Coexistence Curve of Polystyrene/Poly(2-Chlorostyrene) Blends

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Coexistence curves of polystyrene PS($M_w = 3.7 \times 10^4$ g/mole, $M_w/M_n < 1.06$) and poly(2-chlorostyrene) P2ClS($M_w = 2.33 \times 10^5$ g/mole, $M_w/M_n \simeq 1.19$) in the presence of 22.6 wt% of di-*n*-butylphthalate (DBP) and of PS($M_w = 3.7 \times 10^4$ g/mole, $M_w/M_n < 1.06$)/P2ClS($M_w = 11.2 \times 10^4$ g/mole, $M_w/M_n \simeq 1.09$) were determined by using a combination of a novel centrifugal method and synchrotron small-angle x-ray scattering. The coexistence curves could be fitted to yield a β value of ~ 0.33 for the blend *with* DBP and a β value of 0.5 for the blend *without* DBP.

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In polymer blends of long chain molecules, the coexistence curve is predicted to obey a mean-field behavior, except for in the very immediate neighborhood of the critical mixing point. For a ternary polymer–polymer–good-solvent system, deviation from the mean-field behavior could be expected. There have been methods devised to determine the coexistence curve of critical binary mixtures including the use of a differential refractometer [1,2], the method of pulse-induced critical scattering [3,4], or the more standard approaches of laser light scattering (LLS), small-angle x-ray scattering [5] (SAXS), and small-angle neutron scattering [6] (SANS). The differential refractometer method was very successful in coexistence curve determinations of critical binary liquid mixtures but became impractical for polymer blends because of the high fluid viscosity of polymer blends. The scattering techniques are capable of locating spinodal temperatures [7] but not the coexistence curve. While a centrifugal homogenizer [8] could be used to determine the temperature dependence of the phase-volume ratio at several overall concentrations, an improved and less expensive version could be more suitable for our purpose. Thus a centrifuge was modified [9].

The instrument had two separate insulated chambers with individual temperature controls. The insulation permitted temperature control of *air* to ±0.003° up to 300 °C in the inner chamber. The rotor also acted as a fan. The samples which were located inside the rotor could have temperatures maintained constant to better than 0.003 °C. The rotor speed was controlled by computer, since speed variations could also influence the sample chamber temperature. The reading of selected samples was accomplished by using a slotted aluminum plate together with an IR slotted switch [9]. The phase-separation temperature could be measured as a function of centrifuged acceleration up to 1500*g*. With a micrometer precision of ±0.001 mm, the volume ratio of the polymer blend could be measured to better than 0.1%.

The centrifugal apparatus requires only a very small amount (mg) of the precious monodisperse polymer blend components in order to determine the phase-volume ratio. The outer jacket of the sample chamber was made of precision capillary tubing while the inner core was made of solid quartz fiber, leaving the sample volume in the 10-μl range. We have intentionally made the sample chamber dimension much greater than the accessible correlation length.

A detailed test of the coexistence curve measurements using polystyrene in methyl cyclohexane has yielded excellent results [9]. In the coexistence curve studies, each measurement of the coexistence composition needs to be incorporated in a set of simultaneous equations. Thus, each volume composition measurement needs at least two samples with different total polymer volume fractions: ϕ_1 and ϕ_2, with ϕ_p being the volume concentration of the plasticizer. The third sample in each run can be used to check the assumption of equal concentration distribution of the plasticizer among the two phases.

The phase behavior of the polymer blend of polystyrene (PS) and poly(2-chlorostyrene) (P2ClS) has been investigated by many researchers [10–16]. A PS/P2ClS blend has a lower critical solution temperature (LCST). Phase diagrams of PS/P2ClS blends in the presence of 22.6 wt% di-*n*-butylphthalate (DBP) and without the plasticizer (DBP) are presented. DBP is an equally good solvent for both PS and P2ClS polymers.

Polystyrene with weight-average molecular weight $M_w = 3.7 \times 10^4$ g/mole and a narrow molecular weight distribution $M_w/M_n < 1.06$ was purchased from Pressure Chemical Co. Poly(2-chlorostyrene) was radically polymerized in toluene at 60 °C with 2,2′-azobis(isobutyronitrile) as the initiator, and was fractionated by the precipitation method at 35 °C using toluene and methanol as the solvent and the precipitant, respectively. M_w and M_w/M_n were determined by light scattering and gel permeation chromatography to be 2.33×10^5 g/mole and 1.19, respectively, for the blend with DBP and 11.2×10^4 g/mole and 1.09, respectively, for the blend without DBP. Di-*n*-butylphthalate (DBP > 99%) was obtained from Tokyo Kasei Kogyo Co. and used without further purification.

PS/P2ClS blends with different ratios of PS to P2ClS at constant 22.6 wt% DBP were prepared and then dissolved in benzene. The solvent in the stock solution was evaporated to form a highly concentrated solution which was then used to coat a small-diameter (~0.9 mm) quartz fiber. The coated fiber was allowed to dry. The process of coating and drying was repeated until a known amount of the polymer blend (with DBP) was deposited on the quartz fiber tubing. Then the coated fiber was kept in an oven for about 5 h at 70 °C. After that, the coated fiber was under vacuum for about three days to make sure that all the solvent (benzene) had been driven off. The coated fiber was then put into a larger diameter (~1.2 mm) capillary tubing which could be sealed under vacuum with the polymer blend sample and fiber inside. By sealing the polymer blend under vacuum, we could reach temperatures up to 310 °C without any degradation of the PS/P2ClS polymer blend over extended periods of time.

According to the Wegner expansion [17], the coexistence curve data could be analyzed by the following expressions:

$$\phi^+ - \phi^- = \epsilon^\beta (B + B_1 \epsilon^\Delta)\,, \tag{1}$$

$$\phi^+ = \phi_c + a^+ \epsilon^\beta + b^+ \epsilon^{\beta+\Delta}\,, \tag{2}$$

$$\phi^- = \phi_c + a^- \epsilon^\beta + b^- \epsilon^{\beta+\Delta}\,, \tag{3}$$

where ϕ^+ and ϕ^- are volume fractions of PS in the concentrated and dilute coexistence phases, respectively. ϕ_c is the critical volume fraction. ϵ $[=(T-T_c)/T_c]$ is the reduced temperature, with T_c being the critical mixing temperature.

The value of exponent β and of the coefficients a^+, a^-, b^+, and b^- were determined by nonlinear least-squares fitting. Δ was fixed at a value of 0.5. The fitting results of PS/P2ClS blends containing 22.6 wt% DBP and with $T_c = 134.3\,^\circ\mathrm{C}$ are as follows:

$$\beta = 0.33(\pm 0.03)\,,$$

$$a^+ = 53.86,\quad b^+ = -21.49,\quad a^- = -29.93,\quad b^- = 6.16\,.$$

Figure 1 shows the coexistence curve of the PS/P2ClS blend (curve *a*) where the critical temperature T_c was determined independently by a synchrotron SAXS experiment [18]. The details of the method and analysis will be described elsewhere. It is sufficient to note here that the coexistence curve was obtained by using five samples of the polymer blend at different concentrations of ϕ_{PS} (0.299, 0.404, 0.487, 0.559, and 0.612). $\phi_{\mathrm{PS}} = 0.404$ and 0.487 denote the first set while $\phi_{\mathrm{PS}} = 0.299$ (*B*), 0.559 (*C*), and 0.612 (*A*) denote the second set.

Figure 2 shows a fitting of the first-order approximation of Eq. (1) and the corresponding relative deviations (%). The solid line represents the result (with $\log\epsilon < -0.5$) yielding $\beta = 0.30$ and $B = 1.05$. The standard deviation for the first-order fitting is less than 2%.

We fitted the experimental data using different ϵ ranges (see Table I). The results suggest that the β value is around 0.33 for the polystyrene/poly(2-chlorostyrene) blend with 22.6 wt% DBP. The five coexistence curve values at the highest temperatures as shown in Fig. 1(b) have been neglected in the fitting with $\beta \simeq 0.33$.

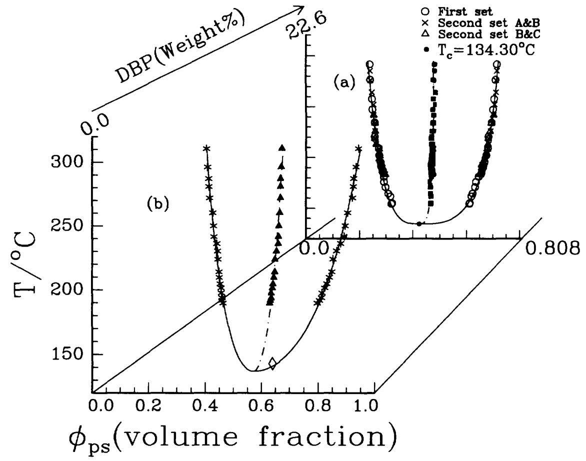

FIG. 1. Coexistence curves of PS/P2ClS blends. Curve *a*: PS with $M_w = 3.7\times10^4$ g/mole, P2ClS with $M_w = 2.33\times10^5$ g/mole, and DBP 22.6 wt%. The solid circle (from synchrotron SAXS) represents the critical mixing point. The results were obtained from two independent sets of experiments with the parameters of Eqs. (1)-(3). *A*, *B*, and *C* of the second set denote the designation of those blend samples with different ϕ_{PS}. Solid squares denote $(\phi^+ + \phi^-)/2$. Curve *b*: PS with $M_w = 3.7\times10^6$ g/mole; P2ClS with $M_w = 2.33\times10^5$ g/mole. The open diamond represents the phase-separation temperatures determined by synchrotron SAXS. T_c for the PS/P2ClS blend without DBP $\cong 137\,^\circ\mathrm{C}$ from Eqs. (1)-(3).

At a given ϕ and different temperatures, we can define a volume fraction ratio f_r by the following relationship:

$$f_r = (\phi^+ - \phi)/(\phi - \phi^-) \quad \text{for } \Delta\phi^+ < \Delta\phi^-\,, \tag{4a}$$

$$f_r = (\phi - \phi^-)/(\phi^+ - \phi) \quad \text{for } \Delta\phi^- < \Delta\phi^+\,, \tag{4b}$$

where $\Delta\phi^+ = (\phi^+ - \phi)$ and $\Delta\phi^- = (\phi^- - \phi)$.

If we substitute the first-order term from Eqs. (1), (2), and (3) into Eq. (4), we then have

$$f_r = (\phi^- - \phi + B\epsilon^\beta)/(\phi - \phi^-) = -1 + B\epsilon^\beta/(\phi - \phi^-)\,, \tag{5a}$$

$$f_r = (\phi - \phi^- + B\epsilon^\beta)/(\phi^+ - \phi) = -1 + B\epsilon^\beta/(\phi^+ - \phi)\,. \tag{5b}$$

From Eq. (5), $f_r = -1$ when $\epsilon = 0$, i.e., $T = T_c$, and $f_r = 0$ at $T = T_p$ (phase-separation temperature) at a given ϕ.

Figure 3(a) shows the volume ratio versus temperature at the compositions ϕ_{PS} of 0.559 and 0.404. The phase-separation temperature T_p could be obtained by extrapolating the volume ratio to zero using different β values.

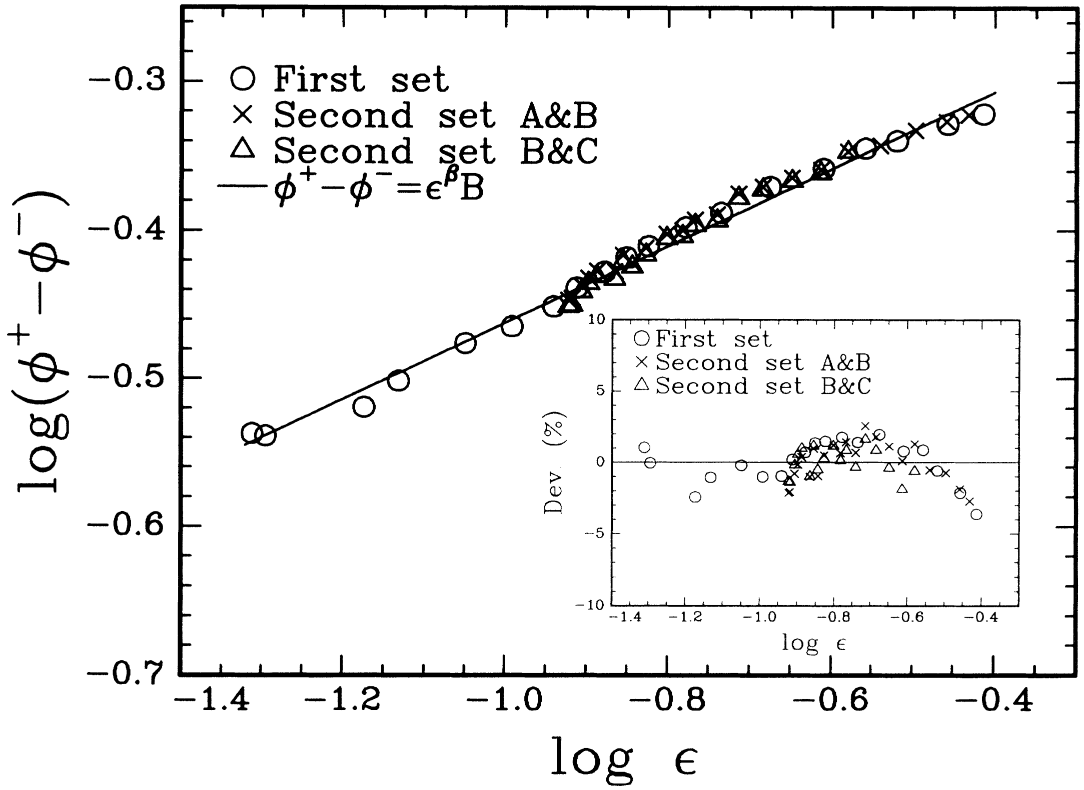

FIG. 2. $\log_{10}(\phi^+-\phi^-)$ vs $\log_{10}\epsilon$. Solid curve represents the fitting by Eq. (1) (without second-order term) with $\log\epsilon < -0.5$. Inset: Plot of relative deviations of data fitting.

Figure 3(b) shows the extrapolated T_p values by nonlinear least-squares fitting of Eq. (5) with different β values. For $\beta=0.5$, $\phi_{\rm PS}=0.559$, $T_p=143.8\,^\circ{\rm C}$ which was 2.8° away from the coexistence curve. For $\beta=0.33$, $T_p=141.3\,^\circ{\rm C}$ which was only 0.3° away from the coexistence curve. For our experimental data, the β values ranged from 0.30 to 0.33 and the T_p values ranged from 140.7 to 141.3 °C. Thus we could conclude that the β value was equal to 0.33. We also obtained a consistent T_p value in agreement with the extrapolated T_p value based on the assumption that DBP was an equally good solvent between PS and P2ClS as denoted by the solid line in Fig. 2. It should be noted that in the semiempirical approach to determine T_p by means of Eq. (5) we have not required an equal solvent quality for DBP with PS and P2ClS.

TABLE I. β values based on different ranges of $\log_{10}\epsilon$ for a PS/P2ClS blend with 22.6 wt% DBP, $M_w({\rm PS})=3.7\times10^4$ g/mole, $M_w({\rm P2ClS})=2.33\times10^5$ g/mole.

Set	$\log\epsilon$ range	β Eq. (5)
First	(a) $(-1.4,-0.4)$	0.26 ± 0.03
	(b) $(-1.2,-0.5)$	0.28 ± 0.02
	(c) $(-1.4,-0.7)$	0.30 ± 0.01
Second *A* and *B*	(d) $(-0.95,-0.4)$	0.27 ± 0.03
	(e) $(-0.95,-0.65)$	0.31 ± 0.01[a]
	(f) $(-0.95,-0.75)$	0.33 ± 0.01[a]
Second *B* and *C*	(g) $(-0.95,-0.5)$	0.29 ± 0.02
	(h) $(-0.95,-0.7)$	0.30 ± 0.01[a]
	(i) $(-0.95,-0.75)$	0.33 ± 0.01[a]

[a] We estimated an accuracy of the critical exponent β (=0.33) to be ±0.03.

By a combination of phase-volume ratio and SAXS experiments, we determined a β value of 0.33 which seems to be independent of the method of our data analysis. In order to assure that our experiments were correct, another polymer blend without DBP was studied. Figure 1 shows a comparison of the temperature-composition diagram for the ${\rm PS}(M_w=3.7\times10^4$ g/mole)/${\rm P2ClS}(M_w=11.2\times10^4$ g/mole) blend without DBP (curve *b*) and the coexistence curve *a* (with DBP) where $\phi_{\rm PS}+\phi_{\rm P2ClS}=1-\phi_{\rm DBP}=0.808$. The solid curve for the polymer blend without DBP can again be represented by Eqs. (1)-(3) with $\Delta=0.5$, $a^+=73.30$, $a^-=-33.77$, $b^+=-22.97$, $b^-=12.96$, $\phi_c=0.57$, $T_c=137\,^\circ{\rm C}$, and $\beta=0.5$. The mean-field behavior with $\beta=0.5$ could be established firmly as expected for the same polymer blend without DBP.

In summary, we have, for the first time to our knowledge, determined a very precise coexistence curve

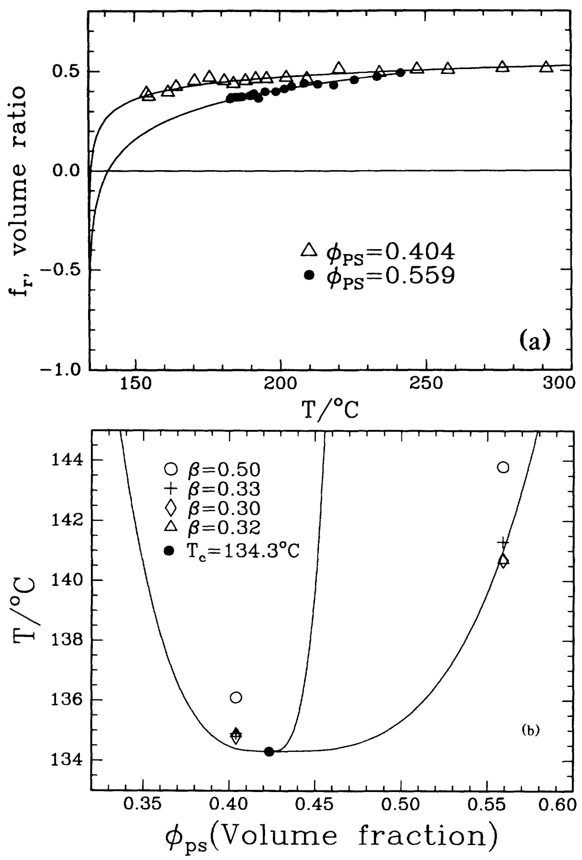

FIG. 3. (a) Fitting of T_p obtained by extrapolating f_r to zero for $\phi_{PS}=0.559$ and 0.404 and $\beta=\frac{1}{3}$. (b) Based on the average of all data in both sets, $T_p=141.0\,°\mathrm{C}$ for composition $\phi_{PS}=0.559$ by means of the computed coexistence curve, which is the solid line (also shown in Fig. 1). The open circle represents the mean-field ($\beta=0.5$) fitting with $T_p=143.8\,°\mathrm{C}$ which is 2.8° above the coexistence curve. The plus represents the Ising ($\beta=0.33$) fitting with $T_p=141.3\,°\mathrm{C}$ which is only 0.3° away from the coexistence curve. The solid circle is the critical mixing point. For composition $\phi_{PS}=0.404$, $\beta=0.30$–0.33 (Ising) is again more consistent with the solid curve.

for a polymer blend in the presence of a plasticizer. It has a β value of $\sim$0.33, implying that the entire coexistence curve covering a temperature range of 150° can be represented by an Ising exponent.

In 1987, Broseta, Leibler, and Joanny [19] presented a theory of phase separation in polymer blends dissolved in a good solvent. Their essential conclusion is that polymer blends in a good solvent should belong to the same universality class as the Ising model with $\beta\simeq0.325$. However, for mixtures of two polymers (without solvent), the critical behavior could be described by the mean-field theory. In the present study, the blend P2ClS/PS with DBP has $\beta\simeq0.33$, and the blend P2ClS/PS without DBP has $\beta\simeq0.5$. The results of the critical behavior of blend P2ClS/PS with and without DBP found in the present work are consistent with their predictions.

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