

## Long-range density fluctuations in a symmetric diblock copolymer

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We present an experimental piece of evidence of the excess small-angle-scattering in a nearly symmetric diblock copolymer. This phenomenon is observed only in the two-phase coexistence region of the ordered and disordered phases near the order-disorder transition temperature, using the ultra-small-angle x-ray scattering method. This excess scattering is found to be caused by the difference of the density between the ordered and disordered phases in the coexistence region. [S1063-651X(99)50610-7]

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If two kinds of polymers are covalently bonded to each other at one of their ends, diblock copolymers are obtained. The “block connectivity” induces the thermodynamic instability at a finite wave number  $q = q_m \neq 0$  [1] and the growth of the dominant mode of the concentration fluctuations with  $q_m$  is known traditionally as “microphase separation transition (MST)” or “order-disorder transition (ODT).” One of the interesting properties of the ODT in block copolymers is fluctuation-induced first-order phase transition [2], in which the nature of the phase transition changes from second-order in mean-field theory [1] to first-order due to the fluctuation effects [3,4]. Experimentally the effects were first illuminated by Bates *et al.* [5] and later by several other groups [6–9].

Recently, we presented a new piece of evidence on the fluctuation-induced first-order phase transition in diblock copolymers: the coexistence of the ordered and disordered phases near the transition temperature [10]. The observations were achieved by using an ultra-small-angle x-ray scattering (USAXS) camera that has a spatial resolution higher than the small-angle x-ray scattering (SAXS) camera by at least one order of magnitude [11]. Although the fluctuation-induced existence of biphasic is expected by recent theoretical studies [3,4,12], the actual phase behavior of the coexisting state in diblock copolymers has never been examined both theoretically and experimentally.

In this Rapid Communication we extensively investigate the two coexisting phases of a nearly symmetric diblock copolymer from the scattering property and show the first evidence, to our knowledge, of *long-range density fluctuations* occurring inside the coexistence region by using the USAXS camera.

The polystyrene-*block*-polyisoprene diblock copolymer (PS-*b*-PI) used has an overall number-average molecular weight  $M_n$  of  $1.9 \times 10^4$ , its polydispersity index  $M_w/M_n = 1.02$ , and a volume fraction of PS block  $f_{PS}$  of 0.46. The specimen for USAXS measurements was first dissolved in toluene, and a homogeneous solution containing 5 wt % polymer was purified through a millipore film of 0.2  $\mu\text{m}$  pore size, since the artifact due to foreign particles in the sample may remarkably increase the USAXS intensities in the lower  $q$  region [13]. Then the solution was cast into a film specimen by slowly evaporating the solvent at room temperature. The sample was kept at each measuring temperature for 2 h before the USAXS measurement was taken to make sure that it was in thermal equilibrium. The sample temperature was controlled with an accuracy of better than  $\pm 0.01$  K.

An example of a USAXS profile in the two-phase coexisting state at  $T = 415.6$  K is shown in Fig. 1, highlighting only near the first-order scattering maximum. The USAXS profile was corrected for air scattering, absorption, and slit-smearing effects. The scattering profiles observed at a narrow temperature range of  $414.2 \leq T \leq 416.4$  K were obviously reproduced by a summation of both the sharp component, typical of the ordered phase, and broad component, typical of the disordered state, as shown in Fig. 1. We should point out that the scattering profiles in the coexistence region were stable for at least 50 h and that no hysteresis was observed within the time scale of our observation, revealing that the coexistence occurs at thermal equilibrium [10,14].

Here in this communication we concentrate on the scattering profile in the small  $q$  region, satisfying  $q < q_m$  obtained from the USAXS measurements, where  $q$  is the magnitude of the scattering vector defined by  $q = (4\pi/\lambda)\sin(\theta/2)$  with  $\lambda$  and  $\theta$  being the x-ray wavelength and scattering angle, and  $q_m$  is  $q$  at the maximum scattering intensity. Figure 2 shows the temperature dependence of the USAXS profiles with  $0.008 < q < 0.45 \text{ nm}^{-1}$ . The scattering maximum at  $q = q_m$  shown in Fig. 1 is seen at the right-hand edge in Fig. 2. It should be noted that all scattering profiles are corrected deliberately only for air scattering to avoid any artifacts caused by the desmearing process. The Leibler random-phase-approximation (RPA) theory predicted that

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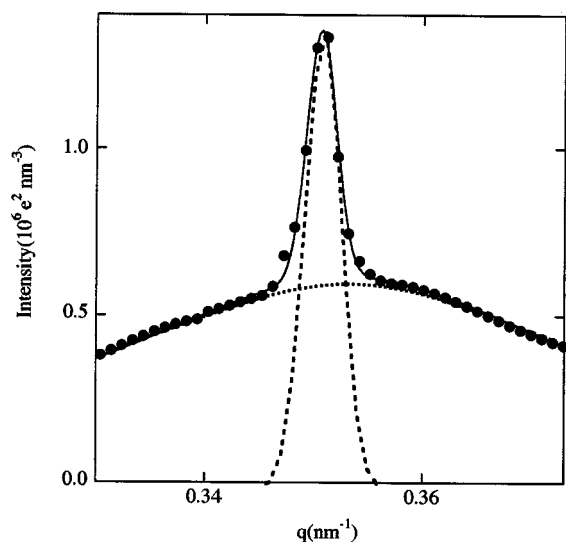


FIG. 1. The scattering profile at  $T=415.6$  K shown by the solid circles is decomposed into a narrow component shown by the broken line and a broad component shown by the dotted line. The solid line represents the best-fit profile.

the connectivity between  $A$  and  $B$  chains in the diblock copolymer completely suppresses concentration fluctuations on the large length scale much larger than the radius of the gyration of the block copolymer chain. That is, the asymptotic value of the scattering profiles  $I(q)$  in diblock copolymer melts is  $\lim_{q \rightarrow 0} I(q) = 0$  for incompressible liquids

[1]. In practice, so far as the fully ordered and disordered phases are concerned, this constraint was valid at least approximately; see, e.g., the observed scattering profile in the disordered state at  $T=417.0$  K shown in Fig. 2 [15]. However, it is striking to note that in the biphasic region of  $414.2 \lesssim T \lesssim 416.4$  K a strong small-angle scattering in excess of that from the fully ordered and disordered phases can be discerned in the very small  $q$  region, smaller than  $\sim 0.04$  nm $^{-1}$ . This excess scattering was increased with increasing temperature on approaching the disordered phase

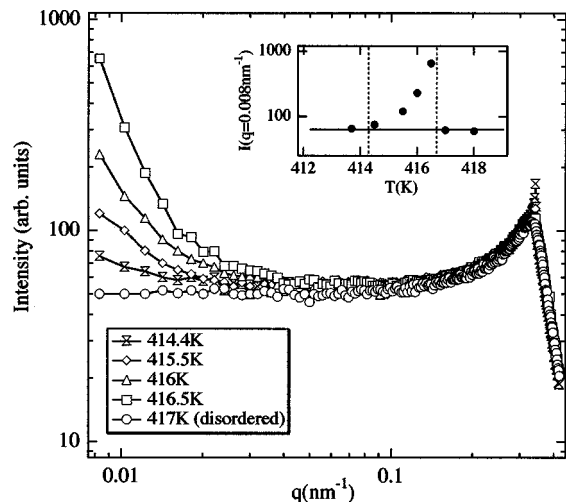


FIG. 2. Temperature dependence of the smeared USAXS profiles near  $T_{\text{ODT}}$ . In the inset, the smeared scattering intensities at  $q=0.008$  nm $^{-1}$  are plotted as a function of temperature.

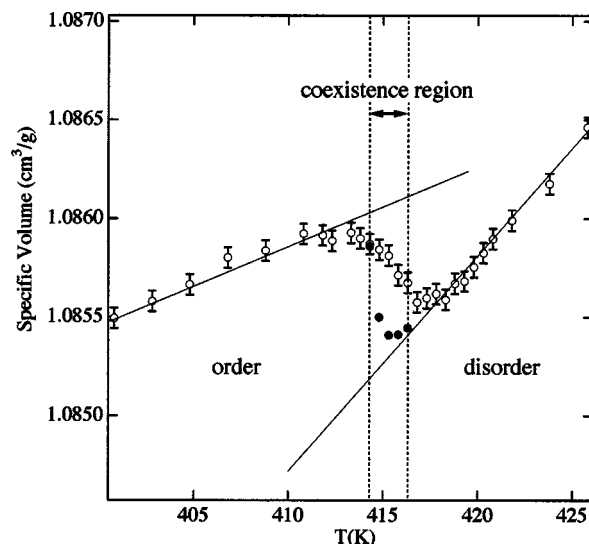


FIG. 3. Temperature dependence of the specific volume of the sample near  $T_{\text{ODT}}$ . The calculated values of the specific volume in the coexistence region,  $V_{\text{CO}}$ , are shown by the solid circles.

and diminished again in the fully disordered phase. As can be seen in the inset of Fig. 2, the temperature dependence of the scattering intensity at the lowest accessible  $q$  ( $=0.008$  nm $^{-1}$ ) in the present study,  $I(q=0.008$  nm $^{-1})$ , is similar to the critical behavior in the second-order phase transition [16]. The  $q$  region where this upturn occurs corresponds to the length scale greater than  $\sim 200$  nm. This excess scattering suggests a possibility that there are long-range density heterogeneities only in the coexistence region. In other words, the incompressibility assumed in the theory [1] is not satisfied. However, the failure of the incompressibility is proven only for the coexistence region.

In order to study the relationship between this anomaly and the density heterogeneities, we measured the temperature dependence of the bulk density near the ODT temperature  $T_{\text{ODT}}$  using a conventional pycnometer. This instrument consists of a glass capillary filled with ethylene glycol in contact with the sample volume and is kept in an oil-filled thermostat, allowing for the measurements of relative volume changes [17]. The temperature increment and the temperature stability for the measurements are  $0.5$  and  $\pm 0.2$  K, respectively. Figure 3 shows the temperature dependence of the specific volume of the sample near  $T_{\text{ODT}}$  corrected for the volume change of ethylene glycol with temperature. The volume rapidly decreases with increasing  $T$  in the narrow temperature range centered around the coexistence region found in the inset of Fig. 2 (shown by the vertical dotted lines), while the volume increases with increasing  $T$  outside the region. This change in the volume is seen to occur over a temperature range slightly larger than the change in  $I(q=0.008$  nm $^{-1})$ . A similar result was reported by Kasten and Stühn [18]. This indicates that the decrease in the volume in the coexisting region is caused by the increase in the volume fraction of the disordered phases.

From the pycnometry and USAXS, an important conclusion can be drawn: the excess small-angle scattering originates from coexistence of the ordered and disordered phases having different electron densities. However, since informa-

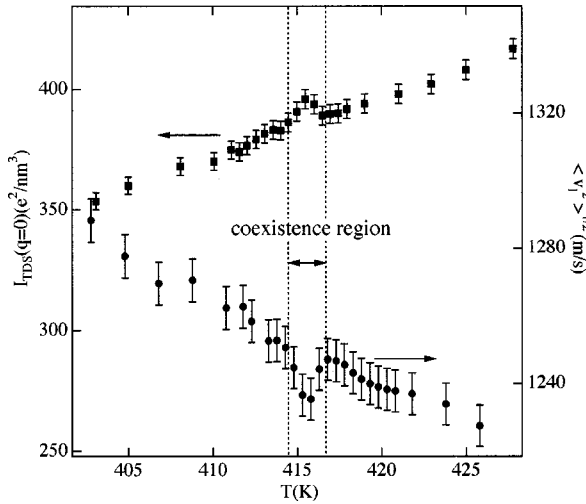


FIG. 4. Temperature dependence of  $I_{\text{TDS}}(0)$  shown by squares and  $\langle v_l^2 \rangle^{1/2}$  shown by circles.

tion of the excess scattering is limited in terms of the accessible smallest  $q$  limit in the present study, it is difficult to discuss this phenomenon quantitatively. Further work on this problem is currently in progress.

The increase in the large length scale density fluctuation upon decreasing temperature from the fully disordered state toward  $T_{\text{ODT}}$  appears to be somewhat analogous to that found in the vitrification process of glass forming liquid [19]. In the glass forming liquid, upon lowering temperature toward the glass transition temperature ( $T_g$ ), the long-range density fluctuations are developed in the system. The origin of the excess scattering in glass forming materials has been predicted by the coexistence of the “liquidlike” and the “solidlike” regions with different relaxation times. The density fluctuations in block copolymer systems occur between the ordered and disordered regions and are suppressed again upon the completion of ordering, the trend of which is different from the glass forming materials. However, if  $T_g$  of the block copolymer is close to the ODT temperature, the density fluctuations developed would not be relaxed but rather would freeze upon lowering temperature.

It is interesting to note that, similarly to the case of our block copolymer, an increase in the bulk specific volume occurs in the process of the condensation of water in the glassy state [20]. By using the molecular dynamics simulation, the presence of two coexisting phases differing in density has been indicated near a liquid-liquid critical point [21]: the systems separate into two phases characterized by different densities, structures, and mobilities, similar to the case of block copolymer at ODT.

An anomaly in the two-phase region is further observed in the thermal diffuse scattering (TDS) at  $q=0$ , as well. TDS is known to be caused by acoustic phonons propagating in the medium via cooperative thermal motion of the molecules. The scattering intensities of TDS,  $I_{\text{TDS}}(q)$ , are approximated by

$$I_{\text{TDS}}(q) = I_{\text{TDS}}(0) \exp(\alpha q^2), \quad (1)$$

where  $\alpha$  is a constant and  $I_{\text{TDS}}(0)$  is an extrapolated scattering intensity at  $q=0$  [22,23]. Figure 4 shows the temperature

dependence of  $I_{\text{TDS}}(0)$  determined by the SAXS method. Details of SAXS analysis are given elsewhere [14]. The values of  $I_{\text{TDS}}(0)$  are estimated from the best-fitting results between Eq. (1) and the experimental data in an intermediate  $q$  region where  $\log I \cdot q^2$  plots show a linear relationship [24]. The temperature dependence of  $I_{\text{TDS}}(0)$  in the fully ordered and disordered phases can be smoothly connected by a straight line, but the values  $I_{\text{TDS}}(0)$  in the two-phase region are higher than the values given by a straight line. According to the TDS’s theory [23],  $I_{\text{TDS}}(0)$  is expressed by

$$I_{\text{TDS}}(0)/\rho_{\text{el}} = \rho_{\text{el}} k_B T / [\rho_m \langle v_l^2(\mathbf{e}) \rangle], \quad (2)$$

where  $\rho_{\text{el}}$  is the average electron density,  $k_B$  is Boltzmann’s constant,  $\rho_m$  is the mass density, and  $v_l(\mathbf{e})$  is the group velocity of acoustic phonons in the direction  $\mathbf{e} = \mathbf{q}/q$ . The contribution of the long wavelength thermal vibration to the total density fluctuation is given by the spherical average of Eq. (2),

$$I_{\text{TDS}}(0)/\rho_{\text{el}} = \rho_{\text{el}} k_B T / (\rho_m \langle v_l^2(\mathbf{e}) \rangle). \quad (3)$$

In order to examine this anomaly further, we tried to separate the contribution of the anomaly in TDS into those from  $\rho_m$  (or  $\rho_{\text{el}}$ ) and  $\langle v_l^2 \rangle^{1/2}$ , assumed that Eq. (3) is valid within the observed temperature range. As seen in Fig. 4, it is clear that the values of  $\langle v_l^2 \rangle^{1/2}$  decrease with increasing  $T$ , and an anomalous drop of  $\langle v_l^2 \rangle^{1/2}$  is discerned in the coexistence region, indicating that the long-range spatial heterogeneities of the system suppress the acoustic phonons. Thus, the anomaly in TDS is found to be related not only to the anomaly in density but also to that in long wavelength acoustic phonons.

Finally, the temperature dependence of the specific volume may be looked into more closely. We tried to estimate the specific volume in the coexistence region,  $V_{\text{CO}}(T)$ , by assuming that  $V_{\text{CO}}(T)$  are approximately described in terms of the weight average of the specific volume in the ordered phase and that of the disordered phase which are obtained by straight lines shown in Fig. 3. The temperature dependence of the fraction for the ordered phases was estimated from the USAXS scattering profiles by assuming that the coexisting scattering profiles could be approximately described by a linear combination of scattering profiles at the temperature just below and above  $T_{\text{ODT}}$  [14]. As shown in Fig. 3, the estimated values of  $V_{\text{CO}}$  (closed circles) are found to be smaller than the observed values under the above assumptions. It would be very important to clarify such complex phenomena associated with a coupling between the two phases, not only in the field of block copolymers but also in other fields of physical science.

To summarize, we have obtained information regarding the two-phase coexistence region for a nearly symmetric diblock copolymer by using combined USAXS and SAXS profiles covering the wide  $q$  range of  $0.008 < q < 6.5 \text{ nm}^{-1}$ . In the coexistence region near  $T_{\text{ODT}}$ , we observed the anomaly in the long range density fluctuation as well as the anomaly in the long wavelength acoustic phonons caused by the spatial heterogeneities of the density.

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