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Nucleation and growth of anisotropic grain in block copolymers near order-disorder transition

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Ordering processes of a nearly symmetric block copolymer of polystyrene-*block*-polyisoprene quenched from the disordered state to the ordered state very close to the order-disorder transition temperature were studied by using primarily transmission electron microscopy. We found that an isolated grain composed of lamellae developed in a disordered matrix and the shape of the grain was anisotropic, whose size along the lamellar normals is much larger than that parallel to the lamellar interfaces. This property was confirmed by the computer simulation of a phenomenological model. [S1063-651X(96)09311-7]

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The order-disorder transition (ODT) of block copolymers has been investigated extensively [1,2] since the introduction of Leibler's pioneering theory [3]. This theory is based on a Landau-type mean-field theory, where the effects of thermal fluctuations on composition fluctuations are neglected. Recently, the properties of block copolymers near the ODT have attracted considerable attention and it has become clear that the effects are important near the ODT [4–10]. Fredrickson and Helfand [4] took into account approximately the effects of thermal fluctuations on the ODT and showed that the ODT, which is a second-order phase transition in mean-field theory, becomes a first-order phase transition due to the fluctuation effects. The experimental results of diblock copolymers showed sharp discontinuous changes in various physical quantities such as the peak intensity I_m [5–10] and the width of the first-order scattering maximum [6,8–10], low-frequency rheological properties [5,11], and birefringence [12] at the order-disorder transition temperature T_{ODT}, which are also interpreted as a result of the fluctuation-induced first-order phase transition.

The ordering processes after the quench from the disordered state to the ordered state near the ODT have not been explored, except for some pioneering works [13–17]. In a previous study [18], we have studied such ordering process very near the ODT by means of time-resolved small-angle x-ray scattering (SAXS) and obtained evidence of a slow nucleation process followed by an incubation time. The SAXS studies clearly support the theoretical concept of the fluctuation-induced first-order phase transition. The nucleation process was further supported qualitatively by transmission electron microscope (TEM) images that indicated multiple grains composed of lamellar microdomains in a less ordered medium. Furthermore, the grains appeared to have highly anisotropic shape. Unfortunately, however, the observed grains resulting from multiple nucleation sites were intricately interconnected, which hindered a straightforward analysis of the nucleation processes such as anisotropic nucleation and growth of the grain. Thus, in this work we aimed to observe seriously *isolated grains* of lamellae developed in the disordered matrix during the nucleation process by using a TEM.

In the present paper, we present definitive results that show growth of isolated grains that are composed of lamellar microdomains and are well separated from other grains in a disordered matrix. We also present results obtained by the computer simulation of a phenomenological model equation for diblock copolymers to interpret the experimental observations in terms of the anisotropic nucleation process.

At first, to explain the properties of a block copolymer used in the present study and elucidate a situation considered in this paper, we review results obtained in a previous study [18] in the following three paragraphs.

The block copolymer studied is a nearly symmetric polystyrene-*block*-polyisoprene having a number average molecular weight $M_n = 1.5 \times 10^4$, volume fraction of polystyrene $f_{\mathrm{PS}} = 0.45$, and heterogeneity index $M_w/M_n = 1.02$, where M_w is weight average molecular weight. Figure 1 shows the reciprocal peak intensity I_m^{-1} obtained from SAXS

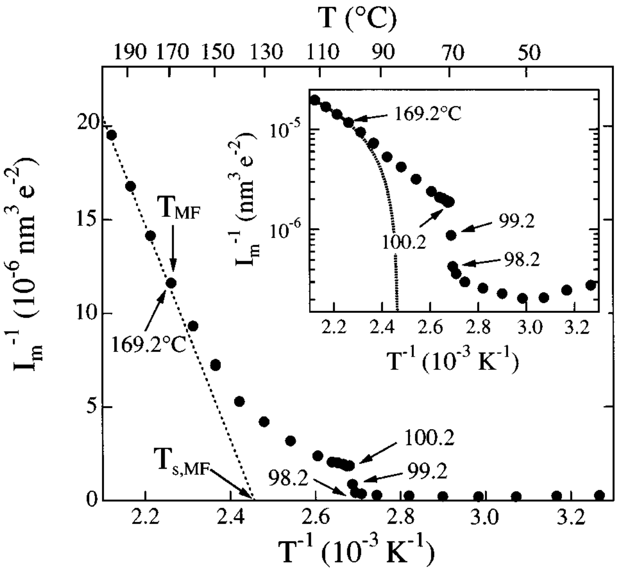

FIG. 1. Temperature dependence of the reciprocal peak scattering intensity I_m^{-1}. The numbers show temperatures in °C. The dotted line shows a fit with Leibler's mean-field theory [18].

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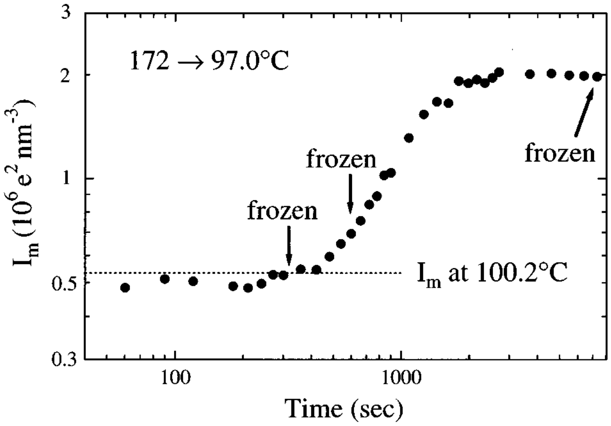

FIG. 2. Time change in the peak scattering intensity I_m after the quench into the ordered state at 97 °C. The horizontal dotted line shows I_m equilibrium at 100.2 °C.

as a function of $1/T$, where T is the absolute temperature. At sufficiently high temperature, I_m^{-1} varies with $1/T$ as predicted by Leibler's mean-theory (the dotted curve). However, upon further lowering of T, I_m^{-1} starts to clearly deviate from the mean-field relationship, especially below the crossover temperature ($T_{\mathrm{MF}} \cong 170$ °C) from the mean-field to the non-mean-field disordered state [10]. I_m^{-1} changes discontinuously at $99.2 < T < 100.2$ °C. This deviation from the mean-field behavior is due to the random thermal force [4] (the Brazovskii effect [19]) and the discontinuous change in I_m^{-1} manifests the thermal-fluctuation-induced first-order transition [4,5,10]. The temperature, below which ordering starts, is shifted from the mean-field spinodal temperature $T_{s,\mathrm{MF}}$($\cong 140$ °C) down to T_{ODT} by the random thermal force. This means that the random thermal force tends to suppress the concentration fluctuations near the ODT. We conclude that T_{ODT} is determined as $99.2 < T_{\mathrm{ODT}} < 100.2$ °C [10,18].

To investigate the ordering process, we studied the 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 Fig. 1). 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 the scattering profile at 172 °C to that at 100.2 °C. 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.

The time evolution of I_m after 60 sec is shown in Fig. 2. It is striking to note that almost no change in the SAXS profile occurs even after the temperature is equilibrated to 97 °C: the scattering profiles remain approximately equal to those in the ''fluctuation-induced'' 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 $400 \text{ sec} \leqslant t \leqslant 3000$ sec. The long incubation time and other dynamical properties of the SAXS profiles discussed in Ref. [18] may suggest that a possible ordering process is essentially a nucleation and growth process rather than spinodal decomposition, as a consequence of the fluctuation-induced first-order transition.

We now present the experimental results obtained in this work. In order to observe 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 observed the structures by a TEM. The specimens were frozen at 330, 640, and 7285 sec (see the arrow labeled ''frozen'' in Fig. 2). Moreover, we also observed the structure equilibrium at 100.2 °C, with the same method, and compared it with the structures frozen during the ordering process. For the purpose of checking whether or not the freezing-in process causes additional ordering in the system, we compared the SAXS profiles measured before and after freezing. The results indicated that the two SAXS profiles measured before and after freezing are almost the same in all the cases as in the case of our previous studies [18]. Thus it is confirmed that the ordering that might occur during the quenching process is not expected to be significant.

The frozen specimens were subjected to microtoming into the ultrathin sections approximately 50 nm thick and the thin sections were stained by osmium tetroxide vapor at room temperature, as detailed elsewhere [18]. A TEM observation was made with a Hitachi H-600 transmission electron microscope at 100 kV.

Figure 3(a) shows the TEM image at 330 sec, which is in the incubation period (see Fig. 2). In this image, there is no long-range-ordered lamellar structure. However, we can see concentration fluctuations with a period of about 20 nm, which is almost the same as that determined from the peak scattering vector in the SAXS profile at 330 sec. It is important to note that we cannot find a significant difference between the structure in Fig. 3(a) and that at 100.2 °C, which is shown in the inset of Fig. 3(a). This indicates that the structure in the incubation period is similar to that in the disordered state at 100.2 °C. This is consistent with the fact that the SAXS profile in the incubation time is almost equal to that at 100.2 °C, as mentioned above.

Figure 3(b) shows the TEM image at 630 sec, at which about 200 sec passed since I_m begins to grow after the incubation period. In this image, we found that an isolated grain composed of alternative lamellae of polyisoprene (the dark phase) and polystyrene (the bright phase) exists in the matrix of the less ordered structure. The structure of the matrix as seen in the inset of Fig. 3(b) is very similar to that in the disordered state in Fig. 3(a). Thus we can conclude that the matrix phase in Fig. 3(b) is the disordered phase and the lamellar grain appears from the disordered phase. 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. Note that the TEM picture previously reported was obtained at 800 sec, a bit later than at 630 sec, so that it showed a network-type grain composed of the lamellae in the disordered matrix [18], as a result of impingement of the grains nucleated in many sites.

The TEM micrograph at 7285 sec after the quench, which is not presented in the present paper, shows that the polygrains of lamellae fill the whose sample space and the shape of one grain is still anisotropic, reflecting the ''memories'' of the ordering process [18]. Therefore, we can conclude from the TEM micrographs that the lamellae phase is

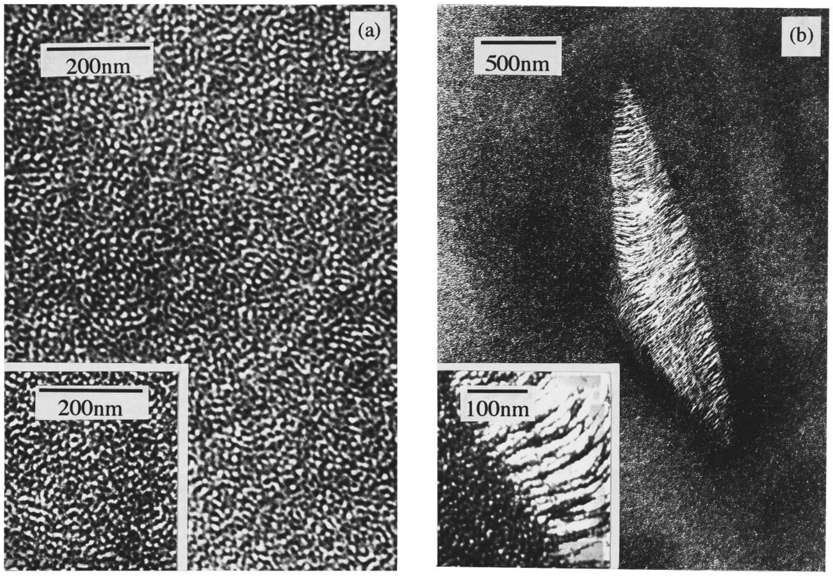

FIG. 3. Transmission electron micrograph of the structure at (a) 330 sec and (b) 630 sec after quenching into the ordered state at 97 °C. The inset in (a) shows the structure equilibrium at 100.2 °C. The inset in (b) shows a magnified micrograph that highlights the disordered matrix (lower left corner) and the boundary between the disordered matrix and the ordered grain (upper right corner).

nucleated in the disordered matrix and grown into the anisotropic grain. There seem to be two possibilities leading to this anisotropic grain shape: (i) The nucleation process itself is anisotropic, yielding the anisotropic critical nucleus with its dimension parallel to the lamellar normal much greater than that parallel to the interface; (ii) the nucleation process develops the isotropic critical nucleus, but the growth is highly anisotropic, leading to the observed shape of the grain.

As for model (i), the shape of the critical nucleus could be estimated if we know the energy of the interface between the ordered phase and the disordered phase, which is called the OD interface. The interfacial energy σ of the OD interface depends on the direction of the lamellae interface at the OD interface: $\sigma=\sigma(\theta)(0\leqslant\theta\leqslant\pi/2)$, where θ is the angle between the direction normal to the lamellar interface and that normal to the OD interface.

Recently, Hohenberg and Swift (HS) [20] obtained the free energy including the thermal noise effects in a certain wave-number region and then estimated the interfacial energy. The free energy is given by [4,17,20]

$$F[\psi]=\int d\mathbf{r}\left\{\frac{e}{2}[(\nabla^2+q_0^2)^2\psi(\mathbf{r})]^2+\frac{\tau}{2}\psi(\mathbf{r})^2+\frac{u}{4!}\psi(\mathbf{r})^4+\frac{w}{6!}\psi(\mathbf{r})^6\right\}, \tag{1}$$

where $\psi(\mathbf{r})$ is the local order parameter and e and w are positive coefficients defined in Ref. [20]. q_0 is a wave number that gives the peak position of the structure factor of ψ near the ODT. In mean-field theory, the bare coefficient u_0 (subscript 0 means the bare coefficient of the corresponding coefficient) is always positive and τ_0 is proportional to $\chi_s N-\chi N$ [4], where χ and N are the Flory χ parameter and the total degree of polymerization of the block copolymer, respectively. $\chi_s N$ gives the mean-field spinodal computed by Leibler [3]. The important point in Eq. (1) is that τ is always positive, while u changes its sign from positive to negative near the ODT. The disordered state $\psi=0$ and the ordered state coexist at the ODT. HS considered two typical cases, $\sigma(0)=\sigma_\parallel$ and $\sigma(\pi/2)=\sigma_\perp$, and concluded that $\sigma_\perp<\sigma_\parallel$ near the ODT. In this case, the equilibrium shape of the lamellar grains is anisotropic; the dimension normal to the lamellar interfaces is larger than that parallel to the interfaces. This tendency is consistent with that of the shape of the lamellar grain in Fig. 3(b).

It is important, however, to note that the approximation used in Ref. [20] is applicable to the small noise case as pointed in the original paper [20]. The strength of the thermal fluctuations in block copolymer systems depends on the degree of polymerization of the block copolymer [4]. In our case, since the degree of polymerization of the block copolymer is relatively small, the strength of the thermal fluctuations is not as small as assumed in the theory. Therefore, we cannot use the theory for quantitative analysis of our results.

On the other hand, if we use the free energy Eq. (1) as a phenomenological model, we can demonstrate the actual shape of the lamellar grain appearing in the disordered phase by computer simulation of Eq. (1). In this case, the time-evolution equation for ψ is written in the form [17,20]

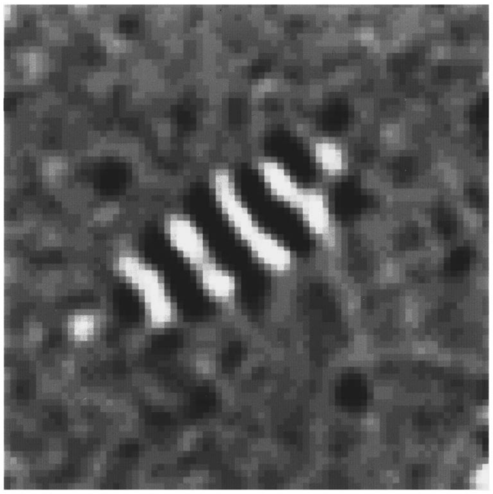

FIG. 4. Snapshot pattern of the order parameter obtained by the computer simulation of Eq. (3). The black (white) region represents the region where $\psi\geqslant 0(\psi<0)$.

$$\frac{\partial}{\partial t}\psi(\mathbf{r},t) = -L\frac{\delta F[\psi]}{\delta\psi(\mathbf{r})} + \sqrt{B}\zeta(\mathbf{r},t), \tag{2}$$

where L is the Onsager kinetic coefficient, which is assumed to be constant in this paper, $\zeta(\mathbf{r},t)$ is the thermal noise that obeys the fluctuation-dissipation relation, and B gives the strength of the thermal noise. By rescaling the variables in Eq. (2) with Eq. (1) as $\tilde{\psi}=\psi/\psi_0$, $\tilde{\mathbf{r}}=\mathbf{r}/\xi_0$, and $\tilde{t}=t/t_0$, where $\psi_0=32\tau/|u|$, $\xi_0=(2q_0^2)^{1/2}$, and $t_0=1/(L\tau)$, we obtain

$$\frac{\partial}{\partial t}\psi(\mathbf{r},t) = -[\tilde{e}(\nabla^2+\tfrac{1}{2})^2\psi(\mathbf{r}) + \psi(\mathbf{r}) - \tfrac{16}{3}\psi(\mathbf{r})^3 + \tfrac{24}{5}\tilde{w}\psi(\mathbf{r})^5] + \sqrt{\tilde{B}}\zeta(\mathbf{r},t), \tag{3}$$

where $\tilde{e}=e/\xi_0^4\tau$, $\tilde{w}=16\tau w/9u^2$, and $\tilde{B}=2k_BT/\psi_0^2\tau\xi_0^d$. In Eq. (3), we omit the tilde above the variables for simplicity. In this unit, the ODT point is given by $\tilde{w}=1$. There are three independent parameters in Eq. (3), $\tilde{e}$, $\tilde{w}$, and $\tilde{B}$, which relate the ratio of the correlation length to the lamellar spacing, the quench depth, and the strength of the thermal noise, respectively.

We have been studying ordering processes after quenching from the disordered state to the ordered state very close to the ODT point using Eq. (3) [21]. In the present paper, we have presented a typical result, where we chose $\tilde{e}=2$, $\tilde{w}=1.1$ (before quenching) and 0.98 (after quenching), and $\tilde{B}=0.12$. We obtained the similar time evolution of I_m as shown in Fig. 2 [21]. In Fig. 4, we show a snapshot pattern of the order parameter obtained after the incubation period by the computer simulation in two dimensions. We find in this figure that a lamellar grain appears in the disordered matrix and the shape of the lamellar grain is anisotropic, which is similar to the experimental result in Fig. 3(b). This result suggests that the anisotropic grain shape is a consequence of the anisotropic nucleation.

In summary, we have presented experimental evidence of the anisotropic shape of an isolated grain composed of lamellar microdomains in a nearly symmetric block copolymer of polystyrene-*block*-polyisoprene quenched from the disordered state to the ordered state very close to T_{ODT}. The anisotropic shape of the grain was confirmed by the computer simulation of the phenomenological model equation for diblock copolymers.

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