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<th>ORDERING PROCESS OF BLOCK COPOLYMERS NEAR ORDER-DISORDER TRANSITION (Session III: Complex Fluids, The 1st Tohwa University International Meeting on Statistical Physics Theories, Experiments and Computer Simulations)</th>
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The order-disorder transition (ODT) of block copolymers has been extensively investigated since Leibler's pioneering theory. This theory is based on a Landau type mean-field theory. Recently some important theoretical and experimental results were obtained for block copolymer melts having relatively weak segregation power. These results conclude that the random thermal force effect neglected in Leibler's mean-field theory is very important near the order-disorder transition temperature, \( T_{ODT} \), and induces sharp discontinuous changes in various physical quantities such as the peak intensity \( I_m^{-1} \) and the width of the first-order scattering maximum, low frequency rheological properties, and birefringence at \( T_{ODT} \).

Figure 1 schematically shows \( I_m^{-1} \) and the characteristic length \( D \), obtained from small angle X-ray scattering (SAXS) or small angle neutron scattering (SANS), as a function of \( 1/T \). \( D \) is given by \( D=2\pi q_m \), where \( q_m \) is the scattering vector at the first-order scattering maximum. At sufficiently high temperature both \( I_m^{-1} \) and \( D \) vary linearly with \( 1/T \) as predicted by Leibler's mean-field theory. The temperature dependence of \( D \) is equal to that of the unperturbed chain dimensions \( R_g(T) \) of the block copolymer. However upon further lowering \( T \), \( I_m^{-1} \) starts to clearly deviate from the linear relationship, showing a downward convex curvature, and the temperature dependence of \( D \) also deviates from that of \( R_g(T) \). \( I_m^{-1} \) changes discontinuously, but \( D \) shows no change at \( T_{ODT} \).

This deviation from the mean-field behavior is due to the random thermal force (the Brazovskii effect), and the discontinuous change in \( I_m^{-1} \) manifests the thermal-fluctuation-induced first-order transition. The temperature below which ordering starts shifts from the mean-field spinodal temperature \( T_{s,MF} \) down to \( T_{ODT} \). It means that the random thermal force tends to suppress the concentration fluctuations near ODT. We defined \( T_{MF} \) as the crossover temperature from the disordered state characterized by the Leibler mean-field theory to the disordered state characterized by the Brazovskii-type non-mean-field theory.

In this paper we present the ordering process of block copolymers in the ordered state near \( T_{ODT} \), especially experimental evidence showing a slow nucleation process followed by an incubation time and an anisotropic growth of lamellar microdomains. The block copolymer studied in this work is a nearly symmetric polystyrene-block-polysoprene (SI), OSI-3, having a number average molecular weight \( M_n = 1.5 \times 10^4 \), volume fraction of polystyrene \( f_{PS} = 0.45 \), and heterogeneity index \( M_w/M_n = 1.02 \) where \( M_w \) is weight average molecular weight.
Figure 2 shows the reciprocal peak intensity \( I_m^{-1} \) from OSI-3 as a function of \( 1/T \) and \( I_m^{-1} \) predicted by the mean-field theory. \( I_m^{-1} \) changes discontinuously at 99.2 < \( T < 100.2^\circ C \), and deviates from the mean-field theory at \( T \leq 170^\circ C \). We conclude that \( T_{ODT} \) is determined as 99.2 < \( T_{ODT} < 100.2^\circ C \) and \( T_{MF} \) is determined as 170°C.

Figure 3a shows that time-evolution of SAXS profiles after quenching the specimen from the disordered state at 172°C, which is above \( T_{MF} \), to 97°C which is just below \( T_{ODT} \) in the ordered state (see Figure 2). The temperature drop (T-drop) from 172°C to 97°C was attained in less than 1 min. After the T-drop, the SAXS intensity increases with time \( t \) as follows. The SAXS profile first changes from curve 1 (solid line) to curve 2 (dotted line) in Figure 3a. The intensity change in this stage may occur quite rapidly in the time scale shorter than about 60 sec, the shortest time covered in this experiment.

It is striking to note, however, that almost no change in the SAXS profile occurs even after the temperature is equilibrated to 97°C as shown in curves 3 and 4 in Figure 3a: the scattering profiles remain approximately equal to those in the disordered state at 100.2°C for a certain incubation period of time (as long as about 400 sec). After the incubation time, the SAXS profile starts to change slowly with time \( t \) in the time scale of 400 < \( t < 3000 \) before reaching an equilibrium profile or equilibrium values \( I_m^e \) and \( \sigma_Q^e \) at \( t \geq 3000 \) sec, where \( I_m^e \) and \( \sigma_Q^e \) are the equilibrium value for \( I_m \) and half width at half maximum (HWHM) of the first-order peak \( \sigma_Q \), respectively. This trend is more clearly shown in Figure 3b in which \( I_m \) and \( \sigma_Q \) are plotted as a function of time \( t \) after the T-drop.
Figure 4 schematically shows the time-evolution of $I_m$ after the $T$-drop from the disordered state to the ordered state very close to $T_{ODT}$. The process in stage I involves the changes in the scattering profile, $I_m$ and $\sigma_q$, in the time scale shorter than 60 sec. This process corresponds to a relaxation of the concentration fluctuations in the disordered phase from those at the initial temperature of 172°C to those at 100.2°C, very close to $T_{ODT}$. The process in stage II is an incubation process where the concentration fluctuations remain similar to those in the disordered state very close to $T_{ODT}$, though the sample temperature is definitely below $T_{ODT}$. The process in stage III is the ordering process from the disordered state.

It is also important to note in Figure 3a that there are two wave numbers $q_{c,S}$ and $q_{c,L}$ in the vicinity of which the scattered intensities do not change much with time, and the intensity increases and decreases at $q_{c,S} < q < q_{c,L}$ and at $q > q_{c,L}$ or $q < q_{c,S}$, respectively. These characteristics cannot be explained on the basis of the linearized theory of spinodal decomposition (SD) with the thermal noise effect and the q-dependent Onsager transport coefficient. These characteristics and the long incubation time may suggest that a possible ordering process is essentially a nucleation and growth process rather than SD, as a consequence of the fluctuation-induced first-order transition.

In order to analyze the ordering process in real-space, we froze the specimen in the ordering process at 97°C below its glass transition temperature ($T_g$) by quenching it into ice-water (0°C), and observe the structures by transmission electron microscopy (TEM). The specimens were frozen at 640 sec and 7285 sec (see the arrow labeled "frozen" in Figure 3b). Moreover we also observed the structure equilibrium at 100.2°C with the same method and compared with the structures frozen during the ordering process. For the purpose of checking whether the freezing-in process causes additional ordering in the system, we compared the SAXS profiles measured before and after the quench. The results indicated that two SAXS profiles measured before and after the quench are almost same in all the cases. Thus it is confirmed that the ordering which might occur during the quenching process is not expected to be significant.

The frozen specimens were subjected to microtoming into the ultrathin sections of ca. 50 nm thickness at -85°C with a Reichert-Jung ultracut E together with a cryogenic unit FC 4E and a glass knife. The ultrathin sections were quickly picked up on 400-mesh copper grids and stained by osmium tetroxide vapor at room temperature. TEM observation was made with a Hitachi H-600 transmission microscope at 100 kV.

Figure 6a shows the TEM picture at 630 sec, where the lamellar-like structure exists in the matrix of the less ordered structure. The matrix structure is very similar to the structure at 100.2°C in the disordered state, which is shown in Figure 5. Thus we can conclude that the matrix phase in Figure 6a is the disordered phase. It implies that the ordered and disordered phases co-exist at 630 sec. Moreover it is striking to notice that the grain composed of lamellae is highly anisotropic in shape, having a large aspect ratio: the dimension normal to the lamellar interfaces is much larger than that parallel to the interfaces. The TEM micrograph thus implies that the lamellae grains are nucleated in the disordered matrix and undergo an anisotropic growth with a greater growth rate along the lamellar normals than parallel to the lamellar interfaces.
Figure 6b shows the TEM micrograph at 7285 sec after the quench. The micrograph shows that the polygrains of lamellae fill the whole sample space, and the shape of one grain is still anisotropic, reflecting the memories of the ordering process.

In summary we obtained experimental evidence of a slow nucleation process with a finite incubation time and anisotropic growth of lamellar microdomains in a nearly symmetric block copolymer of polystyrene-block-polyisoprene quenched to the ordered state very close to TODT.

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