Electron-Microscopic Study of the Coexistence Curve of Polystyrene/Poly(2-chlorostyrene) Blends

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Received August 11, 1992

ABSTRACT: The coexisting curve of a polystyrene (PS, $M_w = 5 \times 10^4$, $M_w/M_n < 1.06$) and poly(2-chlorostyrene) (P2ClS, $M_w = 9.03 \times 10^4$, $M_w/M_n = 1.10$) blend in the presence of 6.9 wt % di-*n*-butyl phthalate was determined using an image analysis of scanning electron micrographs of the fractured surface of the blends phase-separated in the two-phase region. The coexistence curve could be fitted to $\phi' - \phi'' = A\epsilon^\beta$, where ϕ' and ϕ'' are volume fractions of PS in polymers of the coexisting phases ($\phi' > \phi''$) and ϵ is the reduced temperature. The critical exponent β was determined to be 0.39, which was intermediate between those of the Ising type and of the mean-field type. The crossover from Ising to mean-field type behavior was suggested. The Flory–Huggins theory under a quasi-binary approximation could well describe the coexistence curve using the interaction parameter χ that was quite consistent with those previously estimated from the molecular-weight dependence of cloud points, in spite of the deviation of the system from the mean-field type behavior.

Introduction

Determination of the phase diagram must be the first step in static and kinetic studies of phase-separation phenomena, because the phase diagram provides us the basic information of the thermodynamic stability of the system and the volume ratio of the demixed two phases. In the case of polymer blends, however, it is quite difficult to determine the phase diagram due to the high viscosity of polymer melts. The cloud-point curve is expediently used as the phase boundary quite often,[1-5] which is considered to be close to the coexistence curve in some cases and to be the spinodal curve in other cases. The cloud point is not a static property but a kinetic one; thus, its relation to the static phase behavior is not clear especially in viscous polymer mixtures. For example, the heating/cooling rate dependence of cloud points of polymer blends is reported to be nonlinear at very slow rates and make it difficult to determine "true" cloud points. So, the coexistence curve, a well-defined static property, is indispensable for phase-separation studies of polymer blends. The difficulty in determining the compositions of the coexisting phases in polymer blends lies in that the phase domain cannot usually grow large enough to a macroscopic size under ordinary gravity. There have been some attempts to determine the composition of the microphase in polymer blends. In most cases, such studies use the composition dependence of the glass transition temperature determined by differential scanning calorimetry.[6,7] These are not so precise measurements, and it is necessary that the glass transition temperatures of pure-component polymers are not close to each other. By a more elaborate technique, i.e., by the elastic recoil detection, Bruder and Brenn[8] measured the binodal curve of deuterated polystyrene/poly(styrene-*co*-4-bromostyrene) blends. Very recently, Chu et al.[9,10] developed a specially-designed centrifuge apparatus, which could force the viscous mixture to separate macroscopically at a precisely-controlled temperature, and succeeded in determining the coexistence curve of polystyrene/poly(2-chlorostyrene) blends very precisely by measuring the volume ratio of separated phases. But, a close approach to the critical solution point was still not achieved because of the high viscosity and small density difference between the coexisting phases.

In this study, we demonstrate that an electron-microscopic study can be a powerful method for determining the coexistence curve of polymer blends. From scanning electron-microscopic (SEM) pictures of the fractured surface of the phase-separated blends, one can measure the area ratio of the microphases. To evaluate the area ratio of two coexisting phases, we employed the image analysis of the micrographs. From a set of different initial compositions, one can determine the composition of the two coexisting phases based on the conservation of each component. This method can be used if clear SEM pictures are obtained.

We studied a polystyrene/poly(2-chlorostyrene) (PS/P2ClS) blend, which is a suitable system, since the two phases gave a high contrast in electron micrographs without any artificial sample treatment such as dyeing, owing to a higher electron density of chlorine atoms in P2ClS.

In the following sections, we described the details of the experimental procedure used to determine the coexistence curve and discuss the coexistence curve thus determined. The critical exponent for the coexistence curve was evaluated to examine if it is of the Ising or mean-field type and compared with the previous results.[10] The Flory–Huggins interaction parameter χ was calculated as a function of temperature and compared with those estimated previously from the molecular-weight dependence of the cloud point.[4]

Experimental Section

Materials. P2ClS was radically polymerized in toluene with 2,2′-azobis(isobutyronitrile) as initiator and was fractionated by the precipitation method, followed by a further fractionation with preparative gel permeation chromatography. Weight-average molecular weight M_w and polydispersity index M_w/M_n were determined by light scattering and analytical gel permeation chromatography to be 9.03×10^4 and 1.10, respectively. PS was a product of Pressure Chemical Co. with nominal molecular weight $M_w = 5 \times 10^4$ and $M_w/M_n < 1.06$. Di-*n*-butyl phthalate (DBP) used as an additive was a product of Tokyo Kasei Kogyo Co. and used without further purification.

Sample Preparation. DBP was added to the blend to adjust the location of the phase diagram and the phase separation to appropriate ranges of temperature and rate, respectively. The composition of the total polymer (PS + P2ClS) in the blend was fixed at 93.1 wt %, which corresponded to about 92.5 vol %.

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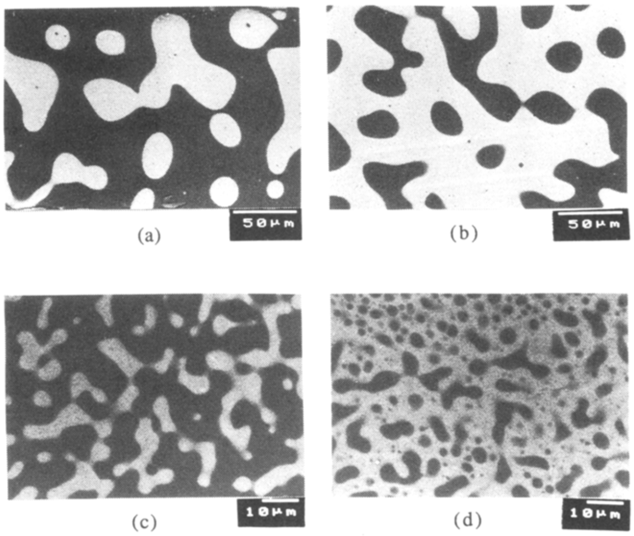

Figure 1. Electron micrographs of the fractured surface of PS/P2ClS blends: (a) PS60, phase-separation temperature $T = 150$ °C, phase-separation time $t = 84$ h; (b) PS46, $T = 150$ °C, $t = 72$ h; (c) PS60, $T = 135$ °C, $t = 231.5$ h; (d) PS46, $T = 135$ °C, $t = 231.5$ h.

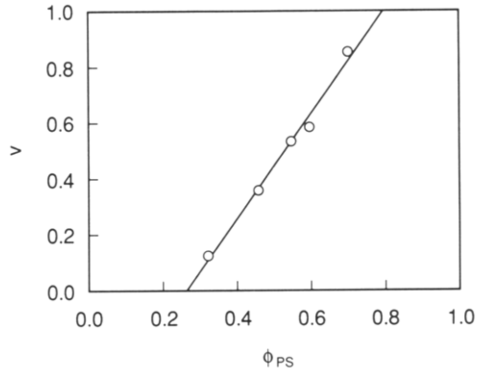

Figure 2. Linear relation of volume fraction v of the PS-rich phase against initial volume fraction ϕ of PS at 165 °C.

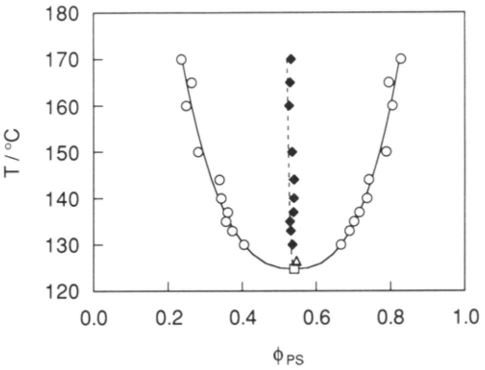

Figure 3. Coexistence curve of PS/P2ClS blends with 6.9 wt % DBP: (○) experimental binodal points; (◆) experimental diameter [$(\phi' + \phi'')/2$ vs T]; (—) calculated coexistence curve (eqs 4 and 5); (- - -) calculated diameter [$(\phi' + \phi'')/2$ vs T] (eq 7); (□) calculated critical point; (△) cloud point of PS55 at the heating rate of 0.1 °C/day.

Ratios of two polymers PS/P2ClS were 66.0/34.0, 55.1/44.9, 50.1/49.9, 41.3/58.7, and 28.3/71.7 wt % or 70.1/29.9, 59.6/40.4, 54.7/45.3, 45.9/54.1, and 32.2/67.8 vol %. In the calculation of the volume fractions, we used densities at 140 °C, namely, 1.005 g mL^{-1} for PS[11] and 1.2098 g mL^{-1} for P2ClS.[12] We refer to these samples as PS70, PS60, PS55, PS46, and PS32, respectively, where the two-digit number indicates the volume fraction of PS. The blends of PS/P2ClS/DBP were cast from about a 3 wt % benzene solution. The cast films were air-dried at 50 °C overnight and then vacuum-dried at 80 °C for 3 days, followed by annealing them in between glass plates with a 0.2-mm-thick spacer at 120 °C in the one-phase region for more than 24 h.

Demixed blend samples for electron-microscopic measurements were obtained by annealing these films in a specially-designed thermostat made of an aluminum block at a desired temperature in the two-phase region, followed by quenching to room temperature, which was much lower than the glass transition temperatures of the two polymers (PS; 100 °C; P2ClS; 130 °C),[4] by taking them out of the thermostat. The temperature was controlled to ±0.03 °C. The annealing time ranged from 5 h to 13 days, depending on the temperature and composition. The time was chosen so that the phase separation reached the late stage, where the composition of the microphase was equal to the equilibrium one, and that a clear, large microdomain was formed.

Electron-Microscopic Measurements. A morphological structure of the fractured surface perpendicular to the film surface was observed by a scanning electron microscope JEOL JSM-T220. Good contrast between the coexisting two phases was obtained without dyeing. Typical micrographs (positive picture) are shown in Figure 1. The dark area and the bright area were identified to be PS-rich and P2ClS-rich phases, respectively, by electron dispersive X-ray analysis.

The area fracton of the dark or bright part in the electron micrograph was computed by using an image analyzer, Pias Co. LA-525. The following requirements must be satisfied in order to regard the area fraction as being identical to the volume fraction: (1) The depth of focus of SEM is shallow enough compared with the domain size, and (2) the sampling number of domains is large enough for taking a statistic average. The micrographs were taken by detecting secondary electrons to check the first requirement. The intensity of the secondary electrons is weak, and only the electrons emitted from thin surface layers can be detected. Morphological structures of microphases observed by secondary electrons were identical with those by the usual reflected electrons, which indicates that an electron-micrographic image is regarded as a domain structure at the surface, being thin compared with the image size.

The compositions ϕ' and ϕ'' (volume fractions of PS in the total polymers) of the coexisting phases can be determined from a pair of information of the phase volume fractions v_i and the initial or total compositions ϕ_i of PS, based on the quasi-binary approximation. In the quasi-binary approximation, the volume fraction of the plasticizer (DBP) is assumed to be constant in any phases. This is considered to be a reasonable approximation for the present system because the amount of DBP was very little and DBP is a thermodynamically good solvent to both PS and P2ClS. In fact, the validity of the quasi-binary approximation was confirmed by the linear relation between v and ϕ, which is required from the lever rule

$$v = (\phi - \phi')/(\phi'' - \phi') \tag{1}$$

as shown in Figure 2. The linear relation has also been obtained for the other PS/P2ClS/DBP.[10] From eq 1, the following equations are derived:

$$\phi' = \{(1 - v_2)\phi_1 - (1 - v_1)\phi_2\}/(v_2 - v_1) \tag{2}$$

$$\phi'' = (v_2\phi_1 - v_1\phi_2)/(v_2 - v_1) \tag{3}$$

ϕ' and ϕ'' were evaluated by using PS60 and PS46 blend samples, and the other samples were used for checking the results.

Results and Discussion

Coexistence Curve and Critical Exponent. Figure 3 shows the coexistence curve obtained. According to the Wegner expanson,[13] the coexistence curve near the critical point could be analyzed by the expressions

$$\phi' = \phi_c + a'\epsilon^{\beta} + b'\epsilon^{\beta+\Delta} \tag{4}$$

$$\phi'' = \phi_c + a''\epsilon^{\beta} + b''\epsilon^{\beta+\Delta} \tag{5}$$

or

$$\phi' - \phi'' = A_-\epsilon^{\beta} + B_-\epsilon^{\beta+\Delta} \quad (6)$$

$$\phi' + \phi'' = 2\phi_c + A_+\epsilon^{\beta} + B_+\epsilon^{\beta} + \beta_+\epsilon^{\beta+\Delta} \quad (7)$$

where $A_- = a' - a''$, $B_- = b' - b'$, $A_+ = a' + a''$, and $B_+ = b' + b''$. ϕ_c is the critical composition, β is the critical exponent, ϵ is the reduced temperature distance from the critical temperature T_c, and Δ is fixed at 0.5. ϵ is usually defined as $\epsilon = (T - T_c)/T_c$. However, another definition $\epsilon = (\chi - \chi_c)/\chi_c$ is sometimes used in polymer blend systems when the interaction parameter χ is known. When the temperature dependence of χ is expressed as a linear function of $1/T$ as usually assumed, $(\chi - \chi_c)/\chi_c$ is proportional to $1 - T_c/T$ and we used the definition of ϵ, that is, $\epsilon = 1 - T_c/T$.

By nonlinear least-squares fitting of the first-order approximation ($B_+ = B_- = 0$) of eqs 6 and 7, the following values were obtained.

$$T_c = 124.8\ °\text{C}, \quad \phi_c = 0.54_1, \quad \beta = 0.38_8, \quad a' = 0.68_6, \quad a'' = -0.73_4$$

The calculated curves fitted by eqs 4–7 are drawn in Figure 3. If β was fixed at the Ising value of 0.33 or the mean-field value 0.5,[14] T_c was evaluated by the least-squares fitting to be 126.8 or 120.3 °C, respectively. Double-logarithmic plots of $\Delta\phi$ (= $\phi - \phi''$) against ϵ with these three values of T_c are shown in Figure 4. The plot with $\beta = 0.33$ gave a slightly upward concave curve and the plot with $\beta = 0.5$ gave a slightly upward convex curve, so that the critical exponent is greater than 0.33 (Ising) but smaller than 0.5 (mean field). This result is quite consistent with the previous results:[10] A PS/P2ClS blend with DBP of 22.6 wt % has the Ising-type critical exponent 0.33, while a PS/P2ClS without DBP shows the mean-field type behavior of the coexistence curve, $\beta = 0.5$. The DBP content of the present blend is intermediate between them, so that the β-value may also be between 0.33 and 0.5.

The intermediate value of β suggests the crossover[15] from Ising to mean-field type behavior. To see this crossover more clearly, $(\Delta\phi)^{1/\beta}$ with $\beta = 0.33$ and 0.5 was plotted against $1/T$ in Figure 5. Because of the lack of accuracy of the data, we cannot identify the crossover region clearly, but the plots with $\beta = 0.33$ appear to show the deviation from the linear relation, suggesting the presence of the crossover region around $10^3T^{-1}/K^{-1} = 2.4$ which corresponds to 143.5 °C. The critical temperature T_c estimated by the extrapolation of the plots with $\beta = 0.33$ in the Ising region was 125.8 °C, which must be the true critical temperature. The mean-field critical point T_{mc} was determined by the $(\Delta\phi)^2$ vs $1/T$ plots in the mean-field region to be 116.7 °C. The crossover region seems to be located around 18 °C higher than T_c and 27 °C higher than T_{mc}. More accurate data of the coexistence curve are necessary to tell about the crossover more definitely.

Since the phase separation becomes extremely slow near the critical temperature, the coexistence curve could not be determined by the present method. In order to estimate the upper bound of the critical temperature, the cloud point of PS55 was visually measured at a very small heating rate 0.1 °C/day to be between 126 and 127 °C, which was shown in Figure 3. The coexistence curve and the critical point must be below this point. This is consistent with the result $0.33 < \beta < 0.5$, recalling that $T_c = 126.8$ °C for $\beta = 0.33$ and $T_c = 120.3$ °C for $\beta = 0.5$.

In the above treatment, we have defined that $\epsilon = 1 - T_c/T$. If ϵ is alternatively defined as $\epsilon = (T - T_c)/T_c$, then the exponent β was obtained to be 0.35_8, which is slightly smaller than the value obtained with the previous definition of ϵ, but the conclusion is not be changed.

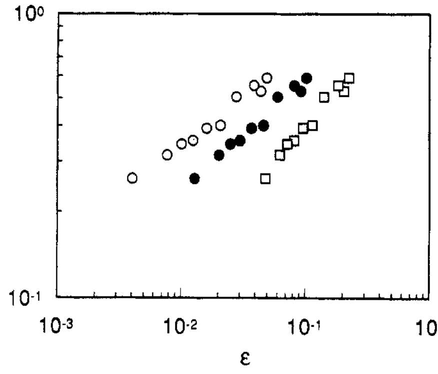

Figure 4. Double-logarithmic plots of $\Delta\phi$ against ϵ (=$1 - T_c/T$) with different T_c (=126.75, 124.80, and 120.33 °C) that give the critical exponent β = 0.33 (○), 0.388 (●), and 0.5 (□), respectively. Plots of ○ and □ are shifted along the ϵ-axis by factors of ±2, respectively.

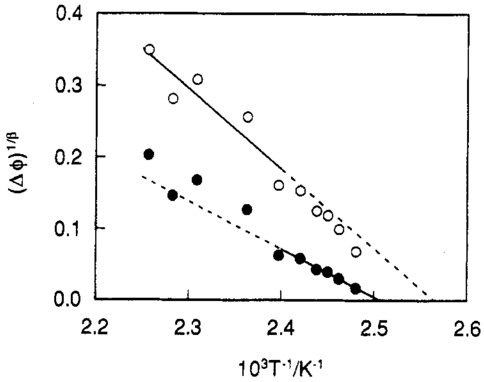

Figure 5. Test of the crossover from Ising to mean-field type behavior: (●) β = 0.33; (○) β = 0.5; (—) linear least-squares fittings for five data points at higher (–○–) and lower (–●–) ranges of temperature: (- - -) extrapolated lines of the fitting line.

Mean-Field Theory and the χ-Parameter. Although the coexistence curve was not of the mean-field type, the χ-parameter as a function of temperature could reasonably be evaluated from the coexistence curve (temperature dependence of ϕ' and ϕ'').

The free energy of mixing ΔF per lattice site is written under the quasi-binary approximation[16] as

$$\Delta F/(\Phi_p kT) = (\phi_1/P_1)\ln\phi_1 + (\phi_2/P_2)\ln\phi_2 + \chi_{eff}\phi_1\phi_2 \quad (8)$$

Here, Φ_p is the volume fraction of total polymers in the blend, ϕ_i is the polymer ratio, i.e., the volume fraction of polymer i in total polymers ($\phi_1 + \phi_2 = 1$), and P_i is the degree of polymerization. χ_{eff} is an effective χ-parameter including solvent (plasticizer) effects, which is related to the real χ-parameter as

$$\chi_{eff} = \Phi_p\chi$$

χ_{eff} was assumed to have no polymer–composition dependence. The volume fractions ϕ_i' and ϕ_i'' of the coexisting phases were calculated from the free energy of eq 8 by conventional thermodynamics for a given set of P_1, P_2, and χ_{eff}. We put $P_1 = 4.97 \times 10^4/103$ (PS) and $P_2 = 7.46 \times 10^4/103$ (P2ClS), taking the molar volume of the PS monomer (103 mL mol^{-1}) as the monomer size.

The value of χ_{eff} was determined such that the calculated value of $\Delta\phi$ agreed with the experimental one. Figure 6 shows the temperature dependence of χ_{eff} thus calculated. It should be noted that the values of χ_{eff} here are those for the PS monomer size of 103 mL mol^{-1}. The linear least-squares fitting to the χ_{eff} vs $1/T$ plots led to the

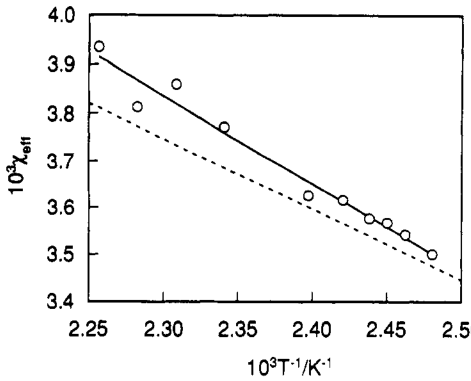

Figure 6. Temperature dependence of the effective χ-parameter of PS/P2ClS with DBP (6.9 wt %): (—) present work (eq 9); (- - -) ref 4 (eq 10 with $\chi_{eff} = \chi\Phi_p$).

equation

$$\chi_{eff} = 0.00810 - 1.85/T\ (\mathrm{K}) \qquad (9)$$

or

$$\chi = \chi_{eff}/\Phi_p = 0.00875 - 2.00/T\ (\mathrm{K}) \qquad (9')$$

where $\Phi_p = 0.925$. This is in good agreement with

$$\chi = 0.0078 - 1.63/T\ (\mathrm{K}) \qquad (10)$$

per the PS monomer size 103 mL mol^{-1}, which was previously determined by the molecular-weight dependence of cloud points for PS/P2ClS blends without DBP.[4] χ_{eff} was calculated from eq 10 as $\chi_{eff} = \chi\Phi_p = 0.0072 - 1.51/T(\mathrm{K})$ and drawn in Figure 6.

Equation 8 gives the critical composition ϕ_c as

$$\phi_c = 1/[1 + (P_1/P_2)^{1/2}] \qquad (11)$$

which predicts $\phi_c = 0.551$ for the present case. This is in very good agreement with the value determined experimentally in the previous section ($\phi_c = 0.54_1$). In Figure 7 is shown the coexistence curve with the diameter [$(\phi' + \phi'')/2$ vs T] calculated by the mean-field equation (eq 8) with the χ-parameter of eq 9, along with the experimental result. The fitting is satisfactory. This result suggests the validity of the present analysis based on the approximations of quasi-binary treatment and composition-independent χ. It should be noted that, if one sees Figure 7 very closely, one can notice a slight disagreement in the shape of the coexistence curve between the theoretical and experimental results. Obviously, the deviation from the mean-field behavior in the present blend is responsible for the disagreement. In this sense, the values of the χ-parameter obtained near the critical temperature are only apparent ones.

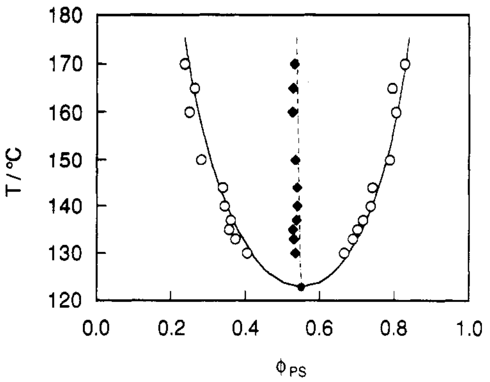

Figure 7. Comparison of the coexistence curve between experiments and the mean-field type calculation: (○) experimental binodal points; (◆) experimental diameter [$(\phi' + \phi'')/2$]; (—) calculated from eq 8 with eq 9; (- - -) calculated diameter from eq 8 with eq 9; (●) calculated critical point.

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Registry No. PS, 9003-53-6; P2ClS, 26125-41-7.