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Concentration fluctuation in a polymer mixture

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The critical behavior in a mixture of polystyrene and polymethylphenylsiloxane has been examined by the angular distribution of the scattered light intensity over $5.7<k<19.6\ \mu\text{m}^{-1}$ and $0.045<T-T_c<2.4\,^{\circ}\text{C}$, where k is the scattering wave number and T_c is the critical mixing temperature. The osmotic compressibility obeys a relation $\chi_T \sim (T-T_c)^{-\gamma}$ with $\gamma=1.22\pm0.02$ and the long-range correlation length $\xi \sim (T-T_c)^{-\nu}$ with $\nu=0.62\pm0.02$, in good agreement with the three-dimensional Ising-model universality.

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INTRODUCTION

It has been found that macromolecular solutions and surfactant solutions in the vicinity of their critical mixing points belong to the three-dimensional Ising-model universality class, as well as other critical binary liquid mixtures [1,2]. Great attention has been focused lately on the critical behaviors in polymer blends with regard to the critical-point universality as a fluid. In early works on polymer blends in the vicinity of their critical mixing point, the mean-field behavior has been reported for binary polymer mixtures [3]. On the contrary, it has recently been found that polymer blends in a good solvent should belong to the same universality class as the three-dimensional Ising model with $\beta \simeq 0.325$, where β is the critical exponent of the coexistence curve [4]. Moreover, several experimental works for the critical behaviors in the polymer-polymer mixtures have been performed confirming the three-dimensional Ising-model universality by means of small-angle neutron scattering (SANS) [5–7] and light scattering [8].

Recently, it has been suggested that the polymer-polymer mixture shows different behaviors in quality concerning the phase separation kinetics, depending on their mobility and temperature range [9]. It is of particular interest to examine the critical behaviors of a polymer blend with low mobility and T_c in the region not far from its glass transition temperature, because the phase separation kinetics in such a system showed a discrepancy from the behavior in the liquid-liquid mixtures. In this paper we report the experimental study of the critical behaviors for the mixture of amorphous-amorphous polymers, polystyrene (PS), and polymethylphenylsiloxane (PMPS), in the homogeneous equilibrium state.

EXPERIMENT

Polystyrene ($M_w=4\times10^3$, $M_w/M_n<1.02$, with M_w and M_n being the weight- and number-average molecular weights, respectively) obtained from Toyo Soda Manufacturing Co. was used in this study. The values of density and refractive index of PS at 25 °C were 1.07 g/cm^3 and 1.591, respectively. Polymethylphenylsiloxane obtained from Shin-Etsu Chemical Co. was fractionated into 12 fractions by the solution fractionation using isopropyl alcohol as a solvent. A fraction characterized by $M_w=1.5\times10^3$ and $M_w/M_n \le 1.03$ was employed as the sample. Our polymers are almost free from the polydispersity effect. The values of density and refractive index of PMPS at 25 °C were 1.10 g/cm^3 and 1.534, respectively. Both the density and the refractive index of PS and PMPS are matched well. The critical point established by the concentration dependence of the spinodal temperature was $T_c=31.9\pm0.1\,^{\circ}\text{C}$ and $W_c=38.1\pm0.1$ wt. % PS [9].

The mixture of 38.1 wt. % PS in PMPS was dissolved in benzene at a total concentration less than 20 wt. % and filtered into a rectangular quartz cell with an optical path of 0.5 mm through a Millipore filter (pore size=0.20 μm). Benzene was subsequently allowed to evaporate at 70 °C for a week and the polymer blend was further heat treated in a vacuum oven at 90 °C for at least six months to remove benzene thoroughly, and then the polymer sample was flame sealed under vacuum. The experimental arrangement is shown in Fig. 1. The incident laser beam of vacuum wavelength $\lambda_0=632.8$ nm passed through a pinhole (P0), a microscope slide (G), a convex lens (L), more pinholes (P2,P3), the sample (S), and it reaches a light trap (LT). The intensity of the incident beam was monitored with a microscope slide (G), pinhole (P1), and

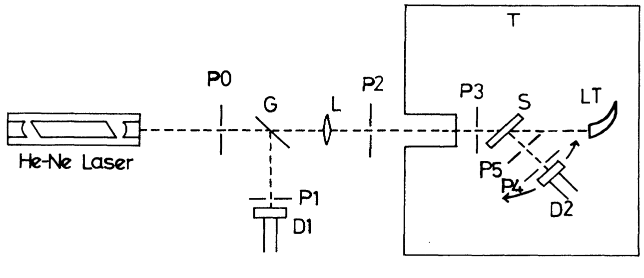

FIG. 1. The schematic diagram of the apparatus. P0, P1, P2, P3, P4, and P5: pinholes; G: microscope slide; L: convex lens; D1 and D2: photodiode; S: sample; LT: light trap; T: silicon oil bath.

photodiode (D1) assembly. Scattered light intensity was detected by pinholes (P4,P5) and photodiode (D2) assembly mounted on the axis of a rotational table. All the pinholes, sample holder, light trap, and silicon oil bath (T) were made of frosted black ebonite to reduce the stray light. Silicon oil in the bath was circulated through a microfilter of 0.45-μm pore size to obtain dust-free silicon oil. The temperature of the silicon oil bath for the sample cell was regulated within 1 mK over 12 hours. After changing the temperature, the sample was allowed to accomplish a thorough equilibrium for 12 hours.

The scattered light intensities were measured for 14 scattering wave numbers $k=(4\pi n/\lambda_0)\sin(\theta/2)$, where n is the refractive index of the medium ($n=1.556$ for the critical PS-PMPS mixture) and θ is the scattering angle, ranging from 5.7 to 19.6 $\mu\mathrm{m}^{-1}$ ($\theta=21.4°$ to $78.4°$). The observed scattered intensity I_s is usually assumed to consist of I_c+I_d, where I_c and I_d are the scattered intensity due to the concentration and density fluctuations, respectively. The background contributions due to the density fluctuations may become significant and have to be taken into account. There are no unique ways to correct for the background-density contribution and the following one which we utilized is merely one of the proposed methods [10]. For performing the corrections of density fluctuations the experimental values of I_s at $\theta=21.4°-78.4°$ vs $\log_{10}(T-T_c)$ were extrapolated to $T-T_c=20\,°\mathrm{C}$ and the resultant estimated values were used as I_d. Angular measurements were corrected for constant incident beam, attenuation, background, refractive index, and reflection. The intensity of the transmitted light I_t for the incident intensity I_0 is given by $I_t=I_0\exp(-\tau L)$ with τ and L being the turbidity and the path length in the cell. The ratio of I_t/I_0 for the sample with an optical path length of 2 mm was constant within the limits of experimental errors in the temperature range far from T_c, $T-T_c\geq 10\,°\mathrm{C}$. The attenuation corrections have been done by measuring the ratio of I_t/I_0 as a function of the temperature. The magnitude of the attenuation correction was 6% at most. The multiple-scattering effect is not significant because of the closeness of the refractive index of each component in our mixture and a short optical path. Reflection was minimized by matching the refractive indices among the sample, the thermostat fluid (silicon oil), and the quartz cell.

RESULTS AND DISCUSSION

The scattered intensity was analyzed by use of the Ornstein-Zernike-Debye (OZD) plot. The reciprocal scattered intensity I_c^{-1} decreased with the decrease of temperature in the OZD plot and obeyed a simple K^2 dependence. No downward curvature at small angles was observed in the experimental range, though Fisher proposed the general scattering formula including the critical exponent η to explain downward turn at small angles in the OZD plot [11]. Hence, the isothermal compressibility $\chi_T \sim I_{c,0}$ (limit of I_c to $K=0$) and the correlation length ξ have been extracted from the relationship:

$$I_c=I_{c,0}/(1+K^2\xi^2)\ . \tag{1}$$

The plots of $I_{c,0}^{-1}$ and ξ^{-2} as a function of T for the critical sample along the isochore are shown in Fig. 2. The critical mixing temperature T_c obtained from the intercept of the abscissa is $31.852\pm0.002\,°\mathrm{C}$ in good agreement with $T_c=31.9\pm0.1\,°\mathrm{C}$ reported previously in the study of the kinetics of phase separation in the spinodal region [9]. These plots cannot be represented by straight lines (mean-field case: $\gamma=1$ and $\nu=0.5$) and deviations from the mean-field behavior are clearly shown in the range of $T-T_c<2.4\,°\mathrm{C}$. In the critical exponent concept, χ_T and ξ above T_c would diverge as

$$\chi_T \sim [(T-T_c)/T_c]^{-\gamma}\ , \tag{2}$$

$$\xi \sim [(T-T_c)/T_c]^{-\nu}\ . \tag{3}$$

Equations (2) and (3) suggest the straight lines with the slopes γ and $-\nu$ in the plots of $\log_{10}I_{c,0}^{-1}$ and $\log_{10}\xi$ as a function of $\log_{10}\epsilon$ with $\epsilon=(T-T_c)/T_c$, respectively. As shown in Fig. 3, linear least-squares fits give the slope values of $\gamma=1.22\pm0.02$ and $\nu=0.62\pm0.02$ and the magnitude of the critical constant ξ_0 is evaluated as $(1.00\pm0.04)\times10^{-7}$ cm. The value of ξ_0 is comparable with those of d-PS–PVME and d-PB–PS blends reported by Schwahn and co-workers [5,6] (PVME denotes polyvinylmethylether). The deviations of the experimental χ_T and ξ from the calculated values are given in Fig. 4. The values of γ and ν are in good agreement with the values expected for the three-dimensional Ising model, $\gamma=1.24$ and $\nu=0.63$, and the corresponding values reported for macromolecular solutions as shown elsewhere [2], and consequently it was verified that the critical exponent concept is equally applicable to the polymer-polymer systems. The present exponents γ and ν approximately satisfy the relation $\gamma=(2-\eta)\nu$, which is derived by the scaling law, within the limits of estimated errors by assuming the theoretical value of $\eta=0.039$ [11].

In the present experimental temperature range, the crossover from the mean-field to the three-dimensional Ising behavior was not observed contrary to the other polymer blends with high molecular weights [5–8]. This is due to the fact that the molecular weights of the present polymer mixture are not so high. According to the classical Ginzburg criterion, the crossover takes place when the fluctuation of the order parameter becomes comparable with the magnitude of the order parameter

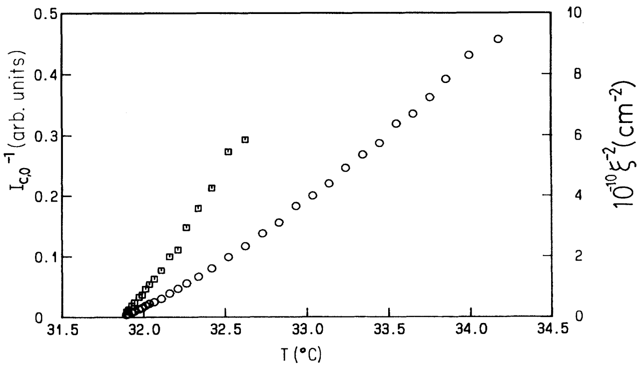

FIG. 2. Plots of $I_{c,0}^{-1}$ (○) and ξ^{-2} (□) against temperature.

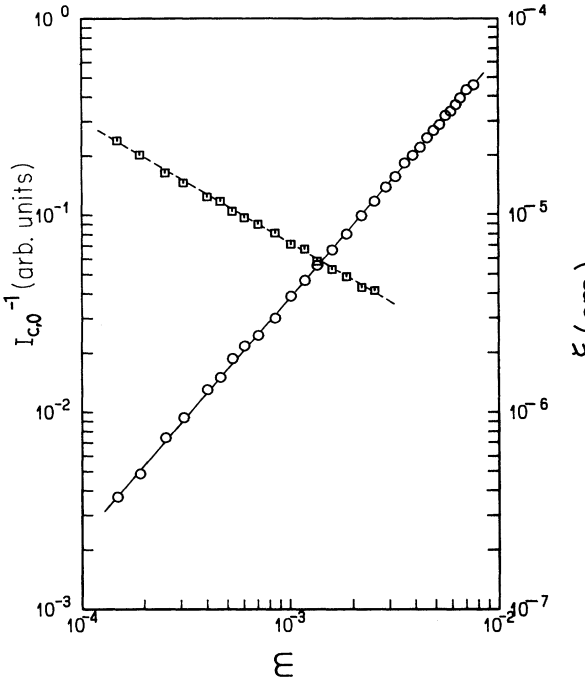

FIG. 3. Log-log plots of $I_{c,0}^{-1}$ (○) and ξ (□) as a function of ϵ. The solid and dashed lines correspond to $\gamma=1.22$ and $\nu=0.62$, respectively.

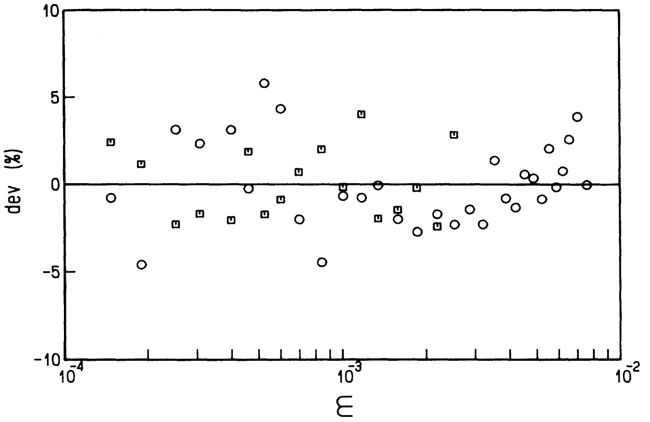

FIG. 4. The deviations of the experimental inverse osmotic compressibility (○) and the correlation length (□) from the calculated values as a function of ϵ.

itself. A simple estimation for the crossover range, ΔT [8,12,13], gives that

$$\Delta T \sim T_c/N \tag{4}$$

with N being the degree of polymerization. Even if N is set at 38.5 (degree of polymerization of PS), ΔT is evaluated as 7.9 K and is beyond the present temperature region.

Schwahn and co-workers have observed from the SANS experiment that a three-dimensional critical behavior occurs within a few degrees above and below the spinodal temperature. Unfortunately, they and Meier and co-workers have not carried out their experiments in the very immediate neighborhood of the critical temperature [5–8]. Bates and co-workers have found the critical behavior over the wide temperature range, which is much wider than the critical region usually expected so far [7]. Their finding might be related to the feature of the amorphous polymer-semicrystalline polymer blend. It is interesting to note that the molecular complexities of polymer blends may provide specific characteristics which vary from system to system. The temperature range where the three-dimensional Ising-like critical behavior is observed should depend strongly on the magnitude of ξ_0 and the distance from the critical point. Though it has been found in the present work that the amorphous polymer-amorphous blend belongs to the same universality class as simple binary liquid-liquid mixtures, further work is still necessary for settlement of the critical exponents for polymer blends.

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