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Critical Fluctuations in a Binary Polymer Mixture

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The critical opalescence of a binary polymer mixture consisting of polyvinyl methyl ether and deuterated polystyrene was measured by small-angle neutron scattering. In accordance with a mean-field treatment, it was found that the critical exponents ν and γ are 0.5 and 1, respectively; the Ornstein-Zernike scaling function describes the scattering data; and the spinodal is parabolically shaped. However, the dependence of the interaction parameter $\bar{\chi}$ on the composition of the polymer mixture is in conflict with the theoretical result.

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De Gennes[1] and Binder[2] have theoretically demonstrated in the limit of infinite molecular weight that a polymer mixture behaves as an ideal mean-field system: (i) In a compatible polymer mixture the interaction between neighboring segments are weak and must be of order N^{-1}, where N is the number of segments of one polymer. McMaster[3] has shown that the weak interaction is of the van der Waals type, which decreases rapidly as r^{-6}. Kwei, Nishi, and Roberts[4] have measured the interaction in a polymer mixture by vapor sorption and Kirste and co-workers[5,6] have measured the second virial coefficient by small-angle neutron scattering. (ii) The conformation in a one-component polymer melt can be satisfactorily described by an unperturbed random coil.[7] In a compatible polymer mixture one expects the same conformations, because for changing the conformation one needs an interaction energy in the order $N^{-1/2}$ in units of k_BT while the interactions between neighboring segments are of order N^{-1}. (iii) The critical behavior of the correlation length and the susceptibility follows a potential law with mean-field exponents $\nu=0.5$ and $\gamma=1.0$. (iv) The angular dependence of the scattering function can be described by a simple Ornstein-Zernike scaling law.

By investigating the concentration fluctuations in the vicinity of the decomposition temperature one is able to explore the validity of these theoretical predictions. This is of particular interest since the theoretical results are derived from approximate calculations of the entropy of mixing and from a crude treatment of the enthalpy term. The scattering law for the polymer mixture is obtained by a random-phase approximation. Mean-field arguments are heavily used in order to simplify the treatment and the final result. As the critical temperature is approached the correlation length of the mixture becomes large so that details of the interaction between the segments are not important for describing the critical phenomena. Small-angle neutron scattering allows observation of concentration fluctuations in the compatible range with the correlation length larger or smaller than the coil dimensions. A sufficient scattering contrast can be achieved by preparing a polymer mixture of protonated and deuterated species.

De Gennes[1] and Binder[2] have calculated the correlation function for compatible polymer mixtures on the basis of mean-field arguments. For the generalized susceptibility χ the dependence on the scattering vector Q is given by

$$\chi^{-1}(Q)=1/N_1\varphi_1 D(Q,R_1)+1/N_2\varphi_2 D(Q_1R_2)-2\bar{\chi}(T), \tag{1}$$

where N is the number of segments, φ the volume fraction, D the Debye scattering function for Gaussian coils, R the radius of gyration, and $\bar{\chi}$ the interaction parameter. The indices 1 and 2 refer to the two components of the mixture. This correlation function holds particularly for the nondilute case, where the coils are strongly overlapping. The interaction parameter $\bar{\chi}$ does not depend on the Q vector, because of the strong r dependence of the segment-segment interaction ($\sim r^{-6}$). Equation (1) describes the critical behavior, because the intensity diverges for $Q=0$ at the spinodal line $\bar{\chi}(T)=\bar{\chi}_s(N_1,N_2,\varphi_1,\varphi_2)$.

The approximation for small Q vectors of $\chi(Q)$ shows the Ornstein-Zernike behavior:

$$\chi(Q\to 0)=\chi(0)(1+Q^2\xi^2)^{-1}, \tag{2}$$

with the correlation length

$$\xi = \tfrac{1}{6} a \{\varphi_1 \varphi_2 [\overline{\chi}_s(Q) - \overline{\chi}(T)]\}^{-1/2}, \tag{3}$$

where a means the length of one polymer segment and $\overline{\chi}_s$ is the value of $\overline{\chi}$ at the spinodal line. ξ diverges with a square root singularity $(T - T_s)^{-1/2}$ on approaching the spinodal temperature. One can see that in this approximation the critical exponents are $\gamma = 1$ and $\nu = 0.5$.

Experiments were carried out with the polymer mixture polyvinyl methyl ether (PVME) and deuterated polystyrene (PSD). This system is a well-known semicompatible mixture described by Nishi[8] and Yang, Hadziioanou, and Stein.[9] The interaction parameter can be changed by varying the temperature. The two interesting regions of negative and positive $\overline{\chi}$ are accessible. A positive $\overline{\chi}$ means that identical segments attract each other more than different segments do, and the opposite is true for negative $\overline{\chi}$. For the small positive value given by

$$\overline{\chi}_s = (N_1 \varphi_1 + N_2 \varphi_2) / \varphi_1 \varphi_2 N_1 N_2 \tag{4}$$

which is of order N^{-1}, the concentration fluctuations are critical. For $\overline{\chi}$ values larger than $\overline{\chi}_s$ the system decomposes spinodally. At $\overline{\chi} = 0$ the mixture is ideal.

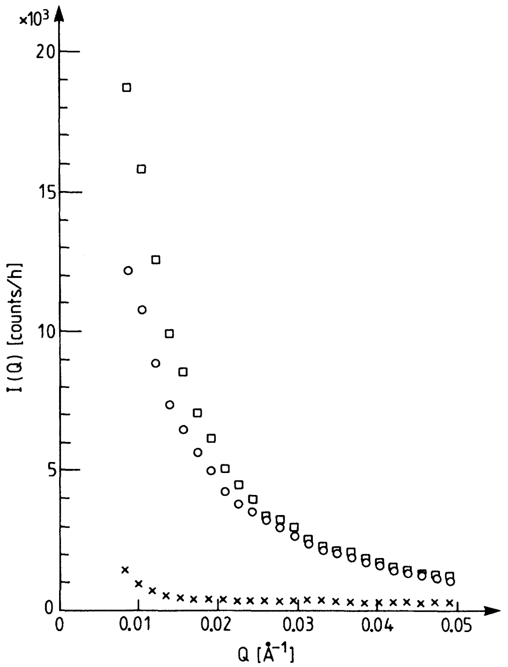

FIG. 1. Small-angle neutron scattering from a binary polymer mixture of PVME and PSD with a volume fraction $\varphi = 0.408$. The scattered intensity is plotted vs the scattering vector Q for the temperatures $T = 20\,^\circ\mathrm{C}$ (crosses), 171.1 °C (circles), 179 °C (squares).

PVME was obtained from the Aldrich Chemical Company ($M_w = 99000$, $M_w/M_N = 2.12$) and PSD was supplied by Pfannenschmidt Hamburg ($M_w = 47000$, $M_w/M_N = 1.06$). Samples were prepared at four volume fractions by dissolving both components in toluene. The toluene was evaporated in a vacuum oven at a temperature of 50 °C for 15 h. For removing the rest of the solvent, the samples were tempered in a vacuum of 10^{-7} bar at 150 °C for 24 h. During the measurements the samples were heated under a helium pressure of 5 bar. The temperature stability was better than 0.1 °C.

The experiments were performed at the neutron small-angle facility at the FRJ-2 in Jülich. The incident wavelength was $\lambda = 7$ Å and a sample-detector distance of $L = 4$ m was used. Background corrections were carried out by measuring the same sample far away from the critical region, in our case at room temperature. Near T_c the probability for first-order scattering is 5% in a sample of 1 mm thickness, so that multiple scattering is less than 1% and cannot be corrected.

In Fig. 1 the scattering behavior of the critical region is shown. The signal grows with increasing temperatures and shifts to smaller Q vectors. The typical critical-scattering behavior of an insignificant change of the scattering intensity at large Q vectors as the temperature approaches the temperature of the spinodal is observed in Fig. 1 for the polymer system.

The corrected scattering data were fitted by the Ornstein-Zernike function [Eq. (2)]. The fit pa-

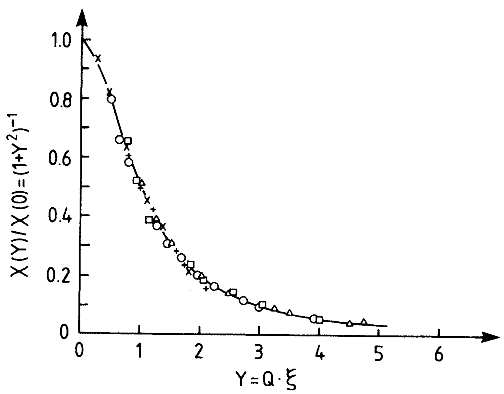

FIG. 2. Ornstein-Zernike scaling plot for $\varphi_{\mathrm{PVME}} = 0.408$ at various temperatures: $T = 138.9\,^\circ\mathrm{C}$ (crosses), 147.9 °C (plusses), 163.0 °C (circles), 173.6 °C (squares), 179.6 °C (triangles).

rameters are the forward scattering $\chi(0)$ and the correlation length ξ. Figure 2 shows a scaling plot, where the scattering intensity normalized by the forward scattering was plotted versus the scaling variable $Y=\xi Q$. In this representation all data measured at different temperatures should fall on one Ornstein-Zernike curve, displayed by the solid line. One can see that for a reduced temperature range of $0.01 \leqslant \tau \leqslant 0.1$, the scaling behavior is obeyed for all the experimental data within the experimental errors. Because of this result the polymer mixture behaves in the critical range as a low-molecular-weight critical mixture.

In Fig. 3 the correlation length ξ^{-2} is plotted against the temperature. The solid line represents a linear least-squares fit through all points in the range $144 \leqslant T \leqslant 178\,^\circ\mathrm{C}$. These points show the typical critical behavior predicted by the mean-field theory, with an exponent $\nu=0.492 \pm 0.017$. From a double logarithmic plot one obtains the critical amplitude $\xi_0=11.3\pm0.2$ Å. This value is very large in comparison with low-molecular-weight critical systems. Schneider *et al.*[10] have measured a ξ_0 value of 3 Å for a critical mixture of isobutyric acid and D_2O. For the polymer system the ξ_0 value compares well with the mean length of the statistical segments of the two polymer species.

The spinodal decomposition temperature was determined from extrapolation to infinite correlation length. We have found a value of $T_s=184.8 \pm 1.2\,^\circ\mathrm{C}$ at the volume fraction $\varphi_{\mathrm{PVME}}=0.408$. In the vicinity of T_s the measured correlation length differs from the straight line. ξ does not seem to diverge at the spinodal line. The limitation of ξ is probably a property of the sample being investigated and is not a phenomenon of polymer mixtures in their critical state. The effect is quite understandable if the samples are inhomogeneous, i.e., the compositions at different positions in the sample are somewhat different. The broad molecular-weight distribution of the PVME component with a polydispersity of $M_W/M_N=2.12$ supports this assumption. On the other hand, the polymer mixture is not completely free from chemical stabilizers which could act as nucleation centers and cause a first-order phase separation. Additional nucleation centers for phase separation could be the aluminum cuvette walls and stress regions in the solid. This observation needs some further investigation by reducing the polydispersity, by eliminating the fraction of stabilizers, by changing the sample thickness and cuvette material, and by annealing the mixtures for very long time.

The susceptibility behaves similarly as the correlation length. From a plot of the reciprocal forward scattering versus temperature one obtains a critical exponent $\gamma=0.997\pm0.085$. In Fig. 4 the spinodal temperatures determined for all four specimens are plotted versus the volume fraction. The parabolic line represents a mean-field spinodal through the measured points. The asymmetric form of this line is due to the different segment numbers of both polymers. The discrepancy with the scattering data is larger at low volume fractions and becomes smaller with increasing volume fraction. From the mean-field theory it is predicted that the interaction parameter does not depend on the composition of the polymer mixture, i.e., on the volume fraction

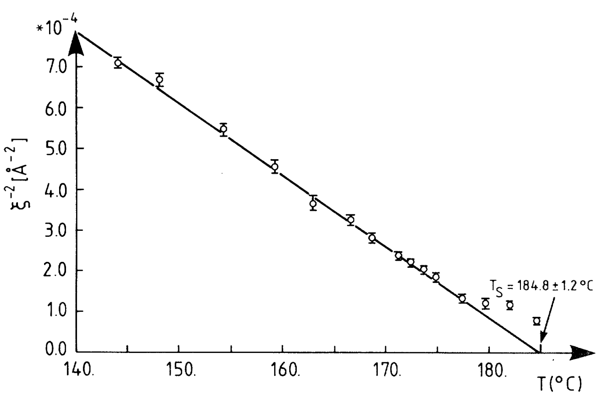

FIG. 3. Correlation length ξ^{-2} vs T for $\varphi_{\mathrm{PVME}}=0.408$. Open circles are experimental data. Extrapolation of the solid line to infinite correlation length determines the spinodal point T_s.

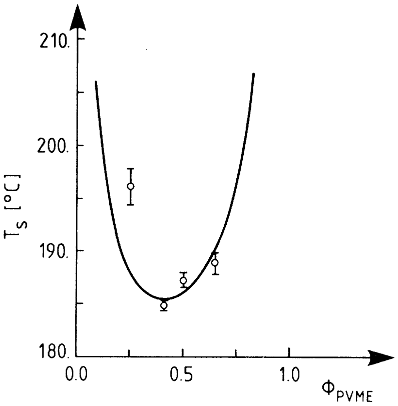

FIG. 4. Spinodal line for binary polymer mixture. Open circles, from present experiment; solid line, calculated from mean-field theory with $\varphi_{\mathrm{crit}}=4.1$ and $T_{\mathrm{crit}}=185.5\,^\circ\mathrm{C}$.

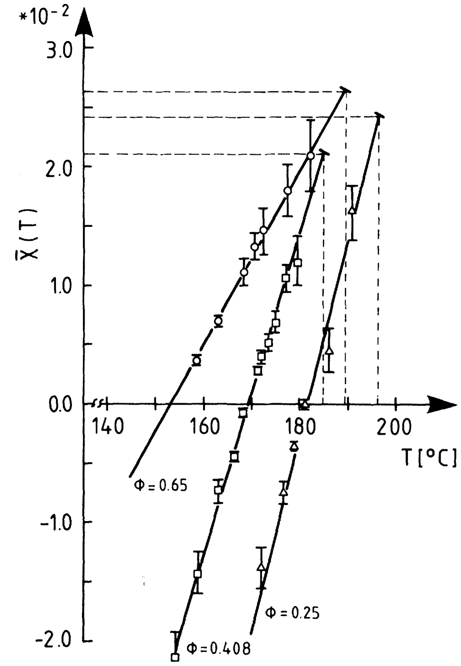

FIG. 5. Interaction parameter $\bar{\chi}$ vs T for three volume fractions. Dotted lines represent the spinodal points.

φ. This theoretical result is quite in contrast with the experimental observation. In Fig. 5 the $\bar{\chi}(T)$ values as determined from the measured scattering data are plotted versus the temperature. The parameter in this plot is the composition of the mixture described by the volume fraction φ of PVME. It is clearly seen that the $\bar{\chi}$ parameter varies linearly with temperature and that both slopes and intercepts are different for different compositions. The dashed lines in Fig. 5 indicate critical temperature and critical $\bar{\chi}$ parameters. It can be verified that the φ dependence of $\bar{\chi}(T)$ is stronger the lower the temperature. This relation is evidence for the assumption that the interaction term in the free-enthalpy expression is theoretically treated less accurately than the entropy term.

The mean-field theory provides a good approximation to the general behavior of the polymer mixture. (i) It was experimentally shown that the critical exponents ν and γ are 0.5 and 1, respectively. (ii) The Ornstein-Zerke scaling function is an excellent description for the scattering data. (iii) The spinodal line shows a typical parabolic mean-field shape. The anomalous behavior of the correlation length and the susceptibility was explained by parasitic phase separation, because PVME material is polydisperse and not perfectly free from stabilizers. (iv) The dependence of the interaction parameter on the composition of the polymer mixture is quite in contrast with the mean-field result. The experimental results indicate that the discrepancy is most severe at low temperatures.

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