

## Coexistence of ordered and disordered phases in a nearly symmetric diblock copolymer near an order-disorder transition point

Tadanori Koga,\* Tsuyoshi Koga, and Takeji Hashimoto<sup>†</sup>

Hashimoto Polymer Phasing Project, ERATO, Japan Science and Technology Corporation, and Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan

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We investigated the phase behavior near the order-disorder transition (ODT) temperature in a nearly symmetric diblock copolymer, using ultra-small-angle x-ray scattering method. In a narrow temperature range very close to the ODT temperature, we observed the scattering profiles that can be interpreted as a linear combination of the scattering from the disordered state and that from the ordered lamellar state. These profiles were stable during the observation time (50 h), revealing that the two-phase coexistence occurs at thermal equilibrium within this temperature range. [S1063-651X(99)50408-X]

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The order-disorder transition (ODT) is well known as one of the cooperative phenomena observed in many physical systems [1]. For a diblock copolymer, which consists of two kinds of polymers covalently bonded to each other at their one ends, the ODT is caused by varying the segregation power between two kinds of segments [2,3]. Theoretically, the Landau-type mean-field theory for diblock copolymer melts led to the fundamental pictures of the ODT [4] and was further generalized by several authors [5–7]. The generalized theories predicted that the effects of random thermal force turn the ODT from a second-order phase transition within the mean-field theory to a first-order phase transition even in a symmetric diblock copolymer. It is well known that this fluctuation-induced first-order phase transition belongs to the Brazovskii universality class [8] and has been observed in many systems, such as soft materials and a structural phase transition in crystal [9]. Many characteristics of the fluctuation-induced first-order phase transition in diblock copolymers are well described by small-angle x-ray scattering (SAXS) or small-angle neutron scattering (SANS) [10–14], rheology [10,15], and birefringence measurements [16].

In the present Rapid Communication we further show a piece of evidence concerning the coexistence of the ordered and disordered phases at thermal equilibrium near the ODT point, further supporting the concept of the fluctuation-induced first-order phase transition. A polystyrene-*block*-polyisoprene diblock copolymer (PS-*b*-PI) used in this study has overall number-average molecular weight ( $M_n$ )  $1.9 \times 10^4$ , molecular weight polydispersity ( $M_w/M_n$ ) 1.02, and volume fraction of polystyrene block ( $f$ ) 0.46.

The SAXS and SANS are useful for investigations of the internal structure of the sample. As will be shown later in Fig. 1, however, the scattering profiles from the ordered phases can be very sharp with their full width at half maximum (FWHM) much smaller than those for the weighting

function of the conventional SAXS and SANS camera. Under this condition the measured scattering profiles cannot be correctly desmeared with the instrumental resolution function [17]. Consequently, it is likely that even after the implementation of the desmearing process the instrumental broadening effects still remain in the profiles, preventing some interesting phenomena from being revealed.

For the present study we employed an ultra-small-angle x-ray scattering (USAXS) camera [18] which increases the spatial resolution by a factor of about 10, compared with the conventional SAXS camera. The USAXS camera uses two channel-cut germanium crystals, one to collimate the incident beam and the other to analyze the scattering radiations. As described elsewhere [19], the instrument permits high-temperature experiments ranging from 258 K to at least 573 K, and the sample cell was set within the temperature controlled copper block with accuracy of  $\pm 0.01$  K. The sample size was 5-mm wide, 15-mm high and 2 mm in thickness. Since the width of the incident x-ray beam is 1 mm, the effect of the finite size on the observed scattering intensity can be ignored in the present study. From the SAXS experiments [20], the ordering process into the lamellar morphology at equilibrium took about 1 h in the temperature region very close to  $T_{ODT}$ ; accordingly, the annealing time was set to 2 h at each temperature.

We shall first demonstrate the ability of the USAXS camera, compared with the SAXS camera. The details of the measurements will be described elsewhere [21(a)]. Figure 1 presents the desmeared USAXS and SAXS profiles around the first-order scattering maximum measured for the same sample specimen in an ordered phase at equilibrium.  $q$  is the magnitude of the scattering vector,  $q = (4\pi/\lambda)\sin(\theta/2)$  with  $\lambda$  and  $\theta$  being the x-ray wavelength and scattering angle, respectively. Both USAXS and SAXS profiles were corrected for air scattering, absorption, and slit-height and slit-width smearing. The absolute intensity was obtained using the nickel-foil method [22]. This figure shows that the two scattering profiles are quite different even after the implementation of the desmearing process: FWHM for the desmeared USAXS and SAXS profiles are  $2.5 \times 10^{-3} \text{ nm}^{-1}$  and  $9.1 \times 10^{-3} \text{ nm}^{-1}$ , respectively, and the intensity of the

\*Present address: Department of Chemistry, State University of New York at Stony Brook, Stony Brook, NY 11794-3400.

<sup>†</sup>Author to whom all correspondence should be addressed at Kyoto University.

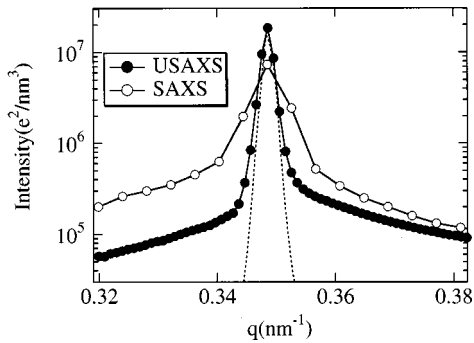


FIG. 1. Absolute intensity results for the USAXS (closed symbols) and the SAXS (open symbols) profiles in the ordered state ( $T=403$  K). The dotted lines show the resolution function of the USAXS camera.

tails in the USAXS profile is quite suppressed [23]. This means that the desmeared SAXS profile does not represent a correct scattering profile [24]. Thus, it turns out that the USAXS method has a great advantage in analyzing the sharp scattering profiles inherent in samples with highly regular structures, such as lamellar morphology in the ordered state.

We now turn to the USAXS observations in the vicinity of  $T_{ODT}$ . Representative results for cooling measurements are plotted in Fig. 2. The figure shows only that portion of the scattering profiles very near the scattering maximum. The scattering profiles at  $T=413.8$  and  $417.5$  K are interpreted as those for the fully ordered (lamellar) and disordered phases, respectively. This is also confirmed by transmission electron microscopy (TEM) observations [21(b)]. As temperature decreased, the scattering intensity at around  $q=0.35$  nm $^{-1}$  ( $0.346 < q < 0.355$  nm $^{-1}$ ) grew, while the intensity outside this  $q$  region decreased. It is important to note that the profiles at each temperature shown in Fig. 2 were stable during the observation time (at least for 50 h in this case). Consequently, these profiles can be regarded essentially as those from the equilibrium state. These profiles obtained at a narrow temperature range of  $414.5$  K  $\leq T \leq 416.1$  K do not belong to those for the fully ordered or fully disordered phase,

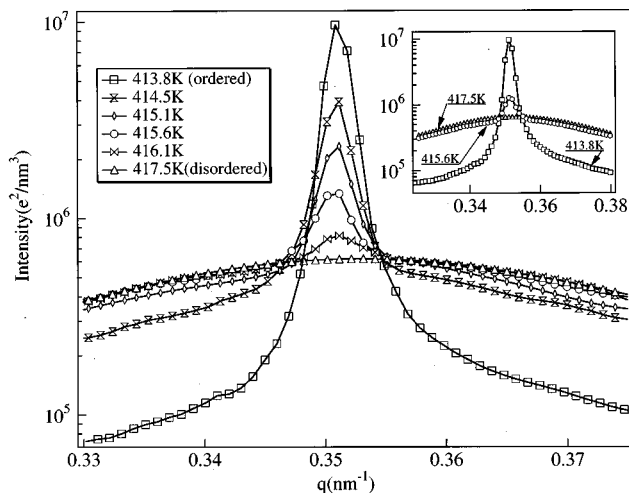


FIG. 2. Temperature dependence of the USAXS profiles near  $T_{ODT}$ . The inset picks up only three profiles at  $T=413.8$ ,  $417.5$ , and  $415.6$  K, representative for fully ordered state, fully disordered state, and order-disorder coexistence state, respectively.

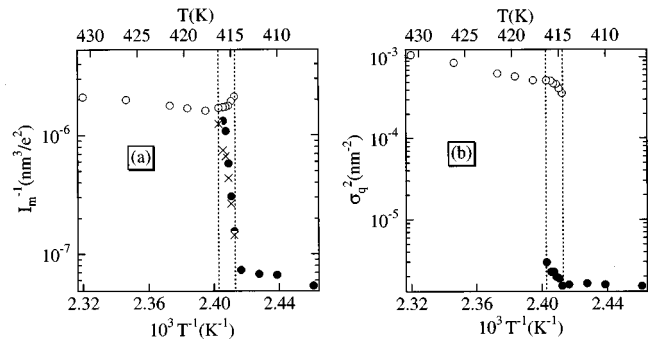


FIG. 3. Temperature dependence of (a)  $I_m^{-1}$  and (b)  $\sigma_q^2$ . In the coexistence region, there are two contributions: one from the broad profile arising from the disordered phase (the data shown by open circles) and the other from the sharp profile arising from the ordered phase (the data shown by closed circles). The observed net peak intensities in the coexistence region are shown by crosses.

and are best interpreted as a superposition of those from the ordered and disordered phases. To emphasize this, we plot three scattering profiles at  $T=413.8$ ,  $415.6$ , and  $417.5$  K in the inset of Fig. 2 [25]. Thus, the lamellar and disordered phases coexist in this temperature range. Since these scattering profiles were observed at a temperature range from  $T_{C,L}=414.2$  K to  $T_{C,H}=416.4$  K, the temperature range for the coexistence is estimated about 2.2 K, where  $T_{C,L}$  and  $T_{C,H}$  are defined as lower and upper bounds of the coexistence region, respectively. The recent theoretical study by Hohenberg and Swift [7] provides, in principle, the thermal-fluctuation-driven two-phase coexistence over a finite temperature range even for block copolymers with no polydispersities in molecular weight and composition. It is noted that the scattering profiles in the coexistence region did not show the temperature hysteresis in the time scale of observation used in this study. This also supports that the nature of ODT for the nearly symmetric block copolymer is a weak first-order phase transition.

To deduce the quantities characterizing the scattering profiles in the coexistence region, the measured profiles were decomposed into the sharp and broad components by fitting them with a linear combination of Gaussian and Lorentzian functions, respectively [26]. Figure 3 depicts the plots of the reciprocal peak intensity  $I_m^{-1}$  (a) and the square of the half width at the half maxima  $\sigma_q^2$  (b) versus  $1/T$  for each of the decomposed profiles. Although the discontinuities in those plots, which reflect the fluctuation-driven first-order phase transition, have been observed by SAXS and SANS experiments [10–14,27,28], the quantitative estimations of the discontinuities obtained from SAXS or SANS are found to be affected considerably by the instrumental resolution [29].

In the coexistence region, there are two contributions on the scattering intensity: one from the ordered phase (closed circles) and the other from the disordered phase (open circles).  $I_m^{-1}$  from the ordered phase in the coexistence region decreases with decreasing  $T$ , reflecting the increase of the volume fraction of the ordered phase with decreasing  $T$ . The fraction of the ordered phases was found to increase exponentially on approaching the fully ordered region [21(a)].  $\sigma_q^2$  for the ordered phase in the coexistence region is slightly larger than that below  $T_{C,L}$  (in the fully ordered

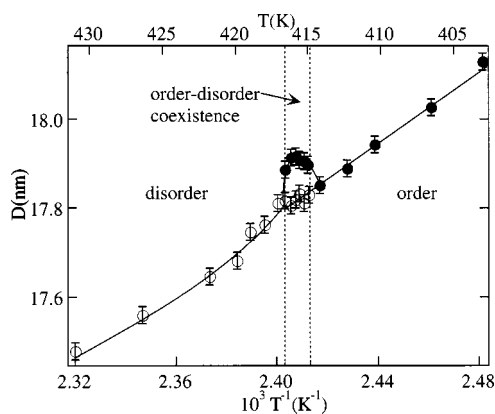


FIG. 4. Temperature dependence of  $D$ . Open symbols,  $D$  for disordered state; closed symbols,  $D$  for ordered state.

region), which is due to the lamellar distortions [30] and/or finite size of the lamellar grains caused by the fluctuation effects.

Figure 4 shows the temperature dependence of the characteristic length  $D (= 2\pi/q_m)$ , where  $q_m$  is the peak position of the scattering maximum. Experimentally, it is well known that  $D$  linearly increases with increasing  $1/T$  near  $T_{ODT}$  [10,13,28,30], except for the data of Stühn *et al.* [11] who reported a small discontinuous decrease at  $T_{ODT}$ . In Fig. 4, the variation of  $D$  with  $T$  in the fully disordered region (open circles), in the fully ordered region (closed circles) and in the disordered phase of the order-disorder coexistence region (open circles) are almost consistent with the previous reports,

i.e.,  $D$  almost linearly increases with  $1/T$ . However, a small jump in  $D$  is clearly observed for the ordered phase (closed circles) in the coexisting region for both heating and cooling processes. The maximum value of the jump in  $D$  is only about 1 Å but is very reproducible. The jump corresponds to only 10 s of arc in  $\theta$  and hence is easily overlooked by the conventional SAXS camera. This excess increase of the spacing  $D$  is not well understood at present and deserves further investigation.

Furthermore, using another PS-*b*-PI diblock polymer having different molecular weight ( $M_n = 1.5 \times 10^4$ ,  $M_w/M_n = 1.02$ ), but the same composition ( $f = 0.45$ ), we found that the temperature range for the two-phase coexistence tends to decrease with increasing  $M_n$ , i.e., with decreasing the first-order character of the phase transition [21(a)]. The same tendency has been reported in the sponge-to-lamellar phase transition in lyotropic liquid crystals which also belong to the Brazovskii's universality class [31]. Thus, the phenomenon is probably universal to any fluctuation-induced first-order phase transition [32]. It should be noted that the jump in  $D$  in the coexistence region is also observed in the lower molecular weight block copolymer [21(a)].

In summary, we show the experimental evidence of the two-phase coexisting region near the ODT temperature for a series of the nearly symmetric diblock copolymers. The findings of this study lead to a conclusion that such coexistence is a substantial phenomenon in the fluctuation-induced first-order phase transition.

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- [25] We note that the small spike at  $q = 0.35 \text{ nm}^{-1}$  on the top of

the broad maximum may be easily overlooked in experiments with the conventional SAXS camera. Even if one can fortunately obtain the profile suggesting the order-disorder coexistence by using SAXS, it is impossible to accurately decompose it into the sharp and broad components corresponding to the ordered and disordered phases, respectively. Thus the USAXS method is quite useful to investigate the order-disorder coexistence.

- [26] The observed broad scattering profiles from the disordered phase are in good agreement with the Leibler's scattering function. Moreover, the Leibler's scattering function around  $q_m$  from the disordered melt can be expressed by Lorentzian form (see, for example, Ref. [27]). On the other hand, as shown in Fig. 1, the scattering profile from the ordered state is close to that of the resolution function for the USAXS camera (Gaussian function), except for the tails around the scattering maximum. A weight average of Lorentzian and Gaussian functions show a quite good agreement with the observed scattering profile in the region of  $0.3 < q < 0.4 \text{ nm}^{-1}$ . The detail will be given elsewhere (Ref. [21(a)]).
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very much on the instrumental resolution, because the profiles in the fully ordered phase are generally very sharp. If the scattering intensity is measured with the limited instrumental resolution, the values of these dimensionless quantities are larger than their intrinsic values. According to the previous reports (Ref. [28]),  $I_{m_o}^{-1}/\Delta I_m^{-1}$  and  $\sigma_{q_o}^2/\Delta\sigma_q^2$  in SAXS results were 0.4 and 0.06, respectively. On the other hand, those of the present case are 0.05 and 0.005, respectively, smaller by a factor of about 10 than the values of the previous reports, clearly revealing superiority using the USAXS camera.

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- [32] The effects of the polydispersity may affect the phase transition in real experimental systems. Unfortunately, since there is no rigorous theory that is applicable to quantitative argument of the phase transition of our diblock copolymers having low molecular weight at this stage and there is no systematic experimental results of the polydispersity effects on the phase transition in diblock copolymer melts, we cannot explicitly show how the polydispersity effects affects the phase transition near the ODT in our system at present. However, we can say that the phase coexistence observed in our experiments cannot be interpreted by the simple argument of the phase separation by the polydispersity effects because we obtained experimental results of the real-space structure at the temperature in the coexistence region by using TEM, which show that the macroscopic two-phase separation of the ordered (lamellar) and the disordered phases does not take place. The details of the method and the results of the TEM experiments will be presented elsewhere [21(b)].