

Mean-Field Ising Crossover and the Critical Exponents γ , ν , and η for a Polymer Blend: d -PB/PS Studied by Small-Angle Neutron Scattering

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(Received 15 October 1991)

The critical behavior of the polymer blend d -PB/PS was investigated by small-angle neutron scattering experiments. 3D Ising behavior was clearly observed with the critical exponents $\gamma=1.26 \pm 0.01$, $\nu=0.59 \pm 0.01$, and $\eta=0.047 \pm 0.004$. The crossover to mean-field behavior occurs at $T^*=T_c+5.4$ K. This is compared with the results of other experiments and the Landau-Ginzburg criterion. The Q dependence of the structure factor $S(Q)$ follows the Ornstein-Zernike form in both regimes.

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

For a great variety of materials the critical behavior has been investigated, in particular, describing the temperature dependence of equilibrium properties such as order parameter, susceptibility, and correlation length. With the corresponding critical exponents, the scaling laws were tested as fundamental relations between the exponents. These investigations have dealt with magnetic materials, alloys, liquid mixtures, ferroelectrics, and ferroelastics (for reviews see [1-3]). It was more recently that one also started to deal with polymer blends, studying the critical phenomena by means of small-angle neutron scattering (SANS). Already in 1977 de Gennes [4] had predicted that a polymer blend should reveal a mean-field behavior; however, a transition to the 3D Ising behavior is expected close to T_c . For the first time, the mean-field behavior was verified for the blend of deuterio-polystyrene (d -PS) and polyvinylmethylether (PVME) by Herkt-Maetzky and Schelten [5] by means of SANS experiments. In a region of $\epsilon=1-T_c/T$ larger than 2×10^{-2} , a linear ϵ dependence of the susceptibility was observed, which means that the structure factor for neutron scattering $S(Q)$ for the wave number $Q \rightarrow 0$ is $S(0)=s_0\epsilon^{-\gamma}$ with an exponent $\gamma=1$. Experiments by Schwahn *et al.* [6] have shown for d -PS/PVME that near T_c , within 2 K or $\epsilon=5 \times 10^{-3}$, a transition from mean-field to non-mean-field behavior occurs with the critical exponent of the susceptibility close to the Ising value $\gamma=1.26$; outside of this region the value of $\gamma=1$ was confirmed in a rather wide temperature region. A similar transition of this kind was found by Bates *et al.* [7] for the blend PEP/PI, again using SANS, and, more recently, in critical light-scattering experiments by Meier, Momper, and Fischer [8] for the PEMS/PDMS blend.

It is the aim of this work to investigate this crossover in a system with a low number of monomers per chain, N , namely, for the system deuterio-polybutadiene/polystyrene (d -PB/PS) with $N(d\text{-PB})=29$ and $N(\text{PS})=19$, both with a polydispersity factor of 1.1. For such a system the crossover temperature T^* should be relatively far from T_c and the Ising region could be easily investigated. In particular, there is a chance to determine not only γ and ν , the critical exponents for the susceptibility and the

correlation length $\xi=\xi_0\epsilon^{-\nu}$, respectively, but the "Fisher exponent" η as well, which is $\eta=2-\gamma/\nu$. For the 3D Ising system, $\gamma=1.24$, $\nu=0.63$, and $\eta=0.039$, whereas $\gamma=1$, $\nu=\frac{1}{2}$, and $\eta=0$ for the mean-field system.

As concerns $S(0)$ we start with the Flory-Huggins formulation of the Gibbs potential of mixing for polymer blends, namely (per molar volume),

$$\Delta G/RT = (\phi_a/V_a)\ln\phi_a + (\phi_b/V_b)\ln\phi_b + \phi_a\phi_b\chi. \quad (1)$$

$\phi_{a,b}$ are the concentrations of the components ($\phi_a + \phi_b = 1$), and V_a, V_b are the chain volumes, respectively; χ is the Flory-Huggins parameter, such that

$$S^{-1}(0) = \frac{\partial^2(\Delta G/RT)}{\partial\phi_a^2} = 2(\Gamma_S - \Gamma), \quad (2)$$

with $\Gamma = -(\frac{1}{2}\partial^2/\partial\phi_a^2)\phi_a(1-\phi_a)$ and $\Gamma_S = \frac{1}{2}[(\phi_a V_a)^{-1} + (\phi_b V_b)^{-1}]$. If χ is only determined by the monomeric interaction energies and an entropic contribution, then Eq. (2) is consistent with the mean-field result. In order to get the Q dependence of the structure factor $S(Q)$ we use the result of the random phase approximation (RPA) [4] which contains χ and the Debye functions for the two polymer components. Expanding the RPA up to Q^2 , an Ornstein-Zernike form for $S(Q)$ is obtained. It is called the "Zimm formula" in polymer physics, and is written as

$$S^{-1}(Q) = S^{-1}(0) + AQ^2, \quad (3)$$

with $A = \frac{1}{3}[R_{ga}^2/V_a\phi_a + R_{gb}^2/V_b\phi_b]$, where $R_{g a,b}$ are the radii of gyration of species a and b , and $\sigma = \Omega(R_g^2/6V)^{1/2}$ is the segment length; Ω is the monomer volume. In our experiments, the error caused by the truncation of the Q^2 expansion is below 0.2%. The polydispersity of the molecular weight is taken into account by introducing the weight averages for V_a, V_b , and the z averages for R_{ga}, R_{gb} , respectively.

Entering the non-mean-field range near T_c , there is no corresponding theory and we use, instead, the scaling prediction [9]

$$S(Q) = S(0)g(Q\xi(\epsilon)), \quad (4)$$

where $\xi(\epsilon)$ is the critical correlation length which is the *only length scale* in this region (in the mean-field case we had $\xi = (R_g^2/6V)[AS(0, \epsilon)]^{1/2}$). For the 3D Ising case, different approximations for $g(Q\xi)$ in various $Q\xi$ regions were proposed [9]. In our experiments ($0.3 < Q\xi < 8.7$) the corresponding Fisher-Burford approximation [2,9] is very close to a simple Ornstein-Zernike formula (within 1%) such that we are allowed to write

$$g^{-1}(Q\xi) = (1 + Q^2\xi^2). \quad (5)$$

Consequently, we maintain the Zimm or Ornstein-Zernike form, where Eqs. (3) and (5) lead to

$$A = \xi^2/S(0) = s_0^{-1}\xi_0^2\epsilon^{-\nu\eta} = \text{const} \times \xi^\eta. \quad (6)$$

Therefore, in the crossover region, A will increase from a constant value $s_0^{-1}\xi_0^2$ to $s_0^{-1}\xi_0^2\epsilon^{-\nu\eta}$ which increases as $\epsilon \rightarrow 0$. The expected transition from the mean-field to a 3D Ising behavior, as soon as fluctuations become large, should occur in the range of relative temperatures $\epsilon \lesssim \epsilon^* = |T^* - T_c|/T_c$, as given by the Ginzburg-Landau criterion, which can be rewritten from the form given in [7] as

$$\epsilon^* = c \frac{[(1/V_a\phi_a^3) + (1/V_b\phi_b^3)]^2}{54\Gamma_\sigma A^3 N_A^2 (1 + \Gamma_\sigma/\Gamma_S)}. \quad (7)$$

Γ_σ is the part of Γ which follows from the segmental entropy contribution in χ and N_A is Avogadro's number.

The scattering experiments were performed at the small-angle neutron diffractometer KWS I at the Jülich FRJ-2 [10]. The samples were 1 mm thick, and installed in a double-shell thermostat [6] with a temperature stability better than 0.01 K. The scattering curves were corrected for background and obtained in absolute units by a Lupolen standard to obtain the structure factor $S(Q)$. We have investigated the influence of multiple scattering

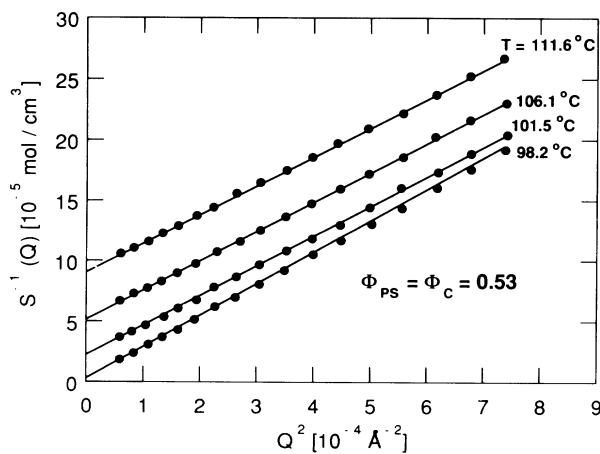


FIG. 1. Selected curves for the inverse structure factor $S^{-1}(Q)$ as a function of Q^2 in the Zimm or Ornstein-Zernike presentation out of 40 curves. $\phi_c = 0.53$ is the measured critical concentration of the PS component.

close to T_c . The critical scattering probability was calculated with Eq. (3) to be $W \approx 0.02$ for $\xi = 400 \text{ \AA}$ at 0.4 K above T_c . Referring to calculations [11] for scattering on a sphere with a radius equal to $5^{1/2}\xi$ we have found that the error in the determination of ξ is negligible under these conditions. The measured patterns were resolution corrected by means of a program from Risø [12]. The resulting changes were only a few 10^{-2} for ν and γ , and $\approx 10^{-3}$ for η .

The structure factor $S(Q)$ was determined as a function of Q for several PS concentrations ϕ , and at 40 temperatures. Figure 1 shows typical Zimm plots of $S(Q)$ for a given sample at various temperatures. Figure 2 presents a typical curve of the extrapolated values $S^{-1}(0)$, as a function of inverse temperature for a concentration which was *off* the critical concentration ϕ_c . For high temperatures one observes the expected linear mean-field behavior. Before crossing the line $S^{-1}(0) = 0$, which defines the spinodal temperature T_S at this concentration in the mean-field approximation, a sharp *upward kink* appears. This kink, already observed in earlier work [6], appears at the temperature where the binodal or coexistence curve is crossed at $T = T_B$. Below this temperature, a separation takes place into two phases, corresponding to the concentrations at the left and the right wing of the coexistence curve (see inset in Fig. 2). Obviously, in these two phases, the difference between the temperature T and the corresponding spinodal temperatures T_{S1} and T_{S2} is larger than it was before phase separation. Therefore, the inverse total critical scattering (in both components) increases sharply. The scattering caused by the *precipitates themselves* appears at Q values much smaller than those accessible at the measurements. This effect should appear already at precipitations with a

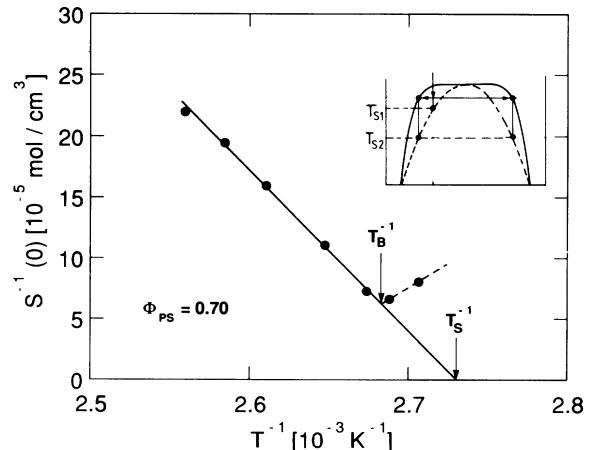


FIG. 2. Extrapolated inverse structure factor $S^{-1}(Q=0)$ as a function of inverse temperature. The binodal is crossed at T_B where the inverse scattering intensity has a kink. T_S is the spinodal at this concentration, as defined by an extrapolation with the mean-field curve. Inset: Decomposition at $\phi \neq \phi_c$ into two regions with the corresponding spinodal temperatures 1 and 2.

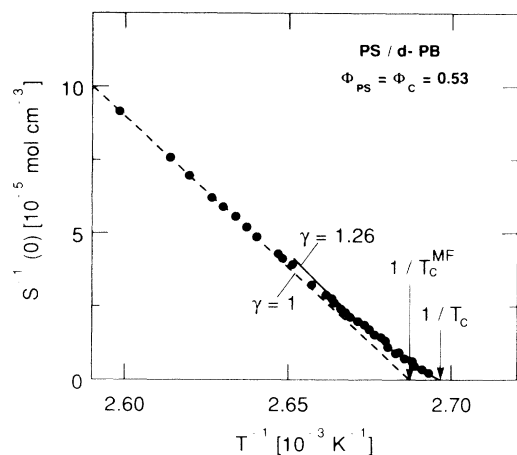


FIG. 3. Inverse structure factor vs T^{-1} . The extrapolated mean-field critical temperature T_c^{MF} (98.9°C) and the true critical temperature T_c (97.6°C) are indicated. One recognizes the crossover from the region with $\gamma=1$ to $\gamma=1.26$.

characteristic length scale of several 100 Å. We believe that this determination of the binodal temperature is more sensitive than cloud point measurements. The phase diagram was determined from these plots; it has an asymmetric shape typical for polydisperse polymer systems [13]. Figure 3 shows a measured $S(Q)^{-1}$ curve where the kink has disappeared, i.e., where spinodal and binodal coincide; this means that this measurement occurred at the critical concentration $\phi_c=0.53$. Above T_c the crossover from the mean-field to a different T dependence can be clearly seen around $T^*=T_c+5.4$ K which yields $c=0.016$ from Eq. (7). From scattering experiments in [6] and [7] one obtains, however, $c=0.29$ and 0.35, respectively. Recent unpublished results on PPMS/*d*-PS [PPMS denotes poly(phenylmethylsiloxane)] [14] lead to $c=0.11-0.13$ [14]. Also earlier work dealing with *d*-PS/PVME [6] gave a much larger value for c .

In order to obtain γ and ν , the measured and resolution-corrected values were log-log plotted versus ϵ [Figs. 4(a) and 4(b)]. T_c was a disposable parameter. The results are $\gamma=1.26 \pm 0.01$ and $\nu=0.59 \pm 0.01$. In the mean-field region the fit gives $\gamma=1.02 \pm 0.01$ and $\nu=0.50 \pm 0.02$. There is a difference of 1.3 ± 0.1 K between T_c [where $S^{-1}(0)$ disappears] and the mean-field extrapolation temperature T_c^{MF} . This implies the inherent ill-definedness of a spinodal as extrapolated by the mean-field approximation. From $\xi(\epsilon)=\xi_0\epsilon^{-\nu}$ we also obtain the characteristic length, namely, $\xi_0=8.6$ Å (mean field) and $\xi_0=7.0$ Å (Ising region) (the segment length is $\sigma=7.1$ Å). The experimental prefactor s_0 for $S(0,\epsilon)$ of the Ising region in relation to the mean-field value is $s_0(\text{Ising})/s_0(\text{MF})=2.4$.

Finally we evaluated the Fisher exponent η . The slope A from the Zimm plots has been drawn versus ξ as ob-

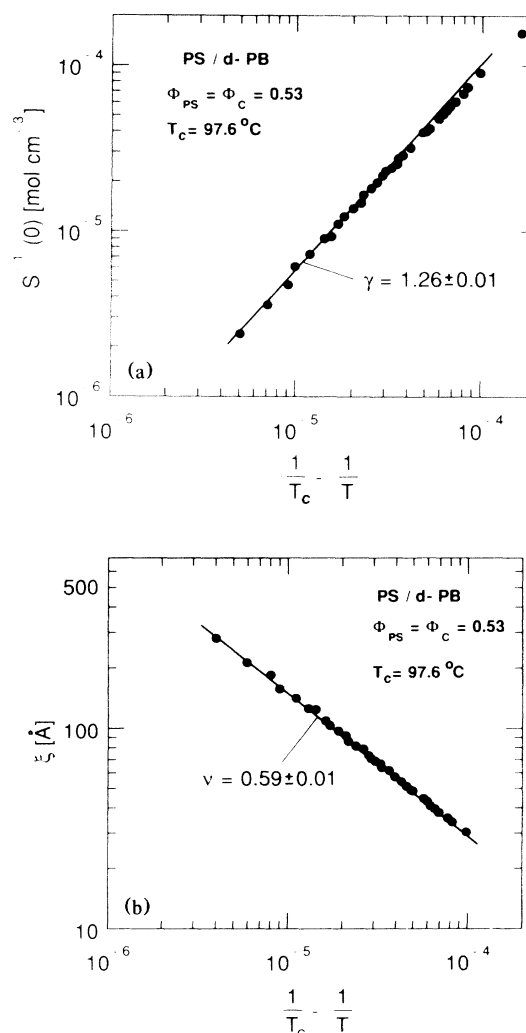


FIG. 4. (a) $S^{-1}(0)$ and (b) correlation length ξ in a log-log plot, both vs the reduced temperature ϵ , for the critical concentration $\phi=0.53$.

tained from Eqs. (3), (5), and (6). Figure 5(a) shows the log-log curve $A(\xi)$ which leads to $\eta=0.047 \pm 0.004$. Figure 5(b) demonstrates how $A(\epsilon)$ starts to increase in the Ising region due to the nonzero η [Eq. (6)]. So we have determined η without an analysis of the *shape* of $S(Q)$, and, as well, without a determination of ϵ (i.e., of T_c), since, instead, ξ is obtained directly from the scattering experiment. Our resulting exponents are finally $\gamma=1.26 \pm 0.01$ [1.238], $\nu=0.59 \pm 0.01$ [0.631], and $\eta=0.047 \pm 0.004$ [0.039]. They agree quite well with the theoretical values given in square brackets and, fairly well, with experiments, e.g., on β -brass [15], Fe_3Al [16], and a fluid mixture [17].

Our experiments have consistently demonstrated the 3D Ising behavior of a polymer blend with a relatively low molecular weight; they yield the theoretically expected exponents γ , ν , and, for the first time, η . Our observed

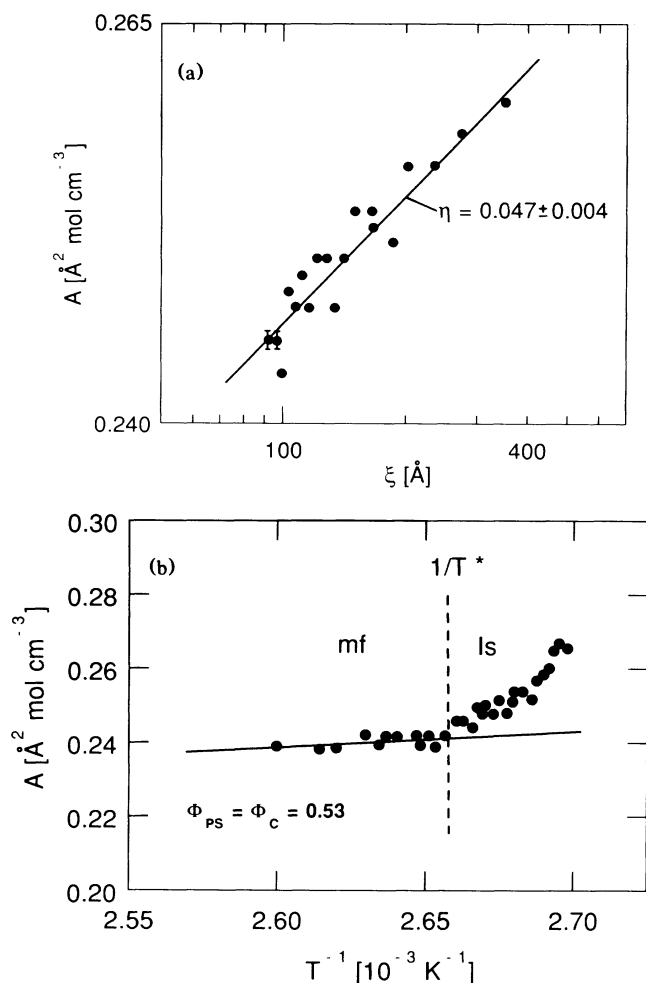


FIG. 5. (a) A vs the correlation length ξ in the Ising region where the slope should yield η . (b) The change of A vs $1/T$ [see Eq. (6)] in the crossover region.

crossover temperature T^* leads to a value of c in Eq. (7) which is much smaller than results from other experiments [7,8] and from [14]. The discrepancy for the case d -PS/PVME [6] may be due to the large polydispersity and the great difference between V_A and V_B . This means that c is not "universal" as quoted in [7] and the crossover needs further explanation and experiments. In our whole temperature region the structure factor $S(Q)$ follows the Ornstein-Zernike form within a few percent, for

$Q\xi$ between 0.7 and 10. This implies that (i) in the mean-field region the prediction of the random phase approximation works very well, and that (ii) the prediction of Fisher and Burford [2], which also approximately yields an Ornstein-Zernike form of $g(Q\xi)$, is valid in our parameter range.

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