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Determination of Order−Order and Order−Disorder Transition Temperatures of SIS Block Copolymers by Differential Scanning Calorimetry and Rheology

Jin Kon Kim,*,† Hee Hyun Lee,† Qi-Jiang Gu,‡ Taihyun Chang,‡ and Yoon Hee Jeong§

Departments of Chemical Engineering and the Polymer Research Institute, of Chemistry, and of Physics,
Pohang University of Science and Technology,
Pohang, Kyungbuk 790-784, Korea

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Numerous studies have been reported on the order−disorder transition (ODT) of block copolymers experimentally determined by either rheology[1,2] or small-angle X-ray (or neutron) scattering (SAXS or SANS) methods. Recently, it was found that some block copolymers have multiple ordered states. The transition from one ordered state to another is referred to as the order−order transition (OOT).[3,4] Previously, the OOT was determined by an abrupt increase in dynamic shear modulus (G') or by a change in the positions of higher order peaks in SAXS profiles with increasing temperature. Leibler[5] and Fredrickson and Helfand[6] predicted that both ODT and OOT are first-order transitions. However, first- and second-order transitions are not determined in principle by rheological methods,[1−4] for instance, the temperature sweep of the storage shear modulus (G') or logarithmic plots of G' and the loss shear modulus (G''), since shear moduli obtained under a flow condition are not a thermodynamic property. To test whether OOT or ODT is a first-order transition, first-order thermodynamic properties such as volume and entropy should be investigated. However, due to difficulty in measurement of entropy change experimentally near a transition, a heat flow or enthalpy change using differential scanning calorimetry (DSC) can be measured. When either an exothermic or endothermic peak is observed from DSC thermograms at a specific transition temperature except a peak corresponding to an enthalpy relaxation near the T_g, such a transition is considered as a first-order transition. Recently, using DSC, some research groups observed an endothermic peak occurring at T_{ODT} for polystyrene-*block*-polyisoprene (SI) copolymers[7] and for other block copolymers.[8]

However, to the best of our knowledge, there is no report that investigates the OOT of a block copolymer using DSC. Thus it is not known whether the OOT is indeed a first-order transition. In this paper, we demonstrate by using DSC that an OOT between a hexagonally packed cylinder (HEX) and body-centered cubic (BCC) is indeed thermally reversible, and we demonstrate a first-order transition in an SIS copolymer having a weight fraction of the PS block of 0.183.

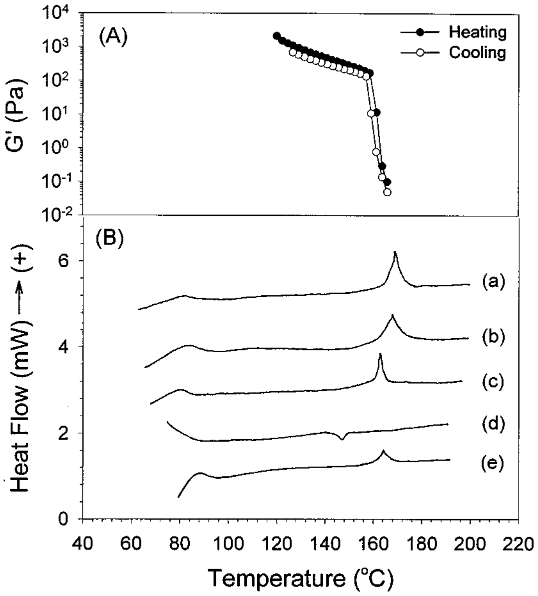

Figure 1. (A) Temperature sweep of G' at $\omega = 0.1$ rad/s and $\gamma_o = 0.05$ for SIS-L1 obtained during heating (●) and cooling (○) at a rate of 1 °C/min. (B) DSC thermograms for SIS-L1. Curves a−c were obtained during the first heating at rates of 20, 10, and 5 °C/min, respectively. Curve d was obtained during the first cooling at a rate of 20 °C/min after annealing for 10 min at 190 °C. Curve e was obtained during the second heating at a rate of 20 °C/min. Heat flows in curves d and e are multiplied by a factor of 4.

Two polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) copolymers, Vector 4111 (total weight-average molecular weight (M_w) of 143 800 and the weight fraction of the PS block of 0.183) and SIS-L1 (M_w of 37 600 and the weight fraction of the PS block of 0.595), were employed in this study. Using synchrotron SAXS and transmission electron microscopy (TEM), we found that SIS-L1 has lamellar microdomains, while Vector 4111 has an OOT between HEX and BCC microdomains.[9] Samples were prepared by solution casting in toluene (~10 wt % in solid) in the presence of an antioxidant (Irganox 1010; Ciba-Geigy Group) and then annealed for 2 days at 100 °C for SIS-L1 and at 140 °C for Vector 4111 in a vacuum oven. Vector 4111 was shear-aligned by an oscillatory shearing with large strain amplitude (100%) to obtain aligned HEX microdomains on a macroscopic scale. Using an advanced rheometric expansion system (ARES) with parallel plates of 25 mm in diameter, dynamic temperature sweep experiments were performed at the frequency (ω) of 0.1 rad/s and the strain amplitude (γ_o) of 0.05 under a nitrogen environment to reduce a possible thermal degradation. DSC thermograms were obtained by using a Perkin-Elmer DSC-7 series under a nitrogen atmosphere at various heating and cooling rates with a baseline correction.

The upper panel in Figure 1 gives the results of temperature sweep of G' during heating and cooling at a rate of 1 °C/min for SIS-L1, from which we observe that G' decreases precipitously at 158 ± 1 °C. According to a rheological criterion,[10] the order-to-disorder transition (ODT) temperature, T_{ODT}, is taken as the temperature where a precipitous decrease in G' appears; the value of T_{ODT} is 158 ± 1 °C. It is of interest to note that the disorder-to-order transition (DOT) during cooling occurs at a temperature almost the same as the T_{ODT}

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* To whom correspondence should be addressed. E-mail: jkkim@postech.ac.kr.

† Department of Chemical Engineering and Polymer Research Institute.

‡ Department of Chemistry.

§ Department of Physics.

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obtained during heating. The lower panel of Figure 1 gives DSC thermograms obtained at various conditions for SIS-L1. It was found that during the first heating, in addition to an enthalpy relaxation peak of the PS block occurring at ~80 °C, an endothermic peak near 165 °C is clearly observed. It is of interest to find that (1) the area of endothermic peak (enthalpy change; ΔH) and the peak temperature gradually decrease with decreasing heating rate, which is generally observed for the DSC melting peak of a semicrystalline polymer; (2) when the heating rate is 5 °C/min (curve c), the peak temperature is almost the same as the T_{ODT} determined from temperature sweep experiments of G'; (3) when the first cooling scan at a rate of 20 °C/min is performed from a disorder state (190 °C) to 40 °C, a small exothermic peak is clearly seen (curve d); and (4) during the second heating at a rate of 20 °C/min, we again observe an endothermic peak (curve e). It should be mentioned that the difference in peak positions during cooling and heating scans is due to a large scan rate of 20 °C/min. The confirmation of exothermic and endothermic peaks during the first cooling and the second heating scan is very important to determine the ODT since the first heating scan may reflect many thermal histories of a sample. For instance, one may argue that an endothermic peak during heating might result from the flowing of a block copolymer in the DSC sample pan due to a rapid decrease in the modulus. Notice that when the original solid sample is placed in the DSC pan, there always exist some empty spaces in the DSC pan where the solid sample does not cover. Thermal conduction through the polymer might be different from that through the empty spaces in the DSC pan. Once a block copolymer begins to flow and becomes molten, the bottom of the DSC sample pan is entirely covered with the block copolymer. Thus, it is speculated that a small amount of heat may be required when a solid sample becomes molten. This suggests that an endothermic peak may be observed even at the temperature where the modulus decreases significantly and the block copolymer starts to flow. Thus, this temperature is not necessarily the same as the T_{ODT}. However, during the cooling from the disordered state and the second heating scans, the above effect could be negligible. Therefore, the endothermic peak obtained during the second heating and exothermic peak obtained during the first cooling, as shown in Figure 1, clearly correspond to the ODT and DOT, respectively. These DSC results are in excellent agreement with rheological results.

The upper panel in Figure 2 gives the results of temperature sweep of G' and G'' during heating for Vector 4111. G' first decreases slowly with increasing temperature and reaches a minimum. Then, G' increases and reaches a maximum and finally decreases again. This behavior was previously reported by Sakamoto et al.[11] When the OOT is taken as the temperature where a minimum in G' appears,[4] the T_{OOT} is estimated to be 181 ± 1 °C. The highlights of DSC thermograms for Vector 4111 are given in the lower panel in Figure 2. We found that all transitions in thermograms are reproducible and quite reliable. It can be seen in curve a that in addition to an enthalpy relaxation peak near T_g of the PS block, there exist two additional peaks: one is an exothermic peak (represented by an upward arrow, ↑) occurring at ~192 °C, and the other is an endothermic peak (represented by downward arrow, ↓) occurring at ~275 °C. When the heating rate was reduced to 5 °C/min (curve b), the exothermic and endothermic peak temperatures were reduced to ~183 and ~255 °C, respectively. The reduction in the transition temperatures with decreasing heating rate is due to a kinetic effect, as shown in the lower panel of Figure 1. It is noted that the temperature where an exothermic peak occurs at 183 °C in curve b is almost the same as the T_{OOT} determined from temperature sweep experiment of G'. Therefore, we conclude that the OOT from HEX to BCC becomes an exothermic process. To the best of our knowledge, it is the first observation that an OOT from HEX to BCC microdomains as determined by DSC becomes a first-order transition and an exothermic process.

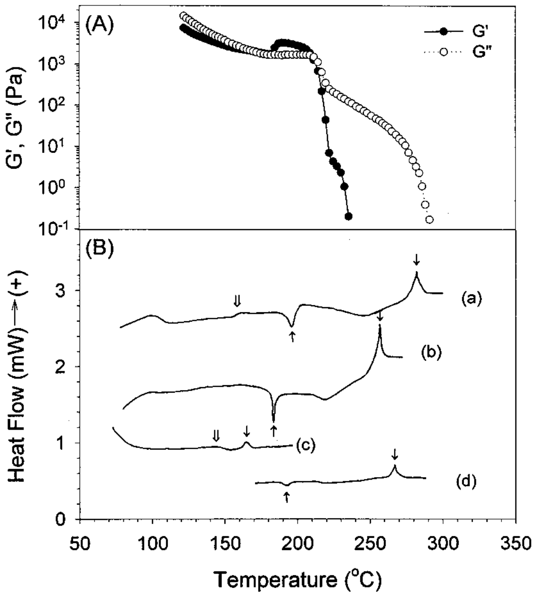

Figure 2. (A) Temperature sweep of G' (●) and G'' (○) at $\omega = 0.1$ rad/s and $\gamma_o = 0.05$ for Vector 4111 during heating at a rate of 1 °C/min. (B) DSC thermograms for Vector 4111. Curves a and b were obtained during the first heating at rates of 20 and 5 °C/min, respectively. Curve c was obtained during the first cooling at a rate of 20 °C/min after annealing at 200 °C for 2 h. Curve d was obtained during the second heating at a rate of 20 °C/min after the above cooling scan was performed and followed by annealing at 160 °C for 2 h.

Now, we consider why an exothermic peak is observed during a transition from HEX to BCC microdomains. The Gibbs free energy change (ΔG) from HEX to BCC microdomains can be written as

$$\Delta G = G_{\mathrm{BCC}} - G_{\mathrm{HEX}} = \Delta H - T_{\mathrm{OOT}}\Delta S = H_{\mathrm{BCC}} - H_{\mathrm{HEX}} - T_{\mathrm{OOT}}(S_{\mathrm{BCC}} - S_{\mathrm{HEX}}) \quad (1)$$

At the T_{OOT}, $\Delta G = 0$, thus the enthalpy change ($\Delta H = H_{\mathrm{BCC}} - H_{\mathrm{HEX}}$) at the T_{OOT} is equal to the entropy change ($\Delta S = S_{\mathrm{BCC}} - S_{\mathrm{HEX}}$) times T_{OOT}. When $\Delta H < 0$, this transition is regarded as an exothermic process, where $\Delta S < 0$ due to the criterion of $\Delta G = 0$. Therefore, an exothermic peak given in curve a in the lower panel of Figure 2 implies that S_{BCC} would be less than S_{HEX}. It may be contradictory to one's expectation that the conformational entropy (S_{conf}) of HEX is smaller than that of BCC. Here, S_{conf} is the entropy resulting mainly from the chain conformations of PS and PI block chains forming a microdomain. According to a self-consistent field theory recently developed by Matsen and Bates,[12] the entropy change at an OOT from HEX to BCC, ΔS_{conf}, for a diblock copolymer becomes positive for $\chi N < 60$, in which χ is the Flory interaction parameter and N is the total number of segments in the block copolymer. The positive value of ΔS_{conf} is attributed to the fact that, in order to satisfy the uniform density requirement, matrix chains in BCC are less stretched than those in HEX, because the curvature of microdomains in BCC is larger than that in HEX. Although Matsen and Bates' theory had been developed for a diblock copolymer, ΔS_{conf} for a triblock copolymer might be assumed to be positive even if bridge and loop conformations of block chains must be considered, which is inconsistent with the above results. Thus, in this study, in addition to S_{conf}, we consider the other entropy, namely, the packing entropy (S_{pack}) resulting from the distribution of many microdomains (or regularity in the packing of the microdomains) in a given volume. The S_{pack} of HEX seems to be similar to that of BCC because both microdomains are fixed in their space groups. Thus, when HEX microdomains are directly transformed into BCC microdomains, an endothermic peak is expected.

However, once undulated cylinders are formed near the transition between HEX and BCC microdomains, the situation becomes quite different. Many research groups[13-16] suggested the formation of undulated cylinders during the transition from HEX to BCC microdomains. We consider that the S_{pack} of undulated cylinders would be much larger than that of BCC microdomains because in the latter the microdomains are fixed at the BCC configuration. Although S_{conf} of undulated cylinders seems to be smaller than that of BCC microdomains, the difference is not large. This is because the curvature in undulated cylinders is similar to that of BCC and there are bridge and loop conformations of block chains preventing free relaxation in matrix phases. Therefore, during the transition from undulated cylinders to BCC microdomains, ΔS_{pack} would dominate over ΔS_{conf}, which leads us to conclude that the entropy change from undulated cylinders to BCC microdomains becomes negative. This implies that an exothermic peak is expected during this transition, which is consistent with results given in the lower panel of Figure 2. However, one might consider that for a diblock copolymer, ΔS_{conf} becomes more important compared with a triblock copolymer, since there is no bridge and loop conformation in the diblock copolymer. The investigation of heat flow change near the OOT in a diblock copolymer is in progress.

Then, a question may be raised as to why an endothermic (or exothermic) peak is not observed in the transition from HEX microdomains to undulated cylinders (or vice versa) at temperatures lower than the T_{OOT}. Although a detailed explanation on this is beyond the scope of this paper, this transition might not be first order. In other words, since HEX microdomains might continuously change their shapes to undulated cylinders as the temperature approaches the T_{OOT}, there is no need for a discontinuity in enthalpy (or in entropy) in DSC thermograms; rather, a slope change in heat flow can be expected. This implies that during the transformation of HEX microdomains into undulated cylinders, both S_{conf} and S_{pack} increase gradually with increasing temperature. We observed that during heating and cooling, a slope change in heat flow near 150 °C (open arrow, ⇒) in curves a and c in the lower panel of Figure 2 was detected. It is noted that this change was very reproducible even if very small. We speculate that an undulated cylinder might start to form at this temperature, although more investigation for this behavior should be done using a synchrotron SAXS near 150 °C.

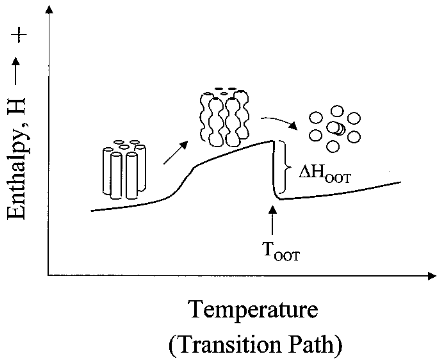

Figure 3. Schematic of the enthalpy change near the OOT between HEX and BCC microdomains.

On the basis of the above argument, we consider that the transition path between HEX and BCC microdomains might be qualitatively drawn in Figure 3. The transition from undulated cylinders to BCC microdomains would be an exothermic first-order transition, while the transition from BCC microdomains to undulated cylinders would be an endothermic first-order transition. This is in qualitative agreement with the result given in curve c of the lower panel in Figure 2, where a clear endothermic peak (↓) is observed at ~165 °C during cooling. The difference in the OOT temperature obtained during cooling and during heating is due to different ordering kinetics between the ordering of HEX from BCC and the ordering of BCC from HEX in addition to a large scanning rate. Previously, we reported that even when a temperature sweep of G' was performed during heating and during cooling at the rate of 0.5 °C/min, the T_{OOT} from HEX to BCC during heating was found to be 15 deg higher than the T_{OOT} from BCC to HEX during cooling.[17] From curve d of the lower panel in Figure 2, we confirmed again the exothermic and endothermic peaks (represented by an upward arrow (↑) and by downward arrow (↓)) during the second heating after annealing at 160 °C for 2 h.

Finally, we briefly mention the ODT of Vector 4111. On the basis of an endothermic peak in curves b and d in the lower panel of Figure 2, the T_{ODT} would be 260−270 °C.[18] This value is consistent with results investigated by Sakamoto et al.[11,20] that the T_{ODT} for Vector 4111 is larger than 220 °C[11] and estimated to be 270−280 °C by the extrapolation, based on a dilution theory, of experimentally measured T_{ODT}'s for several solutions consisting of Vector 4111 and dioctyl phthalate.[20] On the basis of the results in Figures 2, the T_{ODT} of Vector 4111 determined by DSC is 50−60 deg higher than that obtained by the temperature sweep of the G' experiment if the T_{ODT} is assumed to be the temperature where G' drops precipitously. This suggests that the temperature sweep of the G' experiment might not be useful to detect the T_{ODT} for a block copolymer with a lattice disordering transition (LDT), which is often found at a highly asymmetric composition.[11] The existence of LDT or spheres in *liquidlike short-range* orders before reaching the ODT of a block copolymer with highly asymmetric composition has been suggested by SAXS and log G' versus log G'' plots.[11,20,21] For instance, Schwab and Stühn[21] showed that, for an asymmetric SI copolymer (volume fraction of PS is 0.11), spheres in *liquidlike short-range* orders existed between BCC and the homogeneously disordered state, which was deduced from the existence of high-order peaks not corresponding to BCC microdomains in SAXS profiles. However, the existence of LDT might be speculated from the behavior of G'' in Figure 2. After a drop in G'' at ~210 °C, G'' decreases very gradually with increasing temperature up to ~270 °C. It can be considered that as spheres in *liquidlike short-range* order disappear gradually, the G'' (or viscosity) would be decreased gradually, not sharply. Therefore, we speculate that spheres in *liquidlike short-range* orders for Vector 4111 can exist from ~220 °C up to 260−270 °C, which is consistent with results investigated by Sakamoto et al.[11,20] Before closing, we mention that there might exist a broad exothermic peak between the OOT and ODT (curves a and b in the lower panel of Figure 2) and this might be related to the LDT process. However, we found that this change in heat flow (or enthalpy) near the temperature was not quite reproducible, because in the second heating run (curve d) after 2 h annealing at 200 °C, we barely see an exothermic peak, as seen in curve b in the lower panel of Figure 2.[22]

In summary, we have shown that an OOT from HEX to BCC microdomains for the SIS copolymer with the weight fraction of the PS block of 0.183 is an exothermic process due to the undulated cylinders formed during the transition and that the DSC technique can give an alternative method to determine the T_{ODT} of a block copolymer having an LDT.

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(18) Although polyisoprene (PI) can be cross-linked at higher temperatures (e.g., ~230 °C) for longer times,[19] we found that no degradation or gel formation occurred during this DSC experiment. This is because, in addition to the fast scanning rate, the nitrogen environment and an antioxidant were used.

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(22) One might argue that there existed a broad exothermic peak between OOT and ODT that was related to the LDT. This exothermic peak could be explained by using the concepts of ΔS_{conf} and ΔS_{pack} during the LDT. For instance, ΔS_{conf} from BCC to spheres in *liquidlike short-range* orders is less than zero, while ΔS_{pack} becomes positive. This is attributed to the fact that chains connecting two microdomains (tail conformations of PI chains) must be extended (or compressed), thus decreasing the entropy since the distance between spheres in *liquidlike short-range* orders should be longer (or shorter) compared with that in BCC. But, ΔS_{pack} becomes positive because there is no need to have a fixed configuration in the state of spheres in *liquidlike short-range* orders. Therefore, an LDT becomes an exothermic process for $|\Delta S_{\mathrm{conf}}| > \Delta S_{\mathrm{pack}}$, while no detectable peak is expected at an LDT for $|\Delta S_{\mathrm{conf}}| \approx \Delta S_{\mathrm{pack}}$. However, a broad exothermic peak occurring at 220−240 °C is not quite reproducible compared with the exothermic peak found near the OOT. Of course, it would be an interesting subject for a future study.

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