 2 days in a vacuum oven.

the crowding of data points had a single panel been used for all three block copolymers. It is seen in Figure 1 that the log G' vs log G'' plots are independent of temperature over the entire range of temperatures investigated and have a slope of 2 in the terminal region, indicating that all three block copolymers are in the disordered state.[34−36] The inset on the lower right-hand side of each panel in Figure 1 shows the temperature dependence of G' from isochronal dynamic temperature sweep experiments for each triblock copolymer. It is seen from the insets in Figure 1 that values of G' decrease steadily with increasing temperature, as is typically observed in ordinary linear polymers, reinforcing the conclusion drawn above from the log G' vs log G'' plots that all three triblock copolymers are in the disordered state. According to currently held mean-field theory,[37,38] the molecular weight, block copolymer composition, and Flory−Huggins interaction parameter determine whether a block copolymer may undergo microphase separation. Apparently, the change in the Flory−Huggins interaction parameter by end-capping of SIS1 with a −COOH group or a −COONa group was not sufficient to induce microphase separation because the molecular weight of SIS1 might have been much lower than the threshold value at and above which microphase separation may set in. After all, for all intents and purposes the change in molecular weight after end-capping of SIS1 with a −COOH group or a −COONa group is negligibly small. Using the mean-field theory of Mayes and Olvera de la Cruz[39] and the expression for the temperature-dependent Flory−Huggins interaction parameter,[40] $\chi(T) = -0.0419 + 38.5/T$ with T being the absolute temperature, we have estimated the T_{ODT} of SIS1 to be ca. 21 °C, which is far below the measured $T_{\mathrm{g,PS}}$ (46 °C) of SIS1 (see Table 1). Note that the accuracy of the estimated value of T_{ODT} of a block copolymer depends, among other factors, on the choice (or accuracy) of the expression for $\chi(T)$.[41] Use of different expressions for $\chi(T)$ invariably would give rise to different values of predicted T_{ODT} of a block copolymer. Further, the Mayes−Olvera de la Cruz theory,[39] like the Leibler theory,[38] is based on an infinitely high molecular weight block copolymer. Thus, predicted values of T_{ODT}, via currently held mean-field theory, of low molecular weight diblock copolymers (with degree of polymerization less than say 10^3), like the SIS triblock copolymers investigated in this study, must be regarded as being approximate. Nevertheless, currently held mean-field theory has proven to be very useful to gain an insight into the phase transitions in block copolymers.

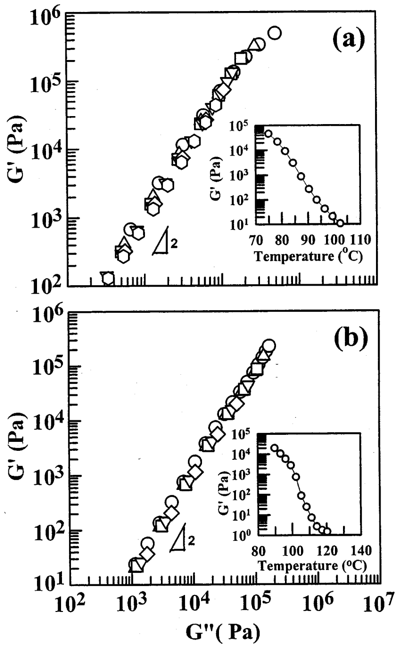

Figure 2. Plots of log G' vs log G'' for: (a) SIS2 at (○) 85, (△) 90, (□) 95, (▽) 100, (◇) 105, and (⬡) 110 °C; (b) SIS2−COOH at (○) 105, (△) 110, (□) 115, (▽) 120, and (◇) 125 °C. The inset on the lower right-hand side of each panel describes the dependence of G' on temperature during the isochronal dynamic temperature sweep experiment at $\omega = 0.1$ rad/s in the heating cycle. The specimens were annealed at 100 °C for 2 days in a vacuum oven.

Figure 2 gives log G' vs log G'' plots for (a) SIS2 and (b) SIS2−COOH at various temperatures. Again, Figure 2 is divided into two panels to avoid the crowding of data points had a single panel been used for both block copolymers. It is seen in Figure 2 that the log G' vs log G'' plots are independent of temperature over the entire range of temperatures investigated and have a slope of 2 in the terminal region, indicating that both block copolymers are in the disordered state.[34−36] We can draw the same conclusion from the insets of Figure 2 describing the temperature dependence of G' from isochronal

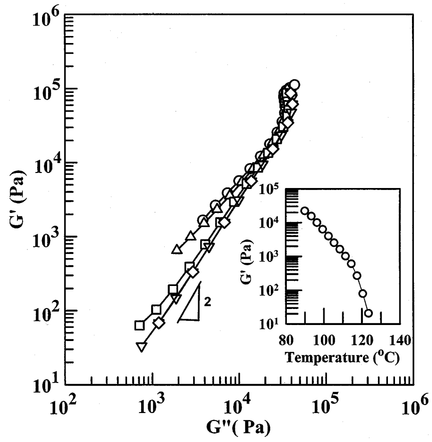

Figure 3. Plots of log G' vs log G'' for SIS2−COONa at: (○) 110, (△) 115, (□) 120, (▽) 123, and (◇) 126 °C, showing that this block copolymer undergoes ODT at ca. 123 °C. The inset on the lower right-hand side describes the dependence of G' on temperature during the isochronal dynamic temperature sweep experiment at $\omega = 0.1$ rad/s in the heating cycle, showing *no* particular temperature at which values of G' begin to drop suddenly. The specimens were annealed at 100 °C for 2 days in a vacuum oven.

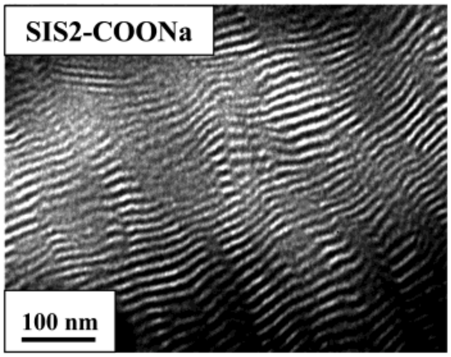

Figure 4. TEM image of SIS2−COONa at room temperature. The specimen was annealed at 100 °C for 1 week.

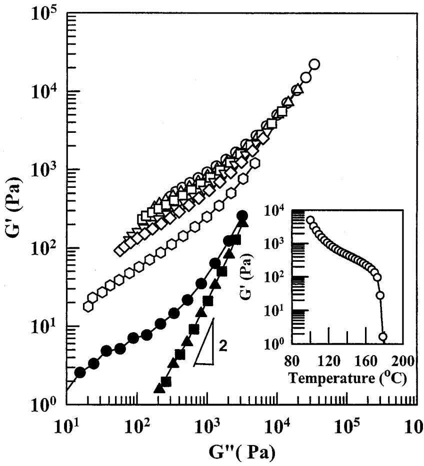

Figure 5. Plots of log G' vs log G'' for SIS3 at: (○) 140, (△) 150, (□) 160, (▽) 170, (◇) 173, (⬡) 176, (●) 179, (▲) 182, and (■) 185 °C, showing that this block copolymer undergoes ODT at ca. 179 °C. The inset on the lower right-hand side describes the dependence of G' on temperature during the isochronal dynamic temperature sweep experiment at $\omega = 0.1$ rad/s in the heating cycle. The specimen was annealed at 120 °C for 3 days in a vacuum oven.

dynamic temperature sweep experiments. Apparently, the molecular weight of SIS2, $M_n = 2.3 \times 10^4$ g/mol (see Table 1), is not sufficiently high to give rise to a microdomain structure. The Mayes−Olvera de la Cruz theory[39] with $\chi(T) = -0.0419 + 38.5/T$ predicts the T_{ODT} of SIS2 to be 47 °C, which is still below the measured $T_{g,PS}$ (67 °C) of SIS2 (see Table 1).

However, we observe a quite different temperature dependence of log G' vs log G'' plots for SIS2−COONa, as can be seen in Figure 3. Here, log G' vs log G'' plots for this block copolymer depend on temperature until reaching 123 °C, at which point they begin to be independent of temperature and have a slope of 2 in the terminal region. Following the rheological criterion of Han and co-workers,[34−36] we conclude from Figure 3 that the T_{ODT} of SIS2−COONa is ca. 123 °C. According to the rheological criterion in the literature,[42−44] the T_{ODT} of a block copolymer may be determined by the temperature at which values of G' from the isochronal dynamic temperature sweep experiments begin to drop precipitously. Then the inset in Figure 3 supports the conclusion drawn from log G' vs log G'' plots. What is of great interest in Figure 3 is that end-capping of homogeneous SIS2 with a −COONa group has induced microphase separation, as indicated by the lamellar microdomain structure shown in the TEM image of Figure 4. To the best of our knowledge, such experimental observation has not been reported until now. The readers are reminded that end-capping of homogeneous SIS2 with −COOH group did not induce microphase separation. The physical origin of the experimentally observed microphase separation in SIS2−COONa must be explained using an argument other than molecular weight, since the increase in molecular weight due to end-capping of SIS2 is negligible. One could make a thermodynamic argument that end-capping of SIS2 with −COONa group might have increased the repulsive segment−segment interactions considerably more than end-capping of SIS2 with a −COOH group. If this is the case, we can then explain the reason why microphase separation was induced in SIS2−COONa, but not in SIS2−COOH. This is because the currently held mean-field theory[38,39] predicts that the Flory−Huggins interaction parameter plays a decisive role in determining whether microphase separation occurs in block copolymers when the molecular weight and block copolymer composition remain constant. We defer further discussion of this subject until presentation of binodal curves for three binary mixtures below: PI/PS, PI/(PS−COOH), and PI/(PS−COONa) mixtures, where PS−COOH denotes PS end-capped with a −COOH group and PS−COONa denotes PS end-capped with a −COONa group.

Figure 5 gives log G' vs log G'' plots for SIS3 at various temperatures, showing that T_{ODT} lies between 179 and 182 °C. The inset of Figure 5 describes the temperature dependence of G' obtained from isochronal dynamic temperature sweep experiments for SIS3, showing that T_{ODT} is ca. 180 °C. Within experimental uncertainties the two different experiments give more or less the same value of T_{ODT} (say 180 °C) for SIS-3. Figure 6 describes the effect of end-functionalization of SIS3 with a −COOH group or a −COONa group on the temperature dependence of G' obtained from isochronal dynamic temperature sweep experiments. Owing to space limitation here, we have not presented log G' vs log G'' plots for SIS3−COOH and SIS3−COONa. In Figure 6, it can be seen that the T_{ODT} of SIS3 is increased from 180 to ca. 182 °C after it was end-capped with a −COOH group and to ca. 228 °C after it was end-capped with a −COONa group. Using the Mayes−

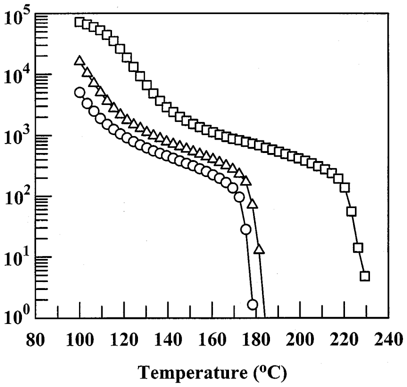

Figure 6. Dependence of G' on temperature during the isochronal dynamic temperature sweep experiment at $\omega = 0.1$ rad/s in the heating cycle for: (○) SIS3, (△) SIS3−COOH, and (□) SIS3−COONa. The specimens were annealed at 120 °C for 3 days in a vacuum oven.

Olvera de la Cruz theory[39] with $\chi(T) = -0.0419 + 38.5/T$, we have estimated the T_{ODT} of SIS3 to be 132 °C, which is far below the measured value, 180 °C. Nevertheless, the predicted T_{ODT} is far above the $T_{g,PS}$ (75 °C) of SIS3, ensuring that indeed SIS3 undergoes ODT. Above we already have mentioned that an estimation of T_{ODT} via currently held mean-field theory depends on the choice (or accuracy) of the expression for $\chi(T)$. We could have obtained a value of T_{ODT} that is closer to the measured value if we had used a different expression for $\chi(T)$, but such a predicted value does not necessarily mean that the mean-field theory employed here is accurate. Figure 7 gives TEM images of SIS3 and SIS3−COONa, showing that the lamellar microdomain structure of SIS3 remains the same after being end-capped with −COONa group. It is clear from Figure 7 that ionic association in SIS3−COONa has not altered the lamellar microdomain structure of the nonfunctionalized counterpart. What is significant in Figure 6 is that an increase in T_{ODT} is much greater for SIS3−COONa than for SIS3−COOH.

The following questions may be raised: (i) What might have contributed to the formation of lamellar microdomains in SIS2−COONa, observed in Figure 4, by end-capping of a homogeneous SIS triblock copolymer (SIS2) with −COONa group, while no microdomains are formed in SIS2−COOH? (ii) What might have contributed to the very large increase in T_{ODT}, observed in Figure 6, when a lamella-forming SIS triblock copolymer (SIS3) was end-capped with −COONa group but very *little* increase in T_{ODT} when the same block copolymer was end-capped with −COOH group? There are two factors that might have contributed to the two experimental observations referred to above: (i) hydrogen-bonding interactions in an SIS triblock copolymer end-capped with a −COOH group and (ii) ion−dipole interactions in an SIS triblock copolymer end-capped with a −COONa group. The −COOH groups present at both ends of an SIS−COOH would form complexes that have short-range interactions, whose activation energy being about 5 kcal/mol and the bond distance being about 0.32 nm.[19] However, the −COONa group present at both ends of an SIS−COONa would form clusters that have long-range interactions whose activation energy being about 20 kcal/mol and the aggregate diameter being about 10−50 nm.[19] That is, the hydrogen-bonding interactions are weaker and do not persist to elevated temperatures to the extent that the ion−dipole interactions. Further, in the molten state the small clusters are formed by ion−dipole interactions in SIS−COONa, whereas in the molten state the hydrogen bonds in SIS−COOH constantly break and re-form with thermal motion. Therefore, the ion−dipole interactions in SIS−COONa are much stronger than the hydrogen-bonding interactions in SIS−COOH. It is appropriate to mention at this juncture that at present we do not have theory that can explain the experimental results presented above. Note that currently held mean-field theory is not applicable to ionomers, in general, because of the specific interactions that dominate the phase behavior.

End-capping of an SIS triblock copolymer does *little* to change the molecular weight and composition of the block copolymer. Therefore, we are left to explore the extent of variations in the segment−segment interactions after an SIS triblock copolymer is end-capped with a −COOH group or a −COONa group. For this, in the present study we conducted cloud point measurements to investigate the phase behavior of binary blends consisting of a PI and a PS end-capped with a −COOH group and the phase behavior of binary blends consisting of a PI and a PS end-capped with a −COONa group.

Figure 8 gives binodal curves, which were obtained from cloud point measurements, for PI6/PS2 mixtures (○), PI6/(PS2−COOH) mixtures (△), and PI6/(PS2−COONa) mixtures (□). It is seen in Figure 8 that the critical temperature of PI6/PS2 has increased from 115 to 120 °C when PS2 was end-capped with a −COOH group, forming PS−COOH, and to 147 °C when PS2 was end-capped with a−COONa group, forming PS−COONa. The above observations suggest that the segment−segment interactions between the PI and PS−COONa phases in SIS3−COONa are much more repulsive than the segment−segment interactions between the PI and PS−COOH phases in SIS3−COOH and that the segment−segment interactions between the PI and PS−COOH phases in SIS3−COOH are only slightly more repulsive than the segment−segment interactions between the PI and PS phases in SIS3. Within the spirit of currently held mean-field theory,[37,38] we conclude from Figure 8 that (i) the formation of lamellar microdomains in SIS2−COONa (see Figure 4) was made possible by a sufficiently large increase in repulsive segment−segment interactions between the PI and PS−COONa phases in SIS2−COONa over the segment−segment interactions between the PI and PS phases in SIS2and (ii) the very large increase in T_{ODT} of SIS3−COONa (see Figure 6) is due to a large increase in repulsive segment−segment interactions between the PI and PS−COONa phases in SIS3−COONa, and the moderate increase in T_{ODT} of SIS3−COOH (see Figure 6) is due to a rather small increase in repulsive segment−segment interactions between the PI and PS−COOH phases in SIS3−COOH. We wish to mention that, in the absence of ionic interactions between the constituent components in a binary mixture, binodal curves may be used to determine the segment−segment interaction parameter using the Flory−Huggins theory. But, in the presence of ion−dipole interactions in the PI6/(PS2−COONa) mixtures and hydrogen-bonding interactions in the PI6/(PS2−COOH) mixtures, the Flory−Huggins theory is not adequate to determine the segment−segment interaction parameter for the binary mixtures. Further discussion of this subject is beyond the scope of this study.

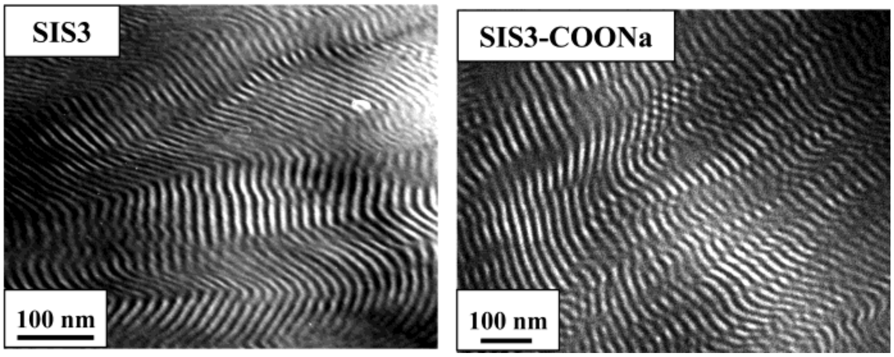

Figure 7. TEM images of (a) SIS3 and (b) SIS3−COONa, each taken at room temperature. The specimens were annealed at 110 °C for 1 week.

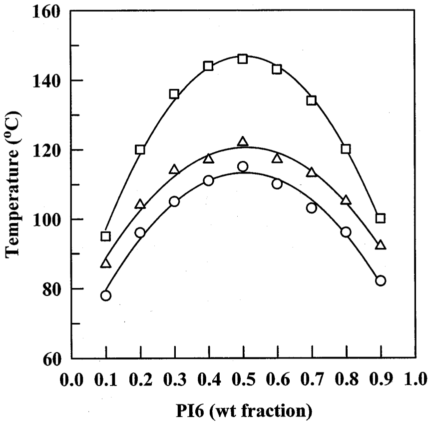

Figure 8. Binodal curves for: (○) PI6/PS2 blends, (△) PI6/(PS2−COOH) blends, and (□) PI6/ (PS2−COONa) blends.

We hasten to point out that in interpreting the phase transition in end-functionalized SIS triblock copolymers observed in this study we used the binodal curves given in Figure 8, which considered only the interactions between PI and PS−COOH in PI/(PS−COOH) binary mixtures and between PI and PS−COONa in PI/(PS−COONa) binary mixtures, and disregarded an unfavorable interaction between the carboxylic acid or salt group and styrene within PS−COOH or PS−COONa. Rigorously speaking, we should have used binary interaction theory and looked at all the binary interactions, and thus the binodal curves given in Figure 8 would not accurately explain phase transition in end-functionalized SIS triblock copolymers. Nevertheless, they offer some clues to the effect of end-functionalization of SIS triblock copolymers on their phase behavior.

Using the definition $\eta_0 = \lim_{\omega\to 0}[G''(\omega)/\omega]$, we have calculated zero-shear viscosities of end-capped block copolymers and the nonfunctionalized counterparts at temperatures that are at an equal distance from the $T_{g,PS}$ of the respective block copolymer, as summarized in Table 2. Such an approach is intended to minimize free-volume effect on η_0 since we wish to compare the viscosities of different polymers within the WLF region. It can be seen in Table 2 that the zero-shear viscosities of end-capped SIS−COONa are much higher than those of end-capped SIS−COOH, and the zero-shear viscosities of end-capped SIS−COOH are only moderately higher than those of the nonfunctionalized counterpart. Such a large increase in zero-shear viscosity of end-capped SIS−COONa is attributable to the very strong ionic association existing in an end-capped SIS−COONa, and a moderate increase in zero-shear viscosity of end-capped SIS−COOH is attributable to the rather weak hydrogen bonding existing in an end-capped SIS−COOH. Earlier, Fetters et al.[20] made similar experimental observation on end-capped PI−COOH and PI−COONa. Also given in Table 2 are values of the viscosity ratios $\eta_{0,\mathrm{COOH}}/\eta_{0,\mathrm{H}}$ and $\eta_{0,\mathrm{COONa}}/\eta_{0,\mathrm{H}}$ at various temperatures, with $\eta_{0,\mathrm{H}}$ being the zero-shear viscosity of the nonfunctionalized counterpart. In Table 2 we observe that (i) the ratio $\eta_{0,\mathrm{SISI-COONa}}/\eta_{0,\mathrm{SISI}}$ decreases from 23.4 to 16.5 and the ratio $\eta_{0,\mathrm{SISI-COOH}}/\eta_{0,\mathrm{SISI}}$ decreases from 6.1 to 3.5 as the temperature increases from $T_{g,PS} + 54$ to $T_{g,PS} + 94$ °C and (ii) the ratio $\eta_{0,\mathrm{SISI2-COONa}}/\eta_{0,\mathrm{SIS2}}$ decreases from 12.7 to 10.0 and the ratio $\eta_{0,\mathrm{SIS2-COONa}}/\eta_{0,\mathrm{SIS2}}$ decreases from 1.4 to 1.2 as the temperature increases from $T_{g,PS} + 34$ °C to $T_{g,PS} + 94$ °C.

4. Concluding Remarks

In this paper we have shown that (i) end-capping of the PS block of a homogeneous SIS triblock copolymer (SIS2) with a −COONa group induced microphase separation, while end-capping of the same block copolymer with a −COOH group did not induce microphase separation, and (ii) end-capping of the PS block of a lamella-forming SIS triblock copolymer (SIS3) with a −COONa group increased its T_{ODT} from 180 to 228 °C, while end-capping of the same block copolymer with a −COOH group increased its T_{ODT} from 180 to 182 °C, only 2 °C. Also, we have shown that in the disordered state (at $T > T_{ODT}$) the zero-shear viscosity of an SIS triblock copolymer (SIS1) end-capped with a −COONa group increased considerably relative to that of its nonfunctionalized counterpart, while the zero-shear viscosity of the same block copolymer end-capped with a −COOH group increased very moderately relative to that of its nonfunctionalized counterpart. This difference in zero-shear viscosity between SIS−COONa and SIS−COOH is attributable to the presence of very strong ion−dipole interactions in an SIS−COONa, which can lead to the formation of ionic clusters having the aggregate diameter of 10−50 nm, while the hydrogen-bonding interactions in an SIS−COOH are rather weak compared to the ion−dipole interactions in an SIS−COONa.

To the best of our knowledge, this is the first study reporting on (i) microphase separation induced by end-capping of a homogeneous block copolymer and (ii) the effect of ionic groups (−COOH groups vs −COONa group) on the T_{ODT} of end-capped SIS triblock copolymers.

It is appropriate to mention at this juncture that earlier Mani et al.[28] reported on experimental observations of the T_{ODT} of lightly sulfonated diblock and triblock copolymer ionomers composed of PS and poly-

Table 2. Temperature Dependence of Zero-Shear Viscosity and Viscosity Ratio for Neat and End-Functionalized SIS Triblock Copolymers Synthesized in This Study

$T - T_{g,PS}$ (°C)	$\eta_{0,SIS}$ (Pa s)	$\eta_{0,SIS-COOH}$ (Pa s)	$\eta_{0,SIS-COONa}$ (Pa s)	$\eta_{0,SIS-COOH}/\eta_{0,H}$	$\eta_{0,SIS-COONa}/\eta_{0,H}$
(a) For SIS1					
54	51	309	1195	6.1	23.4
64	23	112	452	4.8	19.7
74	12	48	206	4.0	17.2
84	6.4	24	106	3.6	16.3
94	3.7	13	61	3.5	16.5
(b) For SIS2					
34	6590	8950	83600	1.4	12.7
44	1390	1800	14210	1.3	10.2
54	380	466	4000	1.2	10.5
64	130	150	1330	1.2	10.2
74	41	48	390	1.2	9.5
84	21	25	207	1.2	9.9
94	11	13	110	1.2	10.0

(ethylene-*alt*-propylene) (PEP) blocks with varying degrees of sulfonation. Their results (Figures 9 and 10 in ref 28) show that the T_{ODT} of sulfonated block copolymer ionomer with free acid derivative was slightly higher than that with sodium salt. This observation stands in contrast with our results in that the T_{ODT} of SIS3 end-capped with −COONa group is much higher (ca. 48 °C) than that of SIS3 end-capped with −COOH (see Figure 6). On the basis of small-angle X-ray scattering data, Mani et al. attributed the observed difference in T_{ODT} to the differences in the microdomain structure between the two sulfonated block copolymer ionomers. Namely, the microstructure of the sulfonated block copolymer ionomer with the free acid derivative was better developed than that with the sodium salt. The lightly sulfonated block copolymer ionomers employed by Mani et al. had physical cross-links provided by ionic association of the sulfonic acid or sodium sulfonate groups, while our block copolymer, SIS3, had the same lamellar microdomain structure before and after being end-capped with −COONa group (see Figure 7), and there were no cross-links in our end-capped SIS triblock copolymer. Therefore, we tentatively conclude that the physical factor(s) which influenced ODT in our end-capped SIS triblock copolymer would be quite different from that which influenced ODT in the sulfonated block copolymer ionomers employed by Mani et al.

In an effort to determine a physical origin that might explain the reason for the very large increase in T_{ODT} observed for SIS3−COONa, we conducted cloud point measurements for binary mixtures of PI and PS, binary mixtures of PI and PS end-capped with −COONa group (PS−COONa), and PI and PS end-capped with −COOH group (PS−COOH). We found from the binodal curves obtained from cloud point measurements that segment−segment interactions between the constituent components become progressively more repulsive in the following order: PI/PS mixtures < PI/(PS−COOH) mixtures ≪ PI/(PS−COONa) mixtures. Thus, we conclude that the very large increase in T_{ODT} observed for SIS3−COONa is attributable, at least in part, to a large increase in repulsive segment−segment interactions between the PI and PS−COONa phases. Earlier, Lu et al.[26] speculated that ionization of one component of a block copolymer may increase the repulsive interactions between the ionic block and nonionic block, increasing T_{ODT}. This is precisely what we have found from this study (see Figure 6), although only the PS end blocks in SIS3 were end-capped with a −COONa group.

It is clear from the literature that ion-containing homopolymers or block copolymers form ionic aggregates. According to Weiss et al.,[23] the characteristic size of the microphase-separated domains is of the order of 10 nm in block copolymers and 1 nm in ionomers. Thus, ionic aggregates are dispersed within the micodomains of the block copolymer, and the ODT in block copolymer ionomers must be preceded by disordering of the ionic microphase. However, we are not certain to what extent such experimental observations may be applicable to our triblock copolymer, SIS3−COONa, because only both ends of each triblock copolymer chain have sodium ions. The number of sodium ions in SIS3−COONa is far fewer than the number of sodium ions, for instance, in end-block-sulfonated triblock copolymer ionomers[23−26] in which many sodium ions are distributed randomly along the entire end-block chain. It seems reasonable to expect that the strength of aggregates in SIS3−COONa would be much weaker than that in end-block-sulfonated triblock copolymer ionomers in which strong ionic interchain interactions exist, since much fewer sodium ions are attached to the chain ends of SIS3−COONa.

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