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Synchrotron Small-Angle X-ray Scattering of Slow Spinodal Decomposition in a Block Copolymer

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ABSTRACT: A block copolymer poly(styrene-*b*-*tert*-butylstyrene) in the frozen "disordered" state has been prepared by fast solution casting. The time changes in the scattered intensity induced by a temperature jump from the frozen disordered state at room temperature to above the glass transition temperature 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 linearized theory. The wavenumber q-dependence of the Onsager coefficient, $\Lambda(q)$, derived from the growth rate, $R(q)$, was discussed.

I. Introduction

Phase transitions of block copolymers have been an important and interesting topic in nonequilibrium statistical physics in recent years. Block copolymers exhibit microphase separation transition and form periodical microdomains. However, most of the studies have been concerned with the phase diagram and the equilibrium structure. Both experimental[1,2] and theoretical[3−5] works explored mainly the various highly ordered structures of block copolymer melts. Hashimoto[6] proposed the Cahn−Hilliard−Cook (CHC) type equations[9,10] for the dynamics of block copolymers in the early stage of phase separation by using the time-dependent Ginzburg−Landau (TDGL) theory. He postulated that the dynamics of the ordering process could occur via the spinodal decomposition in polymer blends. Kawasaki and Sekimoto[7,8] obtained a new stochastic equation to describe the dynamics of block copolymers and predicted that the Onsager coefficient Λ had a wavenumber q-dependence. For the dynamics of spinodal decomposition in polymer blends, the q-dependence of $\Lambda(q)$ was investigated by small-angle neutron scattering.[11,12] Many papers[13−20] reported the experimental results for the ordering process of block copolymers. However, only two papers, by Connel and Richards[15] and by Stühn et al.,[20] compared the experimental results with the CHC theory. However, they did not find the q-dependence of $\Lambda(q)$. The other papers reported that the ordering dynamics of block copolymer progresses via nucleation and growth because the systems were quenched near the order−disorder transition (ODT) point where the fluctuation effects played a very important role.

In this paper we investigated the ordering dynamics in the block copolymer poly(styrene-*b*-*tert*-butylstyrene) quenched deeply by means of small-angle X-ray scattering (SAXS). The experimental results are compared with the CHC equation, and then the q-dependence of $\Lambda(q)$ is obtained.

Table 1. Characterization of the Sample Used in this Study

M_n (10^{-5})	M_w/M_n	PS wt %	$\overline{R}_{g,\mathrm{Block}}$/nm[a]	$\overline{N}_c$[b]
1.63	1.13	50	11.0	158
			PS	PtBS
molar volume of monomer[30] (cm^3/mol)			107	167
segment length[30] (nm)			0.67	0.76
polymerization index between entanglements[30]			128	188

[a] $\overline{R}_g = (R_{g,PS}{}^2 + R_{gPtBS}{}^2)^{1/2}$. [b] $\overline{N}_e = (N_{e,PS} + N_{e,PtBS})/2$.

II. Experimental Method

II-1. Specimens. The diblock copolymer was selected partially because of its high glass transition temperature T_g [T_g of polystyrene (PS) is 100 °C and T_g of poly(*tert*-butylstyrene) (PtBS) is 149 °C]. Thus, we had the following advantages for our experimental study: (i) The "disordered" state obtained through a fast solution casting of the thin film remained disordered even at room temperature which should be the temperature of the ordered region. The frozen-in structure (disordered state in our case) due to the high T_g means that we could measure the dynamics of high molecular weight block copolymers in the bulk. (ii) The dynamics of the ordering process became extremely slow if we quenched to a temperature near T_g. By using these two advantages we could measure the slow dynamics of the ordering process in block copolymers. The characteristics of the sample we used are listed in Table 1.

A benzene solution of the diblock copolymer was quickly dried on a watch glass at 60 °C. Then the diblock copolymer film in the disorder state (which can be demonstrated indirectly at this time; further experiments are under way) was dried in a vacuum oven at 100 °C (below the glass transition temperature), cut into 5 mm squares, stacked, and molded at 105 °C. The thicknesses of the molded samples were on the order of 0.15 mm.

II-2. Experimental Technique. SAXS experiments were conducted at the SUNY X3A2 beamline, National Synchrotron Light Source, Brookhaven National Laboratory. We used a modified Kratky collimator[21] and a one-dimensional position-sensitive detector. The X-ray wavelength λ was 0.154 nm. The sample was subjected to a temperature jump from 23 to 228 °C. All scattered intensity profiles were corrected for background and smearing effects.[22]

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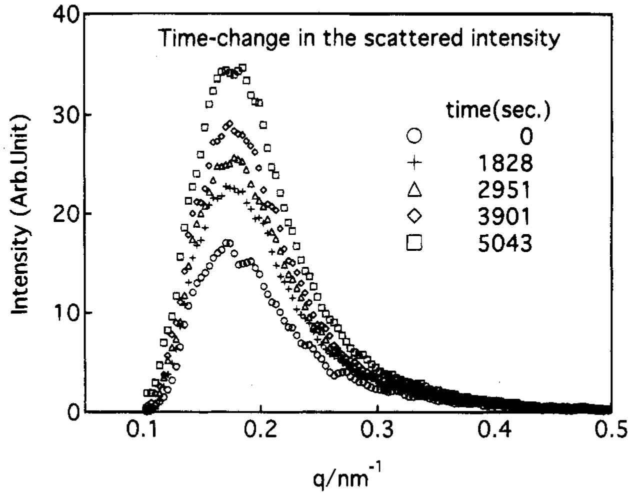

Figure 1. Time change in scattered intensity as a function of q after a temperature jump from 23 to 228 °C. Measurement time per curve was 60 s. Sample thickness was 0.15 mm. It should be noted that we have most likely prepared a disordered diblock copolymer by the quick solvent evaporation procedure at 60 °C. The scattered intensity from the initial "disordered" state (hollow circles) agreed with the estimates (eq 7) of the scattered intensity based on RPA with $\chi = 0.0075$ and parameters listed in Table 1.

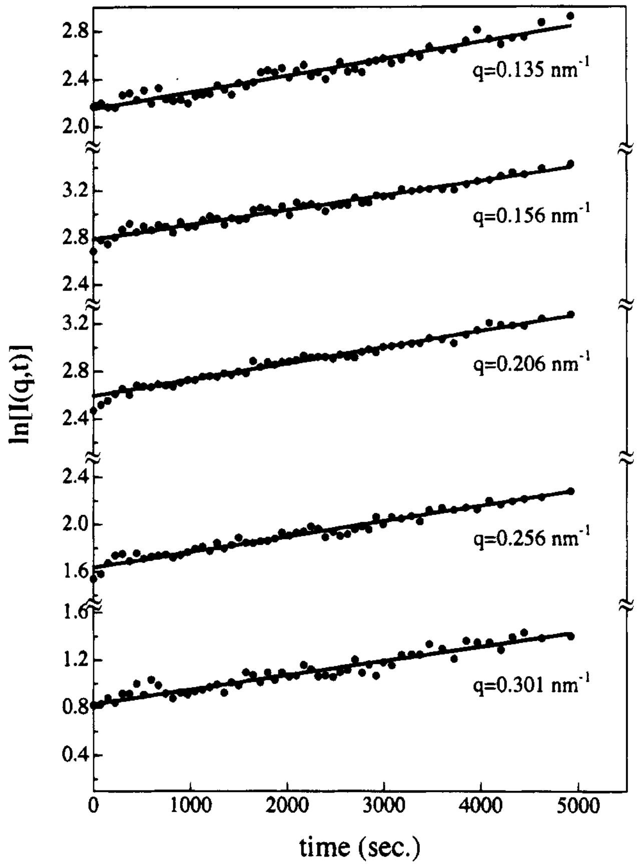

Figure 2. Semilogarithmic plot of scattered intensity as a function of time at various fixed q values.

III. Experimental Results

Figure 1 shows the time change in the scattered intensity plotted as a function of the magnitude of scattering vector $q[=(4\pi/\lambda)\sin(\theta/2)$, with θ being the scattering angle]. The scattered intensity at the observed q-region increased with time; but the peak position did not change with time. It is expected that the peak should shift to smaller q values at later times because of nonlinear effects.

IV. Analyses and Discussion

IV-1. Test of the Cahn Linearized Theory. Figure 2 shows the time change in the scattered intensity $I(q,t)$ as a function of time t at various fixed q values. The semilogarithmic plot indicates that the scattered intensity at various q values increases exponentially up to 4.9×10^3 s. Such an exponential growth was observed in the phase separation dynamics of poly(styrene-*b*-isoprene) in the presence of C_6H_{12}/C_6D_{12}.[15] However, the time region for the exponential growth was only 40 s for the poly(styrene-*b*-isoprene) in the presence of C_6H_{12}/C_6D_{12}.

According to Hashimoto[6] and Kawasaki and Sekimoto,[7,8] the dynamics of spinodal decomposition (SD) in a block copolymer A–B is described by the following TDGL theory:

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

where $\psi(q,t)$, $\Lambda(q)$, and $\mu(q,t)$ are the order parameter of A, the Onsager coefficient, and the chemical potential, respectively. In this study, A and B correspond to PS and PtBS, respectively. The random force $f(q,t)$ obeys the following fluctuation–dissipation relation:

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

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

$$\mu(q,t) = \psi(q,t)/S^T(q) \qquad (3)$$

where $S^T(q)$ is the virtual structure factor. From eqs 1 to 3 we obtain the CHC equation for the structure factor $S(q,t)$:

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

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

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

If the quench depth is deep, the effects of thermal noise become negligible and the time evolution of $S(q,t)$ can be expressed by the Cahn theory:[9]

$$S(q,t) = S(q,0)\exp[2R(q)\,t] \qquad (6)$$

The Cahn linearized theory also predicted that the peak position does not change with time. The experimental results agree with these features and indicate that the time change in the scattered intensity corresponds to the increase in the concentration fluctuations from the homogeneous state. Leibler[4] calculated $S^T(q)$ in the context of the Laudau-type mean-field theory by using the random-phase approximation (RPA). The effects of polydispersity and composition distribution were then taken into account in $S^T(q)$.[23–25] The results suggest that $S^T(q)$ can be expressed by

$$[S^T(q)]^{-1} = \frac{S(q)}{W(q)} - 2\chi \qquad (7)$$

with χ being the Flory–Huggins interaction parameter per segment. According to ref 25, $S(q)$ and $W(q)$ are given by

$$S(q) = S_{AA}(q) + 2S_{AB}(q) + S_{BB}(q) \tag{8}$$

and

$$W(q) = S_{AA}(q)\, S_{BB}(q) - S_{AB}(q)^2 \tag{9}$$

$S_{AA}(q)$, $S_{AB}(q)$, and $S_{AA}(q)$ are expressed by

$$S_{AA}(q) = r_n f_{A,n}{}^2 g_{A,n}{}^{(2)}(q) \tag{10}$$

$$S_{BB}(q) = r_n(1 - f_{A,n})^2 g_{B,n}{}^{(2)}(q) \tag{11}$$

and

$$S_{AB}(q) = r_n f_{A,n}(1 - f_{A,n}) g_{A,n}{}^{(1)}(q)\, g_{B,n}{}^{(1)}(q) \tag{12}$$

with

$$g_{K,n}{}^{(1)}(q) = \frac{1}{x_{K,n}}\left[1 - \left\{\frac{1}{x_{K,n}(\lambda_K - 1) + 1}\right\}^{1/(\lambda_K - 1)}\right] \tag{13}$$

and

$$g_{K,n}{}^{(2)}(q) = \frac{2}{x_{K,n}{}^2}\left[x_{K,n} - 1 + \left\{\frac{1}{x_{K,n}(\lambda_K - 1) + 1}\right\}^{1/(\lambda_K - 1)}\right] \tag{14}$$

where

$$x_{K,n} = N_{K,n} a_K{}^2 q^2/6 \tag{15}$$

and

$$\lambda_K = N_{K,w}/N_{K,n} \tag{16}$$

Here $N_{K,n}$, $N_{K,w}$, and a_K are respectively the number-average degree of polymerization (DP), the weight-average DP, and the statistical segment length of K (K = A or B). r_n and $f_{A,n}$ are respectively the effective number-average DP of the block copolymer and the number-average fraction of A and are defined by

$$r_n = (v_A/v_0)N_{A,n} + (v_B/v_0)N_{B,n} \tag{17}$$

and

$$f_{A,n} = v_A N_{A,n}/(v_A N_{A,n} + v_B N_{B,n}) \tag{18}$$

where v_K denotes the molar volume of K, and v_0 denotes the molar volume of the reference cell of the system given by

$$v_0 = (v_A v_B)^{1/2} \tag{19}$$

Around the peak position q^*, $S^T(q)$ could be approximated by the Orstein–Zernike–Debye (OZD) form[26]

$$S^T(q) = \frac{S^T(q^*)}{1 + \xi^2(q - q^*)^2} \tag{20}$$

where the correlation length ξ is defined by

$$\xi^2 = \frac{1}{4(\chi - \chi_s)}\left[\frac{S(q^*)}{W(q^*)}\right]'' \tag{21}$$

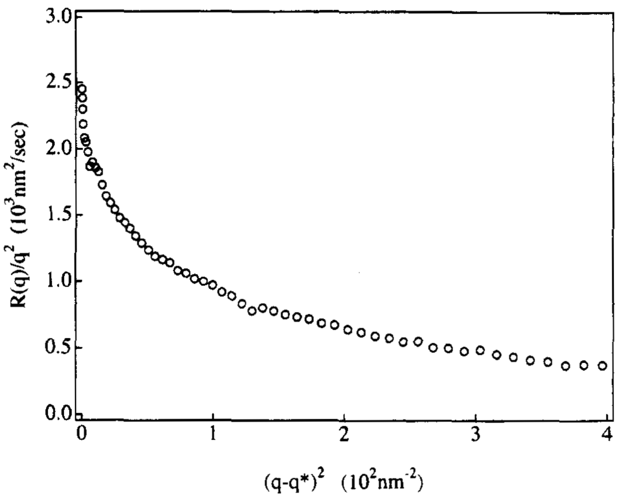

Figure 3. $R(q)/q^2$ as a function of $(q - q^*)^2$ for $q > q^*$.

with χ_s being the value at the spinodal point of the order–disorder transition of a block copolymer or $S(q^*)/W(q^*)$. At $q > q^*$, $S^T(q)$ can be approximated well by eq 20. It is noted that the slope [(slope)$_{OZD}$] and the intercept [(intercept)$_{OZD}$] in an OZD plot or $1/S^T(q)$ vs $(q - q^*)^2$ are described by

$$(\text{slope})_{OZD} = -\xi^2/S^T(q^*) \tag{22}$$

and

$$(\text{intecept})_{OZD} = [2(\chi - \chi_s)] \tag{23}$$

respectively, and that (slope)$_{OZD}$ is independent of temperature. By using eqs 8–19 with the characteristic properties of the block copolymer listed in Table 1, we calculated $\chi_s = 0.007\,49$, (slope)$_{OZD}$ = 0.385, and $q_{cal}{}^* = 0.162$ nm^{-1}, which is in reasonable agreement with $q_{exp}{}^* = 0.17$ nm^{-1}. By substituting eq 20 into eq 5, we obtain

$$R(q) = -q^2\frac{\Lambda(q)}{S^T(q^*)}[1 + \xi^2(q - q^*)^2] \tag{24}$$

If $\Lambda(q)$ is independent of q, a plot of $R(q)/q^2$ vs $(q - q^*)^2$, also known as the "Cahn plot", should show a linear curve. Figure 3 shows the $R(q)/q^2$ vs $(q - q^*)^2$ plot for $q > q^*$. The curve clearly implies that $\Lambda(q)$ is not independent of q.

Kawasaki and Sekimoto[8] proposed the following $\Lambda(q)$ expression.

$$\Lambda(q) = \frac{\Lambda_0}{q^2}[\phi_{PtBS}{}^2\eta_{PS} + \phi_{PS}{}^2\eta_{PtBS} + \phi_{PS}\phi_{PtBS}\eta_{PS}\eta_{PtBS}] \tag{25}$$

where ϕ_K and Λ_0 are the volume fraction of the Kth component and the Onsager coefficient at $q = 0$, respectively. η_K is defined by

$$\eta_K = 1 - \exp(-R_{g,K}{}^2 q^2) \tag{26}$$

where $R_{g,K}$ is the radius of gyration of the Kth component given by

$$R_{g,K}{}^2 = \frac{1}{6}N_K a_K{}^2 \tag{27}$$

with N_K and a_K being the polymerization index and the statistical segment length of the Kth component, re-

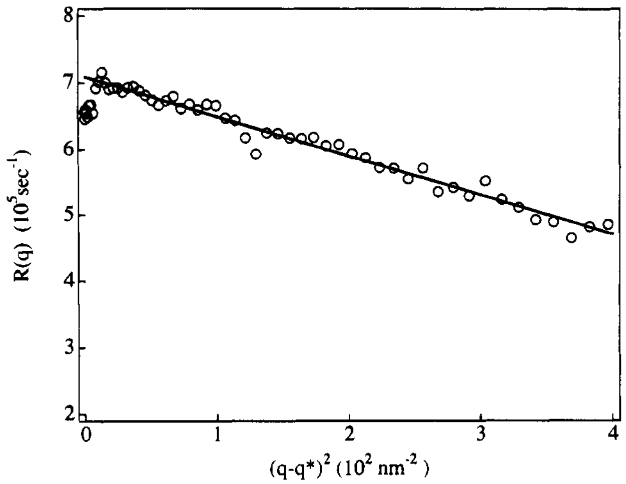

Figure 4. $R(q)$ as a function of $(q - q^*)^2$ for $q > q^*$. The solid line indicates the fitting result with $R(q) = 7.09 \times 10^{-5} – 5.97 \times 10^{-4}\,(q - q^*)^2$.

spectively. Equation 25 denotes the "fast theory", whereby a constant chemical potential for the total monomer density has been assumed.[8] For $qR_{g,PS} \gg 1$ and $qR_{g,PtBS} \gg 1$

$$\Lambda(q) \sim q^{-2} \tag{28}$$

Equation 24 then becomes

$$R(q) = \frac{K}{S^{T}(q^*)}[1 + \xi^2(q - q^*)^2] \tag{29}$$

In eq 29, $R(q)$ is proportional to $(q - q^*)^2$ for $q > q^*$ where K is a constant. In Figure 4, $R(q)$ is plottted as a function of $(q - q^*)^2$ for $q > q^*$. The relationship between $R(q)$ and $(q - q^*)^2$ becomes linear so that $\Lambda(q)$ is found to be proportional to q^{-2} in the high q-region. There is a deviation from the linear relationship around $(q - q^*)^2 = 0$ because q cannot be satisfied with the conditions $qR_{g,PS} \gg 1$ and $qR_{g,PtBS} \gg 1$.

IV-2. Estimations of the χ-Parameter and $\Lambda(q)$. The slope [$(\text{slope})_{R(q)}$] and the intercept [$(\text{intercept})_{R(q)}$] in Figure 4 are given by

$$(\text{slope})_{R(q)} = K\frac{\xi^2}{S^{T}(q^*)} \tag{30}$$

and

$$(\text{intercept})_{R(q)} = K/S^{T}(q^*) = 2K(\chi - \chi_s) \tag{31}$$

respectively. From eqs 23 and 31,

$$\frac{(\text{slope})_{R(q)}}{(\text{slope})_{\text{OZD}}} = -K \tag{32}$$

we then obtained $K = -646\ \text{s}^{-1}$ so that χ at 228 °C can be estimated by using eq 31 with the estimated K. The estimated value of χ is 0.0304, and the thermodynamic force ϵ defined by

$$\epsilon = (\chi - \chi_s)/\chi_s \tag{33}$$

is 3.06 which is more than unity. The value of ϵ indicates that the phase separation condition of the system at 228 °C corresponds to a deep quench and that the thermal noise effects can be neglected at 228 °C.

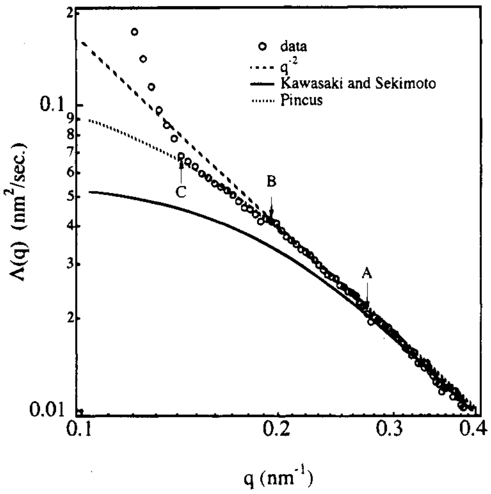

Figure 5. Onsager coefficient $\Lambda(q)$ as a function of q. The solid line and the dotted line correspond to the Kawasaki and Sekimoto theory (eq 25) and the Pincus theory (eq 36), respectively. The broken line has a slope of −2. Data points at $q < 0.14\ \text{nm}^{-1}$ should be ignored.

This result is consistent with the exponential growth of the scattered intensity. Further experiments at other temperatures could determine the temperature dependence of χ. Then the order–disorder transition (ODT) temperature could be estimated.

The theory of Fredrickson and Binder[27] and the experimental results by Bates et al.[16] suggested that the phase separation of block copolymers near the ODT temperature progresses via nucleation and growth because of the fluctuation effects. However, according to Muthukumar,[28] composition fluctuation effects dominante over a narrow range of χN, $(\chi N)_t < \chi N < (\chi N)_t + 1$, where χN is the product of χ and polymerization index N of block copolymers and $(\chi N)t$ is the value of χN at ODT. $(\chi N)_t$ is given by[27]

$$(\chi N)_t = 10.495 + 41.0N^{-1/3} \tag{34}$$

and the value of $(\chi N)_t$ is 14.32 for PS–PtBS. Since the value of χN at 228 °C is 37.51 and is much higher than $(\chi N)_t + 1$. It is, hence, expected that the fluctuation effects become small and that the phase separation occurs via spinodal decomposition in the strong segregation limit.

By using the estimated χ, eqs 8–19, $S^{T}(q)$ can be computed so that we can determine the q-dependence of $\Lambda(q)$. From eq 5, $\Lambda(q)$ is given by

$$\Lambda(q) = -R(q)\,S^{T}(q)/q^2 \tag{35}$$

Figure 5 shows the q-dependence of $\Lambda(q)$ as calculated by eq 35. The solid line is the theoretical results based on the Kawasaki and Sekimoto theory.[8] We fitted the region with a q^{-2}-dependence by using eq 25 and the values of $R_{g,PS}$ and $R_{g,PtBS}$ estimated from the polymerization indices and the statistical segment length of both components. We treated Λ_0 as a floating parameter. In the high q-region, $\Lambda(q)$ is proportional to q^{-2} as represented by the broken line. The q^{-2} dependence at high q values agree with the Kawasaki and Sekimoto result. However, the experimental result bends down at $q = 0.2\ \text{nm}^{-1}$ (point B in Figure 5) which is smaller than that of the theoretical result (point A, $q = 0.28\ \text{nm}^{-1}$ in Figure 5). Furthermore, the experimental data bend upward at $q \approx 0.14\ \text{nm}^{-1}$ (point C in Figure 5) which is not expected in the theoretical prediction. The reason for the upward bend could be an experimental artifact due to strong stray X-rays. Further experiments are needed to ascertain the upward bend at smaller q values.

In the Pincus theory,[29]

$$\Lambda(q) = \Lambda_0 \frac{1 - \exp(-\bar{R}_g^{\,2} q^2)}{\bar{R}_g^{\,2} q^2} \qquad (36)$$

is compared with $\Lambda(q)$ for polymer blends,[11,12] where $\bar{R}_g$ is the radius of gyration of the block copolymer. We fitted the data with eq 36 by treating $\bar{R}_g$ and Λ_0 as floating parameters and obtained $\bar{R}_g = 9.0$ nm and $\Lambda_0 = 0.13$ nm^2/s. The value of $\bar{R}_g$ was about 0.82 times as large as that ($\bar{R}_{g,\mathrm{block}}$) estimated from the molecular weight measurement (see Table 1).

V. Summary

In summary, we have investigated the extremely slow phase separation process via spinodal decomposition in poly(styrene-*b*-*tert*-butylstyrene). The exponential growth of the scattered intensity with time is found to continue up to 4.9×10^3 s, and the early stage of the ordering in the block copolymer can be approximated by the Cahn linearized theory. The value of $R(q)$ and that of the χ parameter at the phase separation temperature, together with the q-dependence of $\Lambda(q)$, are obtained by an analysis of the Cahn linearized theory. At $qR_{g,\mathrm{PS}} \gg 1$ and $qR_{g,\mathrm{PtBS}} \gg 1$, we found that q^{-2}-dependence in $\Lambda(q)$ as predicted by Kawasaki and Sekimoto. The experimental results over the entire q-range, however, were inconsistent with the theoretical predictions as shown in Figure 5.

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