PHYSICAL REVIEW B VOLUME 35, NUMBER 16 1 JUNE 1987

Concentration fluctuations of polystyrene-polybutadiene blends

G. Ronca and T. P. Russell
IBM Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099

(Received 15 December 1986)

Small-angle x-ray scattering analysis of concentration fluctuations in polystyrene-polybutadiene mixtures is interpreted using a recently derived mean-field version of the gradient term of the Landau expansion for the free energy. Available information on the temperature dependence of the interaction parameter, obtained from optical determination of cloud point curves, allows direct comparison between theoretical and experimental correlation lengths at temperatures approaching the spinodal line in the homogeneous phase. Critical wave vectors after quenching below the spinodal line are analyzed in similar fashion. Polydispersity effects on the spinodal line and the structure factor are calculated for an arbitrary shape of the molecular weight distribution. The values of the temperature coefficient of χ obtained separately from cloud point curves and scattering data near the spinodal line are consistent. Comparison after quenching to temperatures below the spinodal line shows systematic overestimation of critical wavelengths.

INTRODUCTION

Concentration fluctuations in polymer blends at temperatures close to the spinodal line are presumably dominated by many chain features.[1] Verification of this assumption requires formulation of a molecular theory accounting for long-range density fluctuations and comparison with experiment. The random-phase approximation (RPA) yields reasonable values of the correlation length for many concentrated polymer systems.[2] However, reference to the decoupled state stresses the approximate character of the method. More intuitive mean-field ideas are often successful in the prediction of the thermodynamic behavior of concentrated systems. In a recent paper,[3] we proposed a mean-field evaluation of the additional contribution to the free energy associated with nonuniform concentration fields. This contribution, additive with respect to the number of chains, comes from configurational distortions induced by concentration gradients causing nonhomogeneous energetics of interaction with the medium. In this paper, we present scattering data obtained for mixtures of polystyrene (PS) with polybutadiene (PBD), at temperatures above and below the spinodal line. RPA predictions of the critical wavelength and temperature dependence of the interaction parameter are compared to our calculations, which provide better agreement with experiment in the range of temperatures considered. Account of polydispersity effects on the spinodal line and the scattering intensity leads to a description in terms of the weight average degree of polymerization.[4] Here, our analysis is extended to the evaluation of the structure factor incorporating polydispersity effects on the form of the gradient term of the Landau expansion.[5]

SPINODAL LINE AND SCATTERING FUNCTION

The spinodal line for polydisperse blends has been treated by Koningsveld and Chermin,[4] whose results confirm those derived earlier by Stockmayer.[6] Restricting, for the moment, our analysis to bulk polymer mixtures without solvent, we devise a technique applicable to the evaluation of the scattering intensity at finite values of the scattering vector.

The free energy ΔG per unit volume Ω of a polydisperse binary blend is given by[4]

$$\begin{aligned}\frac{\Delta G}{k_B T\Omega}[\phi_A,\phi_B]&=g(\phi_A,\phi_B)\\&=\frac{1}{v_A}\sum_{k=1}^{\nu_A}\frac{1}{N_A(i)}\phi_A(i)\ln\phi_A(i)\\&\quad+\frac{1}{v_B}\sum_{i=1}^{\nu_B}\frac{1}{N_B(i)}\phi_B(i)\ln\phi_B(i)\\&\quad-\frac{\bar{\chi}}{v_A}\sum_{j,k}\phi_A(j)\phi_A(k)+(\text{linear terms})\ .\end{aligned}\tag{1}$$

The sets $\phi_A(i)$ and $\phi_B(i)$ define the volume fractions of the molecules of types A and B containing $N_A(i)$ and $N_B(i)$ monomers, respectively. v_A and v_B are the monomer volumes of components A and B and $\bar{\chi}$ is the effective interaction parameter. The value of $\bar{\chi}$ at the spinodal temperature is that value of the reduced interaction parameter for which fluctuations of infinite wavelength become unstable. Our definition and treatment of the spinodal can be extended to finite wavelengths. In the infinite-wavelength limit the contribution of gradient terms to the free energy may be neglected.

Expressing the concentration fields $\phi_A(i,\mathbf{r})$ and $\phi_B(i,\mathbf{r})$ as average values $\Phi_A(i)$ and $\Phi_B(i)$ plus fluctuations $\psi_A(i,\mathbf{r})$ and $\psi_B(i,\mathbf{r})$ and neglecting linear terms which average out after integration over all space, the quadratic expansion of the local free energy (1) yields:

$$g\{\boldsymbol{\phi}_A(\mathbf{r}),\boldsymbol{\phi}_B(\mathbf{r})\}=g(\Phi_A,\Phi_B)+\tfrac{1}{2}\sum_{i=1}^{\nu_A}\frac{\psi_A^2(i,\mathbf{r})}{v_A N_A(i)\Phi_A(i)}+\tfrac{1}{2}\sum_{i=1}^{\nu_B}\frac{\psi_B^2(i,\mathbf{r})}{v_B N_B(i)\Phi_B(i)}-\frac{\bar{\chi}}{v_A}\sum_{i,j}\psi_A(i,\mathbf{r})\psi_A(j,\mathbf{r}) . \qquad (2)$$

Apparent lack of symmetry between the two components A and B results from the assumption of incompressibility which states:

$$\sum_{i=1}^{\nu_A}\psi_A(i,\mathbf{r})+\sum_{i=1}^{\nu_B}\psi_B(i,\mathbf{r})=0 . \qquad (3)$$

Fourier cosine expansion of the fluctuations throughout the volume $V=L^3$ and integration over space yields the total free energy in terms of the Fourier components, $\Psi_A(i,\mathbf{q})$ and $\Psi_B(i,\mathbf{q})$:

$$\int_v g[\phi_A(\mathbf{r}),\phi_B(\mathbf{r})]d^3\mathbf{r}=Vg(\Phi_A,\Phi_B)+\frac{V}{16}\sum_{\mathbf{q}}\sum_{i=1}^{\nu_A}\frac{1}{v_A N_A(i)\Phi_A(i)}\Psi_A^2(i,\mathbf{q})-\frac{V\bar{\chi}}{8v_A}\sum_{\mathbf{q}}\sum_{i,j}\Psi_A(i,\mathbf{q})\Psi_A(j,\mathbf{q})+\frac{V}{16}\sum_{\mathbf{q}}\sum_{i=1}^{\nu_B}\frac{1}{v_B N_B(i)\Phi_B(i)}\Psi_B^2(i,\mathbf{q}) . \qquad (4)$$

Each point of the reciprocal space has a volume π^3/L^3. The partition function is obtained extracting the Boltzmann factor from Eq. (4) and multiplying by a singular weighting factor which incorporates the condition (3). Integration over the Fourier components $\Psi_A(i,\mathbf{q})$ and $\Psi_B(i,\mathbf{q})$ yields the expression

$$Z=\int\exp\left[-\int_V g\{\phi_A(\mathbf{r}),\phi_B(\mathbf{r})\}d^3\mathbf{r}\right]\times\prod_{\mathbf{q}}\delta\left[\sum_{i=1}^{\nu_A}\Psi_A(i,\mathbf{q})+\sum_{i=1}^{\nu_B}\Psi_B(i,\mathbf{q})\right]\times\prod_{\mathbf{q}}\prod_{i}d\Psi_A(i,\mathbf{q})\prod_{\mathbf{q}}\prod_{i}d\Psi_B(i,\mathbf{q}) . \qquad (5)$$

The partition function factorizes, in the absence of gradient terms, into a product of identical contributions:

$$Z=(Z_1)^M , \qquad (6)$$

where M is the total number of available points in the reciprocal space. Introducing the reduced variables

$$x_j\equiv x_j(\mathbf{q})=\Psi_A(j,\mathbf{q})\left[\frac{V}{8v_A}\right]^{1/2} , \qquad y_j\equiv y_j(\mathbf{q})=\Psi_B(j,\mathbf{q})\left[\frac{V}{8v_B}\right]^{1/2} , \qquad (7)$$

after Fourier representation of the δ function in Eq. (5), Z_1 can be expressed as

$$Z_1\propto\int_{-\infty}^{\infty}d\omega\int\left[\prod_{i,j}dx_j dy_j\right]\times\exp\left[-\sum_{i,j}\gamma_{ij}x_i x_j-\sum_j b_j y_j^2+i\omega\left[\sum_j x_j+\left[\frac{v_B}{v_A}\right]^{1/2}\sum_j y_j\right]\right] , \qquad (8)$$

where ω is the auxiliary variable used for the Fourier representation and

$$\gamma_{ij}=\frac{1}{2N_A(j)\Phi_A(j)}\delta_{ij}-\bar{\chi} , \qquad (9a)$$

$$b_j=\frac{1}{2N_B(j)\Phi_B(j)} . \qquad (9b)$$

Integrating first over y_i, then over ω, we obtain the result

$$Z_1\propto\int\left[\prod_i dx_i\right]\exp\left[-\sum_{i,j}\left[\gamma_{ij}+\frac{v_A}{2v_B\sum_k N_B(k)\Phi_B(k)}\right]x_i x_j\right] . \qquad (10)$$

According to our previous discussion, for given sets of average concentrations Φ_A and Φ_B, the spinodal value of the interaction parameter is obtained by determining the appearance of the first nonpositive eigenvalue of the complete matrix of the quadratic form. However, Eq. (10) implies a more trivial conclusion. The molecular weight distribution of polymer B appears in Eq. (10) only through the weight average. By symmetry, Z_1 must depend only on the weight average molecular weight M_w of the two polymers. Passing to the equivalent monodisperse case we get the familiar equation of the spinodal line

$$\frac{\bar{\chi}_s}{v_A}=\frac{1}{2N_{Aw}v_A\Phi}+\frac{1}{2N_{Bw}v_B(1-\Phi)} , \qquad (11)$$

where Φ is the concentration of polymer A, denoted as ϕ

in the monodisperse case. Equation (11) coincides with the result derived by Koningsveld[4] using matrix methods and with the results of Joanny.[7] This has also been reported by Shibayama *et al.*[8] Our formulation in terms of an elementary functional integral becomes more useful in the analysis of correlations, to different degrees of complexity, required for the evaluation of the scattering functions.

We will now focus on the gradient term in the presence of polydispersity. Prediction of the scattering intensity at finite scattering wavelengths above the spinodal temperature requires the introduction of polydispersity into the gradient term of the free energy per unit volume, $Q(\nabla\phi)^2$. The expression for Q previously calculated for monodisperse systems is[3]

$$Q(A,B,\Phi)=\frac{1}{18v_A}(\chi_{AB}-\chi_{AA})^2\phi\langle r_A^2\rangle N_A + \frac{v_B}{18v_A^2}\left[\chi_{AB}-\frac{v_A}{v_B}\chi_{BB}\right]^2(1-\phi)\langle r_B^2\rangle N_B\ , \tag{12}$$

where ϕ is the volume fraction of polymer A. N_A and N_B are the number of monomers of components A and B with monomer volumes v_A and v_B, respectively. χ_{AB}, χ_{AA}, and χ_{BB} are the three separate interaction parameters. In the derivation of Eq. (12) each chain was assumed to interact with its environment by means of an effective χ parameter. In the simplest approximation the energetics of the environment is completely characterized in terms of volume fractions and bulk χ's with no reference to the molecular weights. Conceptually, we are allowed to consider the polymer solvent case and extend the results to other cases of binary mixtures. Previously,[3] we expressed the energy of interaction of a given chain with the medium on the basis of the same probabilistic arguments used for the evaluation of the thermodynamic enthalpy as

$$\frac{E_A}{k_BT}=\sum_{i=1}^{N_c}\{\chi^c_{AA}\phi(x_i)+\chi^c_{AB}[1-\phi(x_i)]\}\ , \tag{13}$$

where $\phi(x)$ is the local volume fraction, N_c the number of effective lattice cubes and $\chi^c=n^c\chi$, where n^c is the number of monomers per statistical cube. Equation (13) implies that concentration gradients introduce alterations to the mass distribution of each chain, resulting in an additional contribution to its configurational free energy. In the case of binary polymer mixtures with no solvent, both sets of molecules contribute. The calculated overall increase of the thermodynamic free energy per unit volume is given by Eq. (12). One chain at a time can be considered in the evaluation of the extra free energy. Division by two avoids improper counting of interactions in the classical derivation of the thermodynamic enthalpy. Motion of each chain through its environment certainly produces changes of the local energetics of the mutual interactions between solvent molecules or chains of the other type. These interactions are not taken into account in Eq. (13). Extension of single chain concepts to the mean field prediction of long-range fluctuations provides a useful check on their consistency. Specifically, we can consider a polymer solution of A molecules in an effective solvent B, subject to small poymer density gradients due to remote boundary conditions. Linear-response theory[1] relates density changes to applied perturbing potentials. Mean-field interpretation, acceptable in the limit of weak long range cooperativity, refers these potentials to total density changes. At *finite solvent amounts,* allowing independent motion of the molecules, the effective single chain potential of the solution for molecules of type A becomes

$$\frac{-u_A}{k_BT}=\sum_{j=1}^{N_c}\{\ln[1-\phi(\mathbf{r}_j)]+\chi^c_{\text{eff}}\phi(\mathbf{r}_j)\}\ , \tag{14}$$

where $\chi^c_{\text{eff}}=\chi^c_{AB}-\chi^c_{AA}$ in keeping with Eq. (13). As we will see, self-consistent evaluation of χ^c_{eff} yields a different result. In the case of slow variations of the density profile, we may write

$$\frac{-\delta u_A}{k_BT}\simeq\sum_{i=1}^{N_c}\left[\bar{\chi}^c_{\text{eff}}-\frac{1}{1-\phi}\right]\delta\phi(\mathbf{r}_i)\ , \tag{15}$$

where ϕ is the polymer volume fraction, proportional to the polymer density. Application of linear-response theory to a system of n_p chains, each containing N_c statistical units, yields

$$\delta\phi(q)\propto\sum_{n=1}^{n_p}\sum_{i=1}^{N_c}\delta\rho_{ni}(q)=S(q\to 0)\left[\chi^c_{\text{eff}}-\frac{1}{1-\phi}\right]\delta\phi(q)\ , \tag{16}$$

where $\rho_{ni}(q)$ is the Fourier transform of the density distribution associated with the ith monomer of the nth chain and $S(q)$ is the complete scattering function. Equation (16) holds for $\xi \ll 1/q \leq D$, where ξ is the correlation length and D is the distance between boundaries. Since

$$S(q\to 0)\propto\left[2\bar{\chi}^c-\frac{1}{(1-\phi)}\right]^{-1}$$

for long molecules and finite solvent amounts, the form of Eq. (16) implies that $\bar{\chi}^c_{\text{eff}}=2\bar{\chi}^c$, where $\bar{\chi}^c$ is the reduced χ parameter per lattice unit. If so, Eq. (13) cannot be correct. The condition $\bar{\chi}^c_{\text{eff}}=2\bar{\chi}_c$ preserves unperturbed statistics between distant boundaries at θ conditions ($\bar{\chi}^c=\frac{1}{2}$) and low concentrations.[9] Calculation of the extra free energy of the general A chain embedded in a density gradient is done subtracting from the effective single chain free energy interactive terms and the ideal contribution. Let $\phi=\phi_0(\mathbf{r}_0)+\mathbf{\Delta}\cdot(\mathbf{r}-\mathbf{r}_0)$ for a particular chain of type A, whose extreme is fixed at $\mathbf{r}=\mathbf{r}_0$. Within the Gaussian approximation, its partition function reduces to the product of three independent factors. The general component Z_x is

$$Z_x=\int\{dx_n\}\exp\left[-\frac{C}{2k_BT}\sum_{m=1}^{N_A^G}x_m^2+2\bar{\chi}^G\Delta_x\sum_{i=1}^{N_A^G}\sum_{m=1}^{i}x_m\right]\ ,$$

where C is the rigidity of each of the N_A^G Gaussian submolecules, x_m is the component of the mth Gaussian bond vector, and $\bar{\chi}^G$ is the interaction parameter per Gaussian strand. After evaluating Z_x, we must subtract the interactive part of the free energy and also the ideal contribution $-\ln[Z_x(\Delta x=0)]$. Summing the contributions of the three Cartesian factors, we obtain a simple formula for the extra free energy *of distortion* per chain of type A:

$$\frac{F'}{k_B T}=\frac{1}{18}(2\bar{\chi})^2 N_A^2 \langle r_A^2 \rangle (\nabla\phi)^2 ,$$

where $\bar{\chi}$ refers, again, to the monomer unit. Interactions must be subtracted because local energetics is already accounted, with or without density fluctuations, by Eq. (1). The complete front factor of the gradient term is easily obtained adding individual chain contribution.

$$Q(A,B,\phi)=\frac{1}{18v_A}(2\bar{\chi})^2\phi\langle r_A^2\rangle N_A + \frac{1}{18v_B}\left[2\bar{\chi}\frac{v_B}{v_A}\right]^2(1-\phi)\langle r_B^2\rangle N_B . \tag{17}$$

Formulation of Q in terms of $\bar{\chi}$ makes comparison with experiment more straightforward. The extension of Eq. (17) to polydisperse systems follows easily due to the additive character of the contributions associated with the partial volume fractions of each molecular weight

$$Q(A,B,\Phi)=\frac{(2\bar{\chi})^2}{18v_A}C_A\Phi N_{Aw}N_{Az} + \frac{(2\bar{\chi}v_B/v_A)^2 v_B^2}{18v_A^3}C_B(1-\Phi)N_{Bw}N_{Bz} , \tag{18}$$

where $\langle r_A^2\rangle = C_A N_A$, $\langle r_B^2\rangle = C_B N_B$, N_w is the weight average number of monomers, and N_z the z average. Reformulation of the partition integral in the presence of fluctuations of finite wavelength leads to the result

$$Z=\prod_{\mathbf{q}}[F(\mathbf{q})\tilde{Z}_1(\mathbf{q})] , \tag{19}$$

where $F(\mathbf{q})$ is a function of the wave vector and $\tilde{Z}_1(q)$ is still expressed by Eq. (10) with a proper redefinition of the matrix γ_{ij}

$$\gamma_{ij}(\mathbf{q})=\gamma_{ij}+v_A q^2 Q[A,B,\Phi] . \tag{20}$$

Fourier expansion of the partial concentrations gives the overall density correlation $\langle\Delta\Phi(\mathbf{r})\Delta\Phi(\mathbf{r}')\rangle$:

$$\langle\Delta\Phi(\mathbf{r})\Delta\Phi(\mathbf{r}')\rangle = \frac{v_A}{V}\sum_{\mathbf{q}}\left\langle\sum_{i,j}x(i,\mathbf{q})x(j,\mathbf{q})\right\rangle\exp[i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')] , \tag{21}$$

where

$$x(i,\mathbf{q})=\left[\frac{V}{8v_A}\right]^{1/2}\Psi_A(i,\mathbf{q}) . \tag{22}$$

From Eq. (21) the scattering function $S(\mathbf{q})$ is readily obtained:

$$S(\mathbf{q})=(2\pi)^3 V\delta(\mathbf{q})\Phi^2+8Vv_A\left\langle\sum_{i,j}x(i,\mathbf{q})x(j,\mathbf{q})\right\rangle . \tag{23}$$

Equations (9a) and (10) yield

$$\sum_{i,j}\langle x(i,\mathbf{q})x(j,\mathbf{q})\rangle = \frac{\partial \ln Z_1(\mathbf{q})}{\partial\bar{\chi}} , \tag{24}$$

with $\gamma_{ij}(\mathbf{q})$ as given by Eq. (20). From Eqs. (9a), (10), (17), and (20) we observe that the molecular weight distribution of polymer B appears in the integral giving $Z_1(\mathbf{q})$ only in terms of N_w and N_z. By symmetry, the same must hold for polymer A. Introducing the "effective" characteristic ratios $C_A'=C_A N_{Az}/N_{Aw}$ and $C_B'=C_B N_{Bz}/N_{Bw}$, we can formally express $Z_1(\mathbf{q})$ and, consequently, the overall scattering function (23), in terms of the equivalent monodisperse formula:

$$S(\mathbf{q})=(2\pi)^3 V\delta(\mathbf{q})\Phi^2 + \frac{4V}{\dfrac{1}{2N_{Aw}v_A\Phi}+\dfrac{1}{2N_{Bw}V_B(1-\Phi)}-\dfrac{\bar{\chi}}{v_A}+q^2 Q} , \tag{25}$$

where

$$Q=\frac{(2\bar{\chi})^2}{18v_A}C_A'\Phi N_{Aw}^2+\frac{1}{18v_B}\left[2\bar{\chi}\frac{v_B}{v_A}\right]^2 C_B'(1-\Phi)N_{Bw}^2 . \tag{26}$$

Equation (25) is easily derived also by calculation of the determinant of the quadratic form and application of Eq. (24). The cumbersome structures of Eqs. (9a) and (10) become very useful in the analysis of partial correlations of fractions with selected molecular weights.

EXPERIMENTAL PART

Mixtures of PS ($M_w=2000$, $M_w/M_n=1.3$) and PBD ($M_w=1000$, $M_w/M_n=1.2$ and $M_w=2500$, $M_w/M_n=1.15$) were prepared by combining preweighed portions of each polymer in a glass-weighing pan at room temperature. Homogeneous mixtures were obtained by heating the mixtures to approximately 90 °C for 15 min under a nitrogen blanket. Using heated pipettes, the homogeneous, single-phased mixtures were transferred to the scattering cell consisting of a stainless-steel ring (1 mm in thickness) with two Kapton windows (8 μm in thickness). The specimens were then allowed to cool to room temperature prior to the experiments.

The samples were mounted into a Mettler FP85 hot stage using a brass collar to center the specimen over the hole through which the collimated x-ray beam passed. Scattering measurements were performed at the small angle scattering facility on beamline I-4 at the Stanford Synchrotron Radiation Laboratory. The white radiation from the storage ring is focussed horizontally using a 1.25-m float glass mirror and a cylindrically bent Si(111) crystal. The size of the beam at the specimen is approximately 1 mm in diameter and at the detector, 50 cm downstream,

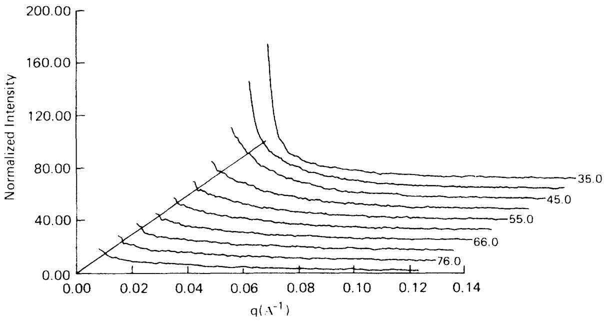

FIG. 1. Small-angle x-ray scattering profiles of a 60% PS ($M_w = 2000$) with 40% PBD ($M_w = 1000$) as a function of temperature.

0.15 and 0.4 mm in the vertical and horizontal directions, respectively. The Si(111) crystal reflected 1.412-Å x rays into the specimen with higher harmonics being filtered previously by the mirror. Scattered x rays were collected using a 1024 pixel, self-scanning photodiode array. Integration times on the detector ranged from 1–2 min. In addition to the scattering profiles, the incident beam monitor counts just before and after the specimen, the temperature of the specimen and the integration time were stored on a hard disk for later use. At least five minutes were given at each temperature prior to collecting a scattering profile to attain thermal equilibrium. Detailed descriptions of the scattering geometry can be found elsewhere.[10–12]

Typical scattering profiles of a 60% PS ($M_n = 2000$) with 40% PBD ($M_w = 1000$) are shown in Fig. 1 as a function of temperature. Only a few representative scattering profiles are shown for this mixture as it is cooled from 82 °C (homogeneous state) to 25 °C (well below the spinodal line). Analysis of one of these scattering profiles in an Ornstein-Zernike manner, i.e., plotting $1/I$ versus q^2, where I is the scattered intensity and q is the scattering vector, is shown in Fig. 2. The average chain dimension of the polystyrene sample is approximately 3 nm, which is well within the experimental resolution. As can be seen over the scattering vector range studied, the q^{-2} dependence of the scattering is evident. It should be noted, however, that as $T \rightarrow T_S$ the correlation lengths, ξ, get quite large and a pronounced downward curvature of these plots was observed. Most likely, this is due to the limited spatial resolution of the small-angle x-ray scattering (SAXS) camera. In the immediate vicinity of T_S, quartic terms in the expansion of the free energy cannot be neglected.[3] This yields a different thermodynamic characterization of the phase transition. However, agreement of experimental scattering data with the Gaussian exponent of the correlation length is clearly observed over an interval of more than ten degrees approaching the spinodal temperature from above.

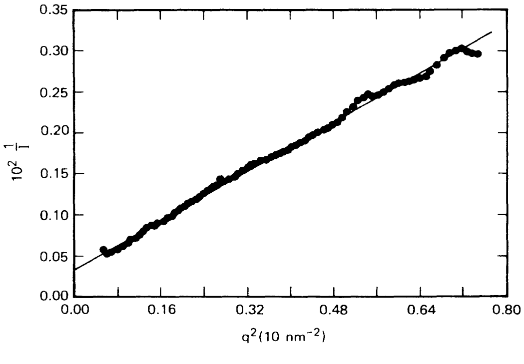

FIG. 2. Ornstein-Zernike plot for a 60% PS ($M_w = 2000$) with PBD ($M_w = 1000$) at 50 °C.

We will now proceed to discuss the analysis of PS-PBD scattering data. Binodal lines determined from optical density measurements[13] using the two fractions of PBD in different relative amounts were analyzed in Ref. 3. In both cases the consolute point corresponds to PS weight fractions of about 50%. Complementary information is obtained from an analysis of scattering data at temperatures approaching the spinodal, with PS weight fractions close to the consolute value, in order to avoid phase nucleation. The RPA version of the gradient term is[1]

$$Q(A,B,\phi) = \frac{\langle r_A^2 \rangle}{36\phi v_A N_A} + \frac{\langle r_B^2 \rangle}{36(1-\phi) v_B N_B} \ . \tag{27}$$

Our mean-field version is given by Eq. (17). We do not consider polydispersity effects for the systems studied. $\langle r_A^2 \rangle$ and $\langle r_B^2 \rangle$ have been evaluated using known values of the characteristic ratios. In the case of PBD, we have chosen a value of C_∞ intermediate between those of the

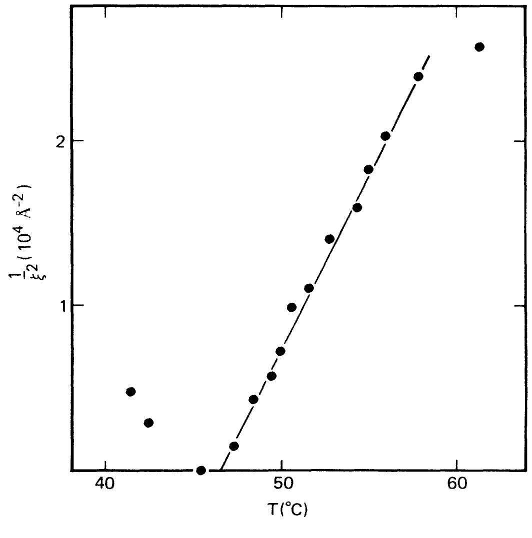

FIG. 3. Plot of the reciprocal square of the correlation length determined from the Ornstein-Zernike analysis as a function of temperature. The intercept at $1/\xi^2 = 0$ yields the spinodal temperature (50% 2 K PS; 1 K PBD).

TABLE I. Quenching temperature T, calculated spinodal temperature T_{SC}, experimental critical wavelength $1/q_c$, RPA prediction, and mean-field estimates. ϕ_{ps} is the weight fraction of PS.

	ϕ_{ps}	T (°C)	T_{SC} (°C)	$1/q_c$ (Å)	$1/q_c$ (Å)	$1/q_c$ (Å)
2000 PS	40%	75	110	43.45	16	72
2500 PBD	60%	60	123	36.36	12	54
2000 PS 1000 PBD	40%	35	58	47.62	15	52

two forms (trans and cis). From Eq. (25), using our previous result $\bar{\chi} \simeq AT^{-\alpha}$, we can express the correlation length ξ at temperatures T close to the spinodal value T_S

$$\frac{1}{\xi^2} = \frac{\alpha \bar{\chi}(T_S)(T-T_S)}{Q(A,B,\phi) v_A T_S} . \tag{28}$$

Figure 3 clearly shows the linear dependence of ξ^{-2} on $(T-T_S)$ for blends containing the shorter fraction of PBD at 50% weight fraction of PS. The experimental values of A and α calculated fitting binodal curves at two different molecular weights of the PBD fraction[3] are $A=6.96\times10^5$ and $\alpha=2.65$. Using these to calculate $\bar{\chi}$ overestimates the spinodal temperature by about ten degrees. Polydispersity may account for this discrepancy, which does not substantially affect the potential use of Eq. (28) for comparison of Eqs. (17) and (27). The corresponding values of α, recalculated using Eq. (28) and the data of Fig. 1 are $\alpha=3.02$ and 0.35, respectively. This discrepancy is remarkable. Independent comparison between the proposed versions of the gradient term is done by considering the kinetics of spinodal decomposition after quenching. Critical wave vectors are obtained from the formula

$$q_c^2 Q(A,B,\phi) - \frac{\bar{\chi}(T)}{v_A} + \frac{1}{2N_A v_A \phi} + \frac{1}{2N_B v_B(1-\phi)} = 0 . \tag{29}$$

Three cases have been analyzed with $\bar{\chi}(T)$ calculated from the analysis of the binodals. The results are shown in Table I. The critical scattering wavelength is considerably larger than the coil radius of gyration. A comparative analysis of the two versions of the gradient term shows that the two models provide opposite bounds.

The practical utility of our mean-field approach to *quasicritical fluctuations* and the opportunity of expressing even single-chain energetics in terms of the Flory effective χ parameter is consistently shown. The value of the exponent α extracted from the analysis of the scattering data using our version of the gradient term is slightly higher than that calculated from the cloud point curves. Account of polydispersity effects, weak in our case, would not increase the discrepancy substantially. Formally (recourse to N_z) and quantitatively similar effect of polydispersity on the gradient term has been predicted by Joanny[7] and Shibayama *et al.*[8] using RPA methods. Our evaluation of the critical wavelength after quenching exceeds the experimental value (see Table I). Increasing dominance of single chain effects must be expected at lower temperatures. Scattering data above the spinodal line are more accurate. The method developed for the evaluation of the global scattering function is applicable to the calculation of the structure factor of restricted sets of labeled molecules in the homogeneous phase close to the spinodal line. Solvent effects contribute additional steric terms to Eq. (17). Our analysis of the cloud point curves[3] did not require introduction of concentration dependence of the χ parameter for PS-PBD mixtures. Careful analysis of biphasic equilibria in the concentration range around the consolute point shows higher sensitivity to polydispersity effects.

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