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Lattice Disordering/Ordering and Demicellization/Micellization Transitions in Highly Asymmetric Polystyrene-*block*-Polyisoprene Copolymers

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ABSTRACT: Two kinds of transitions involving a change in molecular assembly, lattice disordering/ordering transition (LDOT) and demicellization/micellization transition (DMT), in highly asymmetric polystyrene-*block*-polyisoprene (SI diblock) copolymers were investigated using oscillatory shear rheometry, transmission electron microscopy (TEM), and small-angle X-ray scattering (SAXS). For the study, three highly asymmetric SI diblock copolymers having the volume fractions of polystyrene (PS) block of 0.11, 0.13, and 0.16, respectively, were synthesized using anionic polymerization. In highly asymmetric block copolymer, LDOT is defined as a transition where the long-range order of microdomains is lost during heating, giving rise to a disordered arrangement of spheres with short-range liquidlike order (termed disordered spheres or micelles), and DMT is defined as a transition where all microdomains disappear during heating and are transformed into the micelle-free homogeneous state in which the component polymers are mixed on a molecular level and only thermally induced composition fluctuations may exist. DMT may be regarded as a pseudo-phase transition, involving effectively a *finite* number of molecules and hence occurring over a *finite* range (possibly a narrow range) of temperatures. It was found that the three highly asymmetric SI diblock copolymers underwent, during heating, first lattice disordering and then demicellization transitions. The values of LDOT temperature (T_{LDOT}) and DMT temperature (T_{DMT}) for the highly asymmetric SI diblock copolymers were determined by careful analysis of SAXS results, and the value T_{DMT} determined by oscillatory shear rheometry was found in good agreement with SAXS results. The LDOT determined from SAXS was confirmed by TEM, showing the existence of disordered spheres at thermal equilibrium at $T_{\mathrm{LDOT}} \leq T < T_{\mathrm{DMT}}$.

1. Background

During the past two decades, numerous papers dealing with phase transitions in block copolymers have been published. There are too many papers to cite all of them here, and interested readers are referred to some key theoretical papers[1−4] and review papers.[5,6] Today it is well established, theoretically and experimentally, that phase transitions in block copolymers are intimately related to their microdomain structures, which in turn depend on block composition (or block length ratio). The majority of the past experimental studies employed oscillatory shear rheometry and/or radiation scattering methods (e.g., small-angle X-ray or neutron scattering) to investigate order−disorder transition (ODT) from a well-ordered microdomain structure to the homogeneous phase during heating or disorder−order transition (DOT) from the homogeneous phase to a well-ordered microdomain structure. Again, there are too many papers to cite all of them here, and interested readers are referred to our recent papers[7,8] and references therein. Fewer experimental studies have been reported on order−order transition (OOT) in block copolymer from one type of microdomain structure to another type of microdomain structure during heating or cooling.[9−14] Almost all of the experimental studies referred to above dealt with compositionally symmetric or nearly *symmetric* block copolymers having lamellar microdomain structure and/or hexagonally packed cylindrical microdomain structure.

There are, however, a relatively small number of papers[14−20] that dealt with ODT and/or OOT in highly *asymmetric* block copolymers having spherical microdomains. In 1997, using SAXS, we reported that a highly asymmetric polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS triblock) copolymer having a 0.158 volume fraction of polystyrene (PS) block (f_{PS}) underwent, during heating, lattice disordering transition (LDT) before reaching the homogeneous state.[14] Specifically, this particular SIS triblock copolymer (Vector 4111) was found to (i) undergo OOT from hexagonally packed cylindrical microdomains of PS to spherical microdomains of PS in a cubic lattice at 179−185 °C, (ii) have spherical microdomains of PS in the cubic lattice at 185 °C < T < 210 °C, (iii) undergo LDT, upon a further increase in temperature, at temperatures between 210 °C (onset) and 214 °C (completion), giving rise to a disordered arrangement of spheres of PS with short-range liquidlike order (hereafter will be referred to as disordered spheres or micelles), and (iv) have micelles persisting to 220 °C, the highest experimental temperature employed. However, owing to the high molecular weight of Vector 4111, we were not able to attain the micelle-free homogeneous state. In that study, using transmission electron microscopy (TEM), we observed disordered spheres still having sharp interfaces at 220 °C.

In 1997, independently, using SAXS, Schwab and Stühn[18] also reported an observation, similar to that

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reported in our papers,[14,17] in a highly asymmetric polystyrene-*block*-polyisoprene (SI diblock) copolymer having $f_{PS} = 0.11$. In their SAXS experiment, a specimen was cooled from the homogeneous state to an ordered state with PS spheres in body-centered-cubic (bcc) ordered state. Schwab and Stühn[18] observed a new *stable* state of spherical microdomains with liquidlike order (micelles) between the homogeneous state at high temperature and the bcc state at low temperature. They defined the temperature, at which micelles with short-range liquidlike order are transformed during cooling into spheres in the bcc lattice, to be the disorder−order transition temperature (T_{DOT}) which, however, corresponds to the lattice disordering temperature in our SAXS experiment during heating.[14,17]

On the theoretical side, earlier, Semenov predicted the ordering of micelles in a block copolymer.[21] More recently, using a self-consistent mean-field approach, Matsen and Bates[22] identified randomly close-packed spheres over a very narrow range in the intermediate-segregation regime of an AB-type diblock copolymer. Matsen and Bates[22] regarded the randomly close-packed spheres as being part of the disordered phase, because they could not find an appropriate space-group symmetry of the microstructure corresponding to the randomly close-packed spheres.

The randomly close-packed spheres identified by the self-consistent mean-field analysis of Matsen and Bates[22] may correspond to the disordered spheres (or micelles) identified in our previous studies[14,17] and also in the present study that will be discussed below. Since one of our objectives in this study is to clarify whether disordered spheres in highly asymmetric block copolymers represent an equilibrium morphology or are part of thermally induced composition fluctuations with long relaxation times,[16] very recently we synthesized three relatively low molecular weight SI diblock copolymers, each having a highly asymmetric block composition ($f_{PS} = 0.11$, 0.13, or 0.16) and then investigated their phase transitions using oscillatory shear rheometry, transmission electron microscopy (TEM), and SAXS.

To avoid possible confusion when presenting our results later in this paper, we believe that it is very essential for us to first introduce the terminology that will be used throughout this paper. Figure 1 gives a schematic describing the disordering and ordering processes (a) in highly asymmetric sphere-forming block copolymers with T_{LDOT} denoting “lattice disordering/ordering transition temperature” and T_{DMT} denoting “demicellization/micellization transition temperature” and (b) in symmetric lamella-forming block copolymers with T_{ODT}. The distinction made above between the sphere-forming and lamella-forming block copolymers is based on our experimental observations that at T_{LDOT}, during heating, highly asymmetric block copolymers form disordered spheres (micelles) with short-range liquidlike order, and the micelles are a structural entity that exists at thermal equilibrium at any time instance in the time scale of our observation. Here we define the lattice disordering/ordering transition (LDOT) as a transition where the long-range order of microdomains is lost, but the microphase-separated structures (spherical microdomains or micelles) still exist. The demicellization/micellization transition (DMT) is defined as a transition where all the microdomain structures with short-range liquidlike order disappear and are transformed into the micelle-free homogeneous state in which the component polymers are mixed on a molecular level and only thermally induced composition fluctuations may exist. We maintain the view that the formation of micelles is *not* part of thermally induced composition fluctuations in the homogeneous state free from micelles. According to the definitions given in Figure 1, ODT is a transition between microdomains (e.g., lamellae or cylinders) having long-range order and a disordered state free from micelles where the component blocks are mixed on a molecular level with some composition fluctuations (see part b).

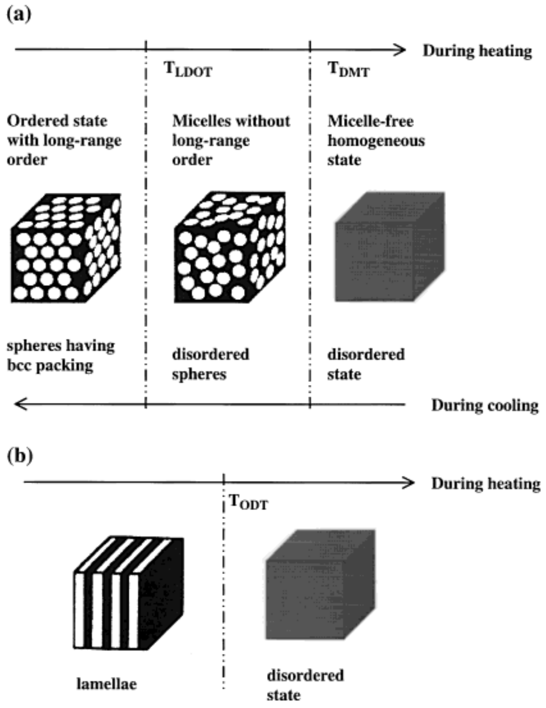

Figure 1. (a) Schematic describing the phase disordering and ordering processes in highly asymmetric sphere-forming block copolymers, namely, (i) transitions' paths, during heating, from spheres with long-range order to disordered spheres (micelles) without long-range order and to the micelle-free homogeneous state or (ii) the phase transitions' paths, during cooling, from the micelle-free homogeneous state to micelles without long-range order and to spheres with long-range order, where T_{LDOT} denotes “lattice disordering/ordering temperature” and T_{DMT} denotes “demicellization/micellization temperature”. (b) Schematic describing the phase disordering process in symmetric or nearly symmetric block copolymer, during heating, from lamellae to the homogeneous state, where T_{ODT} denotes “order−disorder transition temperature”.

We wish to mention that DMT is not a true phase transition from a rigorous thermodynamic point of view, in the sense that it does not occur in effectively infinite system and hence it does not occur at a precise transition point with an infinite sharpness. On the other hand, LDOT is a true thermodynamic phase transition in the sense that it occurs in effectively infinite system and hence at a precise temperature with infinite sharpness. In this sense, LDOT may be defined as order−disorder transition (ODT). However in this paper we use the term LDOT, instead of ODT, to highlight the difference described earlier between the two systems, highly asymmetric and symmetric (or nearly symmetric) block copolymers, above ODT. DMT may be regarded as a pseudo-phase transition in the sense that it involves effectively a *finite* number of molecules and hence occurs over a *finite* range (possibly a narrow range) of temperatures.

It is worth mentioning that earlier Hashimoto et al.[20] reported the lattice disordering transition taking place in polystyrene-*block*-polybutadiene (SB diblock) copolymer in *n*-tetradecane with decreasing polymer concentration at a given temperature or with increasing temperature at a given polymer concentration. Further, Hashimoto et al.,[20] Kinning et al.,[23,24] and Winey et al.[25] reported the lattice disordering transition taking place in binary mixtures consisting of an SI or SB diblock copolymer and homopolystyrene or homopolybutadiene. They observed, via SAXS and TEM, the formation of disordered micelles, upon increase in temperature or increase in homopolymer volume fraction, from ordered morphologies (or ordered micelles) before the onset of DMT (dissolution of micelles into the homogeneous state free from micelles). They emphasized that both spatially ordered and spatially disordered micelles are microphase-separated; thus, the LDT between the ordered morphologies and the disordered micelles is *not* ODT in the sense of ODT in lamella-forming block copolymer, which is equivalent to DMT in our terminology (Figure 1). The LDT defined by Hashimoto et al.[20] and Winey et al.[25] is essentially the same as the LDOT defined in Figure 1 above.

It is appropriate to use different terminology describing the disordering process with increasing temperature when a highly asymmetric block copolymer undergoes first disordering of lattices forming micelles with short-range liquidlike order and then dissolution of micelles, transforming into the micelle-free homogeneous state. It should be mentioned that the entropy of the micellar phase is certainly lower than the entropy of the micelle-free homogeneous phase; thus, micellization is an ordering process and demicellization is a disordering process. Our view is that micelles of spherical shape without long-range order represent a microphase-separated state and still have physically a local order relative to the micelle-free disordered homogeneous state. Consequently, the two phases, the phase with micelles with short-range liquidlike order and the micelle-free homogeneous phase, must be distinguished. This distinction is crucial also for interpretation of the low-frequency rheological properties of the systems as will be discussed later.

It is our view in this paper that the conventional definition of T_{ODT} is applicable only to symmetric or nearly symmetric block copolymers, in which LDOT and DMT degenerate, giving rise to transition between microphase-separated structures with long-range order and micelle-free homogeneous phase. In contrast, highly asymmetric block copolymers undergo first LDOT followed by DMT during heating or undergo first DMT followed by LDOT during cooling.

Table 1. Molecular Characteristics of the SI Diblock Copolymers Synthesized in This Study

sample code	M_{n} (g/mol)[a]	$M_{\mathrm{w}}/M_{\mathrm{n}}$ [b]	w_{PS}[c]	f [d]
SI-7/29	3.6×10^4	1.03	0.19	0.16
SI-10/53	5.7×10^4	1.13	0.16	0.13
SI-12/83	8.7×10^4	1.10	0.13	0.11
SI-9/9	1.8×10^4	1.02	0.51	0.47

[a] Number-average molecular weight (M_{n}) was determined by membrane osmometry. [b] Polydispersity ($M_{\mathrm{w}}/M_{\mathrm{n}}$) was determined by gel permeation chromatography. [c] Weight fraction of PS block (w_{PS}) was determined by nuclear magnetic resonance spectroscopy. [d] Volume fraction of PS block (f) was calculated at room temperature. Note that the value of f varies with temperature, because the temperature dependences of specific volumes of PS and PI are different.

The purpose of this paper is to illuminate experimentally the following ideas which have not been completely clarified in the literature: (i) the existence of LDOT and (ii) the existence of DMT in highly asymmetric neat sphere-forming block copolymers melts; (iii) the existence of micelles in short-range liquidlike order at thermal equilibrium using SAXS, oscillatory shear rheometry, and TEM, i.e., this paper presents experimental evidence that supports the change in molecular assembly with temperature schematically shown in Figure 1. Specifically, in this paper we present the values of T_{LDOT} and T_{DMT} for three *highly asymmetric* SI diblock copolymers, each determined from oscillatory shear rheometry and SAXS. The results will be interpreted with the aid of TEM images. For comparison, the change in molecular assembly with temperature in a *symmetric* SI diblock copolymer will also be presented, demonstrating that indeed the lamella-forming block copolymer does not undergo LDOT and DMT separately and undergoes only ODT directly. It should be mentioned that the terminologies LDT, T_{LDT}, ODT, and T_{ODT} in a series of our previous papers[14,17,19] correspond respectively to LDOT, T_{LDOT}, DMT, and T_{DMT} newly defined in this paper. We believe that the new terminologies are more reasonable in order to highlight the differences between the structural change in lamella- or cylinder-forming block copolymers and the structural changes in sphere-forming block copolymers.

2. Experimental Section

2.1. Materials. In this study we synthesized, via anionic polymerization in cyclohexane, four SI diblock copolymers. We determined the number-average molecular weight using membrane osmometry and polydispersity using gel permeation chromatography of the block copolymers synthesized. Table 1 gives a summary of the molecular characteristics of the polymers.

2.2. Sample Preparation. Samples were prepared by first dissolving a predetermined amount of an SI diblock copolymer (10 wt %) in toluene 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 slowly at room temperature in a fume hood 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. The drying of the samples was continued until there was no further change in weight, and then the specimens were stored in a refrigerator.

2.3. Rheological Measurement. In this study, a Rheometrics mechanical spectrometer (model RMS 800) was used in the oscillatory mode with parallel plate fixtures (25 mm diameter). Two different types of experiment were conducted. (1) Dynamic temperature sweep experiments were conducted; i.e., the dynamic storage and loss moduli (G' and G'') were measured under isochronal conditions during heating. (2) Dynamic frequency sweep experiments were conducted; i.e., G' and G'' were measured as functions of angular frequency (ω) ranging from 0.01 to 100 rad/s at various fixed temperatures in the heating process. 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. The temperature control was accurate to within ±1 °C, and a fixed strain of 0.04 was used at a given temperature, to ensure that measurements were taken well within the linear viscoelastic range of the materials investigated. All the rheological measurements were conducted under a nitrogen atmosphere in order to preclude oxidative degradation of the samples. The

Table 2. Thermal Histories of the Specimens Used for TEM Experiment

sample code	thermal history
for SI-7/29	
sample A	annealed at 60 °C for 12 days followed by rapid quenching in ice water
sample B	annealed at 90 °C for 8 days followed by rapid quenching in ice water
sample C	annealed at 95 °C for 8 days followed by rapid quenching in ice water
sample D	annealed at 115 °C for 5 days followed by rapid quenching in ice water
for SI-10/53	
sample A	annealed at 90 °C for 8 days followed by rapid quenching in ice water
sample B	annealed at 120 °C for 3 days followed by rapid quenching in ice water
sample C	annealed at 140 °C for 2 days followed by rapid quenching in ice water
sample D	annealed at 160 °C for 10 h followed by rapid quenching in ice water
for SI-12/83	
sample A	annealed at 90 °C for 8 days followed by rapid quenching in ice water
sample B	annealed at 120 °C for 3 days followed by rapid quenching in ice water
sample C	annealed at 160 °C for 24 h followed by rapid quenching in ice water
sample D	annealed at 180 °C for 10 h followed by rapid quenching in ice water

thermal histories of the specimens used for the rheological measurements are given in the figure captions.

2.4. TEM Experiment. TEM was conducted in order to determine the microdomain structure of each block copolymer at room temperature as well as at elevated temperatures followed by rapid quenching in ice water. By having recognized the fact that the accuracy of the temperature at which specimens were annealed before rapid quenching was very crucial, a solvent-cast specimen was annealed in a specially designed vacuum oven (Yamato Scientific Co., model DP-22) which can control the temperature to within ±1.5 °C up to 240 °C and can provide temperature uniformity inside the vacuum oven to within ±1.5 °C up to 240 °C. The temperature employed for annealing was guided by the rheological and SAXS studies. The thermal histories of the specimens used for TEM study are summarized in Table 2. The ultrathin sectioning of the quenched specimens was performed by cryoultramicrotomy at −100 °C, below the glass transition temperature ($T_g = -68$ °C) of polyisoprene, to attain the rigidity of the specimen, using a Reichert Ultracut S low-temperature sectioning system equipped with a diamond knife. A transmission electron microscope (JEM 1200EX II, JEOL) operated at 120 kV was used to obtain micrographs of the specimens stained with osmium tetroxide vapor.

2.5. SAXS Experiment. SAXS experiments were conducted under a nitrogen atmosphere in the heating and cooling process, using an apparatus described in detail elsewhere,[26,27] which consists of a newly replaced 18 kW rotating-anode X-ray generator operated at 45 kV × 400 mA (MAC Science Co. Ltd., Yokohama, Japan), a graphite crystal for incident-beam monochromatization, a 1.5 m camera, and a one-dimensional position-sensitive proportional counter. The Cu Kα 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.[28] The absolute SAXS intensity was obtained using the nickel-foil method.[29] In the present study, the temperature dependence of the SAXS profiles was obtained with a large temperature increment (referred to hereafter as the low-temperature-resolution SAXS experiment) and also with a small temperature increment (referred to hereafter as the high-temperature-resolution SAXS experiment) in a temperature enclosure which was sealed by nitrogen gas. This new temperature enclosure and temperature controller enabled us to control the sample temperature to within ±0.002 °C. Figure 2 summarizes schematically the temperature protocols employed in the SAXS experiments for (a) SI-7/29, (b) SI-10/53, (c) SI-12/83, and (d) SI-9/9. Namely, a specimen was exposed to X-ray beam to measure SAXS profiles for the period indicated by each horizontal solid line (typically for 30 min) after 30 min waiting at each temperature increment during the heating process or at each temperature decrement during the cooling process.

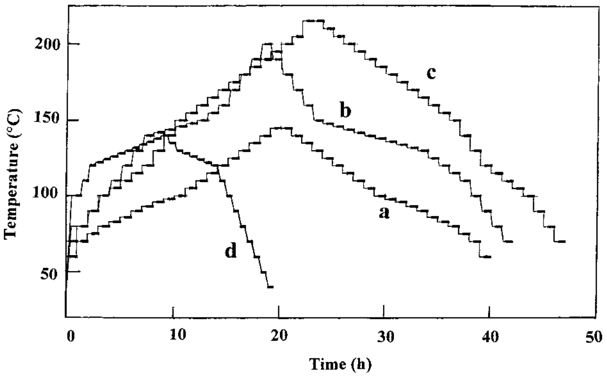

Figure 2. Schematic diagram describing the thermal histories of specimens employed for SAXS experiments: (a) SI-7/29 with 30 min preset time and 30 min exposure time; (b) SI-10/53 with 30 min preset time and 30 min exposure time; (c) SI-12/83 with 30 min preset time and 30 min exposure time; (d) SI-9/9 with 20 min preset time and 20 min exposure time.

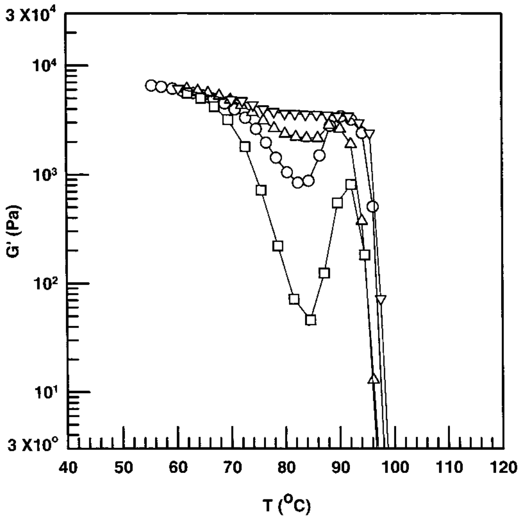

Figure 3. Isochronal dynamic temperature sweep experiment for SI-7/29 at $\omega = 0.01$ rad/s during heating: (○) after annealing at 70 °C for 36 h, (△) after annealing at 90 °C for 8 days, (□) after annealing at 90 °C for 8 days followed by heating to 102 °C, held there for 1 h, then cooled to 60 °C, and held there for 2 h, and (▽) after annealing at 90 °C for 15 days.

3. Results

3.1. Rheology and TEM Results. The temperature dependence of *G*′, which was obtained from the dynamic temperature sweep experiment under isochronal conditions at $\omega = 0.01$ rad/s, is given in Figure 3 for the SI-7/29 ($f = 0.16$) specimens having various thermal histories before being subjected to the dynamic temperature sweep experiment. The following observations are worth noting in Figure 3. For the specimen that was annealed at 70 °C for 36 h, the value of *G*′ goes through

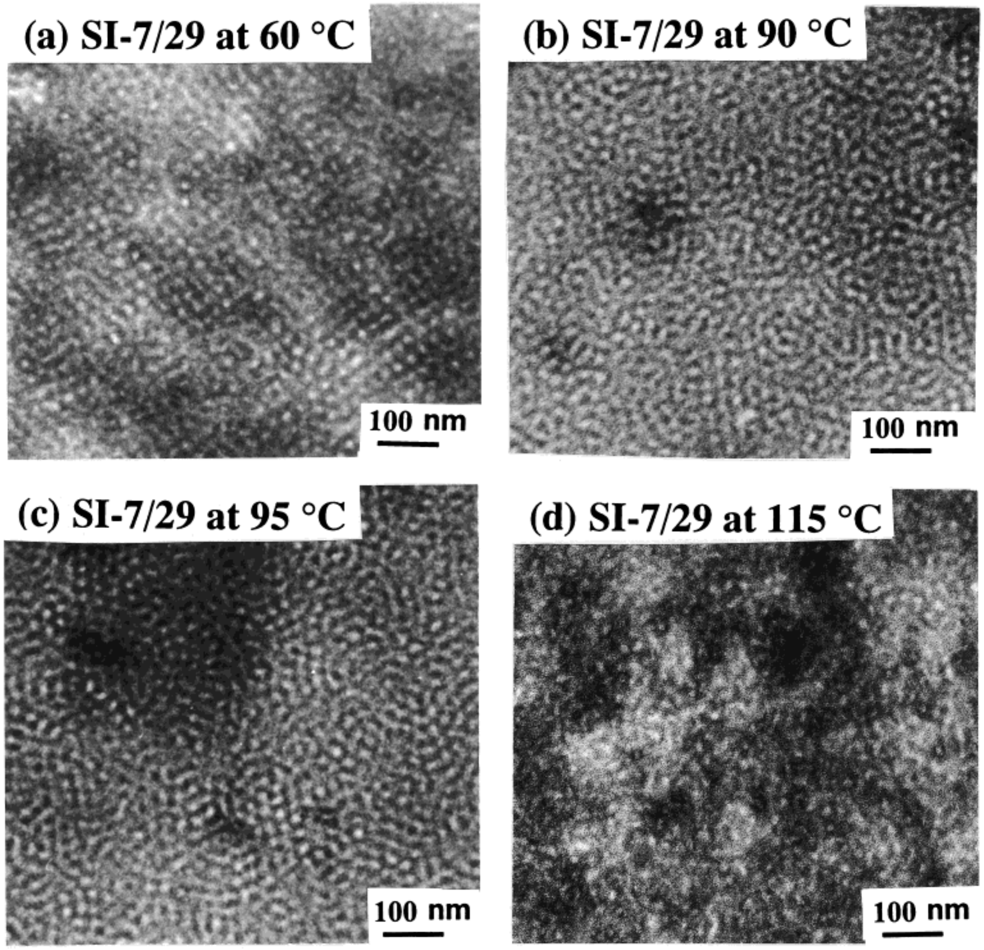

Figure 4. TEM images of SI-7/29: (a) after annealing at 60 °C for 12 days followed by rapid quenching in ice water; (b) after annealing at 90 °C for 8 days followed by rapid quenching in ice water; (c) after annealing at 95 °C for 8 days followed by rapid quenching in ice water; (d) after annealing at 115 °C for 5 days followed by rapid quenching in ice water.

a minimum at approximately 82 °C followed by an increase in G' and then finally starts to decrease very rapidly at approximately 95 °C. According to Almdal et al.,[9] the temperature at which a minimum in G' occurs in Figure 3 may be regarded as being the order−order transition temperature (T_{OOT}) of a block copolymer. However, we will show below that this is not the case for our block polymers. The depth of the minimum in G' is decreased when a specimen was annealed at 90 °C for 8 days. Here, we find a much smaller minimum value of G' at approximately 86 °C (a shift of 4 °C upward) compared to the situation where a specimen was annealed at 70 °C for 36 h. This difference seems to point out that the duration and temperature of annealing definitely affected the minimum value of G' and also a shift of the temperature at which the minimum in G' occurs. Interestingly, when a specimen was first heated to 102 °C and then cooled to 60 °C before being subjected to the dynamic temperature sweep experiment, we observe that the value of G' decreases rapidly with increasing temperature, going through a very large minimum at ca. 84 °C, and then increases rapidly going through a maximum at approximately 93 °C, followed by a rapid decrease again.

When a specimen was annealed at 90 °C for 14 days before being subjected to the dynamic temperature sweep experiment, we observe that a minimum of G' disappears in Figure 3. The above observations suggest that annealing has a profound influence on the dependence of G' on temperature during the dynamic temperature sweep experiment. Similar results were obtained, though not presented here, for SI-10/53 and SI-12/83. The SAXS results to be discussed below will indicate that the minimum in G' observed in the isochronal dynamic temperature sweep experiment for SI-7/29 is due to annealing effect and is *not* an indication of the onset of OOT.

Figure 4 gives the TEM images of SI-7/29 specimens, the thermal history of which is given in Table 2 and also in the figure captions. Similar TEM images were obtained, though not presented here, for SI-10/53 and SI-12/83. In Figure 4, together with the SAXS results to be presented below, we make the following observations. SI-7/29 has spherical microdomains of PS at 60 °C. As the temperature was increased to 90 °C, well-ordered spherical microdomains of PS persist. Interestingly, as the temperature was increased to 95 °C, at which the value of G' begins to drop precipitously (Figure 3), the spherical microdomain structure still persists. As the temperature was increased further to 115 °C, the spherical microdomains appear to have lost long-range order and yet retain a distinct interface, an indication of the presence of disordered spheres (micelles) without long-range order; i.e., SI-7/29 undergoes LDOT. Notice that 115 °C is far above the temperature at which the value of G' in Figure 3 becomes negligibly small. Thus, we tentatively conclude that $T_{LDOT} \cong 95$ °C for SI-7/29.

From Figure 3 one may be tempted to conclude that the T_{ODT} (T_{DMT} in our terminology) of SI-7/29

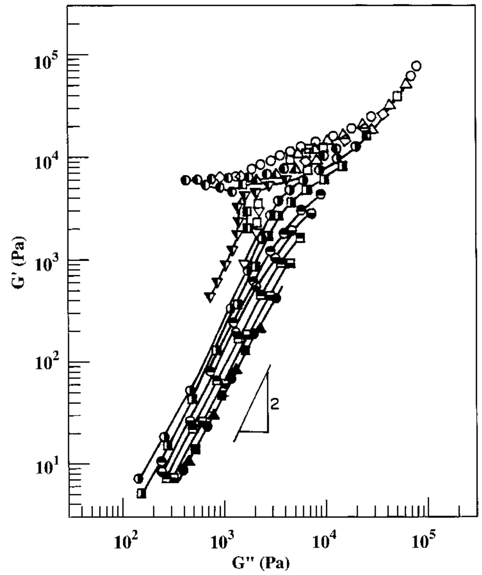

Figure 5. Han plots for SI-7/29 during heating at various temperatures: (○) 60 °C; (△) 70 °C; (□) 75 °C; (▽) 80 °C; (◇) 83 °C; (◐) 86 °C; (◬) 90 °C; (◧) 93 °C; (▼) 96 °C; (◑) 98 °C; (◨) 105 °C; (◓) 115 °C; (◒) 120 °C; (⬒) 125 °C; (⬓) 130 °C; (●) 135 °C; (▲) 140 °C; (■) 145 °C.

is approximately 95 °C if we apply the rheological criterion[30−34] established for cylinder- or lamella-forming block copolymer to sphere-forming block copolymer. However, as already shown above from the TEM images (Figure 4), we know that SI-7/29 has microdomains at temperatures much higher than 95 °C. Therefore, we tentatively conclude that 95 °C represents T_{LDOT} but not the T_{DMT} of SI-7/29. Below we will show from SAXS results that SI-7/29 indeed undergoes LDOT at 93−96 °C before undergoing DMT. Thus, we must conclude that the isochronal dynamic temperature sweep experiment fails completely to determine the T_{DMT} of SI-7/29, a highly asymmetric SI diblock copolymer ($f = 0.16$). A similar conclusion was drawn for SI-10/53 and SI-12/83.

Figure 5 gives log G' versus log G'' plots for SI-7/29 at various temperatures ranging from 60 to 145 °C. Similar plots were obtained, though not presented here, for SI-10/53 and SI-12/83. Following Neumann et al.,[35] below log G' versus log G'' plots will be referred to as Han plots. In Figure 5 we observe that the Han plot begins to exhibit a negative slope at 60 °C and keeps the negative slope (in the region where ca. 4×10^3 Pa $\leq G' \leq$ ca. 7×10^3 Pa and ca. 3×10^2 Pa $\leq G'' \leq$ ca. 1.5×10^3 Pa) until the temperature is increased to 93 °C and finally exhibits a positive slope of 2 in the terminal region at temperatures ranging from 98 to 145 °C, the highest experiment temperature employed. Notice in Figure 5 that the Han plot with a slope of 2 in the terminal region shows the parallel feature at temperatures ranging from 98 to 145 °C and begins to become independent of temperature at 135 °C. Following the rheological criterion of Han et al.,[38] from Figure 5 we determine $T_{\mathrm{DMT}} \cong 135$ °C for SI-7/29. It is of great interest to observe in Figure 5 that the temperature (98 °C) above which the Han plot for SI-7/29 shows a parallel feature, having a slope of 2 in the terminal region, corresponds roughly to the temperature at which the value of G' becomes negligibly small in Figure 3. A similar observation was made, not presented here, for SI-10/53 and SI-12/83. This observation is very significant in that the Han plot is very useful to determine both T_{LDOT} and T_{DMT} of a highly asymmetric block copolymer.

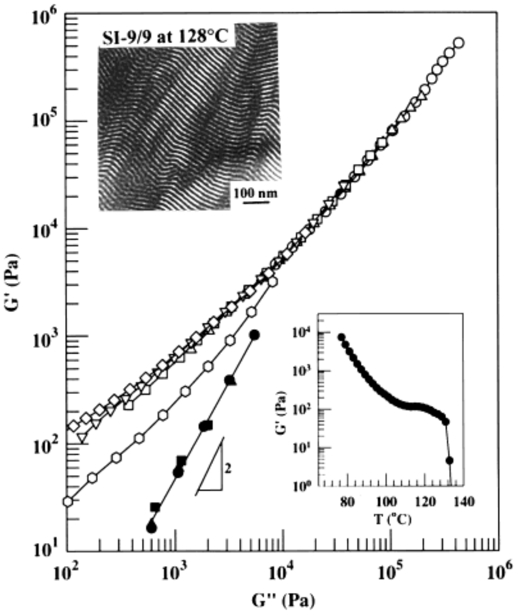

Figure 6. Han plots for SI-9/9 during heating at various temperatures: (○) 80 °C; (△) 90 °C; (□) 100 °C; (▽) 110 °C; (◇) 120 °C; (⬡) 130 °C; (●) 133 °C; (▲) 136 °C; (■) 140 °C. The inset in the lower right side gives the isochronal dynamic temperature sweep experiment for SI-9/9 at $\omega = 0.01$ rad/s during heating after a specimen was annealed at 90 °C for 36 h. The inset in the upper left side gives an TEM image of SI-9/9 specimen after annealing at 128 °C for 1 day followed by rapid quenching in ice water.

For comparison, Figure 6 gives Han plots for SI-9/9 ($f = 0.47$) at various temperatures ranging between 80 and 140 °C, which were obtained from the dynamic frequency sweep experiments. It is worth noting in Figure 6 that the Han plot stays more or less on a single correlation at 80−120 °C with a slope much less than 2 in the terminal region, makes a sudden downward displacement at 130 °C with a slope still less than 2 in the terminal region, and finally makes another sudden downward displacement with a slope of 2 in the terminal region, giving rise to a temperature-independent correlation at 133, 136, and 140 °C. Following the rheological criterion of Han et al.,[38] from the Han plot in Figure 6 we determine the T_{ODT} of SI-9/9 to be approximately 133 °C. In the inset on the lower right side is given the result of the isochronal dynamic temperature sweep experiment at $\omega = 0.01$ rad/s during heating. It can be seen that the value of G' begins to decrease rapidly at approximately 130 °C. According to the literature,[30−34] the temperature at which G' begins to drop rapidly may be regarded as being the T_{ODT} of a block copolymer. Following such a rheological criterion, we determine the T_{ODT} of SI-9/9 to be approximately 130 °C, which is in very good agreement with that determined from the Han plot. Therefore, we can conclude that both the isochronal dynamic temperature sweep experiments and the Han plot produce an almost identical value of T_{ODT} of a nearly symmetric block copolymer. Previously, a similar observation was reported on nearly symmetric poly(ethylene propylene)-*block*-poly(ethylethylene) (PEP-*block*-PEE) copolymers[33,34] and other nearly symmetric SI diblock copolymers[7] and nearly symmetric SIS triblock copolymer.[38c] In the inset on the upper left side is given a TEM image, showing

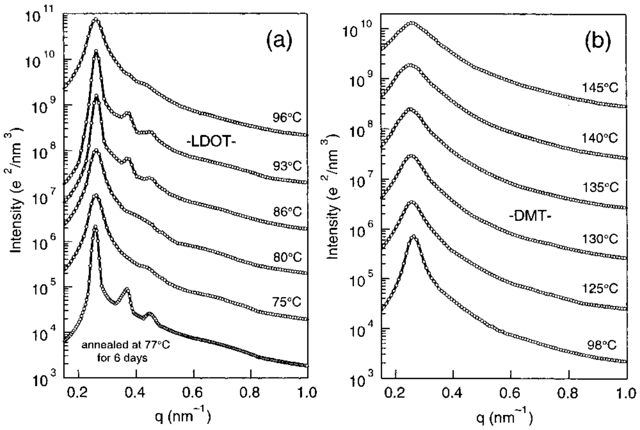

Figure 7. Temperature dependence of desmeared SAXS profiles for SI-7/29 in the heating process at various temperatures: (a) from 75 to 96 °C; (b) from 98 to 145 °C. Note that the profile at 77 °C was obtained for the specimen having a thermal history different from others; namely, it was obtained after annealing an as-cast specimen at 77 °C for 6 days. The intensities of the profiles at 77 and 98 °C shown respectively at the bottom of part a and part b of this figure are actually measured absolute values, and the intensities of other profiles have been shifted up by 1 decade relative to the SAXS intensities immediately below.

lamellar microdomain structure, of the SI-9/9 specimen after annealing at 128 °C for 1 day followed by rapid quenching in ice water. Note that 128 °C is very close to the temperature at which the value of G' begins to drop rapidly during the isochronal dynamic temperature sweep experiment at $\omega = 0.01$ rad/s.

3.2. SAXS Results. Figure 7 gives the desmeared SAXS profiles for SI-7/29 at various temperatures ranging from 75 to 145 °C in the heating process, 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. The following observations are worth noting in Figure 7a. Upon increase in temperature from 75 to 93 °C, the first-order peak becomes intense and sharp, which is followed by increasing intensity and sharpness of higher order peaks at $q = \sqrt{2}q_m$ and $\sqrt{3}q_m$, where q_m is the value of q at the first-order peak. At 75 °C, we observe a broad higher-order maximum at $q = \sqrt{3}q_m$. After annealing the specimen at 77 °C for a long time (6 days), we clearly observe the higher-order maxima at $q = \sqrt{2}q_m$ and $\sqrt{3}q_m$ and a sharpening of the first-order peak. This observation indicates that at 77 °C we have bcc spheres and that the prolonged annealing at 77 °C improved its long-range order. Upon increase in temperature from 75 to 93 °C, the long-range order of bcc lattice increases. Thus, there is no indication that OOT occurs with increasing temperature up to 93 °C, and hence the minimum in the log G' versus temperature plot given in Figure 3 is not due to the OOT but due to the annealing effect, as will be discussed later in section 4.

Upon increase in temperature from 93 to 96 °C, the first-order peak broadens dramatically and the higher-order peaks disappear, indicating an onset of LDOT at approximately 93 °C and completion of LDOT at 96 °C. At $T > 96$ °C, we observe both the gradual broadening and the decay of the intensity of the first-order peak. This observation indicates an apparently continuous change of disordered spheres with short-range liquidlike order to the micelle-free homogeneous melt, as reported earlier by Sakamoto et al.[14,17] At 96 °C < T < 130 °C, the second-order shoulder located at $q \approx 0.4$ nm^{-1} can be discerned, indicative of the existence of spheres. However, at $T > 140$ °C, the shoulder described above cannot be discerned, indicative of the existence of the micelle-free homogeneous melt. Thus, we conclude that SI-7/29 undergoes DMT at 130−135 °C.

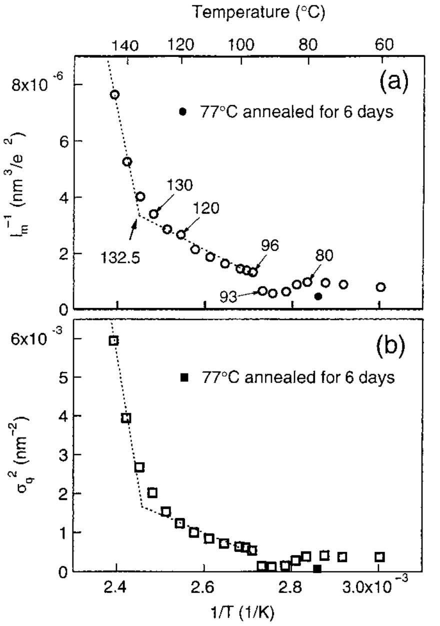

Figure 8. Plots of (a) $1/I_m$ versus $1/T$ and (b) σ_q^2 versus $1/T$ for SI-7/29 in the heating cycle.

Figure 8 gives plots of (a) the reciprocal of the first-order peak intensity ($1/I_m$) versus the reciprocal of the absolute temperature ($1/T$) and (b) the square of the half-width at half-maximum (σ_q^2) versus $1/T$ for SI-7/29 at temperatures ranging from 60 to 145 °C in the heating process. In Figure 8 we observe that I_m^{-1} and σ_q^2 decrease with decreasing $1/T$ (or increasing temperature from 80 to 93 °C), indicating an increase of long-range order of bcc due to the annealing effect as will be discussed later in section 4.

Upon further increase in temperature, I_m^{-1} and σ_q^2 drastically increase over a narrow temperature interval between 93 and 96 °C and then gradually increase almost linearly with $1/T$ in the temperature range between 96 and 120 °C. An abrupt change in I_m^{-1} and σ_q^2 indicates the occurrence of LDOT beginning at approximately 93 °C and completing at approximately 96 °C, i.e., $T_{LDOT} = 93-96$ °C for SI-7/29. Above 96 °C the system has disordered spheres with short-range liquidlike order. The temperature dependence of I_m^{-1} and σ_q^2 changes with $1/T$ at around 132.5 °C, as approximated by two straight lines above and below 132.5 °C. This may imply that SI-7/29 undergoes DMT at 132.5 ± 0.5 °C. It is of great interest to point out that the $T_{LDOT} = 93-96$ °C determined from the SAXS measurement agrees very well with the temperature at which G' begins to decrease precipitously in the dynamic temperature sweep experiment (Figure 3). It should be mentioned that the T_{DMT} of SI-7/29 determined from the SAXS measurement is in very good agreement with that determined from the Han plot (Figure 5).

Since it is very important for us to highlight that the disordered spheres or micelles exist at thermal equilibrium, the desmeared SAXS profiles for SI-10/53 ($f = 0.13$) are given in Figure 9 at temperatures ranging from 160 to 200 °C. It can be seen from the SAXS

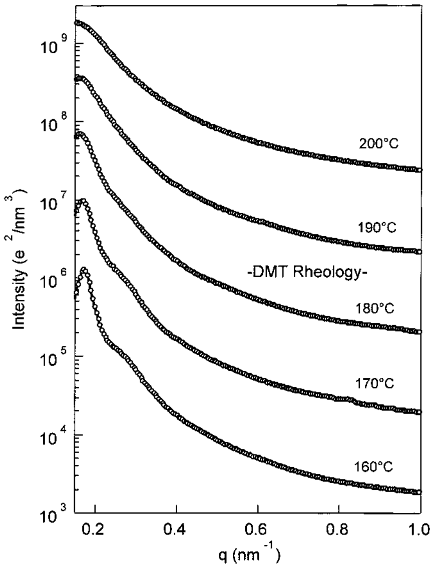

Figure 9. Temperature dependence of desmeared SAXS profiles in the heating process at various temperatures for SI-10/53, the thermal histories of which are described in Figure 2. The intensities of the profile at 160 °C shown at the bottom of this figure are actually measured absolute values, and the intensities of other profiles have been shifted up by 1 decade relative to the SAXS intensities of the profile immediately below.

Table 3. Summary of the Phase Transition Temperatures Determined for the SI Diblock Copolymers Investigated in This Study

	T_{LDOT} (°C)	T_{DMT} (°C)	
sample code	SAXS	rheology	SAXS
SI-7/29	93−96	135 ± 2	130−135
SI-10/53	130−140	185 ± 2	180−190
SI-12/83	165−170	205 ± 2	205−215

profiles of SI-10/53 given in Figure 9 that (i) at 140 °C $< T <$ 180 °C (which is far above the T_g of PS domains) the second-order shoulder at $q \approx 0.3$ nm^{-1} can be discerned, indicative of the existence of disordered spheres with short-range liquidlike order, and (ii) at $T >$ 190 °C the second-order shoulder is hard to discern, indicative of the presence of a disordered melt with thermal composition fluctuations but free from micelles. Thus, we determined the T_{DMT} of SI-10/53 to be 180−190 °C, which is in good agreement with that determined from the Han plot, though not shown here (see Table 3). Also, it was found from the SAXS profiles of SI-12/83, though not presented here, that (i) at 170 °C $< T <$ 205 °C (which is far above the T_g of PS domains) the disordered spheres remain as judged from a broad shoulder existing over the q range of $0.25 \le q \le 0.45$ nm^{-1} and (ii) the disordered spheres may be dissolved into a micelle-free homogeneous melt at $T \ge$ 215 °C. We thus determined the T_{DMT} of SI-12/83 to be 205−215 °C, which again is in good agreement with that determined from the Han plot, though not presented here (see Table 3).

For comparison, a precise temperature dependence of SAXS profile was investigated also for the symmetric block copolymer SI-9/9. Figure 10 gives the desmeared SAXS profiles for SI-9/9 at various temperatures ranging from 110 to 140 °C in the heating process (part a) and 135 to 80 °C in the cooling process (part b). Figure 10a shows that during the heating process the broadening of the first-order peak starts at approximately 130 °C and completes at 132 °C. Figure 10b shows that during the cooling process the sharpening of the first-order peak starts at approximately 130 °C and completes at 128 °C. Also, at 80 °C a higher-order peak appears at $q = 3q_m = 0.961$ nm^{-1}, indicating the formation of alternating lamellae of PS and PI chains having an almost equal volume fraction in the ordered state.

Figure 11 gives plots of (a) $1/I_m$ versus $1/T$ and (b) σ_q^2 versus $1/T$ and (c) the characteristic length ($D = 2\pi/q_m$) versus $1/T$ for SI-9/9 at temperatures ranging from 40 to 140 °C in the heating and cooling processes, respectively. The following observations are worth noting in Figure 11. Upon increase in temperature from 100 to 128 °C (decreasing $1/T$ from 2.68×10^{-3} to 2.49×10^{-3} K^{-1}), the peak intensity I_m decreases slightly and hence I_m^{-1} increases slightly. Upon further increase in temperature, I_m^{-1} and σ_q^2 sharply increase over a narrow temperature interval between 128 and 132 °C and reach nearly constant values between 132 and 140 °C. This observation indicates the onset of disordering at approximately 128 °C and the completion of disordering at approximately 132 °C; thus, we conclude that SI-9/9 undergoes ODT at 128−132 °C. In previous studies,[40,41] Koga et al. found a narrow temperature interval at around T_{ODT} where symmetric or nearly symmetric block copolymers, exhibiting the thermally induced first-order phase transition, can have coexistence of the ordered and disordered phases at thermal equilibrium. The system is expected to be in a non-mean-field disordered state at 132 °C $\le T \le$ 140 °C, the highest temperature covered in this experiment. Almost identical changes in I_m^{-1} and σ_q^2 with temperature across the T_{ODT} are observed during the cooling process, showing almost no hysteresis in the time scale of our observation, consistent with the observation reported earlier by Sakamoto and Hashimoto.[42] The temperature dependence of D does not change across the T_{ODT} within experimental accuracy of D in this study, again consistent with the earlier study by Sakamoto and Hashimoto.[42] It should be mentioned that the T_{ODT} of SI-9/9 determined from the SAXS measurement is in good agreement with that determined from oscillatory rheometry (see Figure 6).

4. Discussion

4.1. Temperature Dependence of Molecular Assembly in Highly Asymmetric Block Copolymers (at LDOT and DMT) and Symmetric or Nearly Symmetric Block Copolymers (at ODT). The results presented in section 3 above clearly support the differences in temperature dependence of molecular assembly, given schematically in Figure 1, between highly asymmetric block copolymers and symmetric or nearly symmetric block copolymers. Specifically, above we have demonstrated that three highly asymmetric SI diblock copolymers (SI-7/29, SI-10/53, and SI-12/83) having a low value of f (say $f \le 0.16$) undergo LDOT and DMT separately, while a nearly symmetric lamella-forming block copolymer (SI-9/9) undergoes only ODT, with LDOT and DMT being degenerated, giving rise to a disordered phase free from micelles. It should be emphasized that at $T_{LDOT} < T < T_{DMT}$ in highly asymmetric block copolymer the ordered phase with long-range order is lost and transformed into disordered spheres in which spherical microdomains exist as static objects, but with only short-range liquidlike order. The

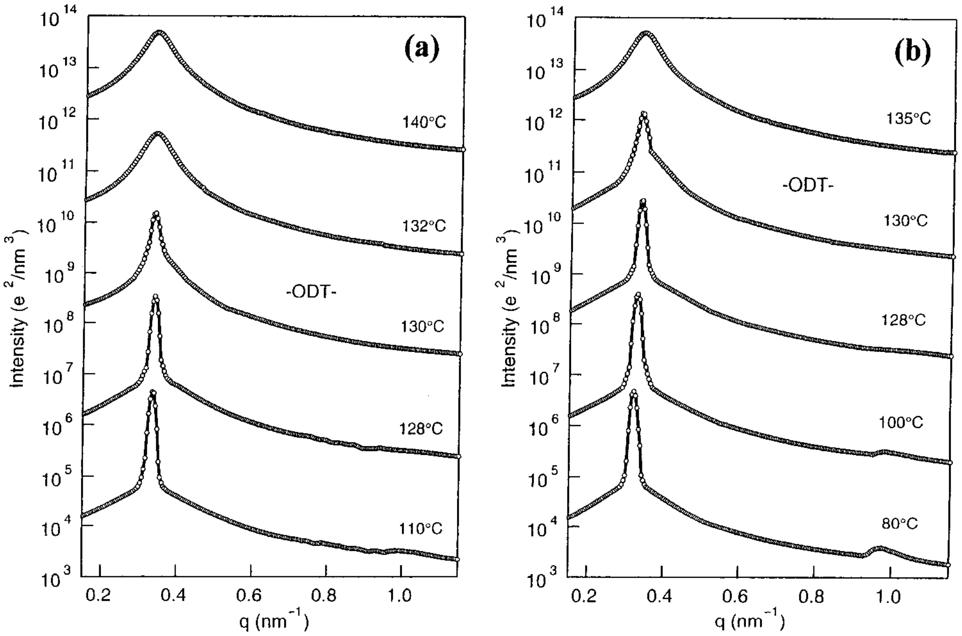

Figure 10. Temperature dependence of desmeared SAXS profiles for SI-9/9: (a) in the heating process; (b) in the cooling process. The intensities of the profiles at 110 and 80 °C shown respectively at the bottom of part a and part b of this figure are actually measured absolute values, and the intensities of other profiles have been shifted up by 2 decades relative to the SAXS intensities immediately below.

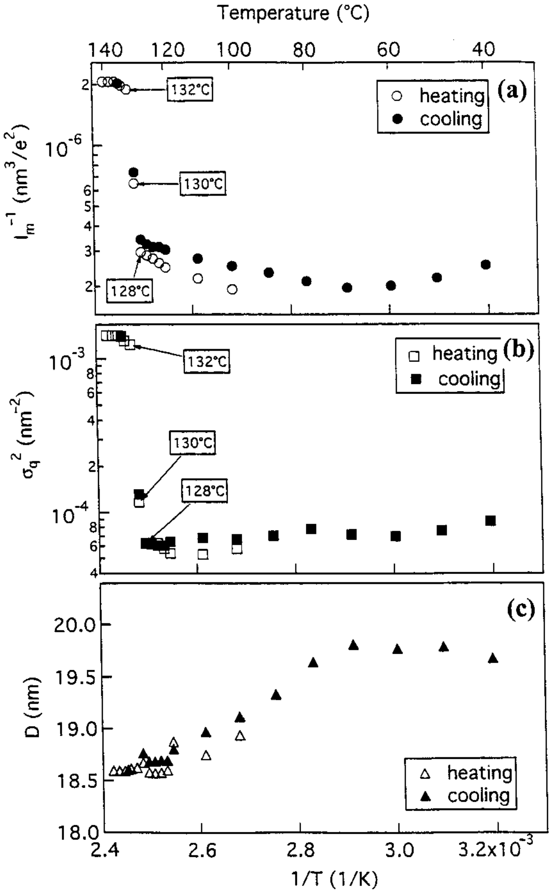

Figure 11. Plots of (a) $1/I_m$ versus $1/T$, (b) σ_q^2 versus $1/T$, and (c) D versus $1/T$ for SI-9/9.

existence of LDOT was clearly identified by a discontinuous change in the $1/I_m$ versus $1/T$ plot and/or σ_q^2 versus $1/T$ plot, which were obtained from SAXS experiments. Further we have presented the following pieces of evidence supporting the presence of disordered spheres in highly asymmetric block copolymer at $T_{LDOT} < T < T_{DMT}$. (1) The higher-order shoulder exists in the SAXS profile at temperatures even above the T_{LDOT}. (2) Scattering from disordered spheres with short-range liquidlike order can be described by the Percus–Yevick theory[43] or by the paracrystal theory based on “hard spheres”.[44,45] (3) Disordered spheres are static structural objects, which exist at any time instance within the time scale of experimental observation and at thermal equilibrium (existing up to 200 °C, for instance). (4) Disordered spheres are *not* dynamical objects which may appear and disappear at a certain relaxation time. If they were dynamical objects, one would not expect to observe a shoulder in the SAXS profile. (5) The Han plot exhibits a parallel shift with increasing temperature between the T_{LDOT} and the T_{DMT} and a liquidlike behavior in the low-frequency region owing to the flow of disordered spheres as a whole. (6) DMT is identified by SAXS and Han plots. Table 3 gives a summary of the T_{LDOT}'s and T_{DMT}'s of the three highly asymmetric SI diblock copolymers determined from the SAXS measurements and the Han plot.

It should be remembered that the Han plots in Figure 6 for the nearly symmetric SI diblock copolymer, SI-9/9 with $f = 0.47$, did not exhibit a parallel feature over the entire range of temperatures investigated, in contrast to the Han plots in Figure 5 for SI-7/29 with $f = 0.16$. There is no evidence suggesting that SI-9/9 with $f = 0.47$ undergoes LDOT and DMT separately over the entire range of temperatures investigated, i.e., the two transitions being degenerated into a single transition conventionally defined as ODT. Needless to say, this degeneracy is clearly supported by SAXS.

We wish to point out that when determining transition temperatures using $1/I_m$ versus $1/T$ and/or σ_q^2 versus $1/T$ plots from SAXS measurements, we applied different criteria to the highly asymmetric SI diblock copolymers (Figure 8). To facilitate our discussion here, we have prepared a schematic shown in Figure 12, in which the left panel represents the situation where we do *not* encounter LDOT and DMT separately, i.e., the

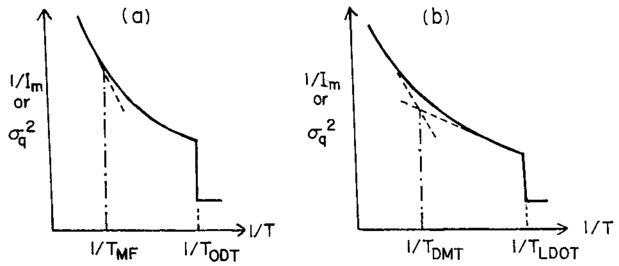

Figure 12. Schematic describing the temperature dependence of $1/I_m$ and σ_q^2 for (a) symmetric or nearly symmetric neat block copolymers having cylindrical or lamellar microdomains which are transformed directly into the micelle-free disordered state and (b) highly asymmetric block copolymer having spherical microdomains that undergo LDOT before reaching DMT.

two transitions being degenerated into ODT, and the right panel represents the situation where the two transitions are separated or not degenerated. So far, we have never encountered the situation where LDOT and DMT are separated when dealing with neat block copolymers having hexagonally packed cylindrical microdomains or lamellar microdomains. In such situations, we determined the T_{ODT} of a block copolymer by the temperature at which a discontinuity in $1/I_m$ or σ_q^2 occurred as indicated in Figure 12a,[34,46-50] in which T_{MF} denotes a crossover temperature[46] above which $1/I_m$ versus $1/T$ plots can approximately be described by the mean-field theory of Leibler;[2] i.e., the T_{MF} may be regarded as being the crossover temperature from the mean-field type to the non-mean-field type disordered state. The corresponding T_{MF} for the highly asymmetric block copolymer may exist at temperatures above T_{DMT} although this could not be determined in the present study.

On the other hand, in the present study dealing with highly asymmetric SI diblock copolymers, we have observed a discontinuity in $1/I_m$ and σ_q^2 at T_{LDOT} and no other discontinuity in $1/I_m$ and σ_q^2 at $T > T_{LDOT}$, as schematically shown in Figure 12b. Hence, in the present study we tentatively have assigned the temperature at which the two dotted straight lines, drawn on the σ_q^2 versus $1/T$ plot or on the I_m^{-1} versus $1/T$ plot (see Figure 8), intersect to be T_{DMT}. We showed that T_{DMT} thus determined from SAXS is in good agreement with T_{DMT} determined from the Han plot. DMT takes place continuously, which may be due to the lack of sensitivity in the current experimental methods. We may expect that demicellization transition takes place when the micellar size becomes smaller than the critical size or the association number (an average number of block copolymer chains per single micelle) becomes smaller than a critical value. The demicellization/micellization transition may cause a discontinuous change in some physical properties if the experimental methods are sufficiently sensitive. At present we have no theoretical basis upon which T_{DMT} can be determined using the procedures described above. We believe that a curvature in the $1/I_m$ versus $1/T$ and σ_q^2 versus $1/T$ plots for the highly asymmetric SI diblock copolymers, obtained from the SAXS measurements in the present study (Figures 8), has *little* to do with thermally induced composition fluctuations in the micelle-free homogeneous state.

4.2. Rheological Methods for Determining the T_{ODT} or T_{DMT} of a Block Copolymer.

Above we have shown very clearly that the isochronal dynamic temperature sweep experiment is useful to determine the T_{ODT} of the nearly symmetric diblock copolymer, SI-9/9 (Figure 6), but not the T_{DMT}'s of the highly asymmetric diblock copolymer, SI-7/29 (Figure 3). This observation should warn those who wish to determine the T_{DMT} of highly asymmetric block copolymers (where, approximately, $0.1 < f < 0.16$) using the dynamic temperature sweep experiment under isochronal conditions. On the other hand, in this study we have shown that the Han plot is very effective to determine both the T_{ODT}'s of nearly symmetric SI diblock copolymers and the T_{DMT}'s of highly asymmetric SI diblock copolymers. The values of the T_{ODT} and T_{DMT} determined from the Han plots agree well with those determined from the SAXS study. The criterion that a threshold temperature, during heating, at which the Han plot having a slope of 2 in the terminal region begins to be independent of temperature can be used to determine the T_{ODT} or T_{DMT} of a block copolymer has as its basis a molecular viscoelasticity theory.[37]

Previously, some investigators[33,34] interpreted the parallel feature of the Han plot, having a slope of 2 in the terminal region, of a block copolymer as being a signature for thermally induced composition fluctuations in the micelle-free homogeneous state. Such an interpretation is not warranted for the three SI diblock copolymers (SI-7/29, SI-10/53, and SI-12/83) investigated in this study, because both the TEM images (Figure 4) and the SAXS results (Figures 7 and 8) show clearly that at $T_{LDOT} \leq T < T_{DMT}$ each of the SI diblock copolymers has disordered spheres with short-range spatial order. The origin of the parallel feature of the Han plot observed in the terminal region at $T_{LDOT} \leq T < T_{DMT}$ (Figure 5) is primarily attributable to flow of the disordered spheres as a whole.[17,20] This flow would control the low-frequency rheological behavior, giving rise to liquidlike rheological response (e.g., $G' \propto \omega^2$ and $G'' \propto \omega$) even though there exist microdomains. Hence, the SI diblock copolymers are in an ordered state or microphase-separated state in comparison with the disordered state free from micelles.

If we were to regard the parallel feature of the Han plot in Figure 5 as being a signature of the presence of thermally induced composition fluctuation effects in the micelle-free disordered state, the following questions must be answered. (1) What would be the T_{DMT} of SI-7/29 if its T_{DMT} is not 135 °C? (2) What would be the T_{DMT} of SI-10/53 if its T_{DMT} is not 185 °C? (3) What would be the T_{DMT} of SI-12/83 if its T_{DMT} is not 205 °C? (4) Why is there *no* parallel feature (thus, negligible thermally induced composition fluctuation effects) in the Han plot for the *nearly* symmetric SI diblock copolymer, SI-9/9, shown in Figure 6? (5) What might be the mechanism that would give rise to thermally induced composition fluctuation effects as much as 37−45 °C only in highly asymmetric SI diblock copolymers (SI-7/29, SI-10/53, and SI-12/83), but not in a nearly symmetric SI diblock copolymer (SI-9/9)? We cannot think of any physical reasons that would give rise to very large thermally induced composition fluctuations *only* in highly asymmetric block copolymers and little in nearly symmetric block copolymers.

It should be mentioned at this juncture that the parallel feature having a slope of 2 in the terminal region of the Han plot, observed in Figure 5, is not unique to highly asymmetric SI diblock copolymers. As a matter of fact, earlier, a similar observation was reported for a highly asymmetric ($f = 0.11$) SIS triblock copolymer.[51] It was also reported earlier that nearly symmetric SIS triblock copolymers did *not* exhibit the parallel feature in Han plots,[38c] consistent with the findings reported above in Figure 6 for the nearly symmetric SI diblock copolymer, SI-9/9.

4.3. Interpretation of a Minimum Observed in the Temperature Dependence of G' from the Isochronal Dynamic Temperature Sweep Experiment. The temperature dependence of G' observed from the dynamic temperature sweep experiment under isochronal conditions at $\omega = 0.01$ rad/s showed a minimum at a particular temperature as shown in Figure 3, which depends on the thermal history of a block copolymer. This trend turns out to be parallel to the improved long-range order as shown in the SAXS results (Figures 7 and 8).

Let us focus on the SAXS results shown in Figure 8. In the heating process from 60 to 93 °C, the long-range order of bcc tends to increase, due to an annealing effect. However, in the temperature range from 60 to 83 °C the time available for the system to improve the long-range order may not be sufficient, so that $1/I_m$ and σ_q^2 remain essentially unchanged. In the temperature range from 83 to 93 °C, above the glass transition temperature of polystyrene spherical microdomains ($T_{g,PS}$), the system may have sufficient mobility, so that it can improve the long-range order within the given time scale of our experiment. In fact, with prolonged annealing at 77 °C, below or near $T_{g,PS}$, the system can achieve almost the same level of long-range order as that obtained by annealing above $T_{g,PS}$ (see the data shown with filled symbols in Figure 8). This interpretation is believed to provide a good explanation for the observed minimum in G' versus temperature plots in Figure 3.

As the temperature is increased toward $T_{g,PS}$, the spherical microdomains soften and hence G' decreases. However, the system tends to achieve a more perfect bcc structure with fewer defects inside the crystal grains and with smaller grain boundary areas or volumes within the given time scale of our rheology experiments, which tends to increase G' with increasing T. The higher the temperature, the more perfect the bcc crystal and hence the higher the modulus G'. Thus, the softening of PS spheres and improved long-range order of bcc crystal due to this annealing effect can explain the observed minimum in G' versus temperature plots. If the system has well-ordered bcc crystals as an initial state, as in the specimen annealed at 90 °C for 14 days (Figure 3), only softening of the PS spheres dominantly occurs upon raising the temperature, so that G' tends to decrease continuously until the temperature reaches T_{LDOT}. We believe that essentially the same explanation can be applied to other asymmetric block copolymers.

4.4. Comparison of the Present Study with Earlier Studies on Highly Asymmetric Block Copolymers. In their 1994 paper, Register and co-workers[15] determined the microphase separation transition temperature (T_{MST}) in highly asymmetric SI and SIS block copolymers from isochronal dynamic temperature sweep experiments and dynamic frequency sweep experiments. Below, we first describe very briefly the highlights of that paper. (1) Without showing SAXS data, they claimed that their SAXS data indicated that their block copolymers showed no lattice over the entire range of temperatures covered. (2) They determined T_{MST} by the temperature at which the change in temperature dependence of G' occurred in the isochronal dynamic temperature sweep experiment and the change in temperature dependence of low-frequency G' occurred in the isothermal dynamic frequency sweep experiments. They indicated that at temperatures above T_{MST} the localization of the block junction at the domain interface was relaxed and the long-time component of the relaxation spectrum vanished and that their highly asymmetric sphere-forming block copolymers were in the homogeneous state with large composition fluctuations as in the case of lamella-forming block copolymers. T_{MST} was meant to correspond to T_{DMT} in our definition, as their system was described to have disordered spheres in our terminology. (3) They concluded that the parallel feature in the Han plot signified the presence of the large-amplitude composition fluctuations near MST, and their block copolymers gave rise to composition fluctuation effects as wide as 40−50 °C in the temperature range.

Considering the fact that the volume fraction of PS block ($f \approx 0.11$) of the SI diblock and SIS triblock copolymers investigated by Register and co-workers[15,16] is very close to that ($f = 0.11-0.16$) of the SI diblock copolymers investigated in this study, we conclude that the values of T_{MST} reported by Register and co-workers[15,16] represent more likely the T_{LDOT} and not the T_{DMT}. According to our results presented in Figures 3−5, T_{LDOT} is considerably lower than T_{DMT}. There is no justification, theoretical or experimental, for determining the T_{MST} of a block copolymer from a change in temperature dependence of low-frequency G' in the isochronal dynamic temperature sweep experiments. In this paper, we have demonstrated that the T_{ODT} (T_{MST} in the terminology by Register and co-workers) of a symmetric or nearly symmetric block copolymer can be determined from the isochronal dynamic temperature sweep experiment *only when* low-frequency G' drops precipitously. Further, we have demonstrated from an independent SAXS experiment that the temperature at which G' drops precipitously for highly asymmetric block copolymers corresponds to T_{LDOT} and not T_{DMT} . As discussed above, the presence of the parallel feature in the Han plot with a slope of 2 observed in the terminal region at $T_{LDOT} \leq T < T_{DMT}$ is attributable to the flow of disordered spheres having short-range liquidlike order (or micelles) as a whole and not to thermally induced composition fluctuations. Thus, it is very clear that our conclusions are quite different from those made by Register and co-workers.[15]

In a subsequent paper,[16] Register and co-workers reported the values of T_{ODT}, which were slightly higher than the values of T_{MST} reported in their earlier paper,[15] of the same block copolymers. They used T_{ODT} in place of T_{MST}. We make the following observations in the 1996 paper of Register and co-workers.[16] They recognized the existence of lattice structure at $T < T_{ODT}$ (using their terminology) by stating that, on the basis of SAXS results (Figure 2 of a paper by Register and co-workers[16]), at $T < T_{LDOT}$ (using our terminology) there are higher-order peaks at $\sqrt{2}$ and $\sqrt{3}$. At $T > T_{ODT}$ there are no higher-order peaks, but there is a "bump" indicative of the existence of micelles with a liquidlike order, which is consistent with our present results. However, they stated that (i) no significant distinction between large-amplitude composition fluctuations and a disordered arrangement of spheres could be made and (ii) because the fluctuations in these asymmetric block copolymers could attain large amplitudes, the styrene-rich regions could severely retard chain diffusion as $T_{g,PS}$ was approached. Such statements are correct when T_{LDOT} approaches $T_{g,PS}$ of the polystyrene-rich region. This should occur in the case when T_{LDOT} is low, so that $T_{LDOT} < T_{g,PS} \cong 60$ °C, where the large-amplitude composition fluctuations may be effectively vitrified and exist as a nonequilibrium structure (i.e., disordered spheres can exist as a nonequilibrium structural entity). However, even in the case when T_{ODT} (in their terminology) or T_{LDOT} (in our terminology) is as high as 164–167 °C (T149 in Table 1 of a paper by Register and coworkers[16]), we observe a bump in the SAXS profile at $T > T_{LDOT}$ (e.g., at $T = 180$ °C in Figure 14 of a paper by Register and co-workers[16]). Thus, we should clearly recognize that the disordered spheres (or micelles) definitely exist at thermal equilibrium. Our results also clearly show that the SAXS bump or shoulder exists at temperatures up to 180 °C for SI-10/53 (Figure 9) or up to 205 °C for SI-12/83 (Table 3). When we recognize the disordered spheres as a structural entity existing at thermal equilibrium, it is reasonable for us to expect that a transition temperature T_{DMT} (which is higher than T_{LDOT}) would exist, at which the disordered spheres disappear over a sufficiently narrow temperature range, forming the micelle-free homogeneous phase.

Register and co-workers[16] regarded the disordered spheres existing at temperatures above T_{LDOT} (in our terminology) as nonequilibrium structures, which are vitrified large-amplitude composition fluctuations or large-amplitude composition fluctuations having very long relaxation times. This may be true only when $T_{LDOT} \leq T_{g,PS}$ or T_{LDOT} is slightly above $T_{g,PS}$. However, there are many cases where $T_{LDOT} \gg T_{g,PS}$ and disordered spheres exist at temperatures even up to ca. 200 °C, in the present study. Thus, we should regard that the disordered spheres exist at thermal equilibrium.

5. Concluding Remarks

In this paper we have introduced new terminologies, LDOT and DMT, to describe temperature dependence of molecular assembly in highly asymmetric block copolymers, as schematically shown in Figure 1. We have pointed out that the distinction must be made between LDOT and DMT in that (i) at temperatures above T_{LDOT} but below T_{DMT} disordered spheres having short-range liquidlike order exist at thermal equilibrium and (ii) at temperatures above the T_{DMT} the micelles disappear and result in thermally induced composition fluctuations with a temperature-dependent characteristic relaxation time. Here we are not claiming that DMT is a well-defined thermodynamic phase transition, but rather that the distinction between the two states (states i and ii described above) is very crucial. In other words, micelles or disordered spheres with well-defined interface undergoing Brownian motion (at $T_{LDOT} < T < T_{DMT}$) should be distinguished from dynamical composition fluctuations in the micelle-free disordered melts (at $T > T_{DMT}$), at least for correct interpretations of the results from SAXS or small-angle neutron scattering and the low-frequency rheological properties. At temperatures below the T_{DMT}, the spheres with a sharp interface may be packed in a bcc lattice if the random thermal force is weak compared to the force forming the lattice as in the case in which the Landau-type mean-field theory is applicable.[2] The DMT defined here is not a thermodynamically precise phase transition in the sense that it does not occur in effectively infinite system and hence with infinite sharpness. It may be rather regarded as a pseudo-phase transition in the sense that it involves effectively a finite number of block copolymer molecules and hence occurs over a finite range (possibly a rarrow range) of temperatures. It may well be regarded as a phase transition for a finite system, clarification of which is beyond the scope of the present study and deserves future theoretical considerations. On the other hand, LDOT is essentially a true phase transition in the rigorous thermodynamic sense described above. However, when it is called ODT, one should note the difference in the molecular assembly above ODT between asymmetric block copolymers and symmetric or nearly symmetric block copolymers (see Figure 1).

We distinguish two different situations in the disordering processes in block copolymer with increasing temperature: (i) one situation involves the transformation of micelles with long-range order with bcc symmetry to those without long-range order followed by transformation into the micelle-free homogeneous state (in the case of micelle- or sphere-forming block copolymers), and (ii) another situation involves a direct transformation of lamellae or cylinders with long-range order into the homogeneous phase free from phase-separated structure, where blocks are mixed on a molecular level with thermal composition fluctuations. In the literature the latter situation commonly has been referred to as ODT. The terms LDOT and DMT may help highlight these two different situations.

What might be possible physical factors that necessitate us to distinguish the two different situations described above? We can think of two factors: (i) thermodynamic stability of domains themselves (e.g., lamellae, cylinders, spheres (or micelles), etc.) and (ii) thermodynamic stability of lattice or long-range order. In sphere-forming block copolymers, the first stability (i) is greater than the second stability (ii); thus, the lattice may be more susceptible to the thermal agitation than the domain, and the lattice may be disintegrated at a lower temperature than the micelles themselves. However, in lamella-forming or cylinder-forming block copolymers, the two factors are equally or nearly equally important. Thus, domains and lattices are destroyed at the same or nearly same temperature as found experimentally. In the context of the Landau-type mean-field theory[2] in which effects of thermal agitation are negligible, the LDOT and DMT are degenerated.

If the temperature is increased toward T_{DMT} during heating, the size of micelle, R, will decrease. If R becomes smaller than a certain critical value, R_c, the micelles become thermodynamically unstable, resulting in disintegration and thus forming the micelle-free homogeneous phase. According to this picture, both micellization and demicellization may occur discontinuously over a narrow range of temperatures and thus they can be regarded as being a phase transition in small systems or a pseudo-phase transition. In the literature we find that such terminologies, as critical micelle concentration and critical micelle temperature, are often used. Therefore, our suggestion for using the terminology “micellization/demicellization transition” in highly asymmetric (sphere-forming) block copolymers seems to be in consonance with the literature.

Now, for the sake of comparison, let us consider micelles in surfactants, e.g., a dilute solution of sodium dodecyl sulfate in water. One may consider that such a system has a phase transition between the micelles in the long-range order and the micelles in the short-range liquidlike order. On the other hand, one may consider that micellization/demicellization is not a well-defined phase transition. From this kind of analogy one may consider that the phase transition in the highly asymmetric block copolymers employed in the present study involves only phase transition of LDOT and thus LDOT can be called ODT. However, one may notice that such an analogy is not necessarily warranted, when one notes that the micelles formed in a dilute solution of sodium dodecyl sulfate have strong interactions (hydrophobic and hydrophilic interactions), and such a solution may not necessarily transform into the micelle-free homogeneous phase over a narrow range of temperatures. If this is the case, the phase transition involving a loss or creation of long-range order of the micelles is the only phase transition, and hence this transition can be called ODT and the phase having micelles without long-range spatial order can just be called disordered phase. The same argument can also be applied to metals. The atoms forming bcc lattice never disappear; thus, the phase transition that involves the disappearance and appearance of bcc symmetry can be called ODT. In the two examples given above, the micelles or atoms are fundamental structural elements. In contrast, the block copolymer melts of our interest have only weak interactions of the London dispersive force, and thus T_{DMT} can exist in a block copolymer though it is only defined over a finite range (possibly over a narrow range) of temperatures. In other words, the spheres or micelles in highly asymmetric block copolymers are not necessarily fundamental structural elements, because they disintegrate into block copolymer molecules in the micelle-free disordered state. Therefore, in this sense, block copolymer melts are different from surfactants and metals.

In this paper we have pointed out that the parallel feature observed in the Han plot, which gives rise to liquidlike rheological responses in the terminal region of the highly asymmetric SI diblock copolymers investigated (SI-7/29, SI-10/53, and SI-12/83), originated from the presence of disordered spheres having short-range liquidlike order as the static structural entity and from flow of these spheres as a whole. The disordered spheres are considered to be the static structural entity because they do not disintegrate and form as a whole with a certain lifetime or relaxation time as in the case of composition fluctuations in the sphere-free disordered state. On the other hand, we did *not* observe the parallel feature in the Han plot for the nearly symmetric SI diblock copolymer, SI-9/9. Thus, we conclude that the parallel feature observed in the Han plot for the SI-7/29, SI-10/53, and SI-12/83 should *not* be construed as being a signature of the presence of thermally induced composition fluctuation effects in the micelle-free homogeneous state, as in the case of lamella-forming block copolymers.

Since the rheological measurements cannot reveal the type of microdomain structure when a block copolymer undergoes OOT, in the present study we conducted TEM and SAXS experiments. Our SAXS experiments reveal that the three highly asymmetric SI diblock copolymers (SI-7/29, SI-10/53, and SI-12/83) do *not* undergo OOT, although a minimum in G' from the isochronal dynamic temperature sweep experiment was observed for certain specimens. We found that such a minimum in G' disappeared when a specimen was annealed for a sufficiently long time. Thus, we concluded that a minimum in G' observed from the isochronal dynamic temperature sweep experiment was attributable to annealing effect. This finding is very significant in that one must make certain that a block copolymer, especially a highly asymmetric block copolymer, is annealed for a sufficiently long time to attain an equilibrium morphology before an isochronal dynamic temperature sweep experiment is conducted.

We wish to mention that, in the past, numerous investigators have reported on the ODT in symmetric or nearly symmetric block copolymers using SAX and/or oscillatory rheometry, without ever having taken differential scanning calorimetry (DSC) measurements. However, in recent years some investigators[40,52−54] reported on the DSC characterization of ODT in nearly symmetric or symmetric block copolymers. Such studies certainly enrich our knowledge on the nature of the ODT. The calorimetric determination of LDOT in *highly asymmetric* block copolymers may be as feasible as that of ODT in *symmetric* or *nearly symmetric* block copolymers. We are of the opinion, however, that the calorimetric determination of DMT in highly asymmetric block copolymer will be extremely difficult, if not impossible. We would like to encourage others to investigate calorimetric determination of LDOT and DMT in highly asymmetric block copolymers as a future study.

In closing, in the present study we have shown, via oscillatory shear rheometry, TEM, and SAXS, that highly asymmetric SI diblock copolymers undergo LDOT before reaching DMT, whereas nearly symmetric SI diblock copolymers undergo only ODT. We believe that such distinction in disordering and ordering processes between symmetric or nearly symmetric block copolymers and highly asymmetric block copolymers would be applicable to other types of block copolymers. We believe further that such distinction is of fundamental importance to a better understanding of changes in molecular assembly in block copolymers with temperature and changes in physical properties associated with the structural changes.

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