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Static Crossover of Critical Behavior in Polymer Blend Solutions: Scaling Analysis of the Ginzburg Number

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ABSTRACT: By means of light scattering, the static critical behavior was investigated for symmetrical polymer blend solutions of polystyrene/poly(methyl methacrylate)/deuterated benzene and polystyrene/poly(2-chlorostyrene)/deuterated benzene with different polymeric indices N and polymer concentrations c. The temperature dependence of the isothermal susceptibility S_T and the correlation length ξ_t near the stability limit showed the static crossover from the mean-field to the three-dimensional Ising behavior in all solutions. The Ginzburg number Gi^{BK} was evaluated with the aid of the crossover function of Belyakov and Kiselev. As c increases from the semidilute region to the bulk limit, the scaled Ginzburg number $gi^{BK} = Gi^{BK}N$ decreased, with the power α of $gi^{BK} \propto c^{\alpha}$ being -1.25 to -2 as expected by the theory based on the blob concept. The values of gi^{BK}(bare) evaluated by the bare interactions were smaller than experimental values.

Introduction

Approaching the critical points, simple or binary fluids exhibit a crossover from the classical mean-field to the three-dimensional Ising (3D Ising) behavior, with changing critical exponents of the thermodynamic properties. This static crossover indicates that the fluctuation of the order parameter becomes infinitely large to be a dominant factor in the thermodynamic behavior. Its location is characterized by the Ginzburg number Gi, which is a system-dependent parameter. Recently, Belyakov and Kiselev[1,2] have derived a simple universal function describing the static crossover of the isothermal susceptibility in terms of Gi on the basis of a renormalization-group method with the ϵ-expansion.

It was first pointed out by de Gennes[3] that polymeric systems, in particular polymer blends, have a narrower 3D-Ising region and tend to exhibit the mean-field critical behavior. Since then, particular attention has been paid to the crossover behavior in polymeric systems and to the dependence of the Ginzburg number on the polymeric index N and/or polymer concentration c. Most of the theoretical[3-7] and experimental[8-18] studies have been devoted to polymer blends. The applicability of Belyakov and Kiselev's universal function has been confirmed for various polymer blends by Meier et al.[15,16] As for semidilute polymer blend solutions, which exhibit a critical behavior mainly due to incompatibility between polymers, Broseta et al.[19] have theoretically studied the crossover behavior on the basis of the blob concept and derived an equation for Gi as a scaling function of c.

In polymer blend solutions, which are ternary systems, a small fluctuation of total polymer concentration c has some influence on the critical behavior, so that a Fisher renormalized Ising region,[21] besides the mean-field and the 3D-Ising regions, must exist in the nearest temperature region to the stability limit. In our previous paper,[20] however, we have experimentally demonstrated that semidilute blend solutions of polymer A/polymer B/good solvent have no Fisher renormalized region in the experimental temperature range, showing a much wider 3D-Ising region than ordinary polymer blend systems. This result is consistent with the theoretical consideration of Broseta et al.,[19] which predicts that the renormalized Ising region is too narrow to be observed under practical experimental conditions. Consequently, we can reasonably suppose a crossover from the 3D-Ising behavior to mean-field behavior for real systems of symmetrical polymer blend solutions.

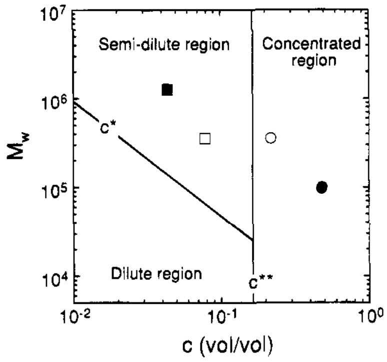

Figure 1. Molecular weight–concentration diagram for polystyrene in toluene or benzene, which was deduced from osmotic pressure measurements by Noda et al.[22,23] Symbols represent the blend solutions used in this study: (□) MA1; (■) MA2; (●) CL1; (○) CL2.

The Ginzburg number Gi of a polymer blend solution must monotonously decrease with increasing polymer concentration from the semidilute region, to the concentrated region, to the bulk limit. Needless to say, the polymeric index N controls Gi and the boundary of the concentration regions as well. The locations of the concentration regions for polymer solutions are illustrated as a c–molecular weight (M) diagram in Figure 1, which was experimentally determined from osmotic pressure for polystyrene in toluene or benzene by Noda et al.[22,23] The dilute and semidilute regions are separated by the overlap concentration c^*, which is defined as

$$c^* \equiv \frac{M}{(4/3)\pi\varrho R_F{}^3 L} \qquad (1)$$

Here, ϱ is polymer density, R_F is the radius of gyration of a polymer chain in a dilute solution of good solvent, and L is the Avogadro number. The boundary c^{**}

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between the semidilute and concentrated regions is independent of M (or N). In the semidilute region, the Ginzburg number Gi is expected to decrease with increasing c, following a scaling law of $(c/c^*)^{-1.25}$.[19] In the concentrated region, it should decrease with a different c dependence, because the excluded-volume effect is partially screened in the semidilute region, whereas it is entirely screened out in the concentrated region as in the bulk.

In this paper we are concerned with the crossover of the critical behavior in polymer blend solutions over a wide range of total polymer concentration c and polymeric index N. The crossover for the isothermal susceptibility S_T and the correlation length ξ_t has been investigated by means of static light scattering for four symmetrical polymer blend solutions of different molecular weights and concentrations. We have applied the Belyakov–Kiselev crossover functions[1,2] and evaluated the Ginzburg number Gi^{BK} to see the c and N dependence of Gi^{BK} over the wide concentration range from the semidilute to the concentrated region and examine the validity of the theoretical prediction based on the blob concept. In the following section, reviewing the theoretical background of the Ginzburg number, we will derive the scaled expressions of Gi as a function of c evaluated from the bare interactions, in other words, on the basis of the mean-field descriptions, covering the semidilute, concentrated, and bulk regions. Then we will describe the details of the experiments, give the results, and present a discussion according to the theoretical consideration.

Theoretical Background

A. The Ginzburg Number *Gi*. In fluid systems, the critical exponents γ and ν for the isothermal susceptibility S_T and the correlation length ξ_T are defined through $S_T \sim \tau^{-\gamma}$ and $\xi_t \sim \tau^{-\nu}$, with the reduced temperature $\tau \equiv |T/T_s - 1|$, where T_s is the temperature at the stability limit. On the crossover from the classical mean-field behavior to the 3D-Ising behavior, the values of γ and ν vary from $\gamma = 1$ and $\nu = 1/2$ to $\gamma = 1.24$ and $\nu = 0.63$,[24] respectively. The location of the static crossover is specified by the Ginzburg number Gi: The mean-field theory holds for $\tau \gg Gi$, while the 3D-Ising model applies for $\tau \ll Gi$. Gi is given as

$$Gi \sim \frac{{b_0}^2}{{a_0}^4}\left(\frac{v_0}{{\xi_{t0}}^3}\right)^2 \tag{2}$$

with the numerical prefactor depending on the definition. Here v_0 is the volume per molecule, and ξ_{t0} is the correlation-length amplitude which is of the order of the molecular radius. a_0 and b_0 are the parameters in the Ginzburg–Landau–Wilson expression, eq 3, of free energy Δf near the stability limit.

$$\Delta f(\psi) = \frac{k_BT}{v_0}\int d^3r\left[\frac{1}{2}a_0\tau\psi^2(r) + \frac{1}{4!}b_0\psi^4(r) + \frac{1}{2}c_0(\nabla\psi(r))^2\right] \tag{3}$$

Here, k_B is the Boltzmann constant and $\psi(r)$ is the order parameter. The bare interaction parameters a_0 and b_0 are explicitly given in terms of the local free energy density f_0 per volume v_0 of the mean-field expression as

$$a_0 = (\partial^2\bar{f}_0/\partial\tau\,\partial\psi^2) \tag{4}$$

$$b_0 = (\partial^4\bar{f}_0/\partial\psi^4) \tag{5}$$

Here, $\bar{f}_0 = f_0(k_BT/v_0)$ is the reduced free energy, and τ is defined as $\tau \equiv |T/T_{sm} - 1|$ with the mean-field spinodal temperature T_{sm}. The bare (unrenormalized) amplitude ξ_{t0} of the correlation length for thermal concentration fluctuations is given by

$$\xi_t = \xi_{t0}\tau^{-1/2} \tag{6}$$

The Ginzburg number Gi(bare) evaluated from these equations (eqs 4–6) must be proportional to the real Gi that is evaluated with the renormalized parameters.

B. Universal Crossover Function. By the renormalization-group calculation, Belyakov and Kiselev have derived the universal function that describes the static crossover of S_T for fluids.[1,2] The crossover function is expressed in terms of the Ginzburg number Gi^{BK} and a_0 as follows.

$$\frac{\tau}{Gi^{BK}} = \{1 + \kappa(S_Ta_0Gi^{BK})^{\Delta/\gamma}\}^{(\gamma-1)/\Delta} \times [(S_Ta_0Gi^{BK})^{-1} + \{1 + \kappa(S_Ta_0Gi^{BK})^{\Delta/\gamma}\}^{-\gamma/\Delta}] \tag{7}$$

$$Gi^{BK} \equiv \frac{{b_0}^2}{32\pi^4{a_0}^4}\left(\frac{v_0}{{\xi_{t0}}^3}\right)^2 = \left|1 - \frac{T_{sm}}{T_s}\right| \tag{8}$$

The gap exponent $\Delta = 0.51$ and the critical exponent $\gamma = 1.24$ are the values for the 3D-Ising model. The value of the universal constant κ is determined to be 2.333 by ϵ^2 expansion. The crossover function, eq 7, is a phenomenologically generalized one to reproduce the 3D-Ising behavior at the limit of $\tau/Gi^{BK} \ll 1$ as follows.

$${S_T}^{-1} = \frac{\kappa^{\gamma/\Delta}a_0(Gi^{BK})^{1-\gamma}}{(1 + \kappa^{\gamma/\Delta})^{\gamma}}\tau^{\gamma} \qquad (\text{3D-Ising};\ \tau/Gi^{BK} \ll 1) \tag{9}$$

Equations 7 and 9 and a presumable mean-field behavior are illustrated in Figure 2, along with the locations of T_s and T_{sm}.

C. Gi^{BK}(bare) for Polymer Blend Solutions with a Blob Model. Here, we will evaluate Gi^{BK}(bare) for a polymer A/polymer B/good solvent system with a blob picture to estimate the N and c dependence of the Ginzburg number Gi. By the use of the blob concept, the system is approximated by binary mixtures of Gaussian chains of blobs. In describing the quasi-binary mixture with the blob model, we impose the basic assumption that the blob volume $v_b(c)$ is common for the two polymers. Furthermore, the segment volume v_s, independent of c, is commonly defined for unlike polymers. Then, since $v_b(c)$ is written by

$$v_b(c) = v_sg(c)/c \tag{10}$$

the number $g(c)$ of segments within a blob is also common for polymers A and B. Using the segment volume v_s, the polymeric indices N_A and N_B are defined by

$$N_A = v_A/v_s, \qquad N_B = v_B/v_s \tag{11}$$

where v_i is the volume of an i-polymer molecule. Then, the mean-field expression of the local free energy density

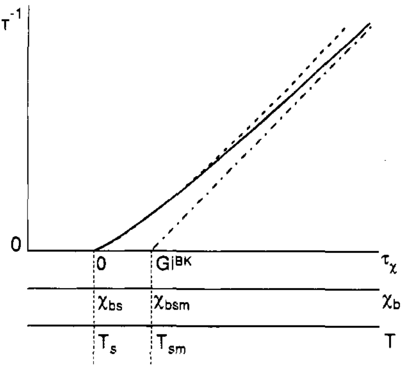

Figure 2. Schematic illustration of the static crossover for the isothermal susceptibility S_T: solid line, the Belyakov–Kiselev crossover function (eq 7); dashed line, the asymptotic Ising behavior (eq 9); broken line, the presumable mean-field behavior.

f_{b0} per $v_b(c)$ is given by[19]

$$\bar{f}_{b0} = \frac{f_{b0}}{k_BT/v_b} = \frac{\phi_A}{N_A/g}\ln\phi_A + \frac{\phi_B}{N_B/g}\ln\phi_B + \chi_b\phi_A\phi_B \tag{12}$$

where ϕ_i is the volume fraction of polymer i in the total volume of polymers ($\phi_A + \phi_B = 1$), which corresponds to the order parameter $\psi(r)$. χ_b represents the Flory–Huggins interaction parameter between unlike blobs. χ_b depends on temperature and the concentration c and is here assumed independent of the composition ϕ_i.

The reduced interaction parameter τ_χ is defined by

$$\tau_\chi \equiv \left|1 - \frac{\chi_b}{\chi_{bs}}\right| \tag{13}$$

and the mean-field definition

$$\tau_{\chi m} \equiv \left|1 - \frac{\chi_b}{\chi_{bsm}}\right| \tag{14}$$

Here, χ_{bs} and χ_{bsm} are χ_b at the actual spinodal temperature T_s and the mean-field spinodal temperature T_{sm}, respectively. It is noteworthy that χ_b has a different dependence on the polymer concentration c between the semidilute and concentrated regions. However, as far as we are observing the phenomena as a function of τ_χ, the c dependence of χ_b does not appear in the formalism of the critical behavior explicitly.

From eqs 4 and 5 with eq 12, the bare constants a_0 and b_0 are derived as

$$a_0 = \frac{1}{(N_A/g)\phi_A} + \frac{1}{(N_B/g)\phi_B} = 2\chi_{bsm} = \left(\frac{\phi_A\phi_B\langle N\rangle}{g}\right)^{-1} \tag{15}$$

$$b_0 = 2\left(\frac{1}{(N_A/g)\phi_A^{\,3}} + \frac{1}{(N_B/g)\phi_B^{\,3}}\right) = 2\left(\frac{\phi_A\phi_B\langle N\rangle}{\langle\phi^{-2}\rangle g}\right)^{-1} \tag{16}$$

The random phase approximation for binary polymer mixtures yields are bare amplitude ξ_{t0} for the present model as[10]

$$\xi_{t0} = \frac{1}{(3a_0)^{1/2}}\left(\frac{R_{gA}^{\,2}(c)}{(N_A/g)\phi_A} + \frac{R_{gB}^{\,2}(c)}{(N_B/g)\phi_B}\right)^{1/2} = \left(\frac{\langle R_g^{\,2}(c)\rangle}{3}\right)^{1/2} \tag{17}$$

$\langle N\rangle$, $\langle\phi^2\rangle$, and $\langle R_g^2(c)\rangle$ in eqs 15–17 are defined as follows.

$$\langle N\rangle = \frac{\phi_A^{\,-1} + \phi_B^{\,-1}}{N_A^{\,-1}\phi_A^{\,-1} + N_B^{\,-1}\phi_B^{\,-1}} \tag{18}$$

$$\langle\phi^{-2}\rangle = \frac{N_A^{\,-1}\phi_A^{\,-3} + N_B^{\,-1}\phi_B^{\,-3}}{N_A^{\,-1}\phi_A^{\,-1} + N_B^{\,-1}\phi_B^{\,-1}} \tag{19}$$

$$\langle R_g^{\,2}(c)\rangle = \frac{R_{gA}^{\,2}(c)N_A^{\,-1}\phi_A^{\,-1} + R_{gB}^{\,2}(c)N_B^{\,-1}\phi_B^{\,-1}}{N_A^{\,-1}\phi_A^{\,-1} + N_B^{\,-1}\phi_B^{\,-1}} \tag{20}$$

Here, the subscripts A and B denote polymers A and B, respectively. $\langle N\rangle$ is alternatively written as

$$\langle N\rangle = \langle v\rangle/v_s \tag{21}$$

where the mean volume $\langle v\rangle$ of the polymer molecules is given by

$$\langle v\rangle = \left[\frac{v_A^{\,-1}\phi_A^{\,-1} + v_B^{\,-1}\phi_B^{\,-1}}{\phi_A^{\,-1} + \phi_B^{\,-1}}\right]^{-1} \tag{22}$$

Then, the bare Ginzburg number Gi^{BK}(bare) is evaluated by eq 8 with eqs 10 and 15–17 to be

$$Gi^{BK}(bare) = \frac{27}{8\pi^4}f_\phi v_s^{\,2}\langle R_g^{\,2}(c)\rangle^{-3}\langle N\rangle^2 c^{-2} \tag{23}$$

where the asymmetry factor f_ϕ for the composition is defined as

$$f_\phi = \phi_A^{\,2}\phi_B^{\,2}\langle\phi^{-2}\rangle^2 \tag{24}$$

which becomes unity when $\phi_A = \phi_B = {}^1/_2$.

Now, the segment volume v_s is defined as

$$v_s = \langle v\rangle^3/\langle R_{g\theta}^{\,2}\rangle^3 \tag{25}$$

with

$$\langle R_{g\theta}^{\,2}\rangle = \frac{R_{g\theta A}^{\,2}v_A^{\,-1}\phi_A^{\,-1} + R_{g\theta B}^{\,2}v_B^{\,-1}\phi_B^{\,-1}}{v_A^{\,-1}\phi_A^{\,-1} + v_B^{\,-1}\phi_B^{\,-1}} \tag{26}$$

where $R_{g\theta i}$ is the unperturbed radius of gyration of an i-polymer molecule. Once the segment size v_s is definitely defined by eq 25, N_A, N_B, $\langle N\rangle$, and g are uniquely defined and cannot arbitrarily be taken hereafter.

By the scaling law, $\langle R_g^2(c)\rangle$ for the semidilute region ($c^* < c < c^{**}$) is described as

$$\langle R_g^{\,2}(c)\rangle = \langle R_{g\theta}^{\,2}\rangle\left(\frac{c}{c^{**}}\right)^{-(2\sigma-1)/(3\sigma-1)} \qquad (c^* < c < c^{**}) \tag{27}$$

where $\sigma \cong 0.588$ is the swelling exponent defined by $R_F \sim N^\sigma$. A detailed discussion on the expression of $\langle R_g^2(c)\rangle$ and c^{**} may be found in the Appendix. For the concentrated region ($c^{**} < c < 1$) including the bulk limit,

$$\langle R_g^{\,2}(c)\rangle = \langle R_{g\theta}^{\,2}\rangle \qquad (c^{**} < c < 1) \tag{28}$$

Using eqs 25–28, one can rewrite eq 23 to obtain the expressions of Gi^{BK}(bare) for the semidilute solution, the concentrated solution, and the bulk limit.

$$Gi^{\mathrm{BK}}(\mathrm{bare}) = \frac{27}{8\pi^4} f_\phi (c^{**})^{-3(2\sigma-1)/(3\sigma-1)} \langle N\rangle^{-1} c^{-1/(3\sigma-1)} \qquad (c^* < c < c^{**}) \quad (29)$$

$$= \frac{27}{8\pi^4} f_\phi \langle N\rangle^{-1} c^{-2} \qquad (c^{**} < c < 1) \quad (30)$$

$$= \frac{27}{8\pi^4} f_\phi \langle N\rangle^{-1} \qquad (\mathrm{bulk}) \quad (31)$$

Under the symmetrical conditions, i.e., $N_A = N_B = N$ and $\phi = 1/2$, eq 29 is reduced to be the following equation written in terms of c/c^* with the coefficient K_R used by Broseta et al.[19] (see Appendix)

$$Gi^{\mathrm{BK}}(bare) = \frac{6}{\pi^2 K_R^{\,3}} \left(\frac{c}{c^*}\right)^{-1/(3\sigma-1)} \qquad (c^* < c < c^{**}) \quad (32)$$

Equation 32 is equivalent to the equation of Broseta et al. (see a note in ref 19). Bates et al.[11,12] defined the Ginzburg number $Gi°$ as

$$Gi° \equiv \left|1 - \frac{\chi_x}{\chi_{sm}}\right| \quad (33)$$

χ_x is the interaction parameter χ at which the asymptotic $S_T^{-1}-\chi$ curve for the mean-field behavior intersects with that for the Ising behavior, and χ_{sm} is χ at the mean-field spinodal temperature. They have derived a theoretical expression equivalent to eq 31, which is related to the present $Gi^{\mathrm{BK}}(\mathrm{bare})$ by

$$Gi° = \tilde{C} f_\phi \langle N\rangle^{-1} = \frac{8\pi^4}{27} \tilde{C}\, Gi^{\mathrm{BK}}(bare) \qquad (\mathrm{bulk}) \quad (34)$$

where $\tilde{C}$ is the constant.

The Ginzburg number may have a $f_\phi \langle N\rangle^{-1}$ dependence in all regions, so that if a scaled Ginzburg number gi is defined as

$$gi^{\mathrm{BK}} \equiv \frac{Gi^{\mathrm{BK}} \langle N\rangle}{f_\phi} \quad (35)$$

then $gi^{\mathrm{BK}}(\mathrm{bare})$ can be expressed by

$$gi^{\mathrm{BK}}(bare) = \frac{27}{8\pi^4} (c^{**})^{-3(2\sigma-1)/(3\sigma-1)} c^{-1/(3\sigma-1)} \qquad (c^* < c < c^{**}) \quad (36)$$

$$= \frac{27}{8\pi^4} c^{-2} \qquad (c^{**} < c < 1) \quad (37)$$

$$= \frac{27}{8\pi^4} \qquad (\mathrm{bulk}) \quad (38)$$

It should be pointed out that since c^{**} is independent of N, gi^{BK} is a function of c alone, irrespective of N, over the semidilute and concentrated regions. Therefore, plots of gi^{BK} vs c for different N and c make a master curve, following eqs 36–38, as long as c^{**} can be regarded as a constant for the set of data.

Experimental Section

Materials. Weight-average molecular weight M_w and polydispersity index M_w/M_n are listed in Table 1 for polystyrene (PS), poly(methyl methacrylate) (PMMA), and poly(2-chlorostyrene) (P2ClS), along with material codes and sources. Numbers in the material codes refer to the molecular weight in ten kilograms per mole.

Samples. Blend solutions used were PS/PMMA/deuterated benzene (Bnz-d_6) solutions and PS/P2ClS/Bnz-d_6 solutions, all of which had a lower critical solution temperature. Two polymer components in respective blend solutions had approximately the same molecular weight, and benzene-d_6 was thermodynamically good for PS, PMMA, and P2ClS. Polymer compositions (ϕ_{PS}) of the samples prepared were close to the critical composition predicted by the Flory–Huggins theory (eq 12). They might not be real critical compositions, but solutions of these compositions could reach a temperature sufficiently close to the stability limit with no phase separation. Details of sample preparation were described in the previous paper.[20] Sample codes and characteristics of the blend solutions are listed in Table 2. M_w and total polymer concentration c of blend solutions are also shown in Figure 1. Samples MA1 and MA2 belong to the semidilute region, while CL1 and CL2 fall within the concentrated region.

Light Scattering. Details of the light scattering apparatus were described elsewhere.[25] An Ar ion laser operated at the wavelength 488 nm was used as a light source. A sample tube of 4.2 mm inner diameter was immersed in a thermostated (±0.05 °C) index-matching oil bath. The scattered light intensity $I(q)$ was measured by the photon-counting method as a function of length q of the scattering vector. Turbidity attenuation and the multiple scattering effect were estimated from the Rayleigh ratio of scattered light intensity to be less than 2×10^{-2} of the observed intensity,[20] so no corrections for them were made.

In a polymer/polymer/solvent system, the scattered light intensity $I(q)$ can be expressed as a sum of structure functions $S_{ij}(q) = \langle \delta c_i(q) \delta c_j(-q)\rangle$ weighted with the refractive index increment, where $\delta c_i(q)$ is the Fourier transform of concentration fluctuations of component i. However, all structure functions show a similar critical divergence near the stability limit irrespective of ij. For a symmetrical system such as the present case, where both polymers have similar polymeric indices and the solvent is sufficiently good for both, quasi-binary treatment is feasible and the critical divergence is governed by fluctuations of the polymer composition. Actually, the scattered light intensity from binary solutions PS/Bnz-d_6 with concentration 0.07–0.22 vol/vol was 1/50 to 1/1000 times of that of used blend solutions, so most of scattered light intensity may come from polymer-composition fluctuations. Thus, the inverse isothermal susceptibility S_T^{-1} and the correlation length ξ_t of polymer-composition fluctuations were evaluated from $I(q)$ by the least-squares fitting to the Ornstein–Zernike equation, eq 39:

$$\frac{I(q)}{I(0)} = (1 + q^2 \xi_t^{\,2})^{-1} \quad (39)$$

$I(0)$ provides S_T^{-1} in an arbitrary scale by $S_T^{-1} \sim T/I(0)$.[20] As examples of the good linearity between $I^{-1}(q)$ and q^2, the results for sample MA1 are shown in Figure 3a. However, the most concentrated solution CL1 exhibited excess intensity deviating from the linearity in the smaller q range as shown in Figure 3b, probably because there remained some heterogeneity in composition owing to their high viscosity. Thus, we had evaluated S_T^{-1} and ξ_t for CL1 by the fitting of $I(q)$ at higher q ($q^2 > 3.8 \times 10^{-4}$ nm^{-2}).

Table 1. Weight-Average Molecular Weight and Polydispesity Index of the Polymers Used in This Study

material code	$M_w \times 10^{-5}$	M_w/M_n	note
polystyrene			
PS10	10.0	≤1.06	a product of Pressure Chemicals
PS36	35.5	1.02	a product of Tosoh
PS126	126	1.05	a product of Tosoh
poly(methyl methacrylate)			
PMMA33	32.7	≤1.10	a product of Pressure Chemicals
PMMA109	109	1.08	radical polymerized
poly(2-chlorostyrene)			
P2ClS12	12.4	1.19	radical polymerized
P2ClS37	36.9	1.23	radical polymerized

Table 2. Characteristics of Polymer Blend Solutions

sample code	system	ϕ_{PS}	c/vol% $(c/c^*)^a$	$\langle N\rangle$	$\langle R_g^2(c)\rangle^{1/2}$/nm^b	f_ϕ
MA1	PS36/PMMA33/Bnz-d_6	0.484	7.82 (8.52)	75.8	21.0	1.01
MA2	PS127/PMMA109/Bnz-d_6	0.497	4.33 (12.7)	259	41.8	1.00
CL1	PS10/P2ClS12/Bnz-d_6	0.469	48.9 (19.7)	17.5	9.1	1.06
CL2	PS36/P2ClS37/Bnz-d_6	0.452	21.8 (23.8)	58.7	18.2	1.08

[a] The values of c/c^* were calculated with the swelling radius R_F (eq 40) and the molecular weight M_w for PS. [b] Calculated by eqs 26–28 with c^{**} = 0.538 vol/vol-solution, σ = 0.595, and the published data[26] for the unperturbed radius $R_{g\theta}$.

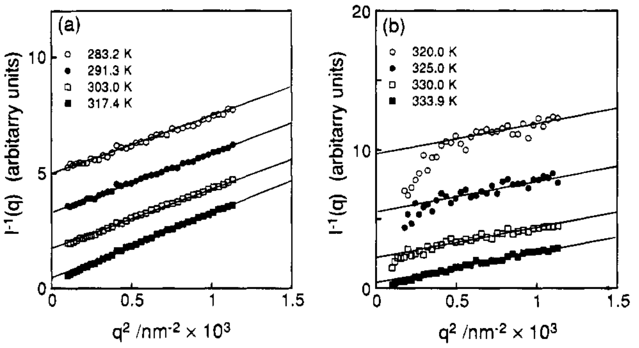

Figure 3. Ornstein–Zernike plots of $I^{-1}(q)$ vs q^2 for blend solutions: (a) MA1; (b) CL1.

Results and Discussion

For data presentation and analysis, we first evaluated v_A, v_B, and v_s for each blend solution to calculate the values of $\langle N\rangle$, $\langle R_g^2(c)\rangle$, and f_ϕ. The volume v_i was calculated from $v_i \equiv M_{wi}/\varrho_L$ with the density ϱ = 1.065 g/cm^3 for PS, and then the value of v_s was obtained from eqs 22, 25, and 26 with reported data[26] for the unperturbed radius $R_{g\theta}/M_w^{1/2}$. The values of $\langle N\rangle$ and f_ϕ for blend solutions were calculated by eqs 18, 19, and 24 and are summarized in Table 2. To evaluate $\langle R_g^2(c)\rangle$ as a function of concentration from eqs 27 and 28, the value of c^{**} was estimated from eq A17 as follows. K_l was first estimated on the basis of eq A4 (see Appendix) by using the following expressions for R_F and $R_{g\theta}$ of the PS chain obtained by Miyaki et al.[27]

$$\overline{R_F^2}/\mathrm{cm}^2 = (1.47 \pm 0.05) \times 10^{-18} M_w^{1.19\pm0.05} \quad (40)$$

$$\overline{R_{g\theta}^2}/\mathrm{cm}^2 = (8.8 \pm 0.2) \times 10^{-18} M_w \quad (41)$$

The value of K_l obtained was 1.27, which was approximately the same as those evaluated for PMMA and P2ClS. Then c^{**} was determined from eq A17 with g_0 = 1 and K_l = 1.27 to be 0.538 vol/vol-solution. Eventually, the values of $\langle R_g^2(c)\rangle$ were calculated from eqs 26–28 with the c^{**} value and σ = 0.595 which was taken so as to be consistent with eq 40. The value of c^{**} = 0.538 vol/vol-solution is much larger than c^{**} = 0.14–0.19 vol/vol-solution determined from osmotic pressure by Noda et al.[22,23] However, the value of c^{**} obtained here is consistent with those estimated from direct measurements of chain dimensions for PS in toluene solutions[28] and for polyisoprene in good solvent solutions.[29,30]

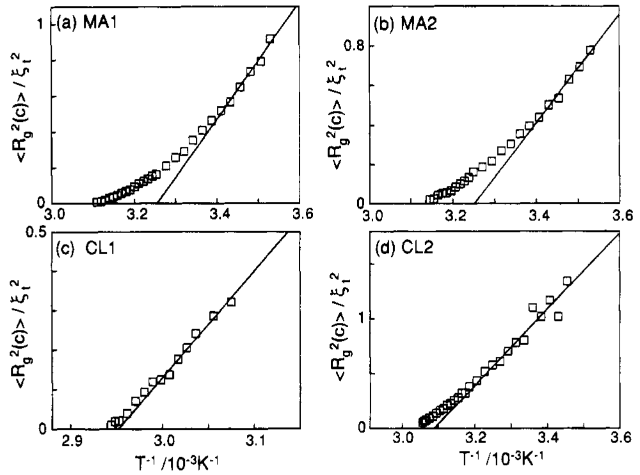

Figure 4. Temperature dependence near the stability limit of the reduced correlation length $\langle R_g^2(c)\rangle/\xi_t^2$ for samples: (a) MA1; (b) MA2; (c) CL1; (d) CL2. Full lines represent the results of fittings of eq 42 to the mean-field regions.

Figure 4 presents the temperature dependence of the correlation length ξ_t near the stability limit as plots of $\langle R_g^2(c)\rangle/\xi_t^2$ vs T^{-1}. In all solutions, ξ_t shows the crossover from the linear region at lower temperatures to the concave region at higher temperatures, which is consistent with the static crossover from the classical mean-field behavior $\xi_t \sim \tau_\chi^{-1/2}$ to the 3D-Ising behavior $\xi_t \sim \tau_\chi^{-0.63}$. Describing the temperature dependence of χ_b as $\chi_b = A - bT^{-1}$ $(A, b > 0)$, the following expression for the mean-field region was derived from eqs 6, 14, and 17.

$$\frac{\langle R_g^2(c)\rangle}{\xi_t^2} = 3\left|1 - \frac{\chi_b}{\chi_{bsm}}\right| = \left(\frac{3b}{\chi_{bsm}}\right)\left|\frac{1}{T} - \frac{1}{T_{sm}}\right| \quad (42)$$

Although the experimental range may not fully cover the mean-field region, we assumed that the linear region at lower temperatures in Figure 4 was described by eq 42 and estimated the values of χ_{bsm}/b and T_{sm} by the least-squares fittings to the linear region. From both values the temperature dependence of χ_b was evaluated to be of the form $\chi_b/b = A/b - T^{-1}$. The obtained values of A/b, χ_{bsm}/b, and T_{sm} are listed in Table 3.

Table 3. Static Critical Properties of Polymer Blend Solutions

sample code	$(A/b) \times 10^3$	$(\chi_{bsm}/b) \times 10^3$	T_{sm}/K	$(\chi_{bs}/b) \times 10^3$	T_s/K	Gi^{BK}	gi^{BK}
MA1	4.17_8	0.92_3	307.2	1.07_0	321.7	0.137	10.1
MA2	4.34_1	1.08_9	307.5	1.22_1	320.6	0.109	28.1
CL1	4.11_4	1.11_1	333.1	1.12_6	334.7	0.0128	0.221
CL2	3.94_8	0.85_9	323.7	0.92_4	330.5	0.0688	3.73

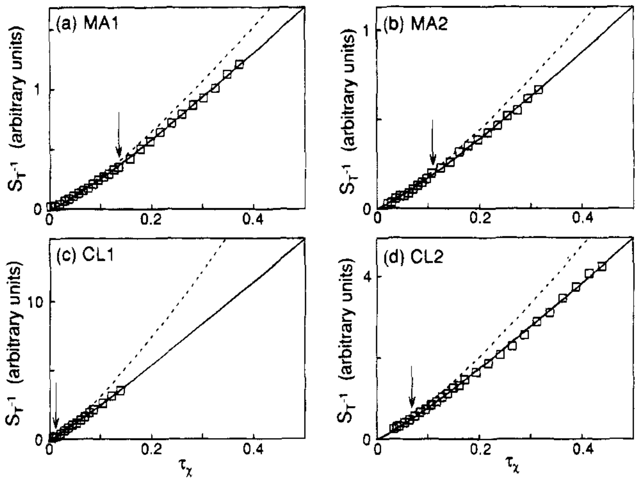

Figure 5. Dependence of the inverse isothermal susceptibility S_T^{-1} on the reduced interaction parameter τ_χ for samples: (a) MA1; (b) MA2; (c) CL1; (d) CL2. Solid lines, the fitting results of the universal crossover function (eq 7); dashed line, the asymptotic Ising behavior (eq 9); arrows, the Ginzburg number Gi^{BK}.

Replacing τ, T_{sm}, and T_s in eqs 7–9 by τ_χ, χ_{bsm}, and χ_{bs}, respectively, the universal crossover function (eq 7 with eqs 8 and 9) was fitted to the experimental $I(0)/T$ vs T relation to obtain the Ginzburg number Gi^{BK}. Here the fitting parameters were T_s and a scale factor for S_T because the experimental S_T was given in an arbitrary scale. T_s provided Gi^{BK} and τ_χ. Figure 5 shows the temperature dependence of the isothermal susceptibility S_T for all blend solutions as plots of S_T^{-1} vs τ_χ. Full lines, dashed lines, and arrows in the plots represent the universal crossover function, the asymptotic Ising behavior, and the redefined Ginzburg number Gi^{BK}, respectively. Although the present fitting ranges of τ_χ (<0.4) and Gi^{BK} ($=0.07-0.14$) do not sufficiently satisfy the required conditions ($\tau_\chi \ll 1$ and $Gi^{BK} \ll 1$) for the crossover function,[31] it describes the experimental data of all solutions well. It should be noted here that, in the fitting to the crossover function, T_{sm} was fixed at the value determined on the basis of eq 42 in Figure 4. Therefore, the Gi^{BK} values obtained are not fully based on the fitting to the Belyakov–Kiselev crossover function, but rely on the T_{sm} evaluation as well and involve uncertainties in these two determining processes. Probably, the value of Gi^{BK} evaluated here may primarily depend on the T_{sm} evaluation and may have slightly been underestimated. The obtained values of χ_{bs}/b, T_s, and Gi^{BK} are also listed in Table 3.

The scaled Ginzburg number gi^{BK} was plotted against the concentration c in log–log scales over the semidilute and concentrated regions in Figure 6. Also plotted were the results reported for symmetrical and asymmetrical bulk polymer blends.[10–12,14,15] The values of $\langle N \rangle$ and f_ϕ for the respective samples were estimated in the same way as for the present systems. The solid line in the figure represents the bare Ginzburg number gi^{BK}(bare) of eqs 36–38 with $\sigma = 0.595$ and $c^{**} = 0.538$ vol/vol-solution, and the broken line represents the gi^{BK}(bare) calculated with $c^{**} = 0.165$ vol/vol-solution, which is the mean value of c^{**} estimated by Noda et al.[22,23] The experimental value of gi^{BK} for the systems with different $\langle N \rangle$ decreases with increasing polymer concentration monotonously as expected from the theoretical consideration in the Introduction. The strength of the concentration dependence is close to that predicted from gi^{BK}(bare) with $c^{**} = 0.165$ vol/vol-solution, being approximately described by the vertically shifted line (dotted line) of gi^{BK}(bare) with $c^{**} = 0.165$ vol/vol-solution.

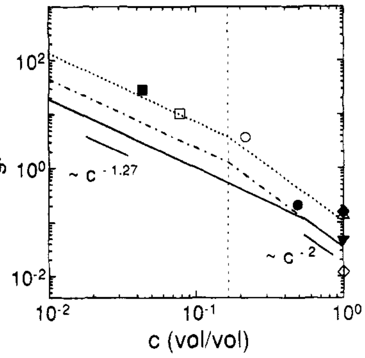

Figure 6. Double-logarithmic plots of the scaled Ginzburg number gi^{BK} vs c. Symbols: (□), (■), (●), and (○) are the same as in Figure 1; (◆), (△) polyisoprene/poly(ethylene–propylene) blends (Stepanek et al.[11,12]); (▼) poly(dimethylsiloxane)/poly(ethylmethylsiloxane) blends (Meier et al.[14]); (◇), deuterated polystyrene/poly(vinyl methyl ether) blends (Schwahn et al.[10,15,16]). Solid and broken lines represent the bare Ginzburg number gi^{BK}(bare) of eqs 36–38 with $c^{**} = 0.538$ and 0.165 vol/vol-solution, respectively. Dotted line represents the calculated curve that was obtained by vertically shifting the broken line [gi^{BK}(bare) with $c^{**} = 0.165$ vol/vol-solution] such that it agreed with the experimental data for blend solutions best.

Poor agreement in the concentration dependence was found between gi^{BK} and gi^{BK}(bare) with $c^{**} = 0.538$ vol/vol which was estimated from $R_g(c)$ behavior. The Ginzburg number appears to show the crossover from the semidilute to the concentrated behavior around the same concentration c^{**} as osmotic pressure[22,23] and viscosity[32,33] do. We may have to keep in mind that the screening of excluded-volume effects in the blend solution is not always the same as in the pure solution, since, in the present treatment $\langle R_g^2(c) \rangle$ has been evaluated on the basis of knowledge of pure polymer solution.

gi^{BK} are much larger than gi^{BK}(bare). This may be attributed primarily to a breakdown of the mean-field treatment near the critical point and possibly to the incompressibility approximation.[5,6] For various bulk blends, Meier et al.[14] reported that the experimental values of a_0 and b_0 were larger than the mean-field values and the deviation for b_0 was larger than that for a_0, which is consistent with the present results.

The vertically shifted line of gi^{BK} with $c^{**} = 0.165$ vol/vol is extrapolated to the bulk limit to a value around 0.1, which falls in the range of reported values for bulk blends. The universality of gi^{BK} for bulk polymer blends is expected from the fixed value of gi^{BK}(bare) $= 27/8\pi^4 = 0.035$. However, gi^{BK} at the bulk blend limit show some scatter as illustrated in Figure 6, suggesting a system dependence of gi^{BK}. The reported values of gi^{BK}

(in bulk) range from 0.019 to 0.158. The universal constant $\tilde{C}$ in the expression of Bates et al.[11,12] (eq 34) was also reported to have *system*-dependent values, that is, $\tilde{C} = 0.016-2.03$.[10,17] More experimental studies on the Ginzburg number *Gi* for blends and blend solutions by the use of the universal crossover function are needed to examine the universality of gi^{BK}.

Appendix

A. Expressions for $\langle R_{\mathrm{g}}^2(c)\rangle$ and c^{**}. The screening of excluded-volume effects on the chain dimensions over the semidilute, concentrated, and bulk regions has not thoroughly been revealed for a blend solution consisting of unlike polymers with different Kuhn lengths. Therefore, in the present treatment, the blob size is assumed common for unlike polymers, and the segment size is commonly defined such that

$$\langle R_{\mathrm{g}\theta}^{\ 2}\rangle = v_{\mathrm{s}}^{\ 2/3}\langle N\rangle \tag{A1}$$

which defines the polymeric indices N_{i} and g uniquely. The blob radius R_{b} must be proportional to $v_{\mathrm{s}}^{1/3}g^{\sigma}$, so we put $R_{\mathrm{b}}^2 = v_{\mathrm{s}}^{2/3}g^{2\sigma}/K_{\mathrm{l}}$ with a common constant K_{l} for i = A and B, since the blob volume v_{b} is the same for unlike polymers. Then for the semidilute region, one has

$$R_{\mathrm{gi}}^{\ 2}(c) = \frac{v_{\mathrm{s}}^{\ 2/3}g^{2\sigma}}{K_{\mathrm{l}}}\left(\frac{N_{\mathrm{i}}}{g}\right) \tag{A2}$$

which leads to

$$\langle R_{\mathrm{g}}^{\ 2}(c)\rangle = \frac{v_{\mathrm{s}}^{\ 2/3}g^{2\sigma}}{K_{\mathrm{l}}}\left(\frac{\langle N\rangle}{g}\right) \tag{A3}$$

(see eq 20), or using eq A1,

$$\langle R_{\mathrm{g}}^{\ 2}(c)\rangle = \langle R_{\mathrm{g}\theta}^{\ 2}\rangle g^{2\sigma-1}K_{\mathrm{l}}^{\ -1} \tag{A4}$$

K_{l} is a system-dependent constant, reflecting the stiffness of the polymer molecules. According to the scaling law, the polymeric index $g(c)$ of a blob has the following c dependence.[34,35]

$$g = K_{\mathrm{g}}c^{-1/(3\sigma-1)} \tag{A5}$$

K_{g} is also a system-dependent constant. Equations A4 and A5 provide the following expression of $\langle R_{\mathrm{g}}^2(c)\rangle$ as a function of c:

$$\langle R_{\mathrm{g}}^{\ 2}(c)\rangle = \langle R_{\mathrm{g}\theta}^{\ 2}\rangle K_{\mathrm{l}}^{\ -1}K_{\mathrm{g}}^{\ 2\sigma-1}c^{-(2\sigma-1)/(3\sigma-1)} \tag{A6}$$

In the concentrated region, since the excluded-volume effect is assumed to be completely screened out, the chain dimension is the unperturbed one, independent of c:

$$\langle R_{\mathrm{g}}^{\ 2}(c)\rangle = \langle R_{\mathrm{g}\theta}^{\ 2}\rangle \tag{A7}$$

Then, assuming a continuous change of $\langle R_{\mathrm{g}}^2(c)\rangle$ at the crossover concentration c^{**}, one can obtain the following relationship among K_{l}, K_{g}, and c^{**} from eqs A6 and A7.

$$(c^{**})^{-(2\sigma-1)/(3\sigma-1)} = K_{\mathrm{l}}K_{\mathrm{g}}^{\ 1-2\sigma} \tag{A8}$$

This relation with eq A6 leads to the following scaling equations, which is a direct consequence of the scaling law with the continuous change of $\langle R_{\mathrm{g}}^2(c)\rangle$ at c^{**}.

$$\frac{\langle R_{\mathrm{g}}^{\ 2}(c)\rangle}{\langle R_{\mathrm{g}\theta}^{\ 2}\rangle} = \left(\frac{c}{c^{**}}\right)^{-(2\sigma-1)/(3\sigma-1)} \qquad (c^{**} < c < c^{**}) \tag{A9}$$

$$= 1 \qquad (c^{**} < c < 1) \tag{A10}$$

In the treatment of Broseta et al.,[19,36] the scaling formula for $\langle R_{\mathrm{g}}^2(c)\rangle$ was given for the symmetrical system by

$$\frac{R_{\mathrm{g}}^{\ 2}(c)}{R_{\mathrm{F}}^{\ 2}} = K_{\mathrm{R}}\left(\frac{c}{c^*}\right)^{-(2\sigma-1)/(3\sigma-1)} \tag{A11}$$

Noting that $R_{\mathrm{F}}^2 = v_{\mathrm{s}}^{2/3}N^{2\sigma}/K_{\mathrm{l}}$, c^* is expressed from the definition of c^* (eq 1) as

$$c^* = \frac{3}{4\pi}K_{\mathrm{l}}^{\ 3/2}N^{1-3\sigma} \tag{A12}$$

and consequently, one has

$$\frac{R_{\mathrm{g}}^{\ 2}(c)}{R_{\mathrm{F}}^{\ 2}} = K_{\mathrm{R}}\left(\frac{4}{3}\pi K_{\mathrm{l}}^{\ -3/2}\right)^{(2\sigma-1)/(3\sigma-1)}N^{1-2\sigma}c^{-(2\sigma-1)/(3\sigma-1)} \tag{A13}$$

Then, noticing that if $N = g$, then $R_{\mathrm{g}}^2(c)/R_{\mathrm{F}}^2 = 1$, and comparing eq A13 with eq A5, one has the relation

$$K_{\mathrm{g}} = K_{\mathrm{R}}^{\ 1/(2\sigma-1)}\left(\frac{3}{4\pi}K_{\mathrm{l}}^{\ 3/2}\right)^{1/(3\sigma-1)} \tag{A14}$$

Using eqs A8, A12, and A14, eq 29 in the text can be rewritten in terms of c/c^* as eq 32 for the symmetrical system.

B. Evaluations of K_{l}, K_{g}, and c^{**}. On the basis of eq A4 with $g = N$, the constant K_{l} can be estimated from the values of the swelling radius R_{F} in a good solvent and the unperturbed radius $R_{\mathrm{g}\theta}$ in a Θ solvent and/or in bulk obtained experimentally. Then, c^{**} can be estimated as a concentration of the crossover for $R_{\mathrm{g}}(c)$ in the following two ways.

(i) The value of K_{R} was theoretically given by Broseta et al.[36,37] to be about 1.4. Equations A8 and A14 with this value yield

$$c^{**} = \frac{3}{4\pi}K_{\mathrm{R}}^{\ (3\sigma-1)/(2\sigma-1)}K_{\mathrm{l}}^{\ -1/2(2\sigma-1)} = 0.92K_{\mathrm{l}}^{\ -1/2(2\sigma-1)} \tag{A15}$$

(ii) In the concentrated region, the scaling law gives[34,35]

$$g = g_0c^{-2} \tag{A16}$$

From the continuity of $R_{\mathrm{g}}^2(c)$ at c^{**}, eq A4 with $g = g_0(c^{**})^{-2}$ leads to the following relation.

$$c^{**} = g_0^{\ 1/2}K_{\mathrm{l}}^{\ -1/2(2\sigma-1)} \tag{A17}$$

If it is assumed that $g = 1$ in bulk, i.e., at $c = 1$, then one can put $g_0 = 1$. Under this assumption, the prefactor $g_0^{1/2}$ of eq A17 becomes unity, which is very close to the prefactor of eq A15, 0.92.

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$$\tau_\chi^* = \frac{16\pi^2}{3{K_\mathrm{R}}^3}\left(\frac{c}{c^*}\right)^{-1/(3\sigma-1)}$$

where η is the composition difference between the coexisting phases at the same τ_χ in the two-phase region. From the definition and relations $S_\mathrm{T}^{-1} = a_0\tau_\chi/v_\mathrm{b}$, $\xi_\mathrm{t} = \xi_{\mathrm{t}0}\tau_\chi^{-1/2}$, and $\eta = 2(6a_0/b_0)^{1/2}\tau_\chi^{1/2}$, τ_χ^* is given in terms of the present parameters as $\tau_\chi^* = (b_0^2/36a_0^4)(v_\mathrm{b}/\xi_{\mathrm{t}0}^3)^2$, which leads to the relation $Gi^\mathrm{BK} = (9/8\pi^4)\tau_\chi^*$. This reproduces eq 32.

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