

# Small-angle X-ray scattering from block copolymers in disordered state: 2. Effect of molecular weight distribution\*

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Spatial segmental density fluctuations occurring in a polystyrene–polyisoprene diblock copolymer in bulk and in disordered state were investigated by small-angle X-ray scattering. The observed wavelength of the dominant mode of the fluctuations was found to be larger than that predicted by the random phase approximation by a factor up to 50%. This discrepancy was found to be essentially removed by taking into account the distributions of molecular weight and composition of the block copolymer.

(Keywords: small-angle X-ray scattering; block copolymer; disordered state; molecular weight distribution; thermal concentration fluctuation; random phase approximation)

## INTRODUCTION

Analyses of the spectrum of thermally induced concentration fluctuations of polymer mixtures and block copolymers in the disordered bulk or condensed state are one of the interesting subjects in polymer physics. This is partly because the analyses lead to the prediction of the thermodynamic stability limits (spinodal points) for the mixtures and block copolymers, and partly because the fluctuations reflect properties of individual polymer molecules in the condensed phase such as their radii of gyration and the thermodynamic interaction parameter  $\chi$  between the dissimilar monomers. The results obtained in such studies also provide key information on the mechanism and dynamics of ordering processes when the systems are quenched inside the spinodal line. Analyses on thermally induced spatial concentration fluctuations of segments can be performed experimentally by elastic scattering of light, X-rays and neutrons.

We previously reported small-angle X-ray scattering (SAXS) analyses of the spatial concentration fluctuations of segments for a particular diblock copolymer HK-17 of polystyrene–polyisoprene (SI) in bulk and in disordered state<sup>1</sup>. We found that the spectrum of thermal concentration fluctuations as observed by the SAXS intensity distribution is in good agreement with the theoretical spectrum predicted by Leibler<sup>2</sup> on the basis of the mean-field random phase approximation (RPA). By best-fitting the experimental SAXS intensity distributions measured as a function of temperature we could

determine the thermodynamic interaction parameter  $\chi$  between dissimilar monomers as a function of temperature. The  $\chi$ -parameter is an important parameter which determines the intensity of the concentration fluctuations  $\langle \eta^2(q) \rangle_T$  for the particular Fourier mode with wavenumber  $q$  and its  $q$ -dependence, and therefore the fluctuation spectrum, where  $\langle \rangle_T$  denotes thermal average.

Another important parameter which also characterizes the fluctuation spectrum is the wavenumber  $q_m$  of the dominant mode of the fluctuations, although the analysis of this parameter was disregarded in the previous paper<sup>1</sup>. This mode with  $q_m$  is the one which gives rise to the maximum value of  $\langle \eta(q)^2 \rangle_T$  and hence to the maximum scattering intensity  $I(q_m)$  at the magnitude of the scattering vector  $q$  equal to  $q_m$ . Here  $q$  is defined by

$$q = (4\pi/\lambda)\sin \theta \quad (1)$$

and

$$q_m = 2\pi/D = (4\pi/\lambda)\sin \theta_m \quad (2)$$

where  $\lambda$  and  $\theta$  are the wavelength of X-ray and half the scattering angle in the medium, respectively,  $D$  is the wavelength of the dominant Fourier mode of the fluctuations, and  $2\theta_m$  is the scattering angle at which the scattered intensity becomes a maximum.

In this paper we re-examine our previous experimental data for HK-17 and compare the experimental value  $D(D_{\text{exp}})$  determined from the peak position  $2\theta_m$  of the scattering profile (equation (2)) with the value  $D(D_{\text{theor}})$  predicted by RPA. The value  $D_{\text{exp}}$ , in turn, is related to the radius of gyration,  $R_{g,\text{exp}}$ , of the block copolymer in disordered state. The value  $R_{g,\text{exp}}$ , which can be determined by best-fitting the experimental and theoretical scattering profiles, can be compared with

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$R_{g,theor}$  calculated from the segmental lengths and polymerization indices of the components of the block copolymer. We found a significant discrepancy between  $D_{theor}$  and  $D_{exp}$  ( $D_{exp}/D_{theor} \approx 1.5$ ) or  $R_{g,theor}$  and  $R_{g,exp}$  ( $R_{g,exp}/R_{g,theor} \approx 1.5$ ) for HK-17, if we adopted the scattering formula presented by Leibler<sup>2</sup> for the diblock copolymer with no composition and molecular weight distributions. A similar discrepancy was reported by Bates for a diblock copolymer of deuterated polybutadiene and protonated polybutadiene<sup>3</sup>. Here we explore the effects of the two kinds of distribution, i.e. the distribution of total molecular weight and that of the fraction of A component in an AB diblock copolymer, on  $R_{g,exp}$  and on the discrepancy. Here we assume that both A and B block sequences obey a Schultz-Zimm type molecular weight distribution<sup>4,5</sup> as used by Leibler and Benoit<sup>6</sup> and by Bates and Hartney<sup>7,8</sup>.

In this paper, we first present experimental data for a particular SI diblock copolymer designated as HK-17 and their analysis with Leibler's theory for a diblock copolymer having no molecular weight and composition distributions. We elucidate the discrepancy between  $D_{exp}$  and  $D_{theor}$  or between  $R_{g,exp}$  and  $R_{g,theor}$ . We briefly describe the theoretical background for elastic scattering from thermal concentration fluctuations, and the scattering formula for a block copolymer with composition and molecular weight distributions. The experimental profiles are then re-examined,  $R_{g,exp}$ ,  $D_{theor}$  and  $\chi$  are re-estimated and the results are compared with the previous analyses. The analyses presented are for HK-17 with a relatively broad molecular weight distribution, as indicated by the large heterogeneity index  $M_w/M_n \approx 1.20$ . Finally, the effects of the distributions on  $D_{exp}/D_{theor}$  and  $R_{g,exp}/R_{g,theor}$  are examined for a series of SI diblock copolymers with different  $M_w/M_n$ .

## EXPERIMENTAL

The SI diblock copolymer HK-17 was subjected to extensive studies for this paper and the results of its characterization are summarized in Table 1, where  $M_w$  is the weight average molecular weight,  $w_{PS}$  is the average weight fraction of polystyrene (PS) block in the SI diblock copolymer and  $R_{g,theor}$  is the unperturbed radius of gyration of the SI block copolymer as calculated from the following equation:

$$R_{g,theor} = (N_{n,PS}a_{PS}^2/6 + N_{n,PI}a_{PI}^2/6)^{1/2} \quad (3)$$

where  $a_{PS}$  and  $a_{PI}$  are the statistical segment lengths for

PS<sup>9</sup> and polyisoprene (PI)<sup>10</sup> block chains as defined by

$$a_{PS} \equiv [\langle R_{PS}^2 \rangle_0 / N_{n,PS}]^{1/2} = 0.68 \text{ nm}$$

$$a_{PI} \equiv [\langle R_{PI}^2 \rangle_0 / N_{n,PI}]^{1/2} = 0.59 \text{ nm}$$

$\langle R_K^2 \rangle_0$  is the mean squared unperturbed end-to-end distance for the K block chains (K = PS or PI), and  $N_{n,PS}$  and  $N_{n,PI}$  are the number average polymerization indices for the PS and PI block chains, respectively. Note that  $a_{PI}$  depends on the microstructure of PI. The value  $a_{PI}$  given above is relevant for polymer prepared by anionic polymerization in THF (tetrahydrofuran) at  $-78^\circ\text{C}$  with sec-butyllithium as initiator<sup>10</sup>. The detailed polymerization method for HK-17 and the microstructure of PI block chains having high vinyl content were described in the previous paper<sup>1</sup>. Note that  $M_n$  was reported to be  $8.5 \times 10^3$  in the previous paper, which turned out to be an overestimate, and we currently believe that the value  $6.8 \times 10^3$  given in Table 1 is the correct one. The average volume fraction  $\phi_{PS}$  of the PS block in the SI block copolymer is estimated to be 0.468 from  $w_{PS}$  and will be used for calculating the scattering functions.

The effect of molecular weight distribution on  $R_{g,exp}$  was also studied for a series of SI-diblock copolymers having different  $M_n$  (number average molecular weight), and  $w_{PS}$ , and their characterizations are summarized in Table 2. In the calculation of  $R_{g,theor}$  for SI block copolymers prepared by sequential living anionic polymerization in benzene, the value  $a_{PI}$  relevant for low vinyl content was used<sup>11</sup>:  $a_{PI} = 0.63 \text{ nm}$ .

The detailed procedures for measuring the SAXS profiles were described in the previous paper<sup>1</sup>. SAXS measurements were made with bulk specimens for HK-17 and with DOP solutions for other SI block copolymers.

## EXPERIMENTAL RESULTS

We first describe the previous analyses and then the remaining problems which we deal with in this paper. Figure 1 shows the de-smear SAXS profiles of HK-17 in bulk and in disordered state measured at various temperatures, (a), and the analyses on the temperature dependence of the scattering profiles, (b). The analyses involve the reciprocal of the peak intensity  $I_m^{-1} = I(q_m)^{-1}$  and the wavelength  $D$  of the dominant mode of the fluctuations determined by equation (2) as a function of the reciprocal absolute temperature  $T^{-1}$ . The linear relationship between  $I_m^{-1}$  and  $T^{-1}$  and the fact that  $D$  is independent of  $T^{-1}$  ensure that the specimens are in

**Table 1** Characterization of SI diblock polymer HK-17 and estimation of its radius of gyration

$10^{-3} M_n^a$	$M_w/M_n^b$	$w_{PS}^c$	$R_{g,theor}^d$	$R_{g,exp}$ (Å)		
				Monodisperse <sup>e</sup>	MW <sup>f</sup>	MW and comp <sup>g</sup>
6.8	1.20	0.50	23.2	35.5	30.6	23.5

<sup>a</sup> Number average molecular weight as estimated by vapour pressure osmometry

<sup>b</sup> Determined by gel permeation chromatography

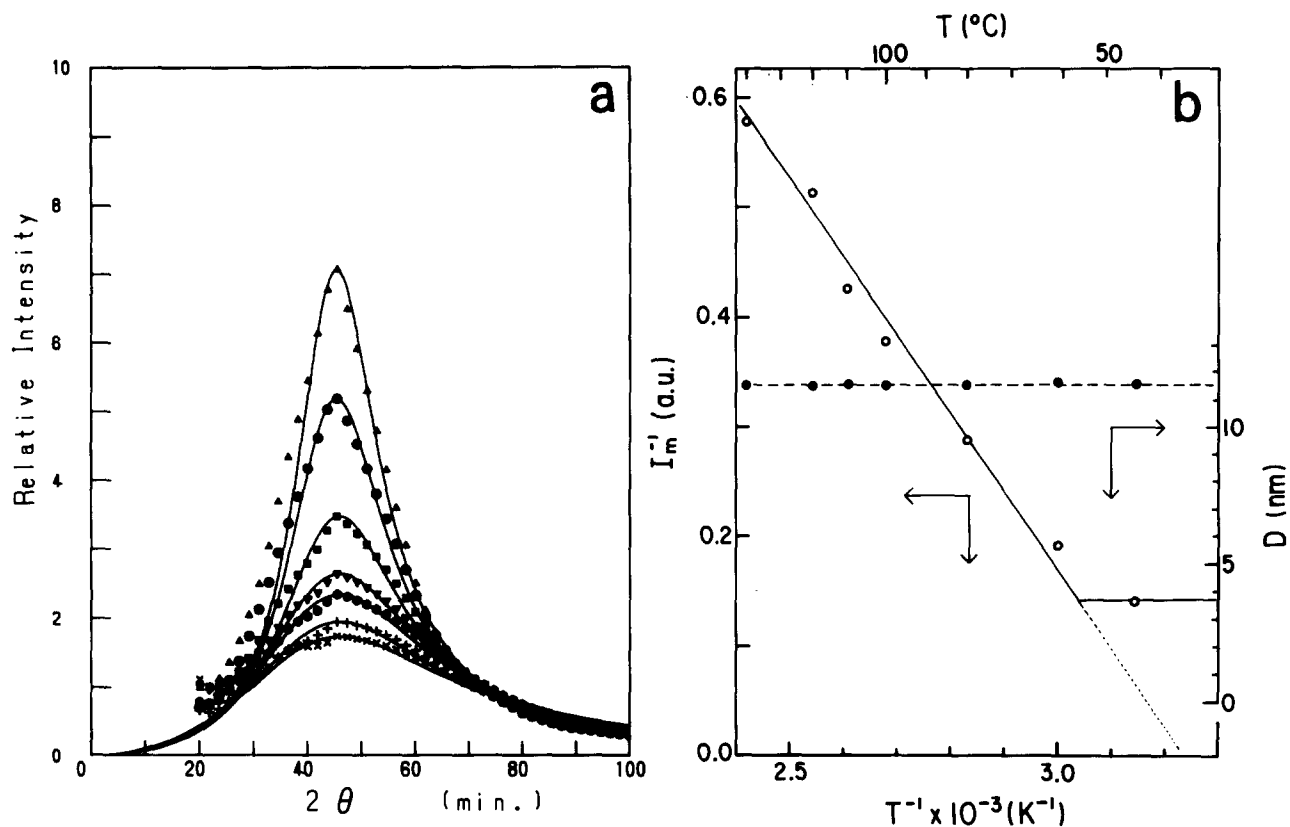
<sup>c</sup> Average weight fraction of PS as determined by elemental analysis

<sup>d</sup> Calculated by using equation (3) in the text;  $a_{PS} = 6.8$  and  $a_{PI} = 5.9 \text{ Å}$

<sup>e</sup> Determined from  $q_m$  by assuming no molecular weight and composition distributions

<sup>f</sup> Determined from  $q_m$  by assuming Schultz-Zimm molecular weight distribution for total molecular weight but no distribution for composition (case II)

<sup>g</sup> Determined from  $q_m$  by assuming distributions in both total molecular weight and composition as predicted by the Schultz-Zimm distribution function (case I)



**Figure 1** (a) Results of best fitting between experimental SAXS profiles of HK-17 (symbols) in the disordered state obtained at various temperatures and the theoretical curves (solid lines) obtained by assuming that the polymer is monodisperse. Temperature ( $^{\circ}\text{C}$ ):  $\Delta$ , 45;  $\circ$ , 60;  $\square$ , 80;  $\nabla$ , 100;  $\diamond$ , 110;  $+$ , 120;  $\times$ , 140. (b) Reciprocal SAXS intensity ( $\circ$ ) measured at  $q = 0.0539 \text{ \AA}^{-1}$  and Bragg spacings ( $\bullet$ ) at the scattering maxima of HK-17 in bulk plotted as functions of reciprocal temperature

the disordered state (see equations (5) and (13)) in the temperature range covered in this experiment.

The measured SAXS profiles shown by the data points in *Figure 1a* were best-fitted with the theoretical profiles (solid lines) given by Leibler<sup>2</sup> for diblock copolymer with neither total molecular weight distribution nor composition distribution. The best fit was obtained by adjusting the  $\chi$ -value, which affects the breadth of the profile and the radius of gyration (defined as  $R_{g,\text{exp}}$  here) of the entire diblock copolymer in the unperturbed state, which affects the peak position  $2\theta_m$  (see equations (5) and (12)). Good agreement between the theoretical and experimental profiles was obtained, indicating that RPA theory predicts the thermal concentration fluctuations of the diblock polymer in the disordered state. The  $\chi$ -value per monomeric unit was determined as a function of temperature, the result of which is shown by curve A in *Figure 5*.

The problem which was ignored in the previous analyses and still remains is a comparison between  $R_{g,\text{exp}}$  thus estimated by best fits and  $R_{g,\text{theor}}$  estimated by using equation (3).  $R_{g,\text{exp}}$  was  $36 \text{ \AA}^*$ , which is about 1.5 times  $R_{g,\text{theor}}$  ( $= 23.2 \text{ \AA}$ ), as shown in *Table 1*. More directly, one can compare  $D_{\text{exp}}$  and  $D_{\text{theor}}$ .  $D_{\text{exp}}$  can be estimated by

$$D_{\text{exp}} = 2\pi/q_{m,\text{exp}} \quad (4a)$$

where  $q_{m,\text{exp}}$  can be directly measured, and

$$D_{\text{theor}} = 2\pi/q_{m,\text{theor}} \quad (4b)$$

where  $q_{m,\text{theor}}$  can be calculated by  $q_{m,\text{theor}} = \alpha/R_{g,\text{theor}}$ ,

\*  $1 \text{ \AA} = 10^{-1} \text{ nm}$

$\alpha$  being a numerical constant which depends on  $f_{\text{PS}} \equiv N_{n,\text{PS}}/(N_{n,\text{PS}} + N_{n,\text{PI}})$  and is given by the scattering theory.  $D_{\text{exp}}$  and  $D_{\text{theor}}$  are 114 and 75  $\text{\AA}$ , respectively, and hence  $D_{\text{exp}}/D_{\text{theor}} \approx 1.5$ .

## THEORETICAL BACKGROUND

*Scattering function from diblock copolymers with monodispersed molecular weight*

Leibler<sup>2</sup> gave the scattering function  $I(q)$  for diblock copolymers in disordered state:

$$I(q)^{-1} \sim S(q)/W(q) - 2\chi \quad (5)$$

where

$$S(q) = S_{AA}(q) + S_{BB}(q) + 2S_{AB}(q) = Ng(f=1) \quad (6)$$

$$W(q) = S_{AA}(q)S_{BB}(q) - S_{AB}^2(q) \quad (7)$$

$$S_{AA}(q) = Ng(f) \quad (8)$$

$$S_{BB}(q) = Ng(1-f) \quad (9)$$

$$S_{AB}(q) = (1/2)N[g(f=1) - g(f) - g(1-f)] \quad (10)$$

$$g(f) \equiv (2/x^2)[fx + \exp(-fx) - 1] \quad (11)$$

$$x \equiv q^2 R_g^2 = (q^2 a^2 / 6) N \equiv yN \quad (12)$$

The function  $S_{ij}(q)$  ( $i, j = \text{A or B}$ ) is the  $q$ -Fourier component of the density-density correlation function

between  $i$  and  $j$  monomers for a Gaussian chain,  $N = N_A + N_B$  is the total polymerization index of AB diblock copolymer,  $N_K$  is the polymerization index of K block chain ( $K = A$  or  $B$ ),  $f = N_A/N$  and  $a$  is the Kuhn statistical segment length, where  $a = a_A = a_B$  is assumed,  $a_K$  being the Kuhn statistical segment length of K block chain.

It should be noted that  $S(q)/W(q)$  has a minimum at  $q = q_m$  and hence intensity has a maximum at  $q_m$ . For a given  $f$ ,  $q_m$  depends only on  $R_g$  but not on  $\chi$ . Since  $S(q)/W(q)$  hardly depends on  $T$  except for a very weak  $T$  dependence via that of  $R_g$ ,  $I_m^{-1}$  should vary linearly with  $T^{-1}$  if the  $T$  dependence of  $\chi$  is given by

$$\chi = A + B/T \quad (13)$$

These two predictions were confirmed by the experimental results shown in Figure 1 and extensively discussed in the previous paper<sup>1</sup>.

When the theoretical scattering intensity from the block copolymer with a given  $f$  is plotted as a function of  $qR_g$ , it has a maximum at  $q = q_m$  satisfying  $q_m R_g = \alpha$ , where the numerical constant  $\alpha$  depends on  $f$ , and the intensity distribution with  $q$  depends upon  $\chi N$ . Therefore the best fit of the experimental scattering profile to the theoretical one determines  $R_g$  (defined as  $R_{g,exp}$ ) and  $\chi N$ . This  $R_{g,exp}$  may be compared with  $R_{g,theor}$  given by equation (3).

#### Effects of composition and molecular-weight distributions

The effects of molecular weight distribution on the scattering function  $I(q)$  were previously treated by Leibler and Benoit<sup>6</sup>, Hong and Noolandi<sup>12</sup> and Bates and Hartney<sup>7,8</sup>. Leibler and Benoit gave the analytical expression for  $I(q)$  using a Schultz–Zimm molecular weight distribution for the symmetric block copolymers with average fraction of  $\phi_A = N_{A,n}/(N_{A,n} + N_{B,n}) = 0.5$  and with identical molecular weight distributions for A and B block chains. Here  $N_{A,n}$  and  $N_{B,n}$  are number average polymerization indices for the A and B block chains, respectively. Bates and Hartney generalized Leibler–Benoit calculations for the asymmetric block polymers with  $\phi_A \neq 0.5$ . This generalization is practically important because most of the block copolymers are asymmetric, as shown in Table 2. However, on executing the detailed

calculations we could not obtain the same formula as those reported by Bates and Hartney. In particular, it is not clear to us whether the abscissa of convergence was properly treated in performing Laplace transformation of the Whittaker function. Thus we summarize our results below and in the Appendix. In calculating  $I(q)$  we further generalized Bates–Hartney calculations by allowing A and B block chains to have different parameters characterizing the Schultz–Zimm distribution functions.

Here we consider two cases: case I in which both A and B block chains have Schultz–Zimm molecular weight distributions; and case II in which  $f$  is fixed and only  $N$  has a Schultz–Zimm distribution. Of course case II is a special case of the general case I. In both cases  $I(q)$  for block copolymers with molecular weight distribution is obtained by substituting, respectively,  $\overline{Ng(f)}$ ,  $\overline{Ng(1-f)}$  and  $\overline{Ng(f=1)}$  for  $Ng(f)$ ,  $Ng(1-f)$  and  $Ng(f=1)$  in equation (5).

The average quantities  $\overline{Ng(f)}$  etc. are given by

$$\left( \frac{\overline{Ng(f)}}{\overline{Ng(1-f)}} \right) \equiv \int_0^\infty \int_0^\infty dN_A dN_B \psi_A(N_A) \psi_B(N_B) \left( \frac{Ng(f)}{Ng(1-f)} \right) \quad (14)$$

for case I, where  $\psi_A$  and  $\psi_B$  are, respectively, the distribution functions for the polymerization index for A and B block chains, which are assumed to be independent and to be given by the Schultz–Zimm equations:

$$\psi_A(N_A) = v_A^{k_A+1} N_A^{k_A} \exp(-v_A N_A) / \Gamma(k_A + 1) \quad (15)$$

and

$$\psi_B(N_B) = v_B^{k_B+1} N_B^{k_B} \exp(-v_B N_B) / \Gamma(k_B + 1) \quad (16)$$

$$v_A = k_A / N_{A,n} = (k_A + 1) / N_{Aw} \quad (17)$$

$$v_B = k_B / N_{B,n} = (k_B + 1) / N_{Bw} \quad (18)$$

$$N_{Aw} / N_{An} = (k_A + 1) / k_A \equiv \lambda_A \quad (19)$$

**Table 2** Characterization of SI diblock copolymers and comparisons of experimental and theoretical values for the wavelength of the dominant mode of the fluctuation

Sample	Polymerization solvent	$10^{-4} M_n^a$	$M_w/M_n^b$	$w_{PS}^c$	$\phi_{PS}^d$	$D_{exp}^e$ (Å)	$D_{theor}$		
							Monodisperse <sup>f</sup>	MW <sup>g</sup>	MW and comp. <sup>h</sup>
HK-15	THF	1.74	1.20	0.55	0.52	161	119 (1.34) <sup>i</sup>	138 (1.16)	184 (0.88)
TSI-3	Benzene	3.2	1.12	0.59	0.56	195	166 (1.17)	182 (1.07)	219 (0.89)
HS-12	Benzene	7.52	1.05	0.46	0.43	309	259 (1.19)	269 (1.15)	291 (1.06)
HS-16	THF	2.3	1.04	0.74	0.72	141	131 (1.07)	135 (1.04)	141 (1.0)
TSI-2	Benzene	3.0	1.12	0.77	0.74	178	149 (1.19)	163 (1.09)	187 (0.95)
HS-15	THF	4.2	1.04	0.76	0.74	216	174 (1.24)	180 (1.20)	181 (1.19)
HS-7	THF	5.1	1.04	0.31	0.28	262	201 (1.30)	206 (1.27)	216 (1.21)
B-2	THF	17.6	1.26	0.85	0.83	376	333 (1.13)	392 (0.96)	436 (0.86)

<sup>a</sup> Number average molecular weight as determined by membrane osmometry

<sup>b</sup> Determined by gel permeation chromatography

<sup>c</sup> Average weight fraction of PS as determined by elemental analysis

<sup>d</sup> Average volume fraction of PS as determined by elemental analysis

<sup>e</sup> Determined using equation (4a)

<sup>f</sup> Determined using equation (4b) for monodisperse molecular weight distribution

<sup>g</sup> Determined using equation (52) by assuming Schultz–Zimm distribution for total molecular weight but not for composition (case II)

<sup>h</sup> Determined using equation (52) by assuming distributions for both total molecular weight and composition (case I)

<sup>i</sup> Values in parentheses indicate  $D_{exp}/D_{theor}$

and

$$N_{Bw}/N_{Bn} = (k_B + 1)/k_B \equiv \lambda_B \quad (20)$$

$N_{Kw}$  and  $\lambda_K$  are, respectively, the weight average polymerization index and the heterogeneity index for K block chain.

By using Laplace transformation of the Whittaker function we obtain the final formula for the averaged quantities for case I:

$$\overline{Ng(f)} = 2(N_n/x_n^2)(G_1 + G_2 - G_3) \quad (21)$$

where

$$G_1 = x_n \frac{z_1(k_A + 1)}{k_A + k_B + 2} F(1, k_A + 2, k_A + k_B + 3; 1 - z_1) \quad (22a)$$

$$\text{for } \phi_A \leq k_A/(k_A + k_B) \quad (22b)$$

$$G_1 = x_n \frac{k_A + 1}{k_A + k_B + 2} F(1, k_B + 1, k_A + k_B + 3; 1 - z_1^{-1}) \quad (23a)$$

$$\text{for } \phi_A \geq k_A/(k_A + k_B) \quad (23b)$$

The quantity  $x_n$  is defined by

$$x_n = yN_n = q^2 N_n a^2 / 6 = q^2 R_{gn}^2 \quad (24)$$

$$N_n = N_{An} + N_{Bn} \quad (25)$$

and  $\phi_A$  is defined by

$$\phi_A = N_{An}/(N_{An} + N_{Bn}) = N_{An}/N_n \quad (26)$$

$R_{gn}$  is the average radius of gyration for the entire block copolymer.  $F(\alpha, \beta, \gamma; z)$  is Gauss's hypergeometric function:

$$F(\alpha; \beta; \gamma; z) = \frac{\Gamma(\gamma)}{\Gamma(\alpha)\Gamma(\beta)} \sum_{n=0}^{\infty} \frac{\Gamma(\alpha+n)\Gamma(\beta+n)}{\Gamma(\gamma+n)} \frac{z^n}{n!} \quad (27)$$

where  $\Gamma$  is the gamma function.  $z_1$  is defined by

$$z_1 = k_B \phi_A / k_A (1 - \phi_A) \quad (28)$$

$G_2$  in equation (21) is given by

$$G_2 = \frac{1}{1 - \phi_A} \frac{k_B}{k_A + k_B + 1} z_2^{k_A + 1} F(1, k_A + 1, k_A + k_B + 2; 1 - z_1 z_2) \quad (29a)$$

$$\text{for } x_n \geq \frac{k_B}{1 - \phi_A} - \frac{k_A}{\phi_A} \quad (29b)$$

$$G_2 = \frac{1}{\phi_A} \frac{k_A}{k_A + k_B + 1} z_2^{k_A} F(1, k_B + 1, k_A + k_B + 2; 1 - 1/z_1 z_2) \quad (30a)$$

$$\text{for } x_n \leq \frac{k_B}{1 - \phi_A} - \frac{k_A}{\phi_A} \quad (30b)$$

where  $z_2$  is defined by

$$z_2 = (1 + x_n \phi_A / k_A)^{-1} \quad (31)$$

Finally,  $G_3$  in equation (21) is given by

$$G_3 = \frac{1}{1 - \phi_A} \frac{k_B}{k_A + k_B + 1} F(1, k_A + 1, k_A + k_B + 2; 1 - z_1) \quad (32a)$$

$$\text{for } \phi_A \leq k_A/(k_A + k_B) \quad (32b)$$

$$G_3 = \frac{1}{\phi_A} \frac{k_A}{k_A + k_B + 1} F(1, k_B + 1, k_A + k_B + 2; 1 - 1/z_1) \quad (33a)$$

$$\text{for } \phi_A \geq k_A/(k_A + k_B) \quad (33b)$$

Note that the conditions (22b), (23b), (29b), (30b), (32b) and (33b) result from the convergence conditions of the Laplace transformation of the Whittaker function (see Appendix). Similarly,  $\overline{Ng(1-f)}$  is obtained by exchanging the subscripts A and B in equations (22)–(33) for  $\overline{Ng(f)}$ .

Finally,  $\overline{Ng(f=1)}$  is given by

$$\overline{Ng(f=1)} = 2(N_n/x_n^2)(G_4 + G_5 - G_6) \quad (34)$$

where

$$G_4 = x_n \quad (35)$$

$$G_5 = \frac{1}{1 - \phi_A} \frac{k_B}{k_A + k_B + 1} z_2^{k_A + 1} z_3^{k_B} F(1, k_A + 1, k_A + k_B + 2; (1 - z_1)z_2) \quad (36a)$$

$$\text{for } \phi_A \leq k_A/(k_A + k_B) \quad (36b)$$

$$G_5 = \frac{1}{\phi_A} \frac{k_B}{k_A + k_B + 1} z_2^{k_A} z_3^{k_B + 1} F(1, k_B + 1, k_A + k_B + 2; (1 - 1/z_1)z_3) \quad (37a)$$

$$\text{for } \phi_A \geq k_A/(k_A + k_B) \quad (37b)$$

$$G_6 = \frac{1}{1 - \phi_A} \frac{k_B}{k_A + k_B + 1} F(1, k_A + 1, k_A + k_B + 2; 1 - z_1) \quad (38a)$$

$$\text{for } \phi_A \leq k_A/(k_A + k_B) \quad (38b)$$

$$G_6 = \frac{1}{\phi_A} \frac{k_A}{k_A + k_B + 1} F(1, k_B + 1, k_A + k_B + 2; 1 - 1/z_1) \quad (39a)$$

$$\text{for } \phi_A \geq k_A/(k_A + k_B) \quad (39b)$$

where  $z_3$  is defined by

$$z_3 = [1 + x_n(1 - \phi_A)/k_B]^{-1} \quad (40)$$

Again the conditions (36b)–(39b) originate from the convergence conditions.

The equations given above become much simpler for the special case of

$$k_A = k_B = k = (\lambda - 1)^{-1} \quad (41)$$

i.e. the case where A and B block chains have the same molecular weight distributions. This is the case previously treated by Bates and Hartney<sup>7,8</sup>. In this case the equations for  $\phi_A \leq 0.5$  are given below:

$$\overline{Ng(f)} = 2(N_n/x_n^2) \left\{ (x_n/2) \frac{\phi_A}{1-\phi_A} F(1, k+2, 2k+3; z_4) + \frac{1}{1-\phi_A} \frac{1}{\lambda+1} \left[ z_2^{\lambda/(\lambda-1)} F\left(1, k+1, 2k+2; 1 - \frac{\phi_A}{1-\phi_A} z_2\right) - F(1, k+1, 2k+2; z_4) \right] \right\} \quad (42)$$

$$z_4 = 1 - \phi_A/(1 - \phi_A) \quad (43)$$

$$\overline{Ng(1-f)} = 2(N_n/x_n^2) \left[ (1/2)x_n F(1, k+1, 2k+3; z_4) + G - \frac{1}{1-\phi_A} \frac{1}{1+\lambda} F(1, k+1, 2k+2; z_4) \right] \quad (44)$$

where

$$G = \frac{1}{\phi_A} \frac{1}{\lambda+1} z_5^{\lambda/(\lambda-1)} F\left(1, k+1, 2k+2; 1 - \frac{1-\phi_A}{\phi_A} z_5\right) \quad (45a)$$

$$\text{for } x_n \geq k[1/\phi_A - 1/(1-\phi_A)] \quad (45b)$$

$$G = \frac{1}{1-\phi_A} \frac{1}{\lambda+1} z_5^{1/(\lambda-1)} F\left(1, k+1, 2k+2; 1 - \frac{\phi_A}{1-\phi_A} \frac{1}{z_5}\right) \quad (46a)$$

$$\text{for } 0 \leq x_n \leq k[1/\phi_A - 1/(1-\phi_A)] \quad (46b)$$

and

$$z_5 = [1 + x_n(1 - \phi_A)(\lambda - 1)]^{-1} \quad (47)$$

Finally  $\overline{Ng(f=1)}$  is given by

$$\overline{Ng(f=1)} = 2(N_n/x_n^2) \left\{ x_n + \frac{1}{1-\phi_A} \frac{1}{\lambda+1} \left[ z_2^{\lambda/(\lambda-1)} z_5^{1/(\lambda-1)} \times F(1, k+1, 2k+2; z_4 z_2) - F(1, k+1, 2k+2; z_4) \right] \right\} \quad (48)$$

Equations (42)–(48) should be compared with those of Bates and Hartney. Note that conditions (45b) and (46b), which originate from the abscissa of convergence in the Laplace transformation of the Whittaker function, depend on  $q$  for a given block copolymer with a given set of  $\phi_A$ ,  $k$  and  $N_n$ . Our equations reduce to those by Leibler and Benoit for the special case  $\phi_A = 0.5$ .

The average quantities for the special case II are simply given by

$$\overline{Ng(f)} = 2(N_n/x_n^2) \{ f x_n - 1 + [k/(k + f x_n)]^k \} \quad (49)$$

$$\overline{Ng(1-f)} = 2(N_n/x_n^2) \{ (1-f)x_n - 1 + [k/(k + (1-f)x_n)]^k \} \quad (50)$$

$$\overline{Ng(f=1)} = 2(N_n/x_n^2) \{ x_n - 1 + [k/(k + x_n)]^k \} \quad (51)$$

where  $f$  is the composition and  $k$  is the parameter characterizing the distribution of  $N$ , i.e.  $k = 1/(\lambda - 1)$ , where  $\lambda = N_w/N_n$  is the heterogeneity index for the total polymerization index.

In both cases I and II, for a block copolymer with a given average composition, the theoretical scattering intensity function can be plotted as a function of  $x_n^{1/2} = q R_{gn}$ . In this case the scattered intensity becomes maximum at  $q = q_m$  satisfying

$$q_{m, \text{theor}} R_{gn} = \beta$$

where the numerical constant  $\beta$  depends upon  $\lambda = N_w/N_n$ , and the width of the scattering maximum depends upon  $\chi N_n$ . Here for case I,  $\lambda$  is the heterogeneity index for PS and for PI block chains, whose indices are assumed to be identical, while for case II  $\lambda$  is the heterogeneity index for the entire block chain. Thus the theoretical scattering profile plotted as a function of  $q$  depends upon  $\lambda$ ,  $R_{gn}$  and  $\chi N_n$  for a given copolymer with a given  $\phi$ . Thus the best fit of the experimental and theoretical profiles for a given  $\lambda$  and  $\phi$  determines  $R_{gn}$  (defined as  $R_{g, \text{exp}}$ ) and  $\chi N_n$ . This  $R_{g, \text{exp}}$  can be compared with  $R_{g, \text{theor}}$  given by equation (3). Alternatively, as in the case of the block copolymer with monodisperse molecular weight distribution, one can estimate  $D_{\text{exp}} = 2\pi/q_{m, \text{exp}}$  directly from the experimental peak position  $q_m$  which is then compared with

$$D_{\text{theor}} = 2\pi/q_{m, \text{theor}} = 2\pi R_{gn}/\beta \quad (52)$$

$R_{gn}$  being given by equation (3). Note that the analyses described above require information on  $\lambda$  only about the Schultz–Zimm molecular weight distribution. Determination of  $\chi$  requires additional information on  $N_n$  which can be estimated by osmometry.

## ANALYSES OF EXPERIMENTAL RESULTS AND DISCUSSION

Here we re-examine experimental scattering profiles of HK-17 shown in *Figure 1a* using the equations described above for cases I and II. We first summarize the assumptions we made for our analyses based on case I:

- (1) The distribution functions for the polymerization index for both PS and PI are independent and are given by a Schultz–Zimm equation.
- (2) PS and PI have identical heterogeneity indices

$$\lambda_{\text{PS}} = \lambda_{\text{PI}} = \lambda = N_w/N_n$$

as adopted by Bates and Hartney<sup>7,8</sup>.

(3)  $\lambda$  can be estimated from the molecular weight distribution curve for the block copolymer as a whole as determined by gel permeation chromatography (g.p.c.)

together with a calibration curve obtained from standard polystyrene samples with very narrow molecular weight distributions.

In the g.p.c. curve we measured the distribution function  $\psi(N_t)$  for the polymerization index  $N_t$  of total block copolymer. This  $\psi(N_t)$  is given by

$$\psi(N_t) = \int_0^{N_t} \psi_A(N_A) \psi_B(N_t - N_A) dN_A \quad (53)$$

where  $\psi_A$  and  $\psi_B$  are the distribution functions for A and B block chains given by equations (15) and (16). Equation (53) can be rewritten as

$$\psi(N_t) \sim N_t^{2k+1} \exp(-v_B N_t) \int_0^1 x^k (1-x)^k \exp[-(v_A - v_B) N_t x] dx \quad (54)$$

where  $k = (\lambda - 1)^{-1} = k_A = k_B$ .  $v_A$  and  $v_B$  are related to  $k$  by equations (17) and (18), where

$$N_{An} = \phi_A N_{n, gpc}, \quad N_{Bn} = (1 - \phi_A) N_{n, gpc} \quad (55)$$

$N_{n, gpc}$  is the total number average polymerization index as determined by g.p.c. Thus the best fit of  $\psi(N_t)$  to the experimental distribution function yields the parameter  $k$  for the distribution function of individual block chain and  $N_{n, gpc}$  for the entire chain.

Figure 2 shows a comparison of the experimental  $\psi(N_t)$  and the theoretical profile. The experimental molecular weight distribution function is seen to be well fitted with the one given by equation (54) based upon the Schultz-Zimm equation. The best fit gives that

$$\lambda = \lambda_{PS} = \lambda_{PI} = 1.398 \quad (56)$$

or  $k = 1 = (\lambda - 1)^{-1} = 2.51$  and  $N_{n, gpc} = 75$ .

By assuming  $\psi_A$  and  $\psi_B$  to be independent, the heterogeneity index  $\lambda_t$  for the entire block chain can be estimated from  $\lambda_{PS}$  and  $\lambda_{PI}$ :

$$\lambda_t - 1 = (\lambda_{PS} - 1)\phi_{PS}^2 + (\lambda_{PI} - 1)(1 - \phi_{PS})^2 \quad (57)$$

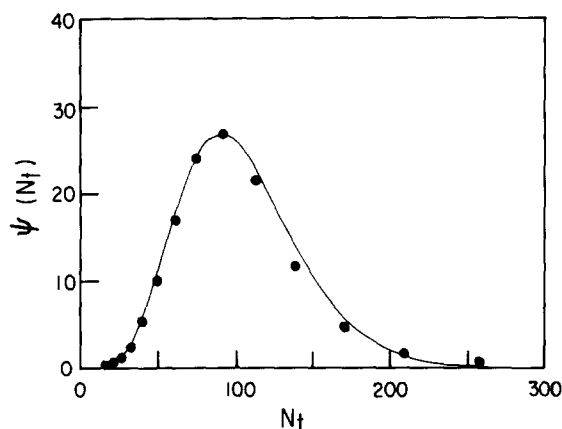


Figure 2 Comparison of the experimental distribution profile of polymerization index for HK-17 (●) and the theoretical curve based on the Schultz-Zimm equation (—)

Since HK-17 has  $\phi_{PS} = 0.468$ , we obtain  $\lambda_t = 1.20$ , which is in good agreement with  $\lambda_t$  directly determined from the experimental distribution function  $\psi(N_t)$ . Here again it should be noted that only the information on  $\lambda$  or  $\lambda_t$  was used for the analyses of the scattering profiles.

Analyses based on case II can be performed using

$$k = (\lambda_t - 1)^{-1} = (1.20 - 1)^{-1} = 5.0 \quad (58)$$

To apply the equations derived above for symmetric block copolymers to asymmetric block copolymers such as PS-PI block copolymers, we define the following quantities after Helfand<sup>13</sup>:

$$\phi_{PS} = (N_{n, PS}/\rho_{0S}) / (N_{n, PS}/\rho_{0S} + N_{n, PI}/\rho_{0I}) \quad (59)$$

where  $N_{n, K}$  is the number average polymerization index for K block chains (K = PS or PI).  $\rho_{0S}$  and  $\rho_{0I}$  are the number density of monomer units for pure PS and PI homopolymers.  $N_{n, PS}$  and  $N_{n, PI}$  can be estimated from  $M_n$  measured by osmometry and  $w_{PS}$ . To calculate  $\chi$ ,  $N_n$  is required, and  $N_n$  is given by

$$N_n = \rho_0 (N_{n, PS}/\rho_{0S} + N_{n, PI}/\rho_{0I}) \quad (60)$$

$$\rho_0 = (\rho_{0S}\rho_{0I})^{1/2} \quad (61)$$

For HK-17 the function  $G$  should be changed from equation (46a) to equation (45a) with increasing  $x_n = q^2 R_{gn}^2$  from conditions (45b) and (46b).

Figure 3 shows results of best fitting between the experimental profiles for HK-17 and theoretical profiles, where the theoretical curves are obtained for case II with the distribution only in the total polymerization index.

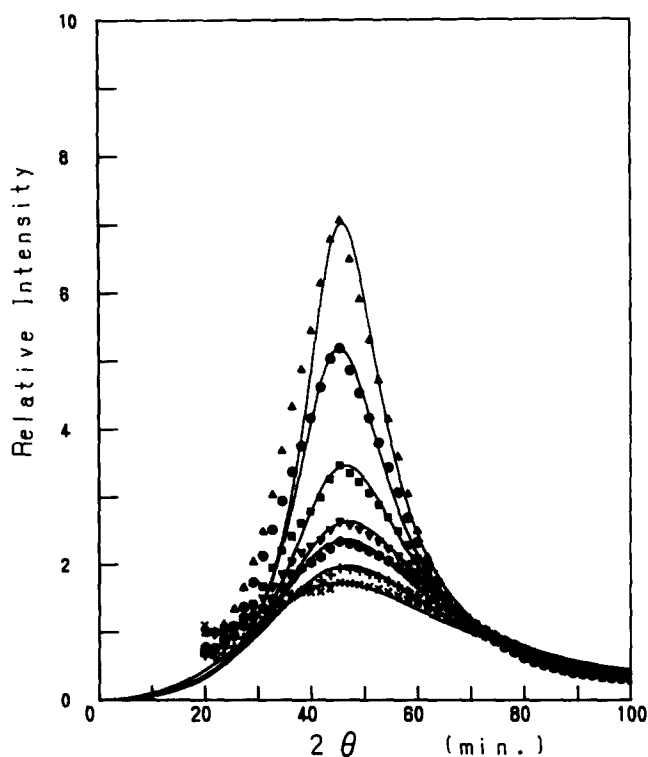


Figure 3 Results of best fitting between the experimental SAXS profiles of HK-17 (symbols) in the disordered state and the theoretical curves (solid lines) obtained for case II with a distribution only in total molecular weight. Temperature (°C):  $\Delta$ , 45;  $\circ$ , 60;  $\square$ , 80;  $\nabla$ , 100;  $\circ$ , 110;  $+$ , 120;  $\times$ , 140

The best fitting yielded  $R_{g,exp} = 30.6 \text{ \AA}$ , as shown in Table 1, and temperature dependence of  $\chi$ , as shown in curve B in Figure 5. The best fits obtained in Figure 3 are as good as those obtained in Figure 1. The introduction of the molecular weight distribution as given by case II is found to decrease the discrepancy between  $R_{g,theor}$  and  $R_{g,exp}$  and hence the discrepancy of the peak positions between the theoretical and experimental scattering profiles. However, the distribution of the total molecular weight alone is not sufficient to account for the discrepancy.

Figure 4 shows the results of best fitting the experimental profiles of HK-17 (data points) with the theoretical profiles (solid lines) calculated for case I, which gives a more realistic model than case II. Again we find that the best fits obtained in Figure 4 are as good as those in Figures 1 and 3. The best fits yielded  $R_{g,exp} = 23.5 \text{ \AA}$ , as shown in Table 1, and the temperature dependence of  $\chi$  as shown in curve C in Figure 5.  $R_{g,exp}$  effectively decreases on introducing the molecular weight distribution and becomes close to the expected value of  $23.2 \text{ \AA}$ . Thus the molecular weight distribution which gives distributions of both total molecular weight and composition explains the large discrepancy between  $R_{g,exp}$  and  $R_{g,theor}$ , as discussed in the preceding section.

The equations of curves A, B and C in Figure 5, which give the temperature dependences of  $\chi$  obtained for monodispersed block copolymer, case II and case I are, respectively,

$$\chi = -0.089 + 72/T \quad (62)$$

$$\chi = -0.063 + 59/T \quad (63)$$

$$\chi = 0.025 + 18.5/T \quad (64)$$

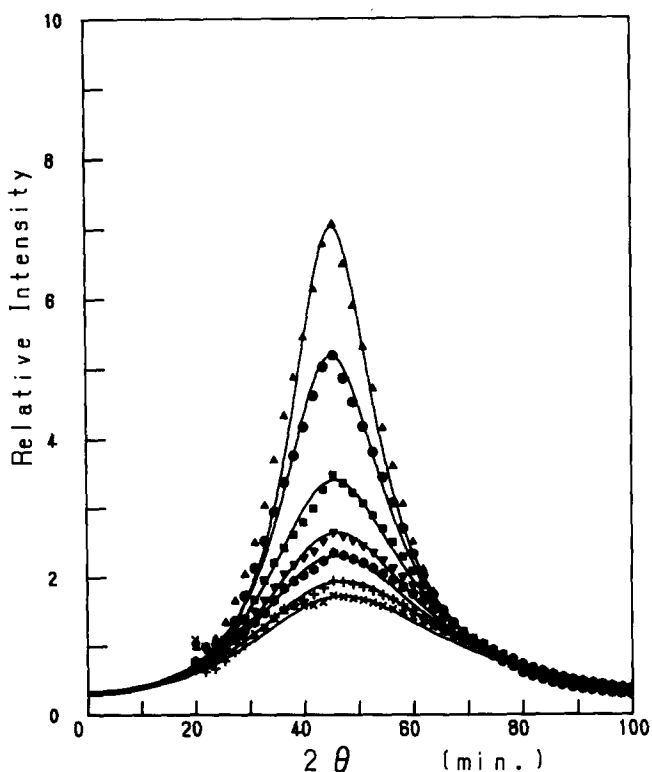


Figure 4 Results of best fitting between the experimental SAXS profiles of HK-17 (symbols) in the disordered state and the theoretical curves (solid lines) obtained for case I with distributions in both molecular weight and composition. Temperature ( $^{\circ}\text{C}$ ):  $\Delta$ , 45;  $\circ$ , 60;  $\square$ , 80;  $\nabla$ , 100;  $\diamond$ , 110;  $+$ , 120;  $\times$ , 140

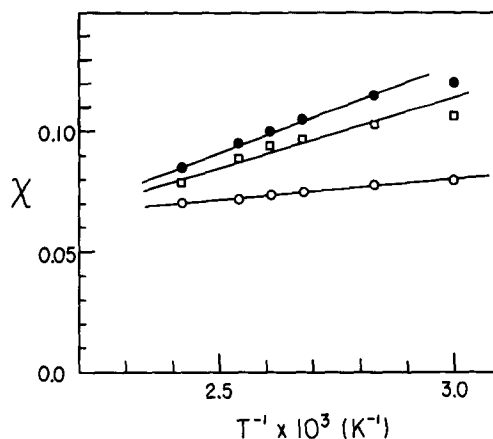


Figure 5 Temperature dependence of the interaction parameter  $\chi$  on monomer units for HK-17 in bulk obtained by best fits of the experimental and theoretical SAXS profiles for three different conditions:  $\bullet$ , monodispersed;  $\square$ , case II (distribution only in total molecular weight);  $\circ$ , case I (distributions in both molecular weight and composition). Curves are referred to as A, B and C respectively, in text

The large molecular weight distribution such as that in HK-17 is a special case for block copolymers prepared by living anionic polymerization. In the next section we examine the effects of molecular weight distribution for other SI diblock copolymers with smaller values of  $M_w/M_n$ .

#### FURTHER DISCUSSION ON THE EFFECT OF MOLECULAR WEIGHT DISTRIBUTION

Similar analyses for the effects of molecular weight distributions on  $D_{exp}$  and  $R_{g,exp}$  were performed for other SI block copolymers and the results are listed in Tables 2 and 3. Table 2 summarizes the characterization of various other SI diblock copolymers prepared by living anionic polymerization with solvents, as indicated in the second column, and values for  $D_{theor}$  as calculated from the peak positions for the theoretical scattering profiles. Comparisons between  $1/D_{theor}$  and  $1/D_{exp}$  correspond to those between theoretical and experimental peak positions for the scattering profiles. As found for HK-17,  $D_{theor}$ s estimated without taking into account the molecular weight distributions ('Monodisperse' column) are slightly but significantly smaller than  $D_{exp}$ s for all the specimens, the ratio  $D_{exp}/D_{theor}$  averaged for all the samples being 1.24. The discrepancy between  $D_{exp}$  and  $D_{theor}$  is slightly improved by taking into account the distribution for total molecular weight (case II) as seen in the 'MW' column, averaged for the seven samples except for B-2 being 1.14. The discrepancy is significantly less if the distributions for both total molecular weight and composition are taken into account (case I), as seen in the 'MW and comp.' column,  $D_{exp}/D_{theor}$  averaged for the seven samples being 1.02. For samples such as HK-15, TSI-3 and B-2, the ratios  $D_{exp}/D_{theor}$  are less than unity, which may be due to error in estimating molecular weight distributions, i.e. our estimations of  $M_w/M_n$  or due to a slight mismatch of the molecular weight distribution from the Schultz-Zimm equation.

Similar conclusions can be drawn by comparing  $R_{g,exp}$  and  $R_{g,theor}$  (Table 3). The values  $R_{g,exp}$  obtained by neglecting molecular weight distribution are significantly larger than  $R_{g,theor}$ , the ratio  $R_{g,exp}/R_{g,theor}$  varying between



**Table 3** Comparison of experimental and theoretical radii of gyration for SI diblock copolymers

Sample	$R_{g,theor}^a$ (Å)	$R_{g,exp}$ (Å)		
		Monodisperse <sup>b</sup>	MW <sup>c</sup>	MW and comp. <sup>d</sup>
HK-15	37.1	50.0 (1.35) <sup>e</sup>	43.5 (1.17)	33.0 (0.90)
TSI-3	51.7	60.5 (1.17)	55.5 (1.07)	46.0 (0.90)
HS-12	80.6	97.0 (1.20)	92.0 (1.14)	86.5 (1.07)
HS-16	42.1	48.3 (1.15)	46.4 (1.10)	44.0 (1.05)
TSI-2	48.8	58.0 (1.19)	54.0 (1.11)	47.0 (0.96)
HS-15	56.7	71.0 (1.25)	68.5 (1.21)	67.0 (1.18)
HS-7	64.5	83.5 (1.29)	79.0 (1.22)	76.0 (1.18)
B-2	115.0	130.0 (1.13)	111.0 (0.97)	92.0 (0.80)

<sup>a</sup> Calculated by using equation (3);  $a_{PS} = 0.68$  nm and  $a_{PI} = 0.59$  nm (for THF) and 0.63 nm (for benzene)

<sup>b</sup> Determined from  $q_m$  by assuming no molecular weight distribution

<sup>c</sup> Determined from  $q_m$  by assuming Schultz-Zimm distribution for total molecular weight but not for composition (case II)

<sup>d</sup> Determined from  $q_m$  by assuming distributions for both total molecular weight and composition (case I)

<sup>e</sup> Values in parentheses indicate  $R_{g,exp}/R_{g,theor}$

1.13 and 1.35, depending upon  $M_w/M_n$  and being 1.22 on average. By taking into account the distribution for total molecular weight only (case II), the discrepancy is reduced, the ratio  $R_{g,exp}/R_{g,theor}$  averaged for the seven samples except for B2 being 1.15. The discrepancy is significantly reduced by taking into account the distributions of case I, the averaged ratio  $R_{g,exp}/R_{g,theor}$  for the seven samples being 1.03.

In conclusion, the analyses presented in this paper clearly indicate that the distributions for total molecular weight and composition of diblock copolymers are one possible source of the discrepancy of the peak position in the experimental and theoretical scattering profiles.

Finally, the values of  $R_{g,exp}$  obtained by the correction for case I are plotted as a function of number average molecular weight  $M_n$  determined by osmometry in Figure 6, where the data points indicate  $R_{g,exp}$  and the solid line indicates  $R_{g,theor}$ . The experimental results show good agreement with the theoretical results and are summarized by the following equation:

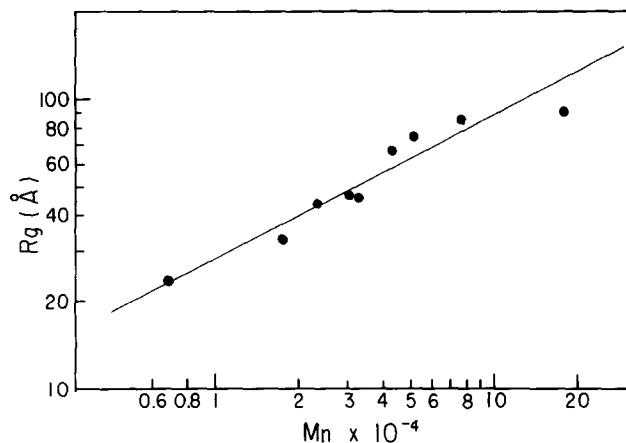
$$R_{g,exp} = (0.29 \pm 0.04)M_n^{1/2} \quad (65)$$

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**Figure 6** Comparison of  $R_{g,exp}$  (●) and  $R_{g,theor}$  (—).  $R_{g,exp}$ s were obtained by best fitting the experimental SAXS profiles and the theoretical curves calculated for case I for various SI block copolymers and are plotted against  $M_n$  determined by osmometry.  $R_{g,theor}$  was calculated for unperturbed polymer chains

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## APPENDIX LAPLACE TRANSFORM OF WHITTAKER FUNCTION AND ITS CONVERGENCE CONDITIONS

We show here an outline for obtaining the general equations (21)–(40). From equations (11) and (14)–(16),  $\overline{Ng(f)}$  is given by

$$\begin{aligned} & \overline{Ng(f)} / [v_A^{k_A+1} v_B^{k_B+1} / \Gamma(k_A+1) \Gamma(k_B+1)] \\ &= \int_0^\infty \int_0^\infty dN_A dN_B N_A^{k_A} \exp(-v_A N_A) N_B^{k_B} \exp(-v_B N_B) (2/y^2 N) \\ & \quad \times [yfN + \exp(-yfN) - 1] \end{aligned} \quad (A1)$$

$$= H_1 + H_2 - H_3 \quad (A2)$$

where

$$H_1 = \int_0^\infty \int_0^\infty dN_A dN_B N_A^{k_A} \exp(-v_A N_A) N_B^{k_B} \exp(-v_B N_B) (2f/y) \quad (A3)$$

$$H_2 = \int_0^\infty \int_0^\infty dN_A dN_B N_A^{k_A} \exp(-v_A N_A) N_B^{k_B} \exp(-v_B N_B) \times (2/y^2 N) \exp(-yfN) \quad (A4)$$

$$H_3 = \int_0^\infty \int_0^\infty dN_A dN_B N_A^{k_A} \exp(-v_A N_A) N_B^{k_B} \exp(-v_B N_B) \times (2/y^2 N) \quad (A5)$$

Let us first calculate  $H_3$ . Noting that

$$\int_0^\infty dN_B N_B^{k_B} \exp(-v_B N_B) (N_A + N_B)^{-1} = \frac{\Gamma(k_B + 1)}{v_B^{(k_B + 1)/2} N_A^{-(k_B - 1)/2} \exp(-v_B N_A/2)} W_{\kappa, \mu}(v_B N_A) \quad (A6)$$

where  $W_{\kappa, \mu}$  is the Whittaker function given by

$$W_{\kappa, \mu}(Z) \equiv \frac{\exp(-Z/2) Z^\kappa}{\Gamma(\mu - \kappa + 1/2)} \int_0^\infty dt \exp(-t) t^{\mu - \kappa - 1/2} \times (1 + t/Z)^{\mu + \kappa - 1/2} \quad (A7)$$

$H_3$  is given by

$$H_3 = \frac{2\Gamma(k_B + 1)}{y^2 v_B^{(k_B + 1)/2}} \int_0^\infty dN_A N_A^{k_A + (k_B - 1)/2} \times \exp[-(v_A - v_B/2)N_A] W_{\kappa, \mu}(v_B N_A) \quad (A8)$$

The integral in equation (A8) can be solved by using the following formula on the Laplace transformation of the Whittaker function:

$$g(p) = \int_0^\infty dt \exp(-pt) t^\nu W_{\kappa, \mu}(at) = \frac{\Gamma(\nu + \mu + 3/2) \Gamma(\nu - \mu + 3/2) a^{\mu + 1/2}}{\Gamma(\nu - \kappa + 2) (p + a/2)^{\nu + \mu + 3/2}} \quad (A9)$$

$$\times F(\nu + \mu + 3/2, \mu - \kappa + 1/2, \nu - \kappa + 2; (2p - a)/(2p + a)) \quad (A10)$$

The abscissa of convergence is  $|a|/2$ , i.e. the convergence condition of equation (A10) is given by

$$p \geq |a|/2 \quad (A11)$$

From equations (A8)–(A10), it follows that

$$H_3 = \frac{2\Gamma(k_B + 1) \Gamma(k_A + 1)}{y^2 (k_A + k_B + 1) v_A^{k_A + k_B + 1}} \left(\frac{v_B}{v_A}\right)^{-k_B} \times F(1, k_A + 1, k_A + k_B + 2; (v_A - v_B)/v_A) \quad (A12)$$

The convergence condition given by (A11) is rewritten as

$$v_A \geq v_B \quad (A13)$$

By using equations (17), (18) and (26), (A13) is further rewritten as

$$\phi_A < k_A/(k_A + k_B) \quad (A14)$$

For

$$\phi_A > k_A/(k_A + k_B) \quad (A15)$$

we obtain

$$H_3 = \frac{2\Gamma(k_A + 1) \Gamma(k_B + 1)}{y^2 (k_A + k_B + 1) v_B^{k_A + k_B + 1}} \left(\frac{v_A}{v_B}\right)^{-k_A} \times F(1, k_B + 1, k_A + k_B + 2; (v_B - v_A)/v_B) \quad (A16)$$

by exchanging subscripts A and B in equation (A12).

One can calculate  $H_1$  and  $H_2$  similarly to  $H_3$ . Here let us calculate  $H_2$ . From equation (A4) and by integrating  $H_2$  first with  $N_B$ , one obtains that

$$H_2 = (2/y^2) \int_0^\infty dN_A N_A^{k_A} \exp[-(v_A + y)N_A] \times \int_0^\infty dN_B N_B^{k_B} \exp(-v_B N_B) (N_A + N_B)^{-1} \quad (A17)$$

The integration of (A17) is obtained by replacing  $v_A + y$  for  $v_A$  in the integration of (A5) to obtain  $H_3$ . Hence,

$$H_2 = \frac{2\Gamma(k_B + 1) \Gamma(k_A + 1)}{y^2 (k_A + k_B + 1) (v_A + y)^{k_A + k_B + 1}} \left(\frac{v_B}{v_A + y}\right)^{-k_B} \times F(1, k_A + 1, k_A + k_B + 2; (v_A + y - v_B)/(v_A + y)) \quad (A18)$$

The convergence condition is given by  $v_A + y - v_B/2 \geq v_B/2$  and therefore by

$$x_n > k_B/(1 - \phi_A) - k_A/\phi_A \quad (A19)$$

Similarly, by integrating  $H_2$  first with  $N_A$ , one obtains

$$H_2 = (2/y^2) \int_0^\infty dN_B N_B^{k_B} \exp(-v_B N_B) \times \int_0^\infty dN_A N_A^{k_A} \exp[-(v_A + y)N_A] (N_A + N_B)^{-1} = \frac{2\Gamma(k_B + 1) \Gamma(k_A + 1)}{y^2 (k_A + k_B + 1) v_B^{k_A + k_B + 1}} \left(\frac{v_A + y}{v_B}\right)^{-k_A} \times F(1, k_B + 1, k_A + k_B + 2; \{v_B - (v_A + y)\}/v_B) \quad (A20)$$

The convergence condition is given by

$$x_n \leq k_B/(1 - \phi_A) - k_A/\phi_A \quad (A22)$$

Note that equations (A20) and (A21) are obtained from equations (A18) and (A19) by exchanging the variables  $k_A$  and  $k_B$ ,  $N_A$  and  $N_B$ ,  $(v_A + y)$  and  $v_B$ . In this way one can obtain an analytical expression for  $\overline{Ng(f)}$ . It is obvious that  $\overline{Ng(1-f)}$  is obtained from  $\overline{Ng(f)}$  by exchanging the suffices A and B for  $\overline{Ng(f)}$ .

From equations (11) and (14),  $\overline{Ng(f=1)}$  is given by

$$\overline{Ng(f=1)} / [v_A^{k_A + 1} v_B^{k_B + 1} / \Gamma(k_A + 1) \Gamma(k_B + 1)] = \int_0^\infty \int_0^\infty dN_A dN_B N_A^{k_A} \exp(-v_A N_A) N_B^{k_B} \exp(-v_B N_B) (2/y^2 N) \times [yN + \exp(-yN) - 1] \quad (A23)$$

The integration can be carried out similarly to the integration for  $\overline{Ng(f)}$ .