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Nucleation and Anisotropic Growth of Lamellar Microdomains in Block Copolymers

Takeji Hashimoto* and Naoki Sakamoto

Division of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-01, Japan

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The order−disorder transition (ODT) of block copolymers has been extensively investigated both theoretically and experimentally.[1,2] One important conclusion obtained is that the nature of the ODT is clarified to be the first-order phase transition,[3,4] showing sharp discontinuous changes of various physical quantities such as the peak intensity I_m[5−9] and the width of the first-order scattering maximum,[6,8,9] low-frequency rheological properties,[5,10] and birefringence.[11] However, the ordering and/or disordering process of block copolymers through ODT has been left relatively unexplored, except for some pioneering experimental[12−17] and theoretical works.[18,19]

In this paper we present experimental evidence showing a slow nucleation process followed by an incubation time and an anisotropic growth of lamellar microdomains in the disordered medium. The block copolymer studied in this work is a polystyrene-*block*-polyisoprene (SI) having number-average molecular weight $M_n = 1.5 \times 10^4$ and heterogeneity index $M_w/M_n = 1.02$ where M_w is the weight-average molecular weight.

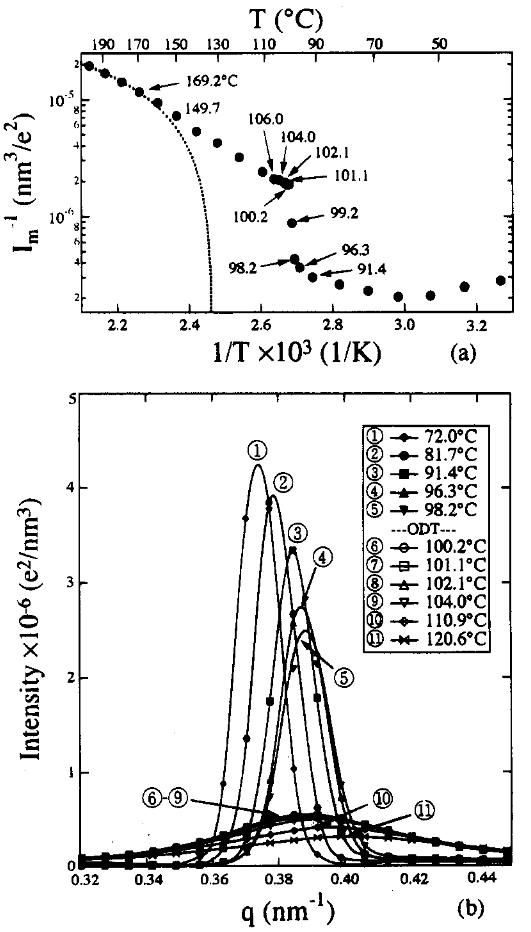

Figure 1. Temperature dependence of SAXS profiles. The scattering profiles were corrected for absorption, background scattering, and slit-width and slit-height smearing effects. The numbers in the top panel show temperatures in degrees Celsius. q is the magnitude of the scattering vector defined by $q = (4\pi/\lambda)\sin(\theta/2)$ where λ and θ are the wavelength of the incident beam (λ = 1.54 Å) and scattering angle, respectively.

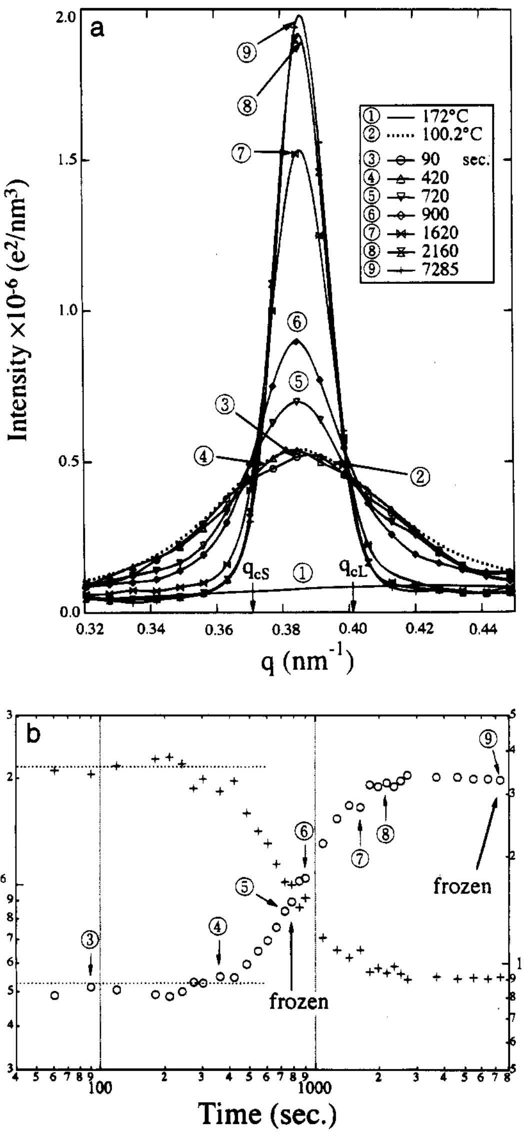

Figure 2. Time changes in the SAXS profile (a) and the peak scattered intensity I_m and hwhm σ_q (b) after the quench into the ordered state at 97 °C (99.2 < T_{ODT} < 100.2 °C). Curves 1 and 2 show the scattering profile equilibrium at 172.0 and 100.2 °C, respectively. The horizontal dotted lines in part b show σ_q and I_m equilibrium at 100.2 °C. The numbers in part b correspond to those attached to the scattering profiles in part a.

Figure 1 shows small-angle X-ray scattering (SAXS) profiles from the SI block copolymers at various temperatures (part b) as well as logarithms of the reciprocal peak intensity I_m^{-1} as a function of $1/T$ (part a). The scattering data were obtained in a cooling cycle, as will be detailed elsewhere.[20] There appears a sharp discontinuous change in the profiles at $T \geq 100.2$ °C and at $T \leq 98.2$ °C, which is more clearly highlighted in the plot of log I_m^{-1} vs $1/T$. We conclude[20] that the block copolymer is in the disordered state at $T \geq 100.2$ °C and the ordered state at $T \leq 99.2$ °C, so that ODT temperature T_{ODT} is determined as 99.2 < T_{ODT} < 100.2 °C. The dotted line in part a shows a fit with Leibler's Landau type mean-field theory:[3] $I_m^{-1} \sim \chi_s - \chi \sim 1/T_s - 1/T$ with T_s = 413 K, where χ and χ_s are the Flory−

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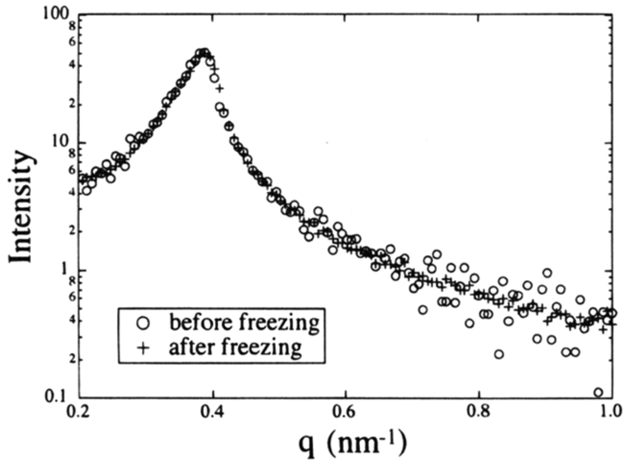

Figure 3. Comparison of the smeared SAXS profiles before and after the freezing to 0 °C from the sample first subjected to the ordering at 97 °C for 800 s. The profiles before (open circles) and after the freezing (+) were obtained with measuring times of 180 and 900 s, respectively; the ordering which might occur during the measuring time is not expected to be significant.

Huggins segmental interaction parameter between polystyrene and polyisoprene at temperature T and at $T = T_s$, respectively. The deviation from the mean-field behavior observed by increasing $1/T$ is believed to be due to the thermal fluctuation effect (Brazovskii effect).[4]

Figure 2a shows time evolution of the SAXS profiles after quenching the block copolymer melt from the initial temperature T_i of 172 °C, far above T_{ODT} in the mean-field disordered state to a measuring temperature T_f of 97 °C just below T_{ODT} in the ordered state. The temperature jump from T_i to T_f was attained in less than 1 min as described elsewhere.[13] After the rapid temperature change, the SAXS intensity from the system increases with time t as follows. The SAXS profile first changes from curve 1 (solid line) to curve 2 (dotted line) in Figure 2a. The intensity change in this stage may occur quite rapidly in the time scale shorter than about 60 s, the shortest time covered in this experiment. The sample temperature is further lowered to T_f where the ordering should take place. It is striking to note, however, that almost no change in the SAXS profile occurs even after the temperature is equilibrated to T_f as shown in curves 3 and 4 in Figure 2a: the scattering profile and hence I_m and the half-width at half-maximum (hwhm) of the first-order peak σ_q 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 s) as shown in Figure 2b. After the incubation time, the SAXS profile starts to change slowly with time t in the time scale of $400 \le t \le 3000$ before reaching an equilibrium profile or equilibrium values I_m^e and σ_q^e at $t \gtrsim 3000$ s.

The *slow ordering process* (slow compared with the relaxation rate of the concentration fluctuations in the disordered state) found here may look somewhat similar to that reported by Schuler and Stühn:[16] our ordering process may appear similar to their second-stage ordering process. However, our result is fundamentally different from their result in that our system shows a single-stage ordering from the disordered phase after the incubation time, rather than the two-stage ordering processes with well-separated relaxation times τ_{fast} and τ_{slow}. We should be able to observe the changes in the scattering profile, I_m, and σ_q in the time scale shorter than 60 s. However, this change in our system should correspond to that in the concentration fluctuations in

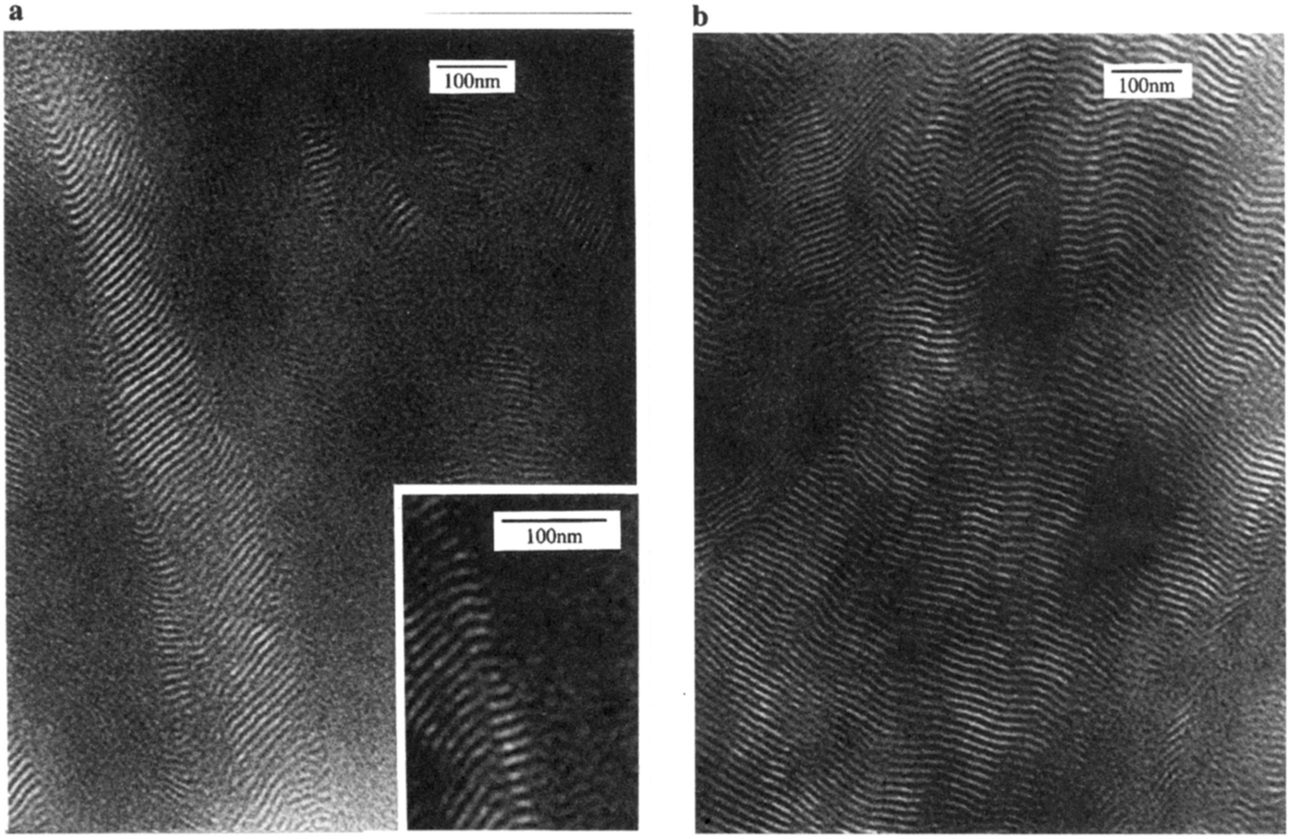

Figure 4. Transmission electron micrograph for the sample first subjected to the ordering at 97 °C for 800 s (a) and for 7285 s (b) and then frozen to 0 °C. The inset in part a shows a magnified micrograph which highlights the disordered matrix and a boundary between the disordered matrix and ordered grain.

the disordered phase. Thus, the process here consists of the following *three stages*: (i) a rapid relaxation of the concentration fluctuations in the disordered phase; (ii) the incubation process (the concentration fluctuations correspond to those at 100.2 °C close to T_{ODT} in the disordered state); (iii) the slow ordering process from the disordered state.

The time evolution of the scattering profiles after the incubation time is seen in curves 4–9 in Figure 2a. The results show the following two characteristic features: (i) the characteristic wavenumber q_{m} for the dominant Fourier mode of the concentration fluctuations remains constant (3.87×10^{-2} Å^{-1}), independent of time; (ii) there are two wavenumbers $q_{\mathrm{c,S}}$ and $q_{\mathrm{c,L}}$ in the vicinity of which the scattered intensities do not change much with time, and the intensity increases and decreases at $q_{\mathrm{c,S}} < q < q_{\mathrm{c,L}}$ and at $q > q_{\mathrm{c,L}}$ or $q < q_{\mathrm{c,S}}$, respectively. The latter characteristics (ii) cannot be explained on the basis of the linearized theory of spinodal decomposition (SD) with the thermal noise effect[17] and the q-dependence of the Onsager transport coefficient.[18]

These characteristics (ii) together with the long incubation time may suggest that a possible ordering process is essentially a nucleation and growth process rather than SD. In order to check this possibility, we made a real-space analysis of the ordering process by means of transmission electron microscopy (TEM) on the specimen frozen below the glass transition temperature (T_g) of the block copolymer. The ordering process at 97 °C was frozen by quenching the system into the ice–water bath at 0 °C at 800 and 7285 s after the quench to 97 °C. In order to check whether the freezing-in process causes an additional ordering in the system, we compared the SAXS profile measured *in situ* at 800 s after the quench (see the arrow labeled "frozen" in Figure 2b) and that measured after the freezing. The results are shown in Figure 3. We clearly observed that the two profiles are identical to each other, indicating that the structure in the frozen specimen is essentially identical to that before the freezing.

The frozen specimens to 0 °C were subjected to microtoning 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 exposure to osmium tetroxide vapor at room temperature. TEM observation was made with a Hitachi H-600 transmission microscope at 100 kV.

A typical TEM micrograph obtained on the specimen frozen at 800 s after the quench is shown in Figure 4a. The grain composed of well-ordered lamellae is clearly seen to exist in the matrix of less ordered morphology. The matrix phase seems to be in the disordered state qualitatively because the SAXS profiles before and after the freezing are identical (Figure 3) and quantitatively because the scattering profile obtained *in situ* at 800 s after the temperature quench to 97 °C can be approximately expressed in terms of the weighted average of the static scattering profile in the disordered state at 100.2 °C and that in the ordered state at 96.3 °C. 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 4b shows the TEM micrograph on the specimens frozen at 7285 s after the quench. The micrograph shows the polygrains which fill the whole sample space and which contain well-ordered lamellae.

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 T_{ODT}.

References and Notes

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