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Synchrotron Small-Angle X-ray Scattering of Relaxation Process in a Nonentangled Diblock Copolymer

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ABSTRACT: The time changes in the scattered intensity induced by a pressure jump within the disordered state of nonentangled poly(styrene-*block*-isoprene) were measured by using time-resolved synchrotron small-angle X-ray scattering. It was found that the time changes in the scattered intensity could be approximated by the Cahn−Hilliard−Cook linearized theory. The analyses yielded the wavenumber q dependence of the Onsager coefficient of the block copolymer. We compared our result the Debye function $\Lambda(q) = 2\Lambda(0)[q^2R_\Lambda{}^2 + \exp(-q^2R_\Lambda{}^2) - 1]/q^4R_\Lambda{}^4$ as proposed by Fredrickson, where R_Λ is the radius of gyration of the block copolymer.

I. Introduction

Block copolymers are polymers where different kinds of polymers connected by covalent bonds and form long-range ordered periodical structure. The size of the periodical structures is on the order of 10−100 nm so that the block copolymer is one of the promising materials of nanotechnologies.[1−3] Thus, the morphological features of the block copolymer have been well investigated from the points of view of experiments, theory, and computer simulations.[4−6]

The dynamics of ordering processes upon the quench from the disordered state has been well investigated experimentally.[7−10] The dynamics of the concentration fluctuations in block copolymers have also received much attention from experimental and theoretical points of view. Akcasu proposed theoretical frameworks based on the dynamic random phase approximation (RPA) for the dynamics of the concentration fluctuations of multicomponent polymer systems.[11,12] Kawasaki and Sekimoto investigated the chain dynamics of entangled block copolymers.[13−15] They obtained a new stochastic equation to describe the dynamics of block copolymers and polymer blends and predicted that the Onsager coefficient Λ had a wavenumber q dependence. Fytas et al. have extensively investigated the dynamic structure factor of entangled melts of diblock copolymer and entangled solutions of high molecular weight diblock copolymers by using dynamic light scattering.[16−23] In this paper, we shall focus on the dynamics of a nonentangled and short diblock copolymer and aim to explore their q dependence of Λ. Theoretically, Fredrickson proposed q dependence of Λ based on Binder's procedure for nonentangeld diblock copolymers.[24] Experimentally, such a q dependence of Λ has been well investigated in the dynamics of the entangled polymer blends. In many papers on the polymer blends, experimentalists measured the time change in the structure factor in the early stage spinodal decomposition upon the quench induced by temperature jump into unstable region from one phase region by using small-angle neutron scattering[25−28] and then successfully obtained the q dependence of Λ by analyzing the time changes with linearized Cahn−Hilliard−Cook (CHC) theory.[29−33] We expect similar experiments on the block copolymer would explore the chain dynamics of diblock copolymers. However, the quench induced by temperature jump which usually takes several seconds to attain the quench cannot be used for our experiment since the changes in the scattered intensity for nonentangled diblock copolymer finish within several seconds as shown later while the time scale of the dynamics of entangled polymer blends is on the order of 10 min. Thus, we employed the pressure-jump technique for the quench and the time-resolved small-angle X-ray scattering (SAXS) with synchrotron radiation. The pressure jump enables us to attain the quick quench, and SAXS with synchrotron radiation enables us to measure the quantitative time change in the scattered intensity very quickly. However, another problem arises from the fluctuation effects[34,35] in diblock copolymers. The phase separation processes of diblock copolymers near the order−disorder transition (ODT) point progresses via nucleation and growth, where we cannot apply the linearized CHC theory due to the fluctuation effects. To avoid this inapplicability of linearized CHC theory, we observed the time change in the scattered intensity induced by the quench within disordered state where the time changes in the scattered intensity can be analyzed by linearized CHC theory. Here, we shall report that we successfully measure the time change in the relaxation process of the concentration fluctuations upon the pressure jump in the disordered state and that we obtained the q dependence of the Onsager coefficient of nonentangled diblock copolymers.

II. Experimental Section

The diblock copolymer used in this study was polystyrene-*block*-polyisoprene (S−I). The characteristics of the sample we used are listed in Table 1. It should be noted that the molecular weight of the S−I is lower than the critical molecular weight M_c from Rouse dynamics to Reptation dynamics since M_c of polyisoprene and polystyrene are respectively 10 000[36] and 31 000.[37] Thus, we expect that the dynamics of the S−I obeys the Rouse dynamics.[37] We prepared the specimen by solvent casting from toluene solution. S−I has the ODT temperature below room temperature. The sample was subjected to pres-

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Table 1. Characterization of the Sample Used in This Study

$M_n(10^3)$	M_w/M_n	PS wt %	$R_{g,block}$/nm[a]
8.38	1.03	52	2.81
		PS	PI
molar vol of monomer[31]		100 cm^3/mol	74.5 cm^3/mol
segment length[32]		0.68 nm	0.66 nm

[a] $R_{g,block} = \sqrt{{R_{g,PS}}^2 + {R_{g,PI}}^2}$.

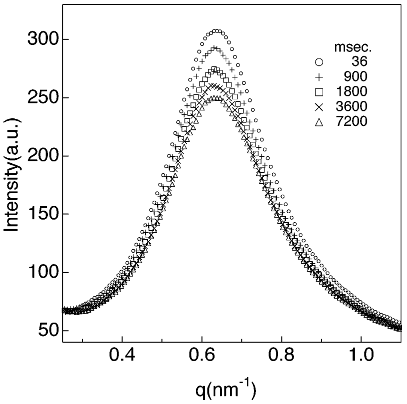

Figure 1. Time change in the scattered intensity as a function of q upon the pressure jump from 80.0 to 0.1 MPa at 33.0 °C.

sure jump from 80.0 to 0.1 MPa at 33.0 and 40.0 °C within the disordered state. We used the cell designed for high pressure and temperature by Kato and Taniguchi.[38] SAXS experiments were conducted at the BL45XU, Spring-8,[39] with the X-ray wavelength λ being 0.11 nm. The quench depth $\Delta\chi$ induced by pressure jump is 1.38×10^{-2} and 2.51×10^{-2} for 33.0 and 40.0 °C. $\Delta\chi$ is defined by $\Delta\chi = \chi_A - \chi_B$, where χ_A and χ_B are respectively the Flory–Huggins interaction parameter per monomer between styrene and isoprene after and before the pressure jump. χ_A and χ_B were obtained from fitting the equilibrium scattered intensity with the scattered intensity calculated by using the random phase approximation.[40] Upon the pressure jump, we measured the time changes in the scattered intensity with the scan rate being 36 ms/scan by using the CCD camera with image intensifier.[41] All scattered intensity profiles were corrected for background and then circularly averaged for further analyses. To obtain the viscosity and the self-diffusion coefficient of the S–I, we carried out linear viscoelastic measurements of the S–I in the disordered state by using ARES, Rheometrics, with a plate–plate geometry of diameter equal to 20.0 mm and angular frequency ω ranging from 0.01 to 100 rad/s. The strain amplitude used here is 1.0%.

III. Results and Discussion

Figure 1 shows the time change in the scattered intensity $I(q,t)$ of the S–I as a function of the magnitude of scattering vector q [$= (4\pi/\lambda)\sin(\theta/2)$, with θ being the scattering angle] upon the pressure jump at 33.0 °C. The scattered intensity at the observed q-region decreased with time, and the slow relaxation process was observed around peak position. The dynamics of the relaxation processes of concentration fluctuations in the S–I is described by the CHC theory.[31,32] The time change in the q-Fourier mode of concentration fluctuations $\psi(q,t)$ of the styrene component in the S–I at time t is expressed by

$$\frac{\partial\psi(q,t)}{\partial t} = -\Lambda(q)q^2\mu(q,t) + f(q,t) \qquad (1)$$

where $\Lambda(q)$ and $\mu(q,t)$ are the Onsager coefficient and the chemical potential, respectively. The random force $f(q,t)$ obeys the following fluctuation–dissipation relation:[30,32]

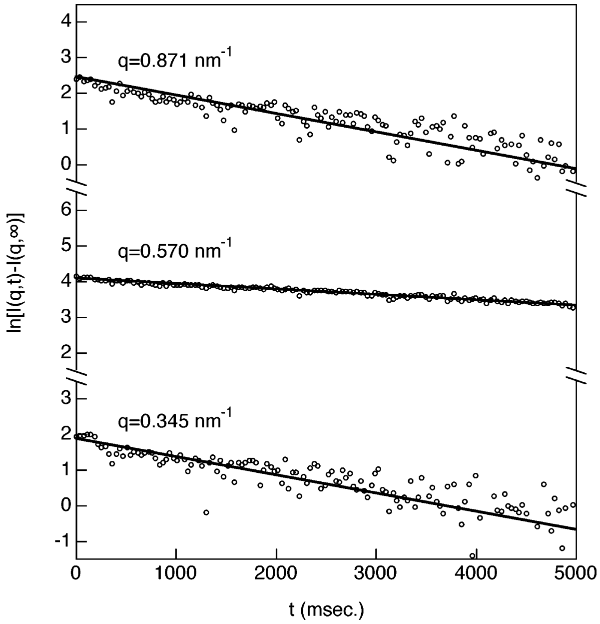

Figure 2. $\ln[I(q,t) - I^T(q)]$ as a function of time at various fixed q values. Solid lines indicate the fitting results with eq 6.

$$\langle f(q,t)f(-q,t')\rangle_T = 2\Lambda(q)q^2\delta(t-t') \qquad (2)$$

with the subscript T denoting a thermal average. If $\psi(q,t)$ is small, $\mu(q,t)$ can be calculated by the relation

$$\mu(q,t) = \frac{\psi(q,t)}{S^T(q)} \qquad (3)$$

where $S^T(q)$ corresponds to the equilibrium structure factor after the pressure jump in this study. From eqs 1–3 we obtain the following linearized CHC equation for the time evolution of the structure factor $S(q,t)$, which is proportional to $I(q,t)$:

$$S(q,t) = \langle|\psi(q,t)|^2\rangle_T = S^T(q) + [S(q,0) - S^T(q)]\exp[-2R(q)t] \qquad (4)$$

where $R(q)$ is the growth rate at q defined by

$$R(q) = q^2\frac{\Lambda(q)}{S^T(q)} \qquad (5)$$

Rearranging eq 4, we obtain

$$\ln[S(q,t) - S^T(q)] = \ln[S(q,0) - S^T(q)] - 2R(q)t \qquad (6)$$

Thus, we can estimate $R(q)$ from the slope of $\ln[I(q,t) - I^T(q)]$ vs t plot where ln denotes natural logarithms. In Figure 2, $\ln[I(q,t) - I^T(q)]$ is plotted as a function of t upon the quench. The linearity between $\ln[I(q,t) - I^T(q)]$ and t can be found in each plot, and the slopes yielded $R(q)$. Figure 3 show the q dependence of $R(q)$. $R(q)$ has the minimum at $q = 0.6$ nm^{-1}, which is near the peak position q_m of the scattered intensity after the pressure jump.

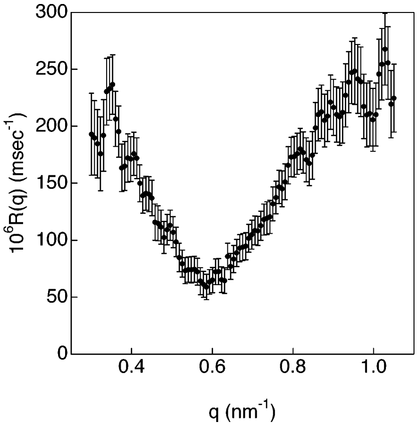

Figure 3. $R(q)$ is plotted as a function of q at 33.0 °C.

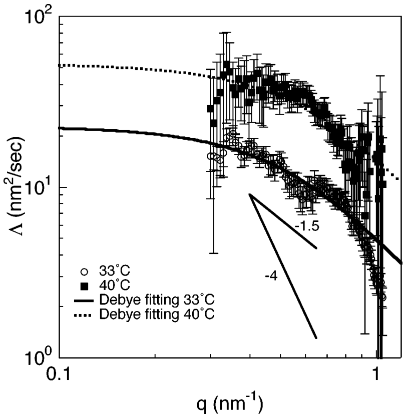

Figure 4. Onsager coefficient $\Lambda(q)$ as a function of q at 33.0 and 40.0 °C. The solid and broken lines correspond to the fitting result with the Debye form (eq 8) at 33.0 and 40.0 °C, respectively.

Next, we estimated the Onsager coefficient $\Lambda(q)$. From eq 5, $\Lambda(q)$ is given by

$$\Lambda(q) = -\frac{R(q)S^{\mathrm{T}}(q)}{q^2} \tag{7}$$

Figure 4 shows the q dependence of Λ as calculated by eq 7. In Figure 4, we also show the q dependence of Λ at 40 °C. The q dependence of Λ can be divided into the following three regions: (i) $\Lambda(q)$ becomes almost constant at $q < q_{\mathrm{m}}$, (ii) $q^{-1.5}$ dependence is observed at $q_{\mathrm{m}} < q < 0.7$ nm^{-1}, and (iii) q^{-4} dependence is observed at 0.7 nm^{-1} $< q$. We employed the Debye form proposed by Fredrickson to express the q dependence of Λ for the time domain where the internal modes are relaxed and tried to fit the data with

$$\Lambda(q) = 2\Lambda(0)\frac{q^2{R_\Lambda}^2 + \exp(-q^2{R_\Lambda}^2) - 1}{q^4{R_\Lambda}^4} \tag{8}$$

by treating $\Lambda(0)$ and R_Λ as floating parameters. Here $\Lambda(0)$ and R_Λ are respectively Λ at $q = 0$ and the radius of gyration of the diblock copolymer. The Debye function agrees with the experimental results at $q < 0.7$ nm^{-1}. However, the Debye function deviates from the experimental results at $q > 0.7$ nm^{-1} since the asymptotic behavior of the Debye function at high q is proportional to q^{-2} while the experimental results shows a q^{-4} dependence. The yielded values of $\Lambda(0)$ and R_Λ are listed in Table 2. We also listed $R_\Lambda/R_{\mathrm{g,block}}$ which are nealry equal to unitiy, indicating that the q dependence of Λ at $q < 0.7$ nm^{-1} is expressed by

$$\Lambda(q) = 2\Lambda(0)\frac{q^2{R_{\mathrm{g,block}}}^2 + \exp(-q^2{R_{\mathrm{g,block}}}^2) - 1}{q^4{R_{\mathrm{g,block}}}^4} \tag{9}$$

Table 2. Fitting Parameters with OZD Form

temp (°C)	$10^{17}\Lambda(0)$ (m^2/s)	R_Λ (nm)	$R_\Lambda/R_{\mathrm{g,block}}$
33.0	2.27	2.84	1.01
40.0	5.27	2.47	0.88

Let us compare $\Lambda(0)$ experimentally estimated with those estimated from independent measurement. According to Ackasu,[12] $\Lambda(0)$ is expressed by

$$\Lambda(0) = \frac{\Lambda_{\mathrm{S}}\Lambda_{\mathrm{I}}}{\Lambda_{\mathrm{S}} + \Lambda_{\mathrm{I}}} \tag{10}$$

where Λ_i is the bare mobility of the ith component [i = S (styrene) or I (isoprene)]. Though we do not show it here, the ω dependence of the storage modulus does not have any plateau region in the disordered state; we expect the chain dynamics obeys the Rouse model. Thus, Λ_i is given by

$$\Lambda_i = \phi_i{\zeta_i}^{-1} \tag{11}$$

where ϕ_i and ζ_i are respectively the volume fraction and the friction coefficient of the ith component. Unfortunately, we do not know the friction coefficient of each component of the S−I in the disordered state so that we used the averaged friction coefficient estimated from the viscoelastic measurement of the S−I. The friction coefficient has the following relationship with the diffusion coefficient:

$$D_{\mathrm{S}} = \frac{1}{\zeta N} \tag{12}$$

with N being the polymerization index of polymers. Nemoto et al. reported that the relationship between the diffusion coefficient D_{S} and the zero-shear viscosity η is well expressed by the following Rouse dynamics for nonentangled system:[42]

$$D_{\mathrm{S}} = \frac{\rho RT{R_{\mathrm{g}}}^2}{6M\eta} \tag{13}$$

where ρ, R, R_{g}, and M are respectively the density of the polymer, the gas constant, the radius of gyration of the polymer, and molecular weight of polymer. We obtained $\eta = 5.83 \times 10^5$ Pa·s at 33.0 °C from viscoelastic measurements. Substituting $\rho = 9.8 \times 10^2$ kg/m^3, R = 8.314 J mol^{-1} K^{-1}, T = 316 K, $R_{\mathrm{g}} = 2.81 \times 10^{-9}$ m, and η into eq 13, we obtained $D_{\mathrm{s}} = 6.52 \times 10^{-19}$ m^2/s, and thus the averaged friction coefficient $\bar{\zeta} = 1.45 \times 10^{16}$ m^{-2} s is obtained with total polymerization index $\bar{N}$ of the S−I being 106 at 33.0 °C. Substituting $\Lambda_{\mathrm{I}} = \phi_{\mathrm{I}}\bar{\zeta}^{-1} = 3.09 \times 10^{-17}$ m^2/s and $\Lambda_{\mathrm{S}} = \phi_{\mathrm{S}}\bar{\zeta}^{-1} = 3.81 \times 10^{-17}$ m^2/s into eq 10, the calculated $\Lambda(0)$, $\Lambda(0)_{\mathrm{cal}}$, is 1.71×10^{-17} m^2/s at 33 °C. A similar procedure with $\eta = 1.06 \times 10^5$ Pa·s at 40.0 °C yielded $\Lambda(0)_{\mathrm{cal}} = 9.62 \times 10^{-17}$ m^2/s at 40.0 °C. The ratio $\Lambda(0)/\Lambda(0)_{\mathrm{cal}}$ is 1.44 and 0.58 respectively at 33.0 and 40.0 °C, which show good agreement. This agreement proves the validity of the value of $\Lambda(0)$ obtained in this experiment.

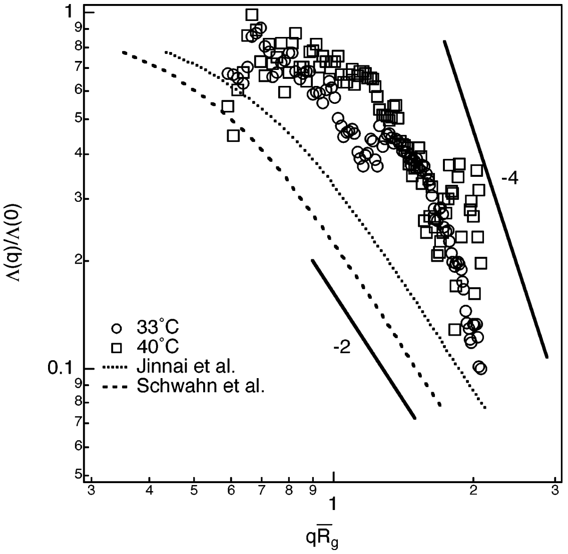

Figure 5. Reduced Onsager coefficient $\Lambda(q)/\Lambda(0)$ are plotted as a function of the reduced wavenumber $q\bar{R}_g$ for S−I diblock copolymer and symmetric polymer blends obtained by Jinnai et al. (dotted line) and by Schwahn et al. (broken line).

Let us compare our result with $\Lambda(q)$ obtained for polymer blends experimentally to explore the effects of the connectivity on the q dependence of the Onsager coefficient. To compare the different systems, we plotted the reduced Onsager kinetic coefficient $\Lambda(q)/\Lambda(0)$ as a function of the reduced wavenumber $q\bar{R}_g$, where $\bar{R}_g$ is the mean radius of gyration of each component for polymer blends and block copolymers. Thus, $\bar{R}_g$ for our S−I system is nearly equal to be $\sqrt{2}R_{g,\text{block}}$. Figure 5 shows the comparison between the q dependence of the Onsager coefficient for polymer blends and that for the S−I diblock copolymer. Jinnai et al.[25] and Schwahn et al.[43] found that the Onsager kinetic coefficient of symmetric polymer blends is given by the following form proposed by Pincus[33]

$$\Lambda(q) = \Lambda(0)\frac{1 - \exp(-q^2{R_\Lambda}^2)}{q^2{R_\Lambda}^2} \tag{14}$$

with $R_\Lambda = 1.7\bar{R}_g$ (Jinnai et al.) and $R_\Lambda = 2.1\bar{R}_g$ (Schwahn et al.). Although the suppression of $\Lambda(q)$ for the polymer blends occurs at lower q region than that for the diblock copolymer, the strong suppression or q^{-4} dependence is observed for the diblock copolymer at higher q region while $\Lambda(q)$ for the polymer blends exhibits the relatively weak suppression. The strong q^{-4} dependence may originate from the connectivity in the diblock copolymer.

IV. Conclusion

We have investigated the relaxation process of the concentration fluctuations in poly(styrene-*block*-isoprene) upon the pressure jump in its disordered state. The time changes in the scattered intensity are found to be well expressed by the Cahn−Hilliard−Cook (CHC) linearized theory. The CHC analysis yielded the q dependence of the Onsager kinetic coefficient $\Lambda(q)$. $\Lambda(q)$ at the lower q region was found to be expressed by the Debye function $\Lambda(q) = 2\Lambda(0)[q^2{R_\Lambda}^2 + \exp(-q^2{R_\Lambda}^2) - 1]/q^4{R_\Lambda}^4$ as proposed by Fredrickson, where R_Λ is nearly equal to the radius of gyration of the diblock copolymer. However, we found the q^{-4} dependence at the higher q region, which does not agree with Debye function. This may originate from the connectivity in the diblock copolymer.

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