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Coexistence curves of polystyrene/poly(dimethylsiloxane) blends

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The coexistence curves of blends of polystyrene (PS, $M_w = 600$ and 2.2×10^3 g mol^{-1}) and poly(dimethylsiloxane) (PDMS, $M_w = 460$, 1400, 3700 and 2.3×10^5 g mol^{-1}) were determined using a specially designed refractometer. The coexistence curve of the oligomer blend PS ($M_w = 600$)/PDMS ($M_w = 460$) was of the upper critical solution temperature type, and sensitively reflected molecular-weight polydispersity of the PS, although the polydispersity index M_w/M_n was less than 1.10. The coexistence curve at the critical composition could be fitted to $\phi_\pm = a_\pm \varepsilon^\beta + b_\pm \varepsilon^{\beta+\Delta}$, where ϕ_+ and ϕ_- are the volume fractions of PDMS of the coexisting phases ($\phi_+ > \phi_-$), the exponent Δ is 0.5 and ε is the reduced temperature. The critical exponent β was determined to be 0.33_6, which was that for non-renormalized Ising behaviour, showing no polydispersity effect. The Flory–Huggins theory could reasonably describe the coexistence curves of blends with different molecular weights, although it showed a slight discrepancy for the effects of molecular-weight asymmetry on the coexistence curve. By fitting the calculated coexistence curves to the experiments, the interaction parameter χ was evaluated as a function of temperature. The obtained χ parameter involved a large enthalpy term, dominating the entropy term, and indicated that PS/PDMS was an extremely immiscible blend compared with other reported blends. Critical fluctuation effects on the coexistence curve were also discussed.

(Keywords: coexistence curve; polystyrene; poly(dimethylsiloxane))

INTRODUCTION

The coexistence curve of a liquid mixture provides us with basic information on the thermodynamic stability of the system and the volume ratio of the two demixed phases, which play important roles in the static and kinetic behaviour of phase-separation phenomena. However, it is very difficult to determine the coexistence curve of polymer mixtures owing to high viscosity. The cloud-point curve is often used as the phase boundary[1–5]. The cloud point involves kinetic effects, so that it is not a well defined static property; and, furthermore, the coexistence curve cannot be approximated by the cloud point in principle as long as the mixture is not a pure binary system. Some attempts have been made to determine the coexistence curve with various approaches: differential scanning calorimetry[6,7] and a more elaborate technique, elastic recoil detection[8], to measure microphase composition in polymer blends, and a specially designed centrifuge apparatus[9,10] and electron micrographic study[11] to determine the volume ratio of coexisting phases.

In this study, we use differential refractometry to determine directly and precisely the composition of coexisting phases. This method is usually restricted to oligomer mixtures owing to the requirement of low viscosity, but is very useful because of the particular significance of coexistence curves of oligomer blends in studying polymer blends. That is, it provides us with quantitative information on the miscibility of polymer blends even for immiscible polymer pairs, since, if the degree of polymerization is low enough, the majority of blends must be partially miscible.

We made a specially designed refractometer, which could be operated at high temperatures up to 200°C, and studied the coexistence curves of polystyrene/poly(dimethylsiloxane) (PS/PDMS) blends with low molecular weights. The critical exponent for the coexistence curve was evaluated to confirm that the exponent for oligomer blends is of Ising type. The Flory–Huggins interaction parameter χ was estimated as a function of temperature for blends of different molecular weights. Effects of critical fluctuations were also discussed.

EXPERIMENTAL

Materials

Poly(dimethylsiloxane)s (PDMS) were products of Shin-etsu Co. Ltd. PDMS of the highest molecular weight was used after being roughly fractionated to eliminate low-molecular-weight fractions. Details of purification and characterization for other PDMS have been described elsewhere[12]. Polystyrenes (PS) were products of Pressure Chemical Co. Sample codes and characteristics of PDMS and PS samples are listed in *Table 1*.

Coexistence curve measurements

Compositions of coexisting phases were measured by a specially designed refractometer, which is schematically illustrated in *Figure 1*. A blended sample (S) was put into

a square optical cell (C) sealed at the top with a Teflon sheet fixed by a screw in an aluminium holder (H). These were dipped in reference liquid in a glass cell (G) such that the cell (C) was tilted by 90° to the light beam. These were installed in a copper-block thermostat (B). A He–Ne laser light beam with thickness of about 1 mm was expanded by two concave lenses to be a parallel beam of 25 mm diameter, and was used as the light source. The light incident on the various surfaces of the square cell was refracted at the surfaces into different directions. The difference in the direction of the refracted light reflected the difference in refractive index between the sample and the reference liquid, which was determined by the composition of the coexisting phases of the phase-separated sample. Upper and lower phases gave different light directions according to their composition difference. The difference in direction of the transmitted light was detected by focusing the light on the diode array of a CCD camera, and was measured by a microcomputer connected to the camera. Temperature could be increased up to more than 200°C, being controlled to within ±0.05°C. PDMS, squarane, di-n-octyl phthalate, poly(phenylmethylsiloxane) and their mixtures were selected as reference liquids according to the refractive indices of the phase-separated samples. The relation between the composition and the difference in refracted light direction

Table 1 Characteristics of samples

	Sample code	M_w	M_w/M_n
PDMS	PDMS5	460	1.0[a]
	PDMS14	1400	1.10
	PDMS37	3700	1.24
	PDMS2K	2.3×10^5 [b]	2[b]
PS	PS6	600	<1.10
	PS22	2200	<1.10

[a] PDMS5 is substantially the pentamer
[b] By size exclusion chromatography with PS standard

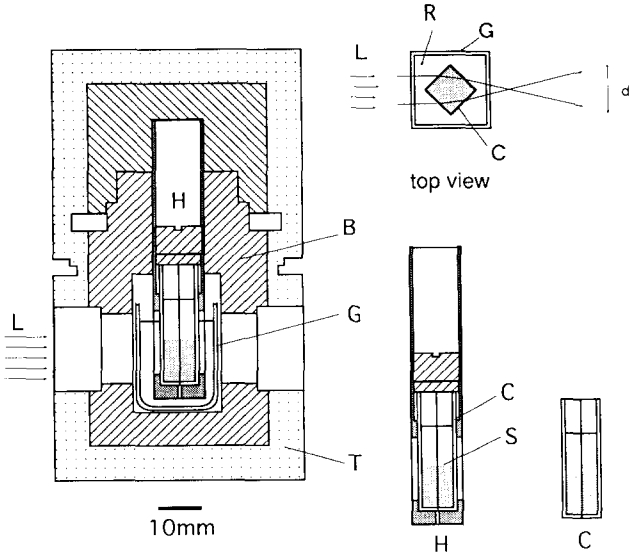

Figure 1 Schematic picture of a refractometer for measuring the composition of coexisting phases: S, sample; C, optical cell; H, aluminium holder; G, glass cell for reference liquid (R); B, copper-block thermostat; T, Teflon thermal insulator; L, light (expanded laser beam); *d*, difference in transmitted-light direction

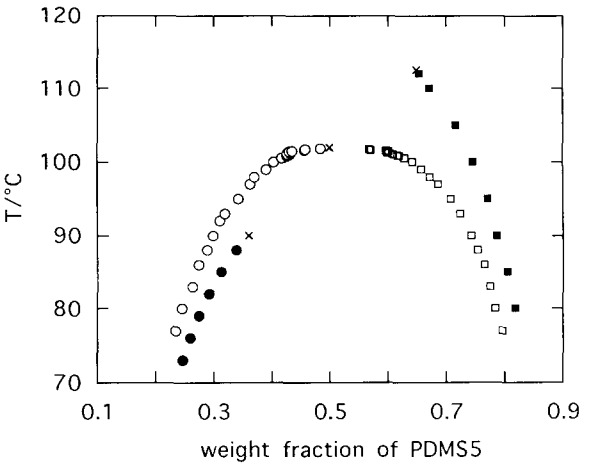

Figure 2 Coexistence curves of PS6/PDMS5 blends with different total compositions W_t: (■) PDMS-rich phase for $W_t=0.65$; (□) PDMS-rich phase for $W_t=0.50$; (○) PS-rich phase for $W_t=0.50$; (●) PS-rich phase for $W_t=0.36$; (×) cloud points

was calibrated before the measurements. In the present configuration of the optical system, the measurable span of refractive index for one reference liquid was about 0.035, and the reading resolution was 4×10^{-5} in refractive index. The difference in refractive index between pure PS and PDMS was about 0.2, so that six liquids with different refractive indices were used as reference liquid, and the resolution was 0.02% in composition of PS/PDMS. The accuracy of composition measurements was less than 0.1% in the present experiments. To obtain the composition in volume fraction, we used the following equations for specific volume v as a function of temperature t (°C), which were based on data from ref. 13 for PS and data provided by Shin-etsu Co. Ltd for PDMS:

$$v(\mathrm{PS})/(\mathrm{ml\,g^{-1}}) = 0.9329 + 6.06\times10^{-4}t \quad \text{for PS6}$$
$$0.9111 + 5.62\times10^{-4}t \quad \text{for PS22}$$

$$v(\mathrm{PDMS})/(\mathrm{ml\,g^{-1}}) =$$
$$1.1455[1+0.00124(t-25)] \quad \text{for PDMS5}$$
$$1.0695[1+0.00106(t-25)] \quad \text{for PDMS14}$$
$$1.0471[1+0.00099(t-25)] \quad \text{for PDMS37}$$
$$1.0225[1+0.00094(t-25)] \quad \text{for PDMS2K}$$

RESULTS AND DISCUSSION

Coexistence curves

Figure 2 shows the coexistence curves of PS6/PDMS5 blends with total composition W_t (before phase separation) of 0.36, 0.50 and 0.65 in weight fraction of PDMS. The compositions of both coexisting phases are shown for $W_t=0.5$, while for $W_t=0.36$ and 0.65 those of one of the coexisting phases, i.e. the majority phase, only are shown. Compositions of the minority phase were not measured because of experimental difficulty, since the volume of the minority phase was so small for these total compositions of mixtures. One can see that the composition of coexisting phase depends on the total composition W_t, indicating the presence of polydispersity in the samples. At the critical composition, the top of the coexistence curve has to be at W_t, so that the blend of $W_t=0.50$ is approximately the critical blend, showing that the critical

temperature $T_c \simeq 102°C$ and the critical composition $W_c \simeq 0.5$. The cloud point can be defined as the temperature at which the composition of the coexisting phase is the same as W_t. Around W_c, the cloud point at PDMS weight fractions larger than W_c is higher than those of lower PDMS contents. This indicates that the polydispersity effect predominantly comes from the polydispersity of PS6 (ref. 5)*, which is consistent with the characteristics of the PS6 and PDMS5 samples. The polydispersity effect might be enhanced by the composition dependence of the interaction parameter[14].

Figure 3 represents the molecular-weight dependence of the coexistence curve for blends of $W_t = 0.5$. The miscibility increases with increasing temperature in any molecular-weight blends, so that the phase behaviour is of upper critical solution temperature (*UCST*) type. As the molecular weight increases, the miscibility of PDMS with PS decreases very rapidly. Higher-molecular-weight component (HMWC) is less dissolved into LMWC-rich phase than LMWC into HMWC-rich phase. This asymmetry due to molecular-weight asymmetry is consistent with theoretical expectation.

Critical exponent

Since the blend of $W_t = 0.5$ is approximately the critical blend, the critical behaviour of the coexistence curve for this particular blend is examined here. According to the Wegner expansion[15], the coexistence curve near the critical point could be analysed by the following expressions:

$$\phi_+ = \phi_c + a_+\varepsilon^\beta + b_+\varepsilon^{\beta+\Delta} \quad (1)$$

$$\phi_- = \phi_c + a_-\varepsilon^\beta + b_-\varepsilon^{\beta+\Delta} \quad (2)$$

or

$$\phi_+ - \phi_- = A_-\varepsilon^\beta + B_-\varepsilon^{\beta+\Delta} \quad (3)$$

$$\phi_+ + \phi_- = 2\phi_c + A_+\varepsilon^\beta + B_+\varepsilon^{\beta+\Delta} \quad (4)$$

where ϕ_+ and ϕ_- are the compositions of the coexisting phases ($\phi_+ > \phi_-$); $A_- = a_+ - a_-$, $B_- = b_+ - b_-$, $A_+ = a_+ + a_-$ 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. The reduced temperature ε is usually defined as $\varepsilon = (T - T_c)/T_c$. However, another definition $\varepsilon = (\chi - \chi_c)/\chi_c$ is sometimes used in polymer blend systems when the interaction parameter χ is known. If 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 $T_c/T - 1$, which we used as the definition of ε, that is $\varepsilon = T_c/T - 1$, in the present analysis. The composition ϕ is hereafter taken as composition in volume fraction of PDMS.

* The effects of molecular-weight asymmetry on phase separation of polymer mixtures appear, as the result of asymmetry of combinatorial entropy, in such a way that the critical consolution point locates at a lower concentration of higher-molecular-weight component (HMWC). This leads to the following prediction. Supposing that polymer A has polydispersity, higher-molecular-weight fractions in polymer A yield higher cloud points at polymer A-lean compositions, while lower-molecular-weight fractions give lower cloud points at polymer A-rich compositions. In view of this, polydispersity of PS must be dominant in the present case, since the cloud point of PS-lean composition is higher

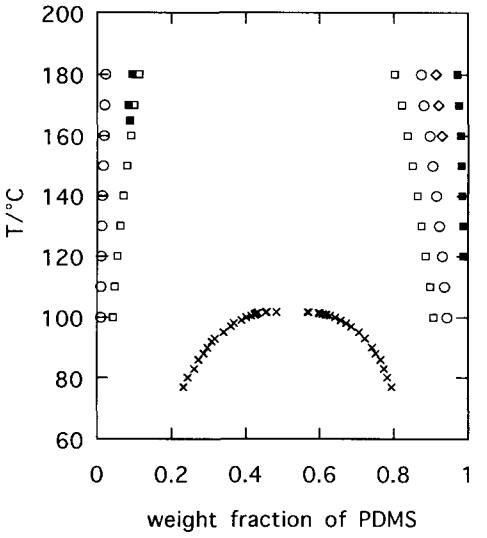

Figure 3 Coexistence curves of PS/PDMS blends with different molecular weights: (×) PS6/PDMS5; (□) PS6/PDMS14; (○) PS6/PDMS37; (◇) PS6/PDMS2K; (■) PS22/PDMS5

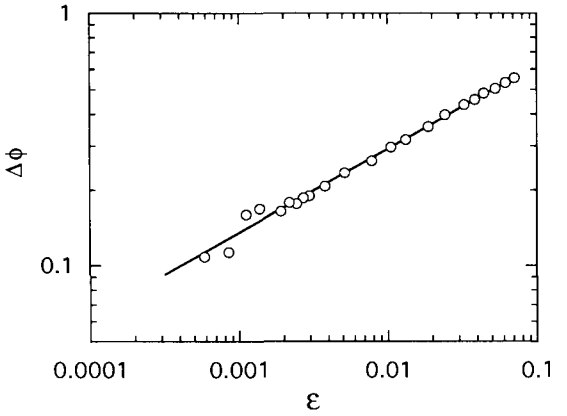

Figure 4 Log–log plots of $\Delta\phi$ against ε for PS6/PDMS5. The full line indicates the calculated value by the Wegner expansion of equation (3) with $\beta = 0.33_6$ ($T_c = 101.92°C$, $A_- = 1.376$ and $B_- = 0.899$)

By non-linear least-squares fitting of equation (3) to the data in the whole experimental range of temperature, taking T_c, β, A_- and B_- as adjustable parameters, the following values were obtained: $T_c = 101.94°C$, $\beta = 0.34_5$, $A_- = 1.444$ and $B_- = -0.2283$. However, it was difficult to determine exact, reliable values of the parameters because of the shallow minimum of the square deviation, although the minimum was located around $\beta = 0.34_5$ (0.33 to 0.36). For this reason, the value of β was first determined by the least-squares fitting of equation (3) to the data of $T \geqslant 93°C$ ($\varepsilon \leqslant 0.024_3$) putting $B_- = 0$, which may be acceptable because of the small value of B_-. Then, using the fixed value of $\beta = 0.336$ thus obtained, values of T_c, A_- and B_- were determined by fitting equation (3) to the data over the whole temperature range ($\varepsilon \leqslant 0.071_1$): $T_c = 101.92°C$, $A_- = 1.376$ and $B_- = -0.0899$. In *Figure 4* are shown log–log plots of $\Delta\phi$ ($= \phi_+ - \phi_-$) against ε (putting $T_c = 101.92°C$), along with the fitting curve of equation (3).

With these values of T_c and β, values of ϕ_c, A_+ and B_+ were determined by equation (4): $\phi_c = 0.56_3$,

$A_+ = 0.2226$ and $B_+ = -1.070$. From these values of A_+, A_-, B_+ and B_-, those of a_+, a_-, b_+ and b_- were calculated. The values finally obtained are summarized as follows:

$$T_c = 101.92°C,\ \phi_c = 0.56_3,\ \beta = 0.33_6,$$

$$a_+ = 0.7993, a_- = -0.5767, b_+ = -0.5798, b_- = -0.4899$$

The coexistence curve and diameter $[(\phi_+ + \phi_-)/2$ vs. $T]$ calculated by using these values are drawn in *Figure 5*, along with the experimental values.

Since the total composition of the blend, which is 0.557 in volume fraction, is very close to the obtained ϕ_c, it is acceptable that the blend has been regarded as the critical blend. In the present temperature range ($\varepsilon \leqslant 0.071_1$), the contribution of the higher-order term $\varepsilon^{\beta+\Delta}$ is minor (see *Figure 4*). The value of the critical exponent β is exactly of Ising type for binary fluid mixtures[16]. Polymer blends must exhibit mean-field-type critical behaviour[17], where $\beta = 0.5$, except very near the critical point. This is not the case in the present oligomer blend because the molecular weights are very low. Impurity in binary mixtures may show the renormalized critical exponent, which is larger than that for pure binary mixtures[18]. In the present system, however, the critical exponent is the non-renormalized one, although the system is not a pure binary system, but has polydispersity.

The mean-field theory and χ parameter

Although the coexistence curve near the critical point 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_-), excluding the vicinity of the critical point.

According to the Flory–Huggins type mean-field theory, the free energy of mixing ΔF per lattice site for a binary polymer mixture is written as:

$$\Delta F/kT = (\phi_1/P_1)\ln\phi_1 + (\phi_2/P_2)\ln\phi_2 + \chi\phi_1\phi_2 \quad (5)$$

Here, ϕ_i is the volume fraction of polymer i ($\phi_1 + \phi_2 = 1$) and P_i is the polymeric index; χ is the interaction parameter per lattice site. The volume fractions $\phi_{i\pm}$ of coexisting phases were calculated from the free energy of equation (5), under the assumption that χ was independent of polymer composition, for a given set of P_1, P_2 and χ, by conventional thermodynamics. The polymeric index P was evaluated by the definition P=(polymer volume)/(lattice-site volume), taking the volume of PS monomer as the site volume v_0. The value of χ was determined such that the calculated value of $\Delta\phi$ ($=\phi_+ - \phi_-$) agreed with the experimental one. *Figure 6* shows the temperature dependence of χ thus obtained. It should be noted that the values of χ here are those per PS monomer of molar volume $V_0 = 103.3$ ml mol^{-1} and 101.6 ml mol^{-1} for PS6 and PS22 at 100°C, respectively.

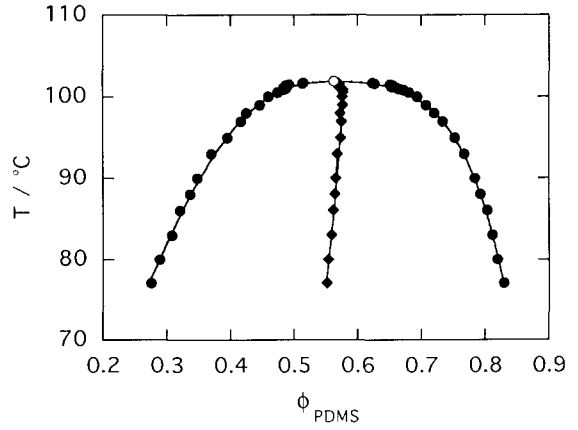

Figure 5 Coexistence curve and diameter $[(\phi_+ + \phi_-)/2$ vs. $T]$ for PS6/PDMS5: (——) fitting curves of the Wegner expansion (equations (1) and (2) — see the text about the parameters); (○) critical point; (●) experimental coexistence curve; (◆) experimental diameter

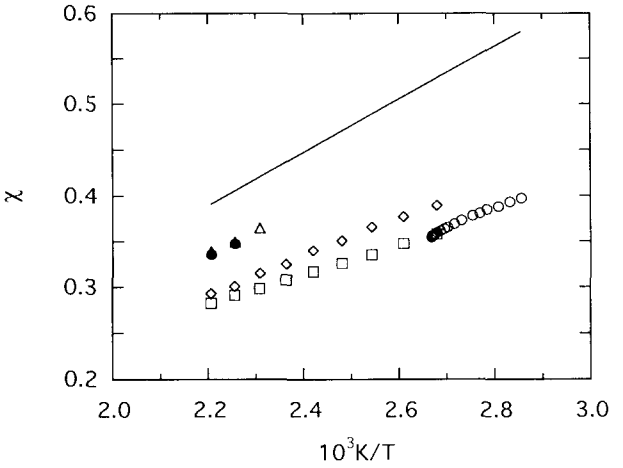

Figure 6 Temperature dependence of χ parameters: (○) PS6/PDMS5; (□) PS6/PDMS14; (◇) PS6/PDMS37; (△) PS6/PDMS2K; (●) PS22/PDMS5; (— · —) high-molecular-weight PS/PDMS (equation (11) with $V_0 = 101.6$ ml mol^{-1})

The value of χ increases slightly with increasing molecular weight, which is likely since the blended liquid with higher molecular weight condenses more densely in the present low-molecular-weight range. One can note that the χ vs. $1/T$ plot for PS6/PDMS5 bends down sharply near the critical point (see also *Figure 8*), which arises from the discrepancy with the mean-field theory. So, the χ values near the critical point are apparent and the rapid change with temperature is artificial. Detailed discussion on this issue will be made later.

The linear least-squares fitting to the χ vs. $1/T$ plots led to the following equations in terms of χ/V_0 (V_0 = molar site volume), which are independent of the site size:

$$(\chi/V_0)/(\text{mol ml}^{-1}) = 1.849/T(\text{K}) - 0.00143 \quad \text{for PS6/PDMS5} \quad (6)$$

$$(\chi/V_0)/(\text{mol ml}^{-1}) = 1.527/T(\text{K}) - 0.00063 \quad \text{for PS6/PDMS14} \quad (7)$$

$$(\chi/V_0)/(\text{mol ml}^{-1}) = 2.027/T(\text{K}) - 0.00164 \quad \text{for PS6/PDMS37} \quad (8)$$

$$(\chi/V_0)/(\text{mol ml}^{-1}) = 2.446/T(\text{K}) - 0.00213 \quad \text{for PS6/PDMS2K} \quad (9)$$

$$(\chi/V_0)/(\text{mol ml}^{-1}) = 2.372/T(\text{K}) - 0.00193 \quad \text{for PS22/PDMS5} \quad (10)$$

In the case of PS6/PDMS5, the fitting was made for the temperature region $T \leqslant 93$°C, excluding the critical region for the reason mentioned above.

Extrapolating the above equations to infinitely high molecular weight for both of PS and PDMS*, the following equation was obtained, which is also shown in *Figure 6:*

$$(\chi/V_0)/(\text{mol ml}^{-1}) = 2.940/T(\text{K}) - 0.00247 \quad (11)$$

for PS/PDMS of high M_w.

Temperature dependences of χ for some other blends of *UCST*-type phase behaviour have been reported: $(\chi/V_0)/(\text{mol ml}^{-1}) = 4.49 \times 10^{-2}/T - 2.20 \times 10^{-5}$ for PDMS/poly(methylethylsiloxane) (PMES)[5] and $(\chi/V_0)/(\text{mol ml}^{-1}) = 0.493/T - 0.81 \times 10^{-3}$ for PS/polybutadiene (PBD)[3]. Comparing the χ value at 400 K, the values of χ/V_0 are 0.090, 0.422 and 4.88 mol ml^{-1} for PDMS/PMES, PS/PBD and PS/PDMS, respectively. One can see that PS/PDMS has a large χ value, being an extremely immiscible blend. If the χ parameter is divided into an enthalpy term χ_H and an entropy term χ_S, $\chi = \chi_H + \chi_S$, where χ_S is negative because of *UCST*-type blends, the two contributions in these blends are as follows: $\chi_H/|\chi_S| = 0.112/0.022$, 1.23/0.81 and 7.35/2.47. Immiscibility of PS/PDMS primarily comes from the enthalpy, i.e. energetic interaction change with mixing, as in the case of PDMS/PMES, although they have a large difference in the magnitude of interactions. PS/PDMS has a rather large $|\chi_S|$, which is larger than χ_S of PS/PBD, but has more energetic interaction change, χ_H, dominating over the entropy change $|\chi_S|$.

Equation (5) gives the critical composition ϕ_c as:

$$\phi_c = [1 + (P_1/P_2)^{1/2}]^{-1} \quad (12)$$

which predicts $\phi_c = 0.504$ for PS6/PDMS5. This is not in good agreement with the value determined experimentally in the previous section ($\phi_c = 0.56_3$). In *Figure 7* are shown the coexistence curves calculated by equation (5) with the χ parameter of equations (7)–(10), along with the experimental results, for blends other than PS6/PDMS5.

All of the calculated curves deviated from the experimental results towards the LMWC-rich side. This may be related to the similar fact that the predicted critical concentration and coexistence curve in polymer solutions deviate from experimental ones to lower concentrations[19]. Agreement in molecular-weight asymmetry effects was quantitatively poor, but qualitatively good.

For more precise description of the experimental coexistence curves, the composition dependence of parameter χ needs to be introduced. However, the χ parameter obtained in the present analysis, which reproduces the experimental $\Delta\phi$, is a quite relevant interaction parameter to express the segregation strength, since $\Delta\phi$ represents the segregation strength itself.

Concentration-fluctuation effects

The Flory–Huggins theory is a mean-field theory, which gives the critical exponent $\beta = 0.5$, while the critical PS6/PDMS5 blend exhibits Ising-type critical behaviour, having $\beta = 0.33_6$, where the mean-field theory breaks down. This is responsible for the anomalous change of apparent χ near the critical point. The true χ of bare segment interaction must change with temperature smoothly without anomalous change even near the critical point. The situations of apparent and true χ, and mean-field and real coexistence curves are represented in *Figure 8*. The coexistence curve of the mean field was calculated by equation (5) with equation (6). Large concentration fluctuations near the critical point make

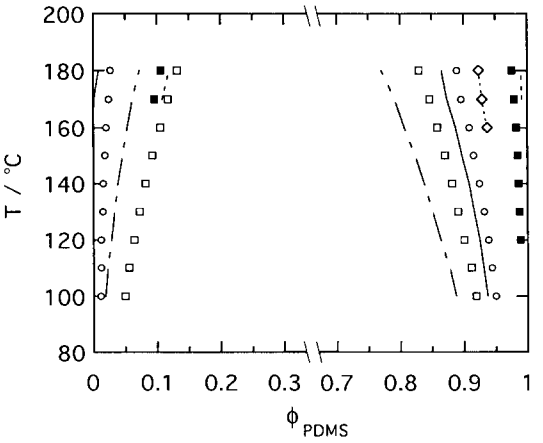

Figure 7 Comparison of experimental coexistence curves (points) and curves calculated by equation (5) with equations (6)–(10): (□, – · –) PS6/PDMS14; (○, ——) PS6/PDMS37; (◇, · · ·) PS6/PDMS2K; (■, – – –) PS22/PDMS5

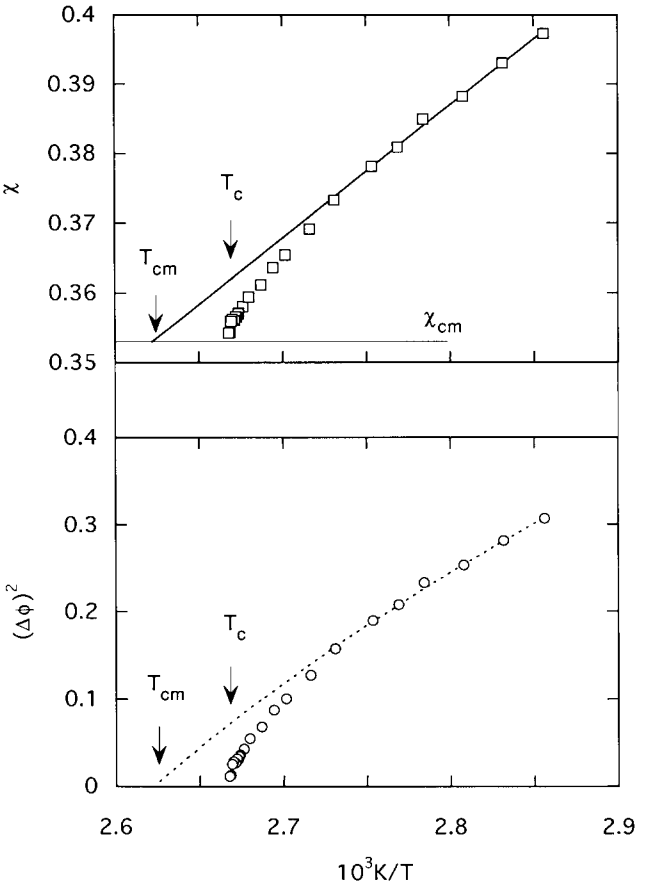

Figure 8 Concentration-fluctuation effects on the coexistence curve of the critical blend of PS6/PDMS5: (○) experimental $(\Delta\phi)^2$; (– – –) calculated $\Delta\phi$ of the mean-field theory (from equation (5) with equation (6)); (——) χ-parameter (equation (6)); (□) apparent χ parameter obtained from the experimental coexistence curve ($\Delta\phi$)

* The extrapolation was made by double extrapolation to zero with respect to both $1/M_w$(PS) and $1/M_w$(PDMS) for the plots of [coefficients of the χ vs. $1/T$ equation] *versus* $1/M_w$(PS) + $1/M_w$(PDMS)

the mixture more miscible and lower the critical temperature from the mean-field critical temperature T_{cm} to the real T_c. Equation (6) predicts that $T_{cm} = 108.22°C$, so that depression of T_c by the critical concentration fluctuation is estimated to be about 6°C in this blend.

If we used an equation of χ vs. $1/T$ obtained by fitting over the whole range of experiments, including the vicinity of the critical point, the theoretical curve reproduced the experimental coexistence curve better as a whole. However, disagreement was found in the shape of the coexistence curve between the theoretical and experimental results owing to the difference of the critical exponent β.

REFERENCES

1 Gordon, M., Irvine, P. and Kennedy, J. W. *J. Polym. Sci. (C)* 1977, **61**, 199
2 Kwei, T. K. and Wang, T. T. 'Polymer Blends' (Eds D. R. Paul and S. Newman), Vol. 1, Academic Press, New York, 1978, Ch. 4
3 Roe, R. J. and Zin, W. C. *Macromolecules* 1980, **13**, 1221
4 Kwak, K. D., Okada, M. and Nose, T. *Polymer* 1991, **32**, 864
5 Horiuchi, H., Irie, S. and Nose, T. *Polymer* 1991, **32**, 1970
6 Kim, W. N. and Burns, C. M. *J. Appl. Phys.* 1986, **32**, 3863; *Macromolecules* 1987, **20**, 1876; *J. Polym. Sci., Polym. Phys. Edn.* 1990, **28**, 1409
7 Yang, H., Ricci, S. and Collins, M. *Macromolecules* 1991, **24**, 5218; Yang, H. and Yetter, W. *Polymer* 1994, **35**, 2417
8 Bruder, F. and Brenn, R. *Macromolecules* 1991, **24**, 5552
9 Chu, B., Linliu, K., Xie, P., Ying, Q., Wang, Z. and Shook, J. *Rev. Sci. Instrum.* 1991, **62**, 2252
10 Chu, B., Linliu, K., Ying, Q., Nose, T. and Okada, M. *Phys. Rev. Lett.* 1992, **68**, 3184
11 Kwak, K. D., Okada, M., Chiba, T. and Nose, T. *Macromolecules* 1993, **25**, 7204
12 Kubo, T. and Nose, T. *Polym. J.* 1992, **24**, 1351
13 Uberriter, K. and Kanig, G. J. *Colloid Sci.* 1952, **7**, 569
14 Koningsveld, R., Keintjens, L. A. and Schoefelers, H. M. *Pure Appl. Chem.* 1974, **39**, 1
15 Wegner, F. J. *Phys. Rev. (B)* 1972, **5**, 4529
16 Stanley, H. E. 'Introduction to Phase Transitions and Critical Phenomena', Clarendon Press, Oxford, 1971, Chs. I and II
17 de Gennes, P. G. *J. Physique Lett.* 1977, **38**, 441; 'Scaling Concepts in Polymer Physics', Cornell University Press, Ithaca, NY, 1979, Ch. 4
18 Fisher, M. E. *Phys. Rev.* 1968, **176**, 257
19 Kurata, M. 'Modern Industrial Chemistry', Vol. 18, Asakura, Japan, 1975, p. 57; Dobashi, T., Nakata, M. and Kaneko, M. *J. Chem. Phys.* 1980, **73**, 6692