Composition fluctuations in binary mixtures of homogeneous polystyrene-*block*-polyisoprene copolymer and polyisoprene

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Abstract

The phase behavior and morphology of binary mixtures of a homogeneous polystyrene-*block*-polyisoprene (SI diblock) copolymer and a polyisoprene (hPI) were investigated using small-angle X-ray scattering (SAXS), light scattering, transmission electron microscopy (TEM), and oscillatory shear rheometry with an aim to elucidate homopolymer-induced microphase separation of a homogeneous block copolymer. For the study, the following polymers were synthesized using anionic polymerization: (i) a symmetric SI diblock copolymer (SI-5/5) having a number-average molecular weight (M_n) of 1.0×10^4, and (ii) two hPIs having $M_n = 1.14 \times 10^4$ (PI-11) and 1.41×10^4 (PI-14). The results of TEM, SAXS and oscillatory shear rheometry showed that SI-5/5 formed a homogeneous single-phase melt, free from any microphase-separated structure in the temperature range of 40–180°C. Binodal curves were constructed, via cloud point measurement, for both (SI-5/5)/(PI-11) and (SI-5/5)/(PI-14) mixtures, and the morphology of the mixtures with and without macrophase separation of hPI was investigated using TEM and SAXS. The TEM study shows the presence of bicontinuous structure in both mixtures, while the SAXS and rheology studies indicate that the mixtures formed a homogeneous single-phase melt. The above observations lead us to conclude that the bicontinuous structure, as determined from TEM, in the (SI-5/5)/(PI-11) and (SI-5/5)/(PI-14) mixtures represents *frozen* composition fluctuations in the disordered phase near order-disorder transition and not the homopolymer-induced ordered structure. An explanation is offered as to why in this study homopolymer-induced microphase separation was not observed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Block copolymers; Composition fluctuations; Small-angle X-ray scattering

1. Introduction

During the past two decades, many research groups have investigated experimentally microdomain structures [1–13], phase transitions [14–19], and phase equilibria [8,20–23] in binary mixtures of microphase-separated block copolymer and homopolymer. What is of great interest is the prospect of inducing microphase separation of a *homogeneous* block copolymer by addition of a homopolymer. Such a prospect was first predicted by Hong and Noolandi [24]. However, in order to experimentally demonstrate homopolymer-induced microphase separation of a homogeneous block copolymer, the system must reach a thermodynamic equilibrium. This can be realized only when the temperature at which homopolymer-induced microphase separation takes place is higher than the glass transition temperatures (T_g) of both the homopolymer added and the block copolymer.

More than a decade ago, Cohen and Torradas [25] reported an experimental observation, based on transmission electron microscopy (TEM) and dynamic mechanical analysis, of homopolymer-induced microphase separation of a *homogeneous* 1,2-polybutadiene-*block*-1,4-polybutadiene (1,2-PB-*block*-1,4-PB) copolymer having the weight-average molecular weight (M_w) of 3.0×10^4 for 1,2-PB block and 1.0×10^5 for 1,4-PB block. Specifically, they reported that microphase separation was induced when a homopolymer 1,2-polybutadiene (1,2-PB) with $M_w = 3.0 \times 10^4$ was added, but not when a homopolymer 1,4-polybutadiene (1,4-PB) with $M_w = 1.0 \times 10^5$ was added, to the 1,2-PB-*block*-1,4-PB copolymer. They reported further that addition of homopolymer 1,2-PB having $M_w = 9.0 \times 10^4$ induced macrophase separation without ever inducing microphase separation. Note that the block copolymer as well as the homopolymers used by them had very low values of T_g, namely, homopolymer 1,4-PB with $M_w = 1.0 \times 10^5$ had $T_g = -79.1$°C and homopolymer 1,2-PB with $M_w = 3.0 \times 10^4$ had $T_g = 9.1$°C. Thus the binary mixtures investigated by Cohen and Torradas could have

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reached a thermodynamic equilibrium state even at room temperature.

We are not aware of any study reporting on homopolymer-induced microphase separation of a homogeneous polystyrene-*block*-polyisoprene (SI diblock) copolymer. When the order–disorder transition temperature (T_{ODT}) of an SI diblock copolymer lies below the glass transition temperature of PS block ($T_{g,PS}$), an experimental observation of microphase separation via TEM and/or small-angle X-ray scattering (SAXS) would be very difficult, if not impossible, owing to the extremely slow kinetics of the ordering process. Thus, here we regard a styrene-based diblock copolymer as being *homogeneous* when the T_{ODT} of the block copolymer lies below $T_{g,PS}$. Therefore, in order to induce microphase separation of a homogeneous SI diblock copolymer, the addition of a polystyrene (hPS) or a polyisoprene (hPI) must raise the T_{ODT} of the block copolymer above $T_{g,PS}$ without first inducing macrophase separation. It should be remembered that the T_g of hPS is much higher than the T_g of hPI. Under such circumstances, the addition of hPS to induce microphase separation of a homogeneous SI diblock copolymer would encounter a practical difficulty, since it might increase the $T_{g,PS}$ of the SI/hPS mixture. In this regard, the addition of hPI, which has a very low T_g (ca $-60°C$), would be effective.

In this study we investigated the possibility of inducing microphase separation in a homogeneous symmetric SI diblock copolymer, having a number-average molecular weight (M_n) of 1.0×10^4, by addition of an hPI. We found that the neat SI diblock copolymer formed a homogeneous single-phase melt, as determined from TEM at room temperature, SAXS at temperatures ranging from 40 to 180°C, and oscillatory shear rheometry at temperatures ranging from 50 to 75°C. We then constructed temperature–composition phase diagrams for SI/hPI mixtures using cloud point measurement and investigated the morphology of the mixtures using TEM and SAXS. In addition, using oscillatory shear rheometry we investigated whether or not the addition of an hPI to neat SI diblock copolymer might have induced microphase separation. In this paper we report the highlights of our findings.

2. Experimental

2.1. Materials and sample preparation

An SI block copolymer (SI-5/5) was synthesized via anionic polymerization with cyclohexane as a solvent. SI-5/5 was found to have a 0.5 weight fraction of polystyrene (PS) block as determined by ^{1}H nuclear magnetic resonance (NMR) spectroscopy, a number-average molecular weight (M_n) of 1.0×10^4 as determined by membrane osmometry and a polydispersity index (M_w/M_n) of 1.05, where M_w is the weight-average molecular weight, as determined by gel permeation chromatography (GPC). The PI block in SI-5/5 was found, via NMR spectroscopy, ca 6 wt% 3,4-addition, ca 94 wt% 1,4-addition, and no detectable amount of 1,2-addition. Two hPIs were also synthesized via anionic polymerization with cyclohexane as a solvent: PI-11 with $M_n = 1.14 \times 10^4$ and $M_w/M_n = 1.04$, and PI-14 with $M_n = 1.41 \times 10^4$ and $M_w/M_n = 1.02$. Varying amounts of each grade of hPI were added to SI-5/5 to prepare binary mixtures.

Samples for TEM, cloud point measurements, and rheological measurements were prepared by first dissolving a predetermined amount of SI-5/5 with and without an hPI into toluene (10% of solid in solution) in the presence of 0.1 wt% antioxidant (Irganox 1010, Ciba-Geigy Group) and then slowly evaporating the toluene. The evaporation of toluene was carried out initially in a fume hood at room temperature for a week and then in a vacuum oven at 40°C for three days. The last trace of solvent was removed by drying the samples in a vacuum oven by gradually raising the oven temperature up to 50°C and annealing there for 15 days. The drying of the samples was continued until there was no further change in weight.

2.2. Rheological measurement

A Rheometrics mechanical spectrometer (Model RMS 800) was used in the oscillatory mode with parallel-plate fixtures (25 mm diameter) to measure the dynamic storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, as functions of angular frequency (ω) at various temperatures. Data acquisition was accomplished with the aid of a microcomputer interfaced with the rheometer. Temperature control was satisfactory to within $\pm 1°C$. In the rheological measurements, a fixed strain in the range from 0.04 to 0.15 was used at a given temperature. The strains used were well within the linear viscoelastic range for the materials investigated at that particular temperature. All experiments were conducted under a nitrogen atmosphere in order to preclude oxidative degradation of the samples. The purpose of the dynamic frequency sweep experiments performed was to determine the T_{ODT}, if any, of SI-5/5 and its mixtures with hPI.

2.3. Transmission electron microscopy

The microdomain structure of SI-5/5, if any, and its mixtures with hPI were examined using TEM. Ultrathin specimens were prepared by cryoultramicrotomy at $-100°C$, below the T_g ($-68°C$) of hPI, to attain the rigidity of the specimen, using a Reichert Ultracut S low-temperature sectioning system. A transmission electron microscope (JEM 1200EX II, JEOL) operated at 120 kV was used for taking images of the specimens stained with osmium tetroxide (OsO_4) vapor in an enclosed flask for 2–4 h at room temperature. Before staining with OsO_4, specimens were annealed at 50°C for 15 days followed by quenching to room temperature and kept in a desiccator at room temperature. The structure existing in the specimens at room temperature just before staining was fixed by this staining method which involves crosslinking and hardening of the

polyisoprene domains [26–28]. After staining with OsO_4, the specimens were kept in a desiccator at room temperature.

2.4. Cloud point determination

In order to determine the cloud point of an SI/hPI mixture we used an apparatus which measured scattered light intensity $I(q)$ at various scattering angles. The apparatus consisted of a He–Ne laser light source with a wavelength of 632.8 nm and a heating stage. The laser beam was collimated through a heating chamber with a 2 mm aperture. The temperature of the hot stage was controlled using a programmable temperature controller (Model CN-2012, Omega). The scattered light intensities at various scattering angles were detected by a one-dimensional silicon diode Reticon detector (Model 1453, Princeton Applied Research) connected to the optical multichannel analyzer (Model 1460, OMA III, EG&G Princeton Applied Research). In order to preclude oxidative degradation, a glass coverslip was placed over the film. During the cloud point measurements, initially the sample was heated well above the cloud point which was roughly determined through a preliminary heating run. The heated sample was allowed to cool at a rate of 0.5°C/min and the scattered light intensities at different values of scattering vector q were recorded at different temperatures. The cloud points determined during the two successive experiments using the same sample had a maximum difference of about ±1.5°C in all cases. In this study, a cloud point was determined by the temperature at which the light intensity $I(q)$ first shows a significant increase during cooling.

2.5. SAXS experiment

SAXS experiments were conducted under a nitrogen atmosphere in the heating and cooling cycles, using an apparatus described in detail elsewhere [29,30], which consists of a newly replaced 18 kW rotating-anode X-ray generator operated at 45 kV × 400 mA (MAC Science), a graphite crystal for incident-beam monochromatization, a 1.5 m camera, and a one-dimensional position-sensitive proportional counter. The CuK_α line ($\lambda = 0.154$ nm) was used. The SAXS profiles were measured as a function of temperature and were corrected for absorption, air scattering and background scattering arising from thermal diffuse scattering, and slit-height and slit-width smearing [31]. The absolute SAXS intensity was obtained using the nickel-foil method [32]. The thermal histories under which the in-situ SAXS experiments were conducted are summarized in Fig. 1. Before SAXS measurement began at each predetermined temperature, 1 h was allowed for temperature equilibration. SAXS measurement lasted for 1 h at each temperature under-nitrogen atmosphere to preclude oxidative degradation.

3. Results and discussion

3.1. Morphology of neat block copolymer SI-5/5

Fig. 2a and b gives, respectively, plots of log G' versus log ω and of log G'' versus log ω for SI-5/5 at 50, 55, 60, 65, 70 and 75°C. It is well established that in the terminal region of homogeneous monodisperse polymers the slope of log G' versus log ω plots is expected to be 2 and the slope of log G'' versus log ω plots is expected to be 1 at all temperatures. Fig. 2 certainly shows such a behavior except for the data at 50°C, which is believed due to the fact that the experimental temperature was very close to the glass transition temperature of the PS phase ($T_{g,PS}$) of SI-5/5. We found from differential scanning calorimetry that the $T_{g,PS}$ of SI-5/5 is 48°C. One of the most effective rheological methods of determining whether a polymer in the molten state is homogeneous or not is to prepare log G' versus log G'' plots which, following Neumann et al. [33],[1] will be referred to as Han plots. Fig. 3 gives Han plots for SI-5/5, showing temperature independence over the entire range of temperatures tested. According to the rheological criterion established by Han et al. [37–39], we can conclude from Fig. 3 that SI-5/5 formed a homogeneous single-phase melt free from microphase-separated structures, because the Han plots having a slope of 2 in the terminal region are independent of temperature over the entire range of temperatures (50–75°C) tested. It should be pointed out that the slope of 2 in the terminal region of the Han plot is *not* necessary [38,41] for a polymer to be regarded as being homogeneous, because polydisperse homopolymers would have a slope of less than 2 in the terminal region of the Han plot unless the experimental angular frequencies are much lower than 0.01 rad/s.

Fig. 4 gives the desmeared SAXS profiles for SI-5/5 at temperatures from 40 to 180°C in the cooling cycle (see Fig. 1 for thermal history), where q is the magnitude of scattering vector defined by $q = (4\pi/\lambda) \sin(\theta/2)$ with λ and θ being the wavelength of X-ray and scattering angle, respectively. In Fig. 4 we observe both the gradual broadening and the decay of the intensity of the first-order peak with increasing temperature, suggesting that SI-5/5 formed a homogeneous single-phase melt over the entire range of temperatures (40–180°C) investigated.

Fig. 5 gives plots of (a) the reciprocal of the first-order peak intensity ($1/I_m$) versus the reciprocal of the absolute

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[1] These authors referred to log G' versus log G'' plots as Han plots. It is Han and Lem [34] who in 1982 first reported that log G' versus log G'' plots show temperature independence for homopolymers. The Han plot has as its basis a molecular viscoelasticity theory for monodisperse homopolymers [35] and also for polydisperse homopolymers [36]. Since then, the Han plot has very successfully been used to determine the order–disorder transition temperature of microphase-separated block copolymer [37–39]. It should be pointed out that the Han plot has *no* relation whatsoever to the Cole–Cole plot [40], which gives a temperature-dependent semi-circle in rectangular coordinates.
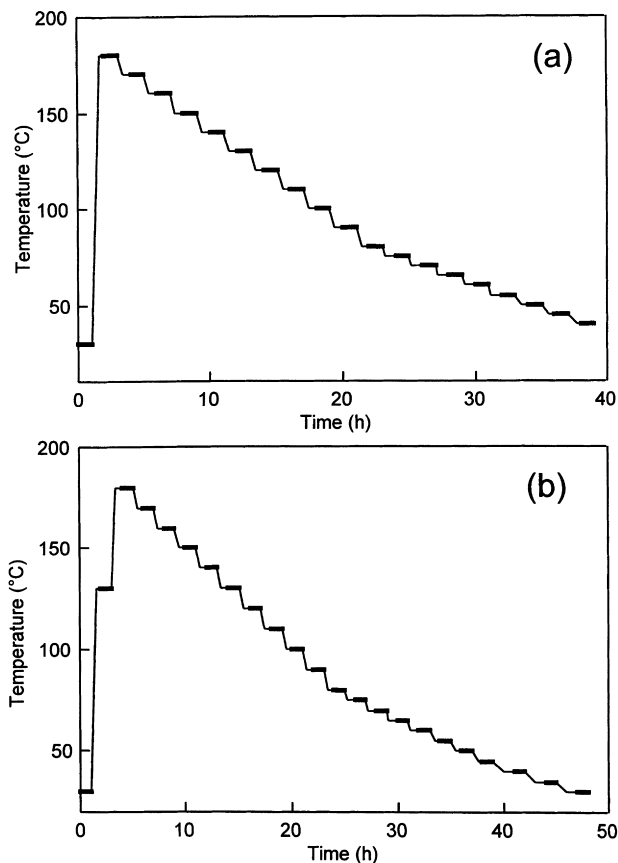
Fig. 1. Thermal histories of (a) SI-5/5 and (b) 75/25 (SI-5/5)/(PI-11) specimens employed for SAXS experiments.

Fig. 2. Plots of (a) log G' versus log ω and (b) log G'' versus log ω for SI-5/5 at various temperatures: (○) 50°C; (△) 55°C (□) 60°C; (▽) 65°C; (◇) 70°C; (○) 75°C.

temperature ($1/T$) and (b) the square of the half-width at half-maximum (σ_q^2) versus $1/T$, and (c) the Bragg spacing (D) versus $1/T$ for SI-5/5 at temperatures ranging from 40 to 180°C in the cooling cycle. In Fig. 5 we observe that I_m^{-1} and σ_q^2 decrease linearly with increasing $1/T$ (i.e. with decreasing temperature), until reaching a certain critical temperature and then they show a curvature with further increasing $1/T$. Note in Fig. 5c that D increases very mildly with increasing $1/T$ (i.e. with decreasing temperature), until reaching a critical temperature. Interestingly, in Fig. 5 we observe a crossover from the disordered state characterized by the Brazovskii-type non-mean-field theory [42] to the disordered state characterized by the Leibler mean-field theory [43] at a value of $1/T$ of approximately $2.48 \times 10^{-3} \, K^{-1}$ (ca 131°C), at which a change in the slopes of I_m^{-1} and σ_q^2, and D versus $1/T$ plots occurs. Such an observation was reported earlier by Hashimoto and Sakamoto [44,45]. In Fig. 5 we observe further that the decreasing trend of I_m^{-1} and σ_q^2 with increasing $1/T$ levels off at approximately $3.18 \times 10^{-3} \, K^{-1}$ (ca 41.3°C as marked by the vertical dotted line). Our experience indicates that this phenomenon would occur in the vicinity of the $T_{g,PS}$ of SI diblock copolymer.

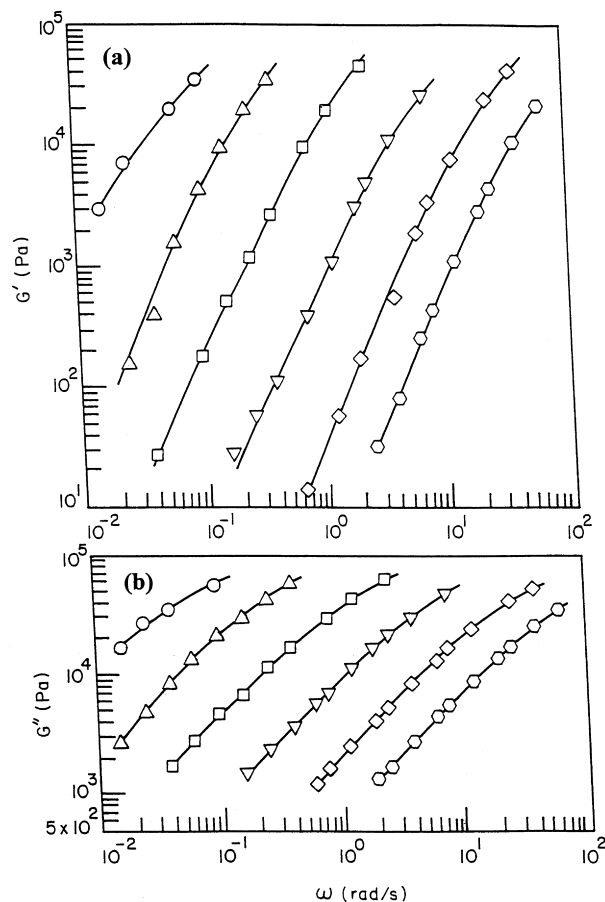Previously, the T_{ODT}s of neat block copolymers [44–49] and binary mixtures of block copolymer and homopolymer

[50] were determined from a sharp discontinuity in the plots of I_m^{-1} and σ_q^2 versus $1/T$. Since in Fig. 5 we cannot observe a sharp discontinuity in the plots of I_m^{-1} and σ_q^2 versus $1/T$ we conclude that SI-5/5 formed a homogeneous single-phase melt over the entire range of temperatures (40–180°C) investigated. This conclusion is consistent with that drawn above from the Han plot given in Fig. 3.

3.2. Phase behavior and morphology of (SI-5/5)/hPI mixtures

Fig. 6 gives the experimental phase diagrams for (a) (SI-5/5)/(PI-11) mixtures and (b) (SI-5/5)/(PI-14) mixtures, which were obtained from cloud point experiments. Fig. 7 gives the TEM images of (a) 64/36 (SI-5/5)/(PI-11) mixture and (b) 85/15 (SI-5/5)/(PI-14) mixture taken at room temperature. Note that the micrographs given in Fig. 7 were taken of (SI-5/5)/hPI mixtures that lie *outside* the binodal curve (Fig. 6). The readers are reminded again that the specimens of the 64/36 (SI-5/5)/(PI-11) and 85/15 (SI-5/5)/(PI-14) mixtures used for taking TEM were annealed at 50°C for 15 days followed by quenching to room temperature, which is below $T_{g,PS}$. We consider that the micrographs
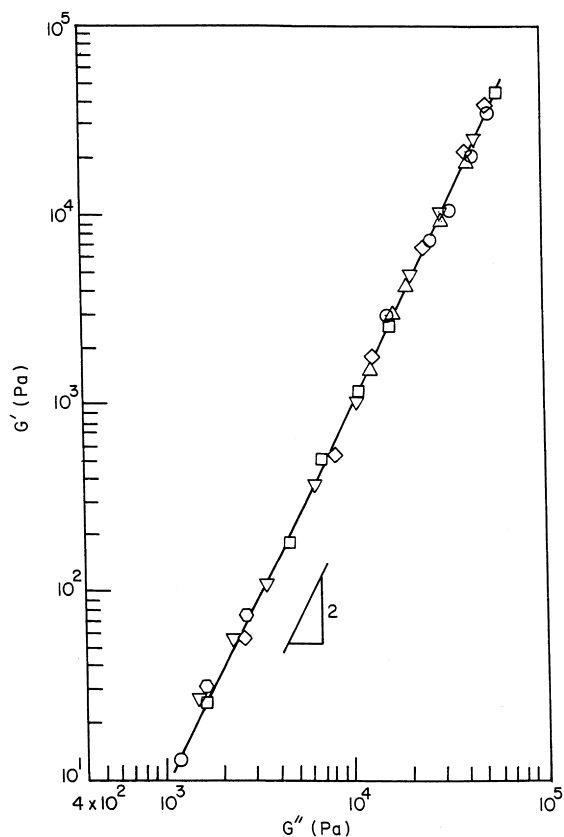
Fig. 3. Han plot for SI-5/5 at various temperatures: (○) 50°C; (△) 55°C; (□) 60°C; (▽) 65°C; (◇) 70°C; (○) 75°C.
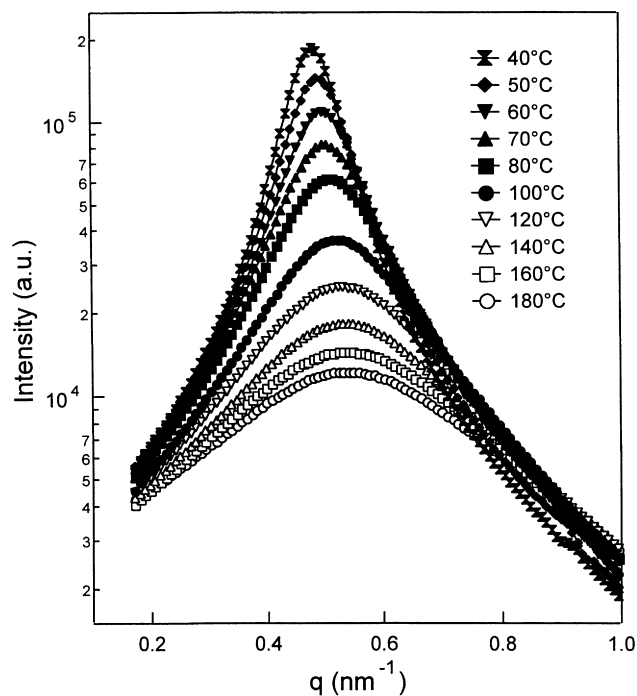

Fig. 4. Temperature dependence of SAXS profiles for SI-5/5 at various temperatures shown in the plot during the cooling cycle. The thermal history of the specimen is given in Fig. 1.
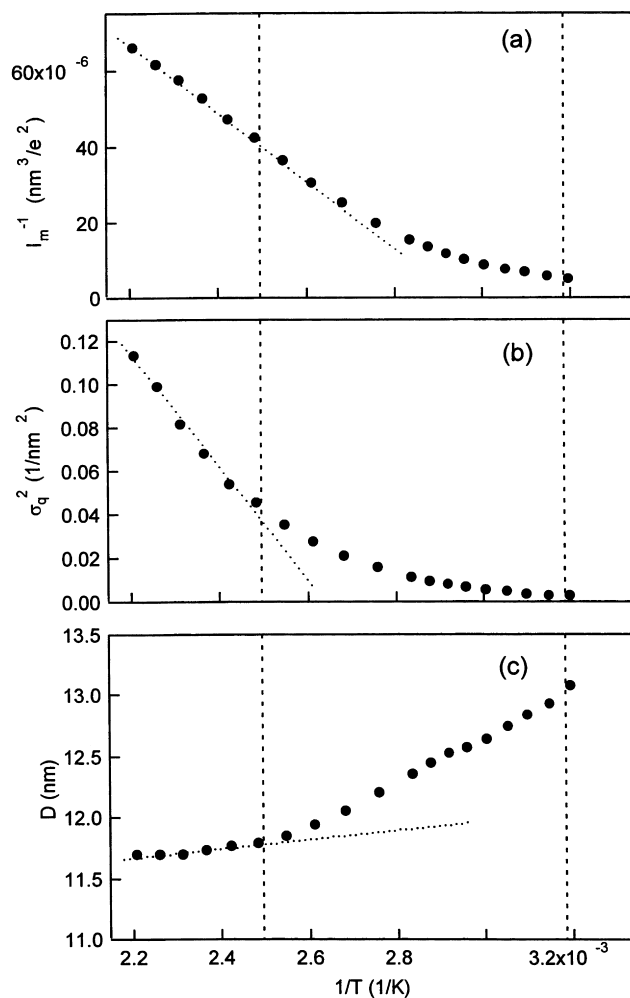

Fig. 5. Plots of (a) $1/I_m$ versus $1/T$; (b) σ_q^2 versus $1/T$; and (c) D versus $1/T$ for SI-5/5. The thermal history of the specimen is given in Fig. 1.

reflect the microstructures that existed at 50°C, which were vitrified as a consequence of the quenching process. One might be tempted to conclude from Fig. 7 that the addition of hPI to the homogeneous block copolymer SI-5/5 induced microphase separation. Note, however, that the micrographs in Fig. 7 do not have well-ordered structure having long-range order. Considering that the volume fraction of PS (f_{PS}) of the 64/36 (SI-5/5)/(PI-11) mixture is 0.27 and $f_{PS} = 0.36$ for the 85/15 (SI-5/5)/(PI-14) mixture, we would expect to observe hexagonally packed cylinders in both mixtures *if* indeed microphase separation were induced by the addition of PI-11 or PI-14 to SI-5/5. Very recently, Sakamoto and Hashimoto [51] presented micrographs, which look very similar to those given in Fig. 7, of an SI diblock copolymer that was frozen from the disordered state, in which they referred to the morphology as 'bicontinuous structure (fluc-tuation-induced disordered (D_F) structure)'. We conclude that the bicontinuous structure in Fig. 7 also reflects the vitrified D_F structure.

Fig. 8 gives the TEM images of the 64/36 (SI-5/5)/(PI-14) specimens which were annealed at 50°C for 15 days
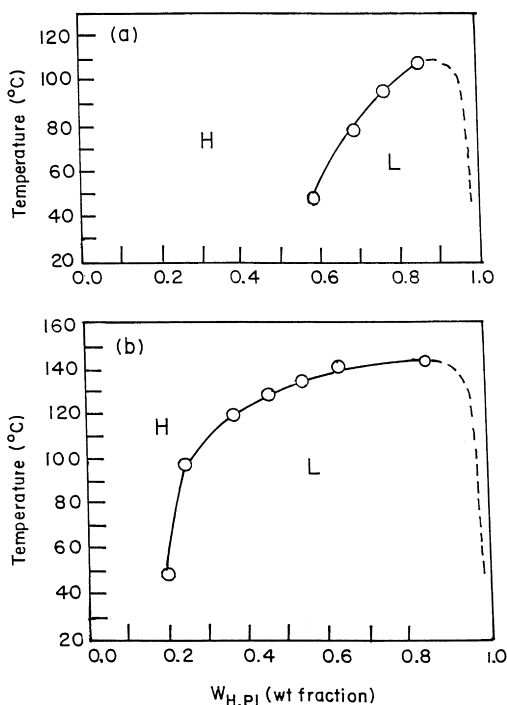
Fig. 6. (a) Temperature–composition phase diagram for (SI-5/5)/(PI-11) mixtures and (b) temperature–composition phase diagram for (SI-5/5)/(PI-14) mixtures, where H denotes a single-phase melt and L denotes two-phase mixtures. The binodal curve was determined from cloud point measurements.

followed by quenching to room temperature. Again, the micrograph reflects the vitrified structures which existed at 50°C. Note that this mixture lies *inside* the binodal curve (Fig. 6b). At a low magnification (Fig. 8a) the mixture shows macrophase-separated PI-14 phase (the dark areas) and the block copolymer SI-5/5 (the bright areas). However, at a large magnification (Fig. 8b) the mixture in the bright areas shows bicontinuous structure, in which the dark areas represent the PI-block-rich areas stained with OsO₄ and the bright areas represent the PS-block-rich areas of SI-5/5. It is clear from Fig. 8 that *inside* the binodal curve (Fig. 6) the

macrophase-separated PI-14 rich phase and the phase having the bicontinuous structure coexist. It is of interest to note that the bicontinuous structure of the 64/36 (SI-5/5)/ (PI-11) and 85/15 (SI-5/5)/(PI-14) mixtures (Fig. 7) *outside* the binodal curve (Fig. 6) looks similar to the bicontinuous structure of the 64/36 (SI-5/5)/(PI-14) mixture (Fig. 8b) *inside* the binodal curve (Fig. 6). That is, the bicontinuous structure observed in both Figs. 7 and 8b does not seem to vary with blend composition, at least under qualitative observations.

Fig. 9 gives the desmeared SAXS profiles for the 75/25 (SI-5/5)/(PI-11) mixture at temperatures from 40 to 180°C in the cooling cycle (see Fig. 1 for thermal history). In Fig. 9 we observe both the gradual broadening and the decay of the intensity of the first-order peak with increasing temperature, suggesting that the 75/25 (SI-5/5)/(PI-11) mixture formed a homogeneous single-phase melt over the entire range of temperatures investigated. Note, with reference to Fig. 6a, that the mixture lies *outside* the binodal curve. Fig. 10 gives plots of (a) $1/I_m$ versus $1/T$ and (b) σ_q^2 versus $1/T$, and (c) D versus $1/T$ for the 75/25 (SI-5/5)/(PI-11) mixture at temperatures ranging from 40 to 180°C in the cooling cycle. In Fig. 10a and b we observe that I_m^{-1} and σ_q^2 decrease with increasing $1/T$ (i.e. with decreasing temperature), behavior little different from that of SI-5/5 (Fig. 5a and b). Since there is no sharp discontinuity in the plots of I_m^{-1} and σ_q^2 versus $1/T$, we conclude from Fig. 10a and b that the 75/25 (SI-5/5)/ (PI-11) mixture formed a homogeneous single-phase melt over the entire range of temperatures investigated. Note that values of I_m^{-1} and σ_q^2 with increasing $1/T$ level off at approximately 3.18×10^{-3} K^{-1} (ca 41.3°C as marked by the vertical dotted line). This temperature is nearly identical to that found in Fig. 5 for SI-5/5 and is expected to reflect the vitrification of PS-rich regions induced by the thermal fluctuations. It is interesting to note that the vitrification temperature ($T_{g,PS}$) really depends on local composition of PS in the PS-rich regions rather than the average composition of PS in the neat block copolymer and its mixture with hPI.
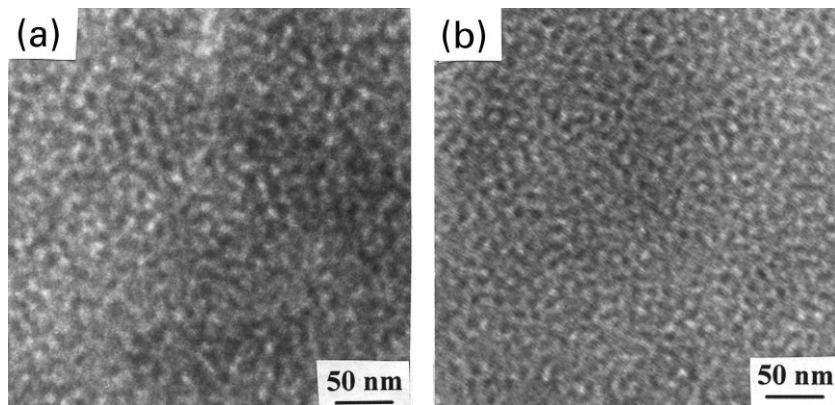

Fig. 7. TEM images of (a) the 64/36 (SI-5/5)/(PI-11) mixture and (b) the 85/15 (SI-5/5)/(PI-14)mixture, where the dark areas represent the PI phase and the bright areas represent the PS phase of the neat block copolymer SI-5/5. Note that both mixtures lie *outside* the binodal curve (see Fig. 6) and the specimens for TEM were annealed at 50°C for 15 days.
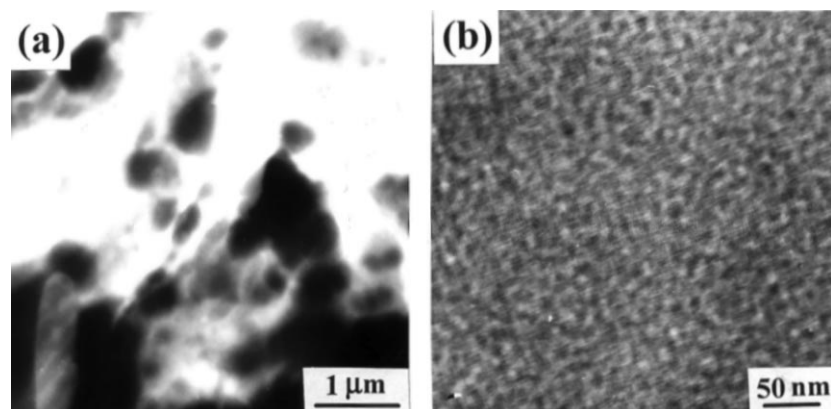
Fig. 8. TEM images of the 64/36 (SI-5/5)/(PI-14) mixture. (a) At a low magnification where the dark areas describe macrophase-separated PI-rich phase and the bright areas describe the block copolymer (SI-5/5)-rich phase. (b) At a high magnification where the dark areas describe the PI-rich phase and the bright areas describe the PS-rich phase within the macrophase rich in the neat block copolymer SI-5/5. Note that this mixture lies *inside* the binodal curve (see Fig. 6b) and the specimen for TEM was annealed at 50°C for 15 days followed by rapid quenching to room temperature. Thus the TEM images reflect vitrified structures which existed at 50°C.

However, as can be seen in Fig. 10c, the temperature dependence of D for the 75/25 (SI-5/5)/(PI-11) mixture is quite different from that for SI-5/5 (Fig. 5c). Specifically, the value of D for the 75/25 (SI-5/5)/(PI-11) mixture decreases steadily with increasing $1/T$ (i.e. with decreasing temperature) and then levels off as the temperature approaches the $T_{g,PS}$ of SI-5/5. A rapid increase in D observed for the 75/25 (SI-5/5)/(PI-11) mixture with decreasing $1/T$ from 2.8×10^{-3} to 2.3×10^{-3} K^{-1} (i.e. with increasing temperature from ca 84 to 165°C) is a behavior typical of this mixture, i.e. a behavior expected

for blends with PI-11. It should be mentioned that Sakamoto et al. [52] made a similar observation when investigating binary mixtures of a polystyrene-*block*-poly-isoprene-*block*-polystyrene (SIS triblock) copolymer and dioctylphthalate (DOP). Following the explanation offered by Sakamoto et al., [52] we speculate that an increase of D with decreasing $1/T$ from 2.8×10^{-3} to 2.3×10^{-3} K^{-1} is due to the predominant contribution of osmotic compressibility between block chains and hPI. At such a high temperature (165°C), the concentration fluctuations between PS and PI blocks of SI-5/5 are negligible compared to the concentration fluctuations between SI-5/5 and homopolymer PI-11. However, unlike the situation of SIS/DOP mixtures, investigated by Sakamoto et al. [52], where the temperature at which D started to increase was regarded as being its T_{ODT}, we do not believe that the temperature at which D starts to increase in the 75/25 (SI-5/5)/(PI-11) mixture (Fig. 10c) signifies an onset of order–disorder transition (ODT) for the following reasons. For the SIS/DOP mixtures investigated by Sakamoto et al. [52], they observed that the temperature at which D started to increase coincided with the temperature at which the Han plot started to become independent of temperature during the heating cycle. However, as can be seen in Fig. 11, for the 75/25 (SI-5/5)/(PI-11) mixture the Han plots having a slope of approximately 2 in the terminal region are independent of temperature over the entire range of temperatures (52–80°C) investigated; that is, there is *no* evidence of microphase separation taking place in the 75/25 (SI-5/5)/(PI-11) mixture. Note that the lowest experimental temperature, 52°C, employed in the rheology measurements (Fig. 11) is well below 66°C, the temperature at which D starts to increase in the SAXS measurements (Fig. 10c). This observation indicates to us that the 75/25 (SI-5/5)/(PI-11) mixture was already in the disordered state before D started to increase.
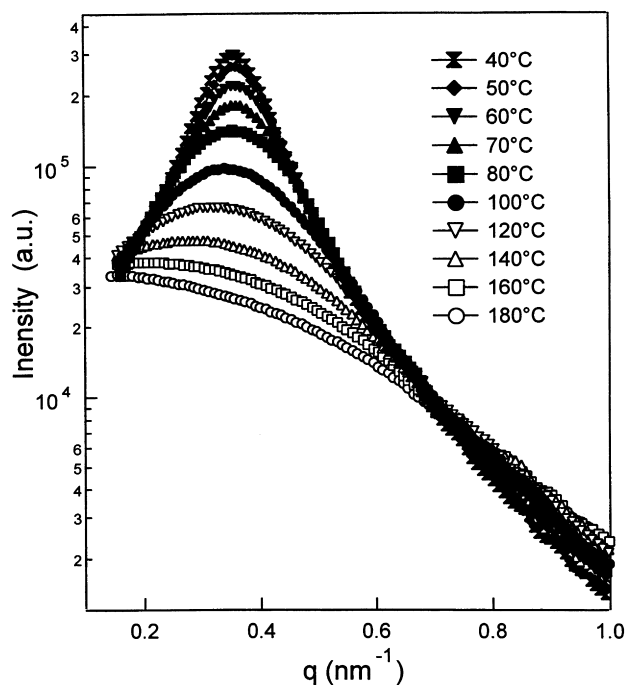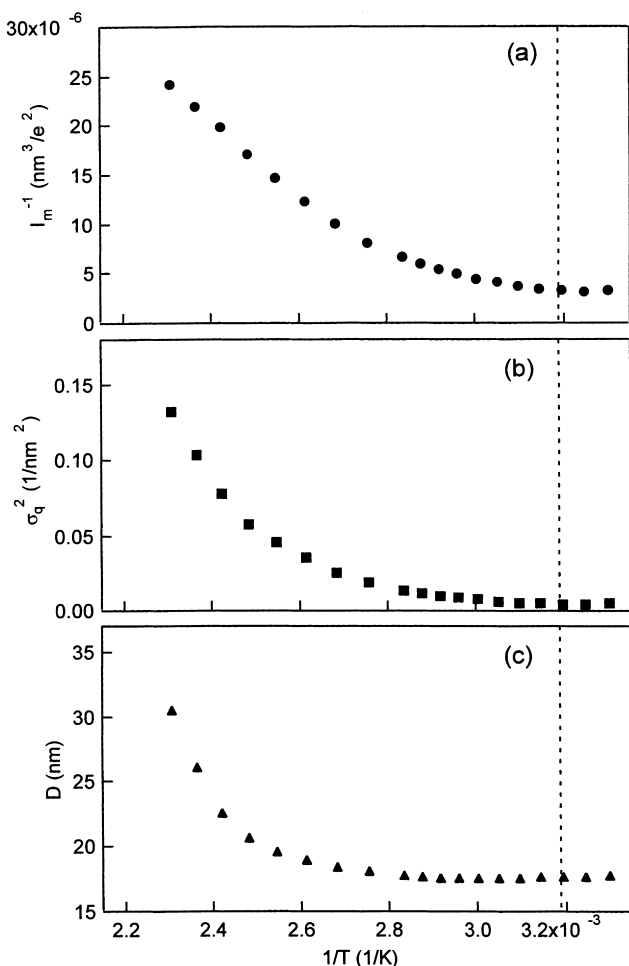

Fig. 9. Temperature dependence of SAXS profiles for the 75/25 (SI-5/5)/(PI-11) mixture at various temperatures shown on the plot during the cooling cycle. The thermal history of the specimen is given in Fig. 1.

Fig. 10. Plots of (a) $1/I_m$ versus $1/T$; (b) σ_q^2 versus $1/T$; and (c) D versus $1/T$ for the 75/25 (SI-5/5)/(PI-11) mixture. The thermal history of the specimen is given in Fig. 1.

3.3. Frozen or vitrified concentration fluctuations in (SI-5/5)/hPI mixtures

Above we have made two seemingly contradictory observations on the morphology of the (SI-5/5)/hPI mixtures; namely, both the Han plot via oscillatory shear rheometry and $1/I_m$ and σ_q^2 versus $1/T$ plots from SAXS suggest that 75/25 (SI-5/5)/(PI-11), 64/36 (SI-5/5)/(PI-11) and 85/15 (SI-5/5)/(PI-14) mixtures formed homogeneous single-phase melts, whereas the TEM images indicate that these mixtures had bicontinuous structure. It is worth mentioning at this juncture that earlier, using a symmetric SI diblock copolymer that is very similar to SI-5/5 investigated in the present study, Spontak et al. [53,54] inferred from an TEM image that their block copolymer was in a thermodynamically disordered state at room temperature. The morphology of the (SI-5/5)/hPI mixtures given in Fig. 7 is very similar to that observed by Spontak et al. [53,54], and also by Saka-moto and Hashimoto [51]. Based on the SAXS results presented above we tentatively conclude, following Saka-moto and Hashimoto [51], that the bicontinuous structure of
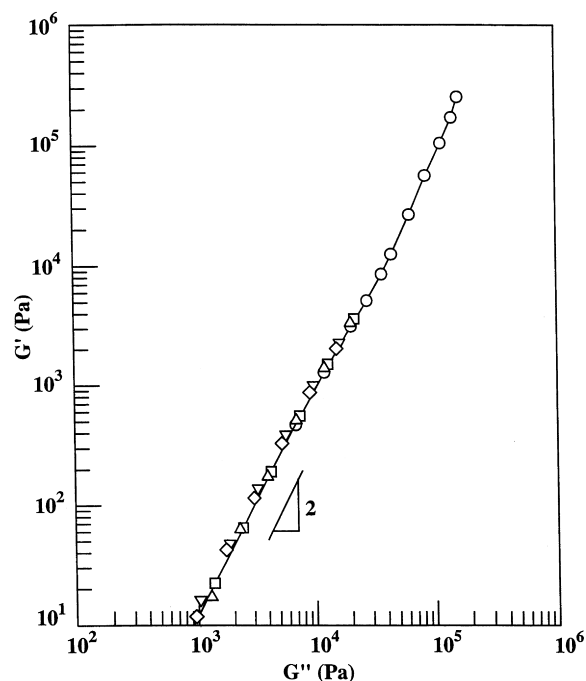

Fig. 11. Han plots for the 75/25 (SI-5/5)/(PI-11) mixture at various temperatures: (○) 52°C; (△) 57°C; (□) 62°C; (▽) 70°C; (◇) 80°C.

the (SI-5/5)/hPI mixtures observed from our TEM study (Figs. 7 and 8b) might have originated from 'frozen' or vitrified concentration fluctuations in the disordered singe-phase state. The amplitude of the concentration fluctuations is sufficiently large to be observed in TEM image. Further, we believe that the relaxation time of the concentration fluctuations that might have occurred in the present study is very large at 50°C owing to the proximity to the $T_{g,PS}$ of SI-5/5, which may freeze the thermal concentration fluctuations at 50°C by quenching below the $T_{g,PS}$ and by the OsO$_4$ staining.

It is reasonable to speculate that there would be very little chance of composition fluctuations if the T_{ODT}s of SI-5/5 and

Table 1
Predicted T_{ODT} for SI-5/5 using various expressions for the interaction parameter in the literature

Expression for the interaction parameter	Equation	Reference	Predicted T_{ODT} (°C)	
			Leibler theory	Helfand theory
$\alpha = -0.00118$ $+ 0.839/T$ (1)	Eq. (1)	[39]	120	38
$\chi = -0.0419$ $+ 38.54/T$ (2)	Eq. (2)	[56]	27	-49

its mixtures with hPI lie very far below the $T_{g,PS}$ (48°C) of SI-5/5. Let us now estimate the T_{ODT} of SI-5/5 using currently held mean-field theory. As shown in our previous paper [55], the estimated value of T_{ODT} of block copolymer would depend on the expression for the interaction parameter chosen. In the present study we used two different expressions for the interaction parameter for PS/PI pair and they are given in Table 1. The predicted values of T_{ODT} for SI-5/5 using the Leibler theory [43] and Helfand–Wasserman theory [57], respectively, are also given in Table 1. It should be mentioned that the interaction parameter α given in Table 1 has dimensions of mol/cm^3 and is related to the Flory–Huggins interaction parameter χ by $\chi = V_{ref}\alpha$ with V_{ref} being the molar volume of a reference component. In using the Leibler theory to predict the T_{ODT} of SI-5/5 given in Table 1, we used the following expression for V_{ref}:

$$V_{ref} = \{([M]_{PS}v_{PS})([M]_{PI}v_{PI})\}^{1/2} \tag{3}$$

where $[M]_{PS}$ and $[M]_{PI}$ denote the molecular weights of styrene and isoprene, respectively, and the following expressions for the specific volumes for PS [58]

$$v_{PS} = 0.9199 + 5.098 \times 10^{-4}(T - 273)$$

$$+ 2.354 \times 10^{-7}(T - 273)^2$$

$$+ (32.46 + 0.1017(T - 273))/M_{w,PS} \tag{4}$$

and for PI [39]

$$v_{PI} = 1.0771 + 7.22 \times 10^{-4}(T - 273)$$

$$+ 2.46 \times 10^{-7}(T - 273)^2 \tag{5}$$

in which v_{PS} and v_{PI} have units of cm^3/g, T is the absolute temperature, and $M_{w,PS}$ is the molecular weight of PS.

As can be seen in Table 1, the predicted values of T_{ODT} greatly depend on the particular expression for the interaction parameter used, and the Leibler theory [43] predicts much higher values of T_{ODT} than the Helfand–Wasserman theory [57]. This presented a great dilemma to decide which of the predicted T_{ODT}s might represent the true T_{ODT} of SI-5/5. Our previous study [55] indicated that for a series of SI diblock copolymers the predicted T_{ODT} from the Helfand–Wasserman theory with Eq. (1) was much closer to experiment, while the predicted T_{ODT} from the Leibler theory with Eq. (2) was much closer to experiment. Therefore, from Table 1 we tentatively assume that $T_{ODT} = 38°C$ predicted from the Helfand–Wasserman theory with Eq. (1) and $T_{ODT} = 27°C$ predicted from the Leibler theory with Eq. (2) are acceptable for our purposes here. Under this assumption we observe that the true T_{ODT} of SI-5/5 is not too far away from the $T_{g,PS}$ (48°C) of SI-5/5.

Our next task is to find out whether or not the addition of PI-11 or PI-14 will increase the T_{ODT} of SI-5/5 sufficiently, such that it could be determined by experiment. According to Hong and Noolandi [24], the ratio of degree of

polymerization of hPI ($Z_{H,PI}$) and degree of polymerization of block copolymer (Z_C) must be greater than 0.25 in order to have the T_{ODT} of (SI-5/5)/hPI mixtures higher than the T_{ODT} of SI-5/5. We have $Z_{H,PI}/Z_C = 1.12$ for the (SI-5/5)/(PI-11) mixtures and $Z_{H,PI}/Z_C = 1.36$ for the (SI-5/5)/(PI-14) mixtures. We then expect that addition of PI-11 or PI-14 to SI-5/5 would increase its T_{ODT}, suggesting a possibility of inducing microphase separation from the *homogeneous* diblock copolymer SI-5/5. However, the experimental results of SAXS (Figs. 9 and 10) and oscillatory shear rheometry (Fig. 11) indicate that the 75/25 (SI-5/5)/(PI-11) mixture formed a homogeneous single-phase melt. This observation appears to suggest that addition of PI-11 or PI-14 to SI-5/5 did not increase its T_{ODT} sufficiently above the $T_{g,PS}$ of SI-5/5 before macrophase separation sets in. There can be another possibility that prevented us from observing experimentally an onset of microphase separation in the SI/hPI mixtures: the true T_{ODT} of SI-5/5 might be much lower than the predicted value, 27°C (Table 1).

4. Concluding remarks

In this study we synthesized a symmetric SI diblock copolymer, SI-5/5, having M_n of 1.0×10^4 and $T_{g,PS}$ of 48°C. We found that SI-5/5 formed a homogeneous single-phase melt (i) at room temperature as investigated by TEM, (ii) at 40–180°C as investigated by SAXS, and (iii) at 50–75°C as investigated by oscillatory shear rheometry. Then we aimed to investigate homopolymer-induced microphase separation of the homogeneous block copolymer. When an hPI having $M_n = 1.14 \times 10^4$ or 1.41×10^4 was added to SI-5/5, our SAXS study indicates that the (SI-5/5)/hPI mixtures were still in the homogeneous state (Figs. 9 and 10) before microphase separation set in, while our TEM study shows that the (SI-5/5)/hPI mixtures formed bicontinuous structure (Figs. 7 and 8b). We believe that the bicontinuous structure, observed from TEM, in the (SI-5/5)/hPI mixtures is not an ordered microdomain structure, but that it originated from '*frozen*' thermal composition fluctuations in the single-phase state near ODT in the fluctuation-induced disordered structure (D_F) [51], instead of the homopolymer-induced ordered structure. Here we define ODT by a thermally-induced phase transition during heating at which a block copolymer or its mixtures with homopolymer is transformed from an ordered state to homogeneous single-phase melts free from the microphase-separated structure.

We have pointed out that one of the most important aspects of inducing microphase separation of a homogeneous block copolymer by adding a homopolymer is to choose the right type of homopolymer which, when added, would *not* increase the glass transition temperature of the block copolymer. Since the T_g (−68°C) of hPI is much lower than that (100°C) of hPS, in this study we used hPI, instead of hPS, to investigate whether or not we

could induce microphase separation of SI-5/5. From our experimental study we could not observe microphase separation occurring in the (SI-5/5)/hPI mixtures. Using currently held mean-field theories, we offered possible explanations on the experimental observations.

We wish to point out that had there been no information on SAXS (Figs. 9 and 10) and rheology (Fig. 11) available to us, using the TEM images alone (Fig. 7) we might have reached an erroneous conclusion that the addition of PI-11 or PI-14 induced microphase separation of the homogeneous diblock copolymer, SI-5/5. This is because we cannot determine whether the bicontinuous structure in Figs. 7 or 8b originated from thermal concentration fluctuations in the disordered state near ODT, which are also vitrified by quenching below the $T_{g,PS}$ and fixed by OsO_4 staining, or whether it is a microdomain structure frozen upon quenching from the disordered state to a temperature below T_{ODT}. If it is the frozen microdomain structure, then after a sufficiently long time the bicontinuous structure would develop into lamellar microdomain structure, since SI-5/5 is a nearly symmetric diblock copolymer. It should be mentioned that the bicontinuous structure observed in a study of Sakamoto and Hashimoto [51] is vitrified thermal concentration fluctuations of a compositionally nearly symmetric SI diblock copolymer having T_{ODT} between 98.5 and 100.1°C, as determined by SAXS. The bicontinuous structure is a stable dynamical structure at $T \geq 101$°C, but it later grew to lamellar microstructure after a sufficiently long time at $T \leq 98.5$°C. The above observations point out that extreme caution is needed to interpret TEM images of block copolymers.

The subject dealt with in this paper is not as simple as it may seem at first glance, because there are very intricate relationships existing among several variables. They are: (i) the ratio of the molecular weights of added homopolymer and corresponding block in the copolymer ($M_{H,A}/M_{C,A}$), (ii) the ratio of degrees of polymerization of added homopolymer A and the entire block copolymer ($Z_{H,A}/Z_C$), (iii) the composition of block copolymer, and (iv) the weight (or volume) fraction of added homopolymer ($w_{H,A}$). Also, the glass transition temperature of added homopolymer ($T_{g,H}$) and the glass transition temperature of block copolymer ($T_{g,C}$) play an important role in determining whether or not microphase separation of a homogeneous block copolymer can be induced upon addition of a homopolymer. At present we do not have a comprehensive theory enabling us to predict such intricate relationships. This subject requires the further attention of polymer scientists in the future.

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