Mean-Field and Ising Critical Behavior of a Polymer Blend

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(Received 27 January 1987)

The critical fluctuations of a polymer blend (PVME/d-PS) were investigated by neutron small-angle scattering. A mean-field behavior was observed, except in a region very close to the critical temperature where a transition to an Ising-type behavior occurs. The width of this region is $T-T_c \simeq 2.4$ K for a mixture with average molecular weights of 89000 (PVME) and 232000 (d-PS).

PACS numbers: 64.60.Fr, 05.70.Jk, 61.12.Ex, 61.41.+e

Polymer blends are supposed to behave in a mean-field manner as long as the number of chain segments is sufficiently large.[1,2] However, a transition to non-mean-field (Ising) critical behavior is expected close to the critical temperature T_c, in a region whose width is estimated on the basis of the Ginzburg-Landau relation[1,2]; this leads to

$$(\chi/\chi_c-1)^{1/2} \gg (N_1N_2)^{-1/4}, \tag{1}$$

where $\chi = H_{\text{mix}}/kT$ is the Flory-Huggins interaction parameter, H_{mix} is the enthalpy of mixing, and N_1, N_2 are the numbers of statistical segments for the components 1 and 2, respectively. A typical segment consists of about ten monomers.[2] χ_c refers to the critical temperature T_c. The system under consideration has a compensation temperature T_{comp} where χ passes through zero.[3] Consequently, we write near T_{comp}, which is close to T_c,

$$\chi/\chi_c = (T-T_{\text{comp}})/(T_c-T_{\text{comp}}), \tag{2}$$

and the criterion Eq. (1) reads

$$T_c - T \gg (T_c-T_{\text{comp}})/(N_1N_2)^{1/2}. \tag{3}$$

In the case of our investigation, the right-hand side of (3) is about 0.1 K.

However, recent Monte Carlo studies[4] indicate a non-mean-field behavior for a chain length as high as 32 statistical segments. From these calculations it can be stated that experiments on polymer blends of high molecular weight should show a mean-field to non-mean-field crossover "without need of unrealistic small values of T_c-T."[4]

The first investigation of critical scattering of neutrons on the system polyvinylmethylether (PVME)–deutero polystyrene (d-PS) by Herkt-Maetzky and Schelten[5] and by Yang *et al.*[6] clearly showed a mean-field behavior, in particular the critical exponent $\gamma=1$. Our paper deals with recent experimental work on the same system in the critical region, in order to identify a crossover as expected by theory.

The scattering function for the critical fluctuations according to the mean-field random-phase approximation[1] can be written as

$$S(Q)^{-1} = S_1^0(Q)^{-1} + S_2^0(Q)^{-1} - 2\chi(Q), \tag{4}$$

where $S_{1,2}^0$ is the Debye function of a single chain multiplied by ϕV (ϕ is the composition and V the molecular volume, 1 and 2 correspond to the two components). An expansion of (4) to fourth order of the scattering vector Q leads to

$$S(Q)^{-1} = S(0)^{-1} + AQ^2 + BQ^4. \tag{5}$$

$S(0)^{-1}$, the reciprocal cross section in the forward direction, is related to the reduced temperature $\epsilon = (T_c-T)/T_c$ by

$$S(0)^{-1} \propto \epsilon^{\gamma} \tag{6}$$

with $\gamma=1$. This form of the scattering function is not affected by polydispersity, i.e., by a distribution of the molecular weights.[7,8] In the case of Ising behavior, we may approximately maintain the validity of Eq. (6) with $\gamma=1.26$. This exponent holds for ordinary liquid mixtures (e.g., see Schwahn, Belkoura, and Woermann[9]).

The scattering function Eq. (4) holds for the homogeneous region of the phase diagram. On crossing of the binodal, thus entering the metastable region, a heterogeneous domain structure appears (see the phase diagram of the system PVME/d-PS in Fig. 1[8]). This leads to strong extra scattering at very small scattering vectors because of the large domain size (typical values are microns), which cannot be resolved. At the same time, the critical scattering due to fluctuations decreases, since the spinodal temperature has increased in the decomposed regions.

The sample was a mixture of d-PS with an average molecular weight of $M_w=232000$ and PVME with $M_w=89000$. The ratio of the weight and number average is a measure for the polydispersity of molecular mass. The mass distribution is broad for PVME with $M_w/M_n=2.5$ and rather narrow for d-PS with $M_w/M_n=1.08$. The strong polydispersity of PVME causes the unusual shape of the binodal as seen in Fig. 1. The sample was prepared by dissolving both components in to-

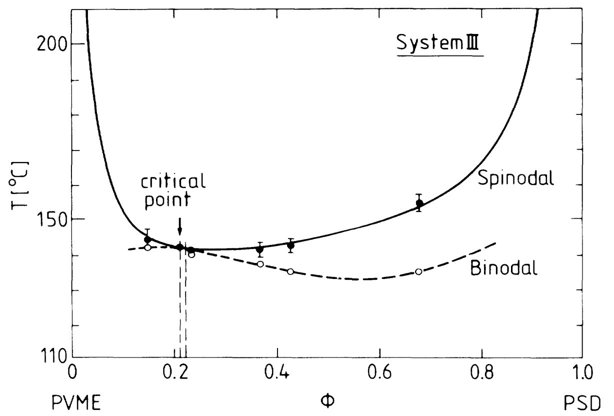

FIG. 1. Phase diagram of the polymer blend PVME and d-PS, determined by neutron small-angle scattering (see text). Dashed line: guide for the eye. Solid line: interpolation between the measured points by the thermodynamic theory of Koningsveld (Refs. 8 and 10). The vertical lines indicate the path of the experiments.

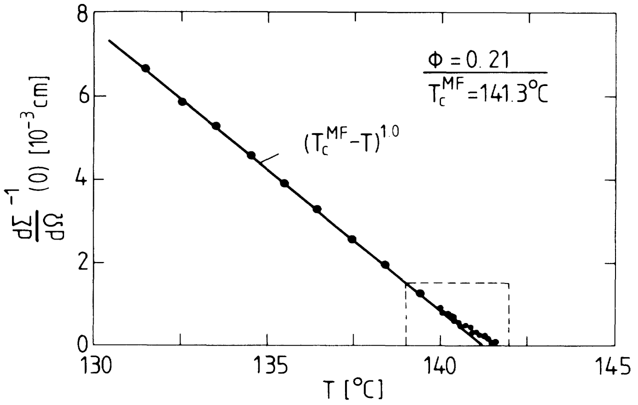

FIG. 3. The same function as in Fig. 2, but measured at the critical composition.

luene and was finally dried by heating in vacuum. Contact with air was avoided during the whole experiment. The temperature control of the specimen was better than 0.01 K.

The small-angle neutron-scattering experiments (SANS) were performed with the cold-neutron source instrument at the Risø National Laboratory. The lowest Q value was 5×10^{-3} Å^{-1}. The scattering patterns were measured with a 64×64 multichannel area detector. Multiple scattering was small. It is determined by the magnitude of the single-scattering probability

$$w = \tfrac{1}{2} D(\lambda/2\pi)^2 \int 2\pi Q (d\Sigma/d\Omega)\, dQ,$$

where d is the sample thickness, $d\Sigma/d\Omega$ the macroscopic cross section, and λ the wavelength of the neutrons. w is then proportional to $(\epsilon^{2\nu}/\epsilon^{\gamma})\ln(1+Q_{\max}^2\xi^2)$ where $\xi=[AS(0)]^{1/2}$ is the correlation length and $Q_{\max}=0.03$ Å^{-1}. With $\gamma=2\nu$, the quantity w changes only weakly with ϵ and the scattering probability is 0.06 for our smallest ϵ.

Figure 2 presents the inverse scattering cross section $(d\Sigma/d\Omega)^{-1}$ as a function of temperature, extrapolated to $Q=0$ by a least-squares fit of Eq. (5), for a concentration of $\phi=0.22$. This composition obviously differs from the critical composition: Namely, at 140.6 °C, a sharp change of the slope is observed; it is caused by domains which appear when the binodal is crossed (see above and Fig. 1). A small deviation from the linear behavior is also visible between 139.8 °C and the binodal temperature. This is tentatively interpreted by a behavior with a critical exponent $\gamma=1.26$ and accordingly extrapolated to the spinodal.

Figure 3 shows data at $\phi=0.21$. Far from T_c, the

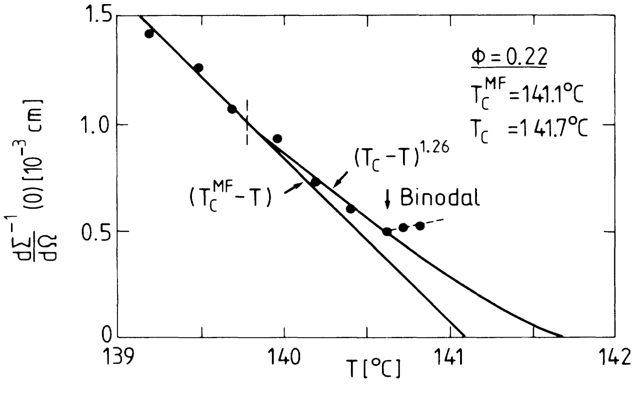

FIG. 2. Inverse cross section for critical scattering extrapolated to a scattering vector $Q=0$ by Eq. (5). Above 140.6 °C, the blend decomposes by nucleation and growth. T_s (MF), spinodal temperatures extrapolated by the mean-field behavior. T_s, spinodal temperature extrapolated with a critical exponent $\gamma=1.26$.

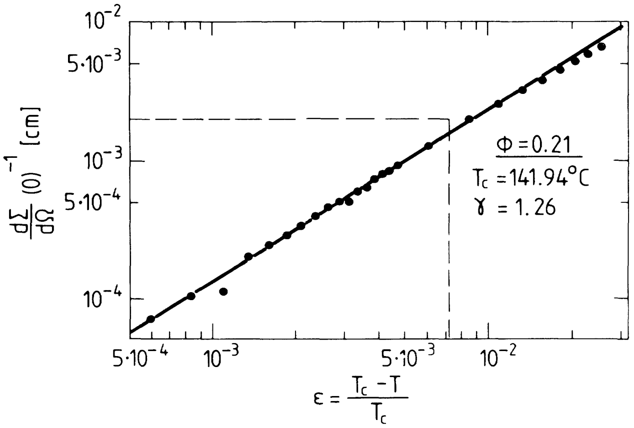

FIG. 4. Same data as in Fig. 3, in a double log plot, vs $\epsilon=(T-T_c)/T_c$ with $\gamma=1.26$.

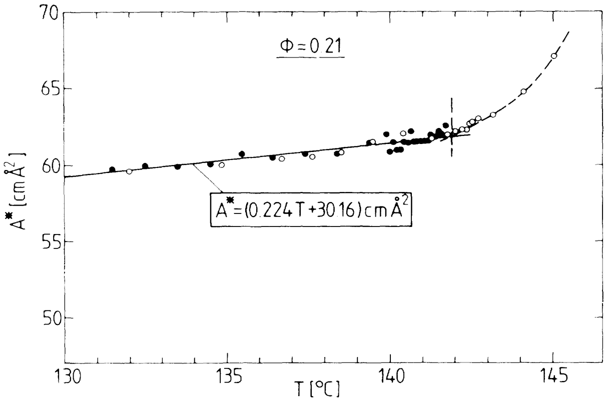

FIG. 5. The coefficient A in Eq. (5) as a function of temperature T. The strong increase of A indicates the appearance of spinodal decomposition for $T > T_c$.

linear mean-field behavior is again clearly observed as in Fig. 2, with an extrapolated $T_c^{\mathrm{MF}} = 141.3\,°\mathrm{C}$. The kink, as seen in Fig. 2, does not appear. Thus, we assume that the composition 0.21 corresponds to the critical one. Instead, the deviation from the linear curve appears very clearly. Figure 4 shows the data of Fig. 3 in a double log scale, and the fit in the region near T_c with $\gamma = 1.26$ leads to $T_c = 141.94\,°\mathrm{C}$.

In Fig. 5 we have also plotted the coefficient A of Eq. (5) versus T. It varies smoothly with T below T_c, but there is an anomalous change of the curve at T_c. Above T_c, the fit leads to a negative extrapolated value of $d\Sigma/d\Omega(0)$ which means that Eq. (5) loses sense. This is to be expected when the unstable decomposition region is entered. The open and closed circles correspond to two independent scattering experiments with different specimens. The very good agreement of the two sets of data demonstrates their reproducibility.

We conclude that a crossover from mean-field to Ising behavior with $\gamma = 1.26$ occurs in the interval $\delta\epsilon \simeq (2.4\ \mathrm{K})/T_c = 5.8 \times 10^{-3}$. Our conclusion is based on the assumption that the mean-field scattering function $S(Q)$ in Eq. (5) holds in the whole temperature region. Furthermore, we have to assume that the fluctuations near T_c are not affected by polydispersity. This is plausible because, even for the largest molecular weights of the system, the mean square radius of the molecular chains is smaller than the critical correlation length ξ. Also we draw attention to the fact that, following the Flory-Huggins theory, the spinodal remains sharp for a polydisperse system.[10] Our analysis of the data *at* and *off* ϕ_c has proven that the change in slope in Fig. 3 is not caused by the appearance of domains which, in fact, were observed at compositions different from ϕ_c (Fig. 2).

For the first time, it is shown that the universality principle, predicting an Ising-type exponent $\gamma = 1.26$ for all binary fluid mixtures close enough to their critical point, is consistent with the critical behavior of the polymer blend which has been studied. Our results also point out the need for a quantitative theoretical description for the crossover from Ising to mean-field behavior.

The authors gratefully acknowledge critical discussions and many suggestions by Professor K. Binder from the University of Mainz and by Professor T. Springer from Institut für Festkörperforschung in the Kernforschungsanlage Jülich, The furnace was constructed and built by B. Huy, A. Baur, and J. L. Harings.

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