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Small-Angle X-ray Scattering from Block Polymers in the Disordered State. 3. Validity of the Pseudobinary Approximation for Block Polymer Solutions

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ABSTRACT: We investigated the validity of the pseudobinary approximation proposed in our earlier work (Hashimoto, T.; Shibayama, M.; Kawai, H. *Macromolecules* **1983**, *16*, 1093) for scattering from semidilute-to-concentrated solutions of block copolymers in the disordered (or single) phase. The validity, which has never been checked carefully, was investigated by comparing scattering functions numerically calculated on the basis of the pseudobinary approximation and that of the full mean-field equation reported by Benmouna and Benoit (Benmouna, M.; Benoit, H. *J. Polym. Sci., Polym. Phys. Ed.* **1983,** *21*, 1227). The criteria for the pseudobinary approximation to be valid were found to be (i) the optical θ condition and (ii) nonselectivity of solvent for the block polymer chains being satisfied. An enormous simplification of the scattering equation brought by this approximation makes it possible to further elaborate the scattering theory to incorporate the nonclassical effects as reported recently (Olvera de la Cruz, M. *J. Chem. Phys.* **1989**, *90*, 1995; Fredrickson, G.; Leibler, L. *Macromolecules* **1989**, *22*, 1238).

Introduction

Small-angle scattering of X-rays (SAXS)[1] or neutrons (SANS)[2] from bulk block polymers in the single-phase (or disordered) state arises from their thermal composition fluctuations and yields important information on the nature of inter- and intramolecular interactions of polymers in the bulk.[3,4] However, many of the existing block polymers are comprised of highly immiscible constituent polymers, and hence their disordered state exists only at very high temperatures where the polymers become thermally unstable. This makes their quantitative and detailed studies difficult. In order to circumvent this difficulty, one has to lower the order-disorder transition temperature T_b by lowering the degree of polymerization N of entire block polymers or by the addition of a solvent. One can estimate the range of N to be $140 < N < 160$ if one wishes to keep T_b in the range $100 < T_b < 180$ °C for polystyrene-polyisoprene block polymer SI having equal polymerization indices N_S and N_I for polystyrene (PS) and polyisoprene (PI) blocks.[5] The range of N is quite low in order to study the connectivity effect of polymers. One good method to avoid this shortcoming involves studies of the block polymer systems in a semidilute-to-concentrated solution regime using neutral solvents. Thus in this paper we are concerned with static scattering from semidilute-to-concentrated solutions of block polymers in the disordered state.

Pseudobinary Approximation

Before Benmouna and Benoit[7] reported the full mean-field theory, we proposed a "pseudobinary approximation" for analyses of SAXS profiles for block polymer solutions in the disordered state.[8] This is a naive and intuitive picture of a one-to-one correspondence between the melts and the solutions, in which the Flory interaction parameter χ_{AB}, radius of gyration R_g, and scattering power $(a-b)^2$ (a and b being the scattering lengths or electron densities of the constituent polymers A and B in the A-B block polymer) in the melt are replaced, respectively, by χ_{eff}, R_g, and $(a-b)_{eff}^2 = (a-b)^2\phi_p$ in the presence of the solvent. Thus the scattering from the solutions is given on the basis of the scattering from the melts

$$I(q) = \phi_p(a-b)^2N/[F(q^2R_g^2,f) - 2\chi_{eff}N] \qquad (1)$$

where F and f are defined in the original Leibler theory[3] for the melts and q is the scattering vector. We applied eq 1 for the semidilute Θ state, so that χ_{eff} is replaced by $\chi_{AB}\phi_p$

$$\chi_{eff} = \chi_{AB}\phi_p \qquad (2)$$

which was justified in the weak-interaction limit by the renormalization group (RG) analyses of Onuki and Hashimoto.[9]

We applied eq 1 for the analyses of the scattering in the disordered state and in the order-disorder transition by investigating quantitatively I_m^{-1} and D as a function of reciprocal absolute temperature T^{-1}, where $I_m \equiv I(q=q_m)$ and $D \equiv 2\pi/q_m$; q_m is the q value at which the scattering function shows a maximum intensity. However, we found that the experimental profile does not necessarily fit very well with the predicted profile based on eq 1, especially at $q \ll q_m$, when toluene was used as a common solvent or n-tetradecane (C-14) was used as a selective solvent.[8] Thus we could not conduct detailed fitting of the profiles to extract χ_{eff} or $\chi_{AB} = \chi_{eff}/\phi_p$ and R_g. We found later[10] that the fits between the predicted and observed profiles become almost perfect down to relatively low polymer concentrations when dioctyl phthalate (DOP) is used as a solvent, as shown in Figure 1 for 50 wt % SI solution over a wide temperature range. The block copolymer SI has the number-average molecular weight $M_n = 3.2 \times 10^4$ and the heterogeneity index $M_w/M_n = 1.16$, M_w being the weight-average molecular weight, and contains styrene monomers by 59 wt %. The predicted and observed profiles are shown by solid lines and data points, respectively. The analyses yielded $R_g = 46$ Å independent of T and χ_{eff} given by

$$\chi_{eff} = 0.001 + 6.323/T \qquad (3)$$

The two results provide fundamental information on polymer physics, and hence further extension of this research as a function of wide ranges of ϕ_p and T is badly needed.

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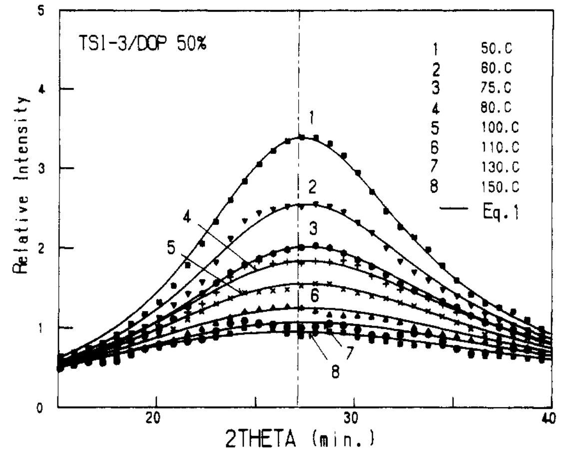

Figure 1. Experimental SAXS profiles from the 50 wt % solutions of SI with DOP in the disordered state (shown by data points). The solid lines are the profiles best fitted by eq 1 based upon a pseudobinary approximation.

Equation 1, derived on the basis of the mean-field approximation, has been further generalized by the incorporation of two kinds of nonclassical effects as elaborated by Olvera de la Cruz[11] and Fredrickson and Leibler.[12] These are (i) the nonclassical effect of polymer solutions, i.e., the deviation from mean-field behavior of polymer solution due to local fluctuations in solvent concentration (ψ_2), and (ii) the nonclassical effect of local composition fluctuations of segments A and B (ψ_1), i.e., deviation from Landau type mean-field behavior, where ψ_1 and ψ_2 are the corresponding order parameters. The first nonclassical effect was incorporated by using RG treatment based on the blob theory,[11,12] while the second effect was incorporated by taking into account the Brazovskii effect.[3,13] Thus in the event when the pseudobinary approximation is valid, i.e., in an experiment where the scattering depends only on $\langle\psi_1(\mathbf{q})\psi_1(-\mathbf{q})\rangle$ but not on $\langle\psi_1(\mathbf{q})\psi_2(-\mathbf{q})\rangle$ and $\langle\psi_2(\mathbf{q})\psi_2(-\mathbf{q})\rangle$, $I(q)$ is given by $I(q) = (a-b)^2\phi_p{}^2\langle\psi_1(\mathbf{q})\psi_1(-\mathbf{q})\rangle$, the generalized equation corresponding to eq 1 is given, using the Hartree approximation,[13] by[11,12]

$$I(q) = (a-b)^2\phi_p Z/\{\epsilon + F[q^2R_g{}^2(\phi_p),f] - 2\kappa\} \qquad (4)$$

$$\epsilon = 2\kappa - 2\chi_{\text{blob}}Z + c^3 d\lambda/(\epsilon Z)^{1/2} \qquad (5)$$

and

$$R_g{}^2 = Z\xi^2/6 \qquad (6)$$

where $Z(\phi_p)$, $\xi(\phi_p)$, and $\chi_{\text{blob}}(\phi_p)$ are coarse-grained parameters that describe, respectively, the number of blobs per chain, blob size, and the interaction between blobs A and B. These parameters, in turn, are given as a function of ϕ_p and T in terms of microscopic parameters such as N, the Kuhn segment length l, and the bare interaction parameter χ_{AB} between the A and B monomers. In the Θ solution with a weak-interaction limit,[9] $\chi_{\text{blob}}Z = \chi_{AB}\phi_p N$, which results in the original pseudobinary approximation.[8]

Thus in the context of the pseudobinary approximation one obtains the generalized eq 4. However, in order to apply this equation for the experimental analyses, we should be cautious of the validity of this approximation, which has never been carefully investigated. The investigation of validity of this approximation is the sole objective of this paper. It is obvious that the generalized eq 4 also fits very well with the experimental SAXS profiles shown in Figure 1, although the bare interaction parameter χ_{AB} determined from eq 4 is generally different from that determined from eq 1. It is also obvious that eq 4 does not fit well with the SAXS profiles obtained with the toluene and C-14 solutions, as eq 1 does not do so.

Validity of Pseudobinary Approximation

The validity of eq 4 can be determined sufficiently from the validity of eq 1 derived in the mean-field approximation level. Thus, the validity of the approximation can be investigated by comparing eq 1 with the scattering equation derived by Benmouna and Benoit (B–B) (eq 30 in ref 7) which explicitly includes the solvent and incorporates the contribution of ψ_2 to $I(q)$ (a full mean-field theory). Although this theory is general in the context of the mean-field approximation, it has limitations inherent to this approximation, and a direct generalization of this theory to account for the two kinds of nonclassical effects discussed earlier is seemingly very difficult. This gives us a strong motivation to check the validity of eqs 1 and 4.

Since $I(q)$ derived from B–B (a full equation) is very complicated, it is very difficult to find analytically the criteria in which the B–B equation becomes identical with eq 1. One can find analytically the criteria only for a few particular cases as described below. (i) The B–B full equation is easily reduced to eq 1 in the high-concentration limit of $\phi_p \rightarrow 1$. (ii) $I(0)$, i.e., $I(q)$ at $q = 0$, of the full equation is given by

$$I(0) = [af + b(1-f)]^2[(\phi_p N)^{-1} + f^2(\phi_s{}^{-1} - 2\chi_{AS}) + (1-f)^2(\phi_s{}^{-1} - 2\chi_{BS}) + 2f(1-f)(\phi_s{}^{-1} - \chi_{AS} - \chi_{BS} + \chi_{AB})]^{-1} \qquad (7)$$

where χ_{KS} (K = A or B) is the χ parameter between K polymer and solvent, $\phi_s = 1 - \phi_p$, and $f = N_A/N$; hence $I(0)$ becomes zero when

$$af + b(1-f) = 0 \qquad (8)$$

This is the "optically Θ condition" of block polymer solutions,[10] corresponding to that of the solution of polymer mixtures of A and B.[14] Thus if eq 8 is valid, then $I(0)$ is not affected by ψ_2 and can be described only by ψ_1. Hence eq 8 gives a criterion of the pseudobinary approximation at $q = 0$. (iii) The B–B full equation is reduced to eq 1 for a special case of $f = 0.5$, $\chi_{AB} = 0$, and $\chi_{AS} = \chi_{BS}$ as inferred by Duval et al.[15]

Obviously, eq 1 implicitly assumes the nonselectivity of the solvent

$$\chi_{AS} = \chi_{BS} \qquad (9)$$

as f is assumed to be unchanged by the solvent. However, this nonselectivity restriction can be removed by treating f in eqs 1 and 4 as an effective fraction as defined by $f = Z_A/Z$, where Z_A is the number of A blobs in the selective solvent, and by recalculating χ_{blob} for the selective solvent. Thus, in this sense, eq 9 is a rather weak requirement for validity of the pseudobinary approximation.

Numerical Test of Pseudobinary Approximation

In order to prove that eqs 8 and 9 are indeed criteria for the validity of the pseudobinary approximation at all q's, we pursued numerical calculations of the scattering profiles predicted by eq 1 and the B–B full theory and quantitatively compared the two profiles. We summarize below the conditions we set up for the comparisons: (1) We assume that the structure factor for a single chain in solution is given by a Debye function, e.g.

$$g(f) = (2/x^2)[\exp(-fx) + fx - 1] \qquad (10)$$

for an A block chain with $x = q^2R_g{}^2$. This assumption is justified by the theoretical work by Ohta et al.[16] and an

Table I
Fundamental Data and Contrast Factors for SI/DOP and SI/Toluene Solutions

sample	mass density $\rho_{m,K}$, g/cm^3	monomer mol wt $M_{0,K}$	monomer density $10^3\rho_{s,K}$, mol of monomers/cm^3	mol of electrons/mol of monomers $Z_{el,K}$	electron density $10\rho_{el,K}$, mol of electrons/cm^3	excess electron density $10^2\Delta\rho_{el,K}$	
						DOP	toluene
PS	1.052	104	10.1	56	5.656	2.46	9.35
PI							
1,4[a]	0.913	68	13.4	38	5.092	−3.14	3.71
vinyl[b]	0.925	68	13.6	38	5.17	−2.4	4.49
DOP	0.986	390	2.53	214	5.41		
toluene	0.868	92	9.44	50	4.721		

[a] 1,4-Rich PI prepared by living anionic polymerization in a nonpolar solvent, e.g., benzene. [b] Vinyl-rich PI prepared by living anionic polymerization in a polar solvent, e.g., tetrahydrofuran.

experiment by Lodge et al.[17] They showed that the single-chain structure factor as a function of qR_g for a solution with a good solvent is almost identical with that in the Θ solvent, both given by the Debye function (eq 10 with $f = 1$). (2) We neglect the polydispersity effect[6,18] and asymmetry effect.[1] (3) The contrast factors a and b for SAXS are given by

$$a = \rho_{el,A} - \rho_{el,S} \tag{11a}$$

$$b = \rho_{el,B} - \rho_{el,S} \tag{11b}$$

where $\rho_{el,K}$ is the electron density of the K species (K = A, B, or solvent S) in units of mol of electrons/cm^3. $\rho_{el,K}$ can be calculated from the mass density $\rho_{m,K}$ (g/cm^3), monomer molecular weight $M_{0,K}$, and number of electrons per monomer $Z_{el,K}$ (mol of electrons/mol of monomers)

$$\rho_{el,K} = \rho_{m,K}Z_{el,K}/M_{0,K} \tag{12}$$

Table I summarizes $\rho_{m,K}$, $M_{0,K}$, monomer density ($\rho_{s,K}$), $Z_{el,K}$, and $\rho_{el,K}$ for PS and PI block chains as well as for solvents (DOP and toluene).

The parameters required for the comparisons are (i) contrast factors a and b, (ii) N, (iii) f, (iv) ϕ_p, and (v) χ_{AS} and χ_{BS}. From Table I, $a/b \cong -1$ for the DOP solution of the SI with the PI block rich in vinyl linkage (the SI copolymer prepared in a polar medium such as tetrahydrofuran (THF)) and −0.77 for the DOP solution of the SI with the PI block rich in 1,4-linkage (the SI copolymer prepared in a nonpolar medium such as benzene). Thus the SI specimens in DOP shown in Figure 1 and L-8 in DOP[8] closely satisfy the optical Θ condition, while L-8 and L-2 in toluene are far from the optical Θ condition, giving rise to the deviations of the experimental profiles[8] from those predicted by eq 1. For numerical comparisons we set $a/b = -1$ or 2, the latter corresponding to the case of SI in toluene, $N = 200$ or 500, $f = 0.5$, 0.6, and 0.75, and ϕ_p from 0.2 to 0.8. These values of ϕ_p are much larger than ϕ_p^*, the overlap concentration, $\phi_p^* = 1.7 \times 10^{-2}$ and 0.34×10^{-2} for $N = 200$ in Θ and good solvents and 1.07×10^{-2} and 0.17×10^{-2} for $N = 500$ in Θ and good solvents, respectively.

Figure 2 shows comparisons of the theoretical scattering profiles calculated by the two kinds of theories where the profiles drawn by the solid line and dots are those calculated by the full theory (B–B) and the approximate theory of eq 1, respectively. The profiles were calculated for a set of parameters of $a/b = -1$, $f = 0.5$ (the optical Θ condition of eq 8 being satisfied), $\chi_{AS} = \chi_{BS} = 0.5$ (nonselectivity of eq 9 being satisfied), $\chi_{AB} = 0.03$ and $N = 200$. The profiles given by eq 1 are identical with those given by the full theory down to a level of ϕ_p as low as 0.2 at all q's. The same conclusion was obtained also for $N = 500$. Thus eqs 8 and 9 are numerically proven to be necessary conditions for the pseudobinary approximation to be valid, at least for $\phi_p > 0.2$ ($\phi_p/\phi_p^* \geq 10$). Hence we can justify our previous analyses based on the pseudobinary approximation.[19]

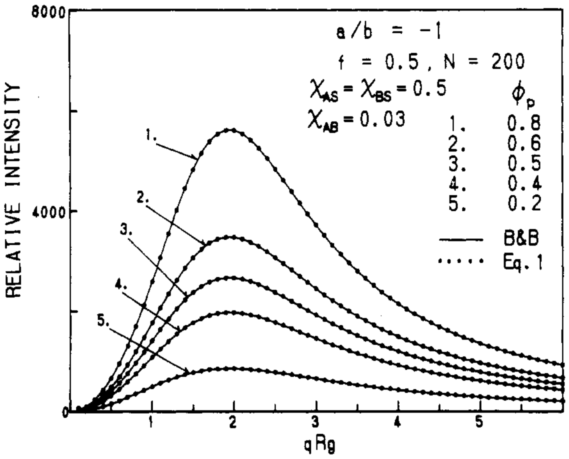

Figure 2. Comparisons of the scattering profiles for the block polymer solution in the disordered state calculated by the full theory (solid lines marked B&B) and by eq 1 (profiles shown by dots). The profiles were calculated for various volume concentrations ϕ_p's of SI for $N = 200$; $a/b = -1$, $f = 0.5$, $\chi_{AS} = \chi_{BS} = 0.5$, and $\chi_{AB} = 0.03$.

Effects of violating eq 8 on the scattering profiles are shown in Figure 3, where parts a and b show, respectively, those due to the changes of f from 0.5 to 0.75 and of a/b from −1 to 2, the rest of the parameters being kept unchanged except for χ_{AB} (=0.05). Obviously, the violation of the optical Θ condition causes an error in the theory for eq 1. The error generally increases with decreasing ϕ_p for a given f or a/b. The error increases with increasing $|f - 0.5|$ for a given ϕ_p and $a/b = -1$ and with increasing $|af + b(1 - f)|$ for a given ϕ_p and f. Parts a and b of Figure 3 correspond to the cases of $af + b(1 - f) = 0.5a$ and $0.75a$, respectively. Thus the violation due to the change of a/b causes much larger errors than that due to the change of f. In any case, the error at a high concentration $\phi_p > 0.6$ is very small. The error in part a of Figure 3 is significant at $q \cong q_m$, while that in part b is significant at $q \cong 0$.

We performed a computer experiment to check the accuracy of the theory for eq 1. For a given set of parameters, we first obtained the scattering profile using the full theory. Then this profile was best fitted by that given by eq 1 using the given N, ϕ_p, and a/b and by adjusting χ_{AB} in eq 1. The estimated χ_{AB} designated as $\chi_{AB,det}$ should be identical with a given χ_{AB} if the pseudobinary approximation is valid. The discrepancy between $\chi_{AB,det}$ and χ_{AB} is a measure of the accuracy of the pseudobinary approximation. Table II shows such analyses as discussed above on $\chi_{AB,det}$ and χ_{AB} as a function of ϕ_p, N, and χ_{AB} for a given set of parameters of $f = 0.6$ (or 0.4), $a/b = -1$, and $\chi_{AS} = \chi_{BS} = 0.5$. For a given N, the higher the concentration, the closer is the value $\chi_{AB,det}$ to the true

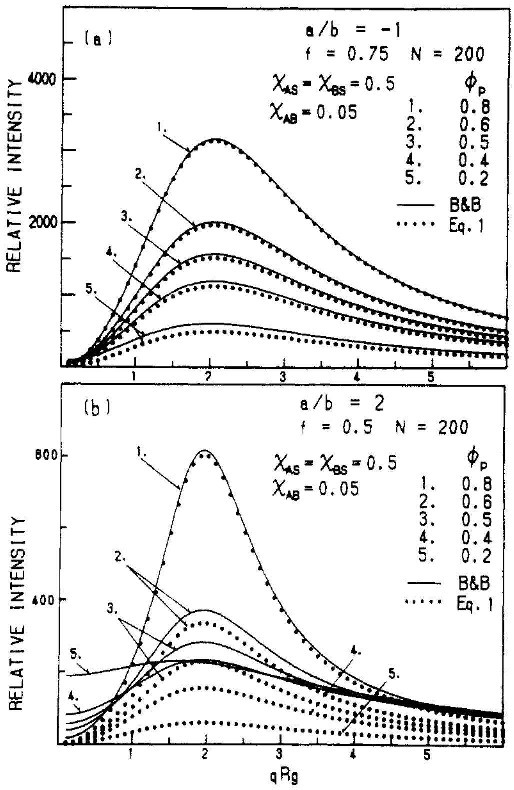

Figure 3. Comparisons of the scattering profiles for the block polymer solution in the disordered state calculated by the full theory (solid lines) and by eq 1 (profiles shown by dots). The profiles were calculated for various ϕ_p's of SI for (a) $a/b = -1$ and $f = 0.75$ and (b) $a/b = 2$ and $f = 0.5$. Other parameters are set to be common: $N = 200$, $\chi_{AS} = \chi_{BS} = 0.5$, and $\chi_{AB} = 0.05$.

Table II
Relation between the Preassigned χ_{AB} (0.03 or 0.05) and Estimated χ_{AB} ($\chi_{AB,det}$, the Values in the Columns) Based on the Approximate Theory as a Function of ϕ_p, N, and χ_{AB} for the Set of Parameters $f = 0.6$, $a/b = -1$, and $\chi_{AS} = \chi_{BS} = 0.5$

	$\chi_{AB} = 0.03$		$\chi_{AB} = 0.05$
ϕ_p	$N = 200$	$N = 500$	$N = 200$
0.8	0.03000	0.03000	0.05000
0.6	0.03015	0.03000	0.05015
0.5	0.03032	0.03000	0.05030
0.4	0.03072	0.03012	0.05070
0.2	0.03621	0.03113	0.05600

Table III
Relation between the Preassigned χ_{AB} (0.05 or 0.01) and Estimated χ_{AB} ($\chi_{AB,det}$, the Values in the Columns) Based on the Approximate Theory as a Function of ϕ_p, N, and χ_{AB} for the Set of Parameters $f = 0.75$, $a/b = -1$, and $\chi_{AS} = \chi_{BS} = 0.5$

	$\chi_{AB} = 0.05$		$\chi_{AB} = 0.01$
ϕ_p	$N = 200$	$N = 500$	$N = 200$
0.8	0.05050		0.01050
0.6	0.05220	0.05040	0.01230
0.5	0.05470	0.05078	0.01480
0.4	0.06050	0.05178	0.02080
0.2	0.12750	0.06550	0.09150

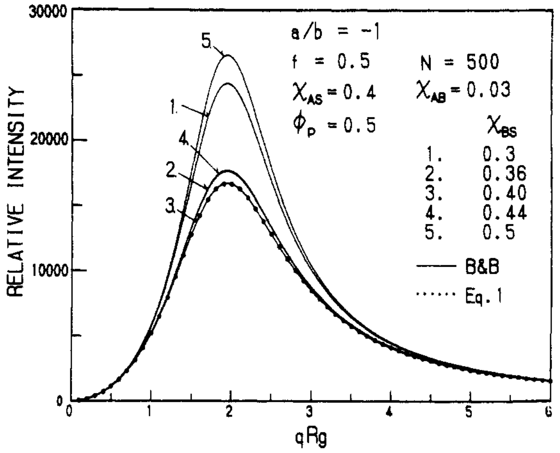

Figure 4. Comparisons of the scattering profiles for the block polymer solution in the disordered state calculated by the full theory (solid lines) and by eq 1 (profiles shown by dots). The profiles were calculated for various χ_{BS}'s for $\chi_{AS} = 0.4$ and $\phi_p = 0.5$. Other parameters are set to be common: $a/b = -1$, $f = 0.5$, $N = 500$, and $\chi_{AB} = 0.03$.

value χ_{AB}. For a given ϕ_p, the higher the value of N, the smaller the relative error $E_r \equiv (\chi_{AB,det} - \chi_{AB})/\chi_{AB}$. For the given N and ϕ_p, the larger the value χ_{AB}, the smaller the relative error E_r. Thus the approximation works better for the higher values of N, ϕ_p, and χ_{AB}. For the SI block polymer with $f = 0.555$ shown in Figure 1, the estimated $\chi_{AB,det}$ based upon the approximation is accurate with a relative error much below 10% if $\phi_p > 0.4$. A similar test of the approximation was performed for the case of $f = 0.75$ (or 0.25) and $\chi_{AB} = 0.05$, the results of which the summarized in Table III. The same trends as described in Table II are also observed here, but the trend is more enhanced for the case of $f = 0.75$ (or 0.25) than for $f = 0.6$ (or 0.4). For example, let us compare the case of $\chi_{AB} = 0.05$, $N = 200$, and $\phi_p = 0.4$ in Tables II and III. For the case of $f = 0.6$, $E_r = 0.014$, while for the case of $f = 0.75$, $E_r = 0.21$.

Figure 4 shows the effect of the solvent selectivity on the scattering profiles where χ_{BS} is changed, keeping $\chi_{AS} = 0.4$ and other parameters fixed; $a/b = -1$, $f = 0.5$, $N = 500$, $\chi_{AB} = 0.03$, and $\phi_p = 0.5$. The discrepancy of the two results is larger for a larger difference of $\Delta\chi = |\chi_{AS} - \chi_{BS}|$, and a complete agreement of the two results is obtained for $\Delta\chi = 0$. Thus eq 1 works for the neutral solvent. The violation of the solvent neutrality causes errors in eq 1 at $q \cong q_{max}$, causing overestimation of χ_{AB}.

In conclusion, eqs 8 and 9 provide criteria for validity of the pseudobinary approximation and hence for the use of the mean field eq 1 or the generalized eq 4 for the scattering analyses of block copolymer solutions in the single-phase state. Finally, it should be noted that Onuki and Hashimoto[9] discussed in detail the pseudobinary approximation for scattering from semidilute solutions of polymer blends.

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