

# Interfacial tension between demixed symmetrical polymer solutions: Polystyrene–poly(dimethylsiloxane)–propylbenzene system

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Interfacial tension between demixed symmetrical polymer solutions of polystyrene–poly(dimethylsiloxane)–propylbenzene was measured as a function of temperature near the critical point at a fixed critical temperature (60.0°C) for molecular weights from 9000 to  $1.0 \times 10^5$ . The interfacial tension increased as the molecular weight was lowered. The order of magnitudes of the interfacial tension was in good agreement with the theoretical prediction proposed previously by Nose. The critical exponents  $\beta$  and  $\mu$  were estimated as near the values found for ordinary binary mixtures or liquids. Cloud point curves and coexistence curves were also obtained and properties related to incompatibility were also briefly discussed.

**Keywords** Interfacial tension; phase diagram; polymer solution; ternary system; critical behaviour; molecular weight dependence

## INTRODUCTION

Interfacial tension between demixed polymer solutions or polymer mixtures depends greatly on whether the phase diagrams of the mixtures are symmetrical or asymmetrical. The theory of interfacial tension proposed by Nose<sup>1</sup> predicts that the interfacial tensions of the two systems behave in different ways. For a polymer–solvent system, which is asymmetrical, the behaviour of the interfacial tension near the critical temperature was clarified as a function of temperature and molecular weight in previous studies<sup>2,3</sup>. The results were compared with the classical theories proposed by Nose<sup>1</sup> and by Roe<sup>4</sup> and were found to be in qualitative agreement. Measurements of interfacial tension in the symmetric system must be carried out using a polymer–polymer or a polymer–polymer–solvent system. For polymer–polymer systems, the interfacial tension has been extensively measured<sup>5</sup>. However, these studies are limited to a temperature region far from the critical point. The interfacial tension behaviour of a symmetric polymer–polymer system near the critical point has not, as yet, been investigated experimentally.

For a polymer–polymer–solvent system, measurements, covering the region near the critical point, were made by Langhammer and Nestler<sup>6</sup> with polymer pairs of the same order of molecular weights. They measured the interfacial tension for the solution containing poly(vinyl acetate), chlorinated poly(vinyl chloride), with ethyl-oxalate as solvent, and they found a very low value in the range of  $10^{-4}$ – $10^{-2}$  dyne  $\text{cm}^{-1}$ . Vrij<sup>7</sup> derived an equation for interfacial tension and compared it with the values measured by Langhammer and Nestler<sup>6</sup> and found qualitative agreement.

Here we have measured the interfacial tension of demixed solutions of polymer pairs of comparable size in a common solvent: polystyrene–poly(dimethylsiloxane)–propylbenzene. Although a

polymer–polymer system is preferred, very few polymer–polymer systems show compatibility and measurements of interfacial tension near the critical temperature are extremely difficult because of the high viscosity. Therefore, the above ternary system was chosen for investigating the properties of symmetrical polymer solutions. In this system the molecular weight dependence of the interfacial tension is somewhat different from that for a polymer–polymer system and this will be discussed in the next section.

Ternary systems of this type have been studied in another context, termed incompatibility. This denotes a phenomenon where a solution of two different polymers in a common solvent usually separates into two phases at relatively low percentages of polymer. Recently Esker and Vrij<sup>8</sup> investigated incompatibility experimentally in polystyrene–poly(isobutylene)–toluene with particular interest in the interface properties between the demixed phases. Studies by many workers in this field are listed in detail in their article. The present study gives a brief discussion related to this topic.

## THEORY

The state of the phase equilibrium in the symmetrical polymer–polymer–solvent system, i.e. two kinds of polymer with the same chain length in a common solvent, is given by<sup>9</sup>

$$\ln \theta_1' N(1 - \phi_0) \chi_{12} (1 - \theta_1')^2 = \ln \theta_1'' + N(1 - \phi_0) \chi_{12} (1 - \theta_1'')^2 \quad (1)$$

where  $N$  is the number of segments in a polymer,  $\chi_{12}$  the interaction parameter between the two polymers;  $\phi_0$  is the volume fraction of the solvent, and  $\theta_i'$  and  $\theta_i''$  ( $i = 1, 2$ ) are the reduced volume fractions of polymers in the

coexisting two phases, defined by

$$\theta_i = \phi_i / (1 - \phi_0) \quad (2)$$

where  $\phi_i$  ( $i = 1, 2$ ) is the volume fraction of polymer  $i$ . The condition (1) is the same as that for a symmetrical polymer-polymer system with the interaction parameter  $(1 - \phi_0)\chi_{12}$ ; therefore, we may regard this ternary system as a pseudo-two-component system. The critical concentrations are given by<sup>9</sup>

$$\theta_{1c} = \theta_{2c} = 1/2 \quad (3)$$

$$\phi_{1c} = \phi_{2c} = 1/(N\chi_{12}) \equiv \phi_{pc} = (1 - \phi_{0c})/2 \quad (4)$$

When we fix  $\phi_0$  at the critical concentration given by equation (4), equation (1) is independent of  $N$ , and therefore,  $\Delta\theta_i \equiv \theta_i - \theta_i'$ , compared at the same temperature distance from the critical temperature, is also independent of  $N$ .

As can be seen from equation (4), the critical concentration of polymers,  $\phi_{pc}$ , is proportional to  $N^{-1}$ . However, the scaling theory predicts another power law<sup>10</sup>. The theory assumes that  $\phi_{pc}$  is essentially the same as the overlap concentration  $\phi^*$ . Then,

$$\phi_{pc} \sim \phi^* \sim N/R^3 \quad (5)$$

where  $R$  is the polymer coil dimension. When the chains are dissolved in a good solvent usually  $R$  is proportional to  $N^{3/5}$ ; hence,  $\phi_{pc}$  is proportional to  $N^{-4/5}$  from equation (5). This power law has not yet been confirmed experimentally.

The equation of interfacial tension derived by Nose<sup>1</sup> can be extended to the present ternary symmetrical system as follows:

$$\begin{aligned} \sigma\omega / \{ (1 - \phi_0)kT_c\lambda \} &= 2(1 + Nb^2)^{1/2} N^{-1} (\Delta T/T_c)^{3/2} \\ &\simeq 2N^{-1/2} b (\Delta T/T_c)^{3/2} \end{aligned} \quad (6)$$

where  $\omega$  is the volume of the segment which is assumed to be equal to that of a solvent molecule  $\omega_s$ ,  $\lambda$  is the interaction length of the segments,  $b$  is given by  $b^2 = (\langle r^2 \rangle_0 / 9M) / \lambda^2 (\langle r^2 \rangle_0)$ ; unperturbed mean square end-to-end distance,  $M$ : molecular weight of the polymers, and  $\Delta T \equiv T_c - T$ . According to equation (4),  $1 - \phi_{0c}$  is proportional to  $N^{-1}$ ; then, the interfacial tension is proportional to  $N^{-3/2}$  when the critical temperature is fixed in the measurements.

However, if the pseudo-two-component system belongs to the same symmetry class as a binary solution or a liquid with regard to the critical phenomena associated with demixing, another type of molecular weight dependence is predicted from the scaling laws we have proposed<sup>11</sup>. Defining the exponents characterizing the molecular weight dependences of the correlation length  $\xi$ , the interfacial tension  $\sigma$ , and the critical temperature  $T_c$  as

$$\begin{aligned} \xi &\propto N^u (\Delta T/T_c)^{-v}, & \sigma &\propto N^m (\Delta T/T_c)^\mu \\ T_c &\propto N^s \end{aligned}$$

we have derived the following exponent-relation from the

concept of the two-scale-factor universality<sup>11</sup>:

$$m = -(d-1)n + s \quad (7)$$

where  $d$  is the space number dimension. Esker and Vrij<sup>8</sup> found experimentally that the direct correlation length (the factor in front of  $\Delta T/T_c$ ) was essentially the same as the polymer coil dimension; therefore,  $n = 1/2$ , and we obtain  $m = -1$  with  $d = 3$  and  $s = 0$  from equation (7). This value disagrees with the one predicted by equation (6), i.e.  $m = -1.5$ .

## EXPERIMENTAL

### Materials

Polystyrene samples were Pressure Chemical Co. products with molecular weights  $M_w = 9000, 17500, 5.0 \times 10^4$ , and  $1.0 \times 10^5$ , where the  $M_w/M_n$  ratios were less than 1.06. These samples were purified by repeated precipitation with benzene and methanol and complete drying in a vacuum oven for a few days. Poly(dimethylsiloxane) samples (Shin-etsu Kagaku Co.) were prepared by fractionating from dilute benzene solutions with methanol as a precipitant. The molecular weights of the poly(dimethylsiloxane) samples were determined by vapour pressure osmometry or intrinsic viscosity measurements to be 11 000 ( $M_n$ ), 16 000 ( $M_n$ ),  $5.0 \times 10^4$  ( $M_w$ ), and  $1.0 \times 10^5$  ( $M_w$ ); these molecular weights are almost equal to those of the polystyrene samples. Propylbenzene used as a solvent was purified by fractional distillation.

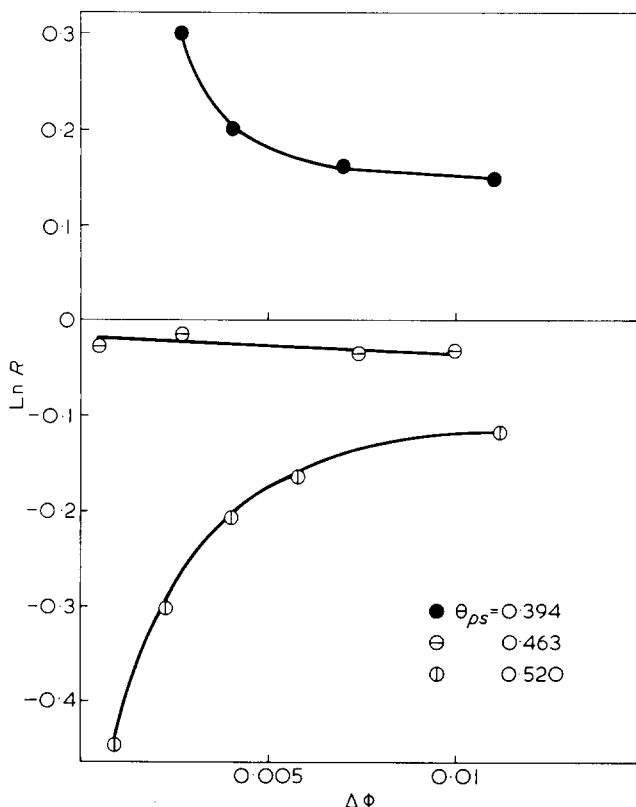


Figure 1 Determination of critical point at 60.0°C. The plots of  $\ln R$  vs.  $\Delta\phi$  for various  $\theta_{ps}$ , where concentrations are in weight fractions

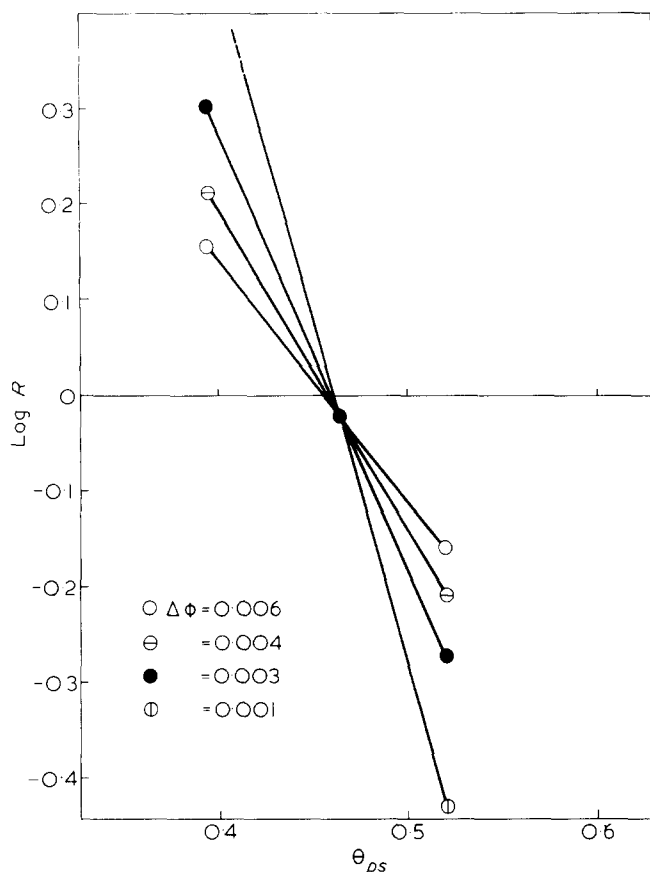


Figure 2 Determination of critical point. The plots of  $\ln R$  vs.  $\theta_{ps}$  for various  $\Delta\phi$ , where concentrations are in weight fractions

#### Methods

For the determination of the cloud point curves at 60.0°C, solutions of known amounts of the two polymers were placed in graduated glass tubes and diluted gradually with the solvent until the phase separation disappeared at 60.0°C. The concentrations of the solvent were then measured and the cloud point curves were determined. We employed a complicated method to determine the critical concentrations at 60.0°C which involved finding a point on each cloud point curve at which the volume ratio  $R$  ( $\equiv V_{up}/V_{low}$ ;  $V_{up}$  is the volume of the upper phase and  $V_{low}$  that of the lower phase) of the demixed two phases was unity. The procedure for the determination is described as follows; firstly, we prepared a solution with a reduced-concentration of polystyrene,  $\theta_{ps}$ , being  $\sim 1/2$  and a certain total-polymer concentration  $\phi_p$ , and then diluted the solution with the solvent until the phase separation disappeared, measuring the volume ratios of the two demixed phases. Figure 1 shows the volume ratio  $R$  as a function of  $\Delta\phi \equiv \phi_p - \phi_{cl}$  for  $M_w$  (polystyrene) = 17 500, where  $\phi_{cl}$  is the concentration of total-polymer on the cloud point curve at given  $\theta_{ps}$  (concentrations are in weight fractions in the plots). From this figure, Figure 2 was obtained, which shows  $R$  as a function of  $\theta_{ps}$  with  $\Delta\phi$  as a parameter. Then, critical values of  $\theta_{ps}$ , i.e.  $\theta_c$  were determined by extrapolating the values of  $\theta_{ps}$  at  $R=1$  to the limit  $\Delta\phi \rightarrow 0$ . The critical concentrations  $\phi_{pc}$  were then determined from the cloud point curves.

Measurements of the interfacial tension were carried out using a sessile bubble method which has been described elsewhere<sup>2</sup>. The density difference,  $\Delta\rho$ , was measured with a float which was set within the solution to

cross the interface. The values of  $\Delta\rho$  were calculated from the changes in position of the float relative to the interface when weights on it were altered. The volume ratios of the demixed two phases were also measured so as to obtain the coexistence curves of the pseudo-two-component system.

Temperature fluctuations were less than  $\pm 0.05^\circ\text{C}$ .

#### Experimental procedure

Firstly, polymer pairs of comparable molecular weights were dissolved in a solvent, and the cloud point curve and the critical concentration at 60.0°C for each pair were determined. Then the solutions with those critical concentrations were prepared and temperatures were lowered below 60.0°C. In this way we obtained two demixed phases of the pseudo-two-component system and measured its interfacial tension and other quantities such as density difference  $\Delta\rho$  between the two demixed phases and the volume ratios,  $R$ , of the two phases. The interfacial tension was measured over a temperature range between 60° and 40°C at intervals of 1°–2°C.

#### RESULTS

Cloud point curves at 60.0°C are shown in Figure 3. The curves shift to lower total-polymer concentrations as the molecular weight is raised. The curves are almost symmetrical and their peaks lie at  $\theta_{ps}$  values slightly larger than 1/2. The critical concentrations  $\theta_c$  and  $\phi_{pc}$  are listed in Table 1 and shown in Figure 3 by the arrows. The

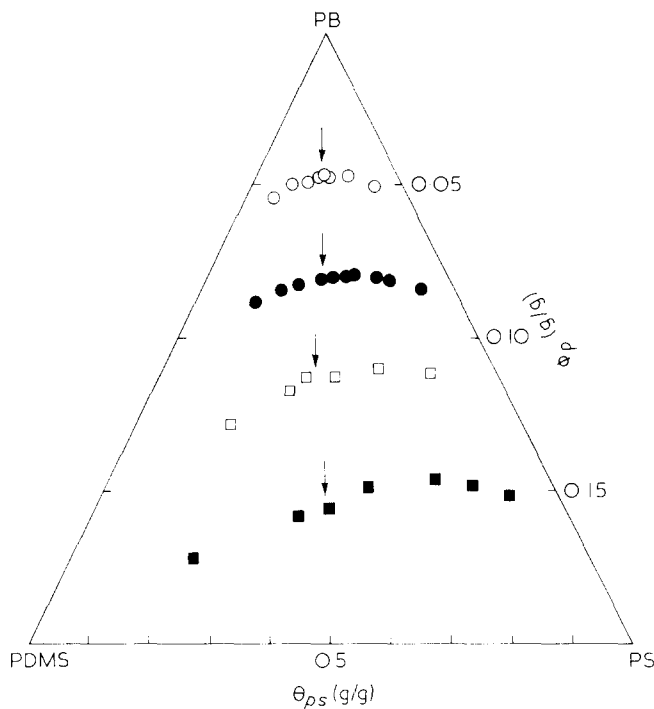


Figure 3 Cloud point curves for  $M_w$  (polystyrene) =  $1.0 \times 10^5$  (○),  $5.0 \times 10^4$  (●), 17 500 (□) and 9000 (■). Arrows indicate the critical points

Table 1 Critical concentrations  $\theta_c$ ,  $\phi_{pc}$  and  $\theta'_c$  for various polystyrene  $M_w$  values

$M_w$ (polystyrene)	9000	17500	50000	$1.0 \times 10^5$
$\theta_c$ (g/g)	0.491	0.463	0.482	0.462
$\phi_{pc}$ (g/g)	0.155	0.112	0.0805	0.0484
$\theta'_c$ (g/g)	0.489	0.456	0.490	0.410

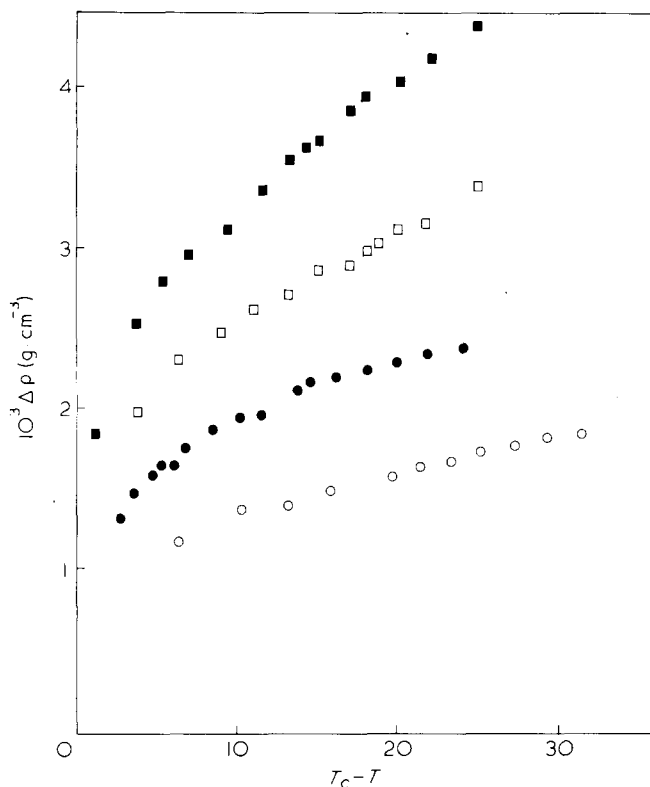


Figure 4 Density difference  $\Delta\rho$  as a function of  $T_c - T$ ; symbols as for Figure 3

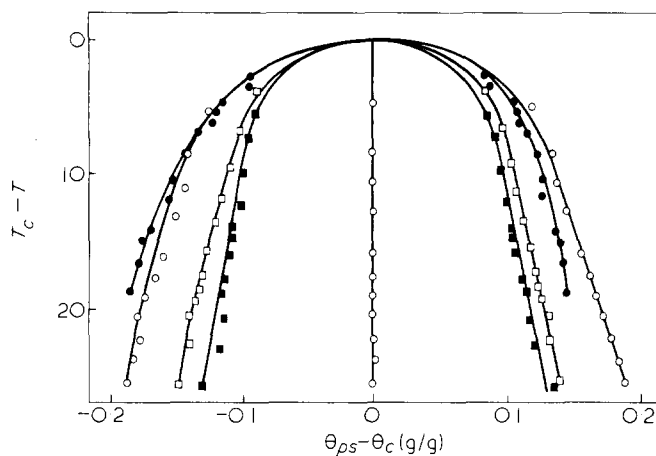


Figure 5 Coexistence curves for  $M_w$  (polystyrene) =  $1.0 \times 10^5$  (○),  $5.0 \times 10^4$  (●), 17 500 (□) and 9000 (■). The diameter is for  $M_w = 100\,000$

concentrations are shown in weight fractions. The critical concentrations  $\theta_c$  are close to  $1/2$  for all the systems and thus, we may regard the systems as symmetrical. The total-polymer concentrations at the critical point,  $\phi_{pc}$ , become smaller as the molecular weight is raised.

The density difference  $\Delta\rho$  between the two demixed phases is shown in Figure 4 as a function of  $\Delta T$  ( $\equiv T_c - T$ ), the distance from the critical temperature  $T_c$  ( $=60.0^\circ\text{C}$ ). The higher the molecular weight the smaller is  $\Delta\rho$ .

The coexistence curves for all the systems are shown on a common graph in Figure 5 which were calculated from the values of  $\Delta\rho$  and the volume ratios  $R$  of the two demixed phases. In the calculation we assumed that concentrations of the solvent in the two demixed phases were the same because the system was almost symmetric. The diameter shown, for  $M_w = 1.0 \times 10^5$ , shifts to a slightly higher concentration region of polystyrene near  $T_c$ ; this

feature was observed in all the systems measured. The higher the molecular weight the wider the coexistence curve. The critical concentrations  $\theta_c$  determined from these coexistence curves are listed in Table 1, which agree quite well with the  $\theta_c$  values.

The interfacial tension is shown in Figure 6 as a function of  $T_c - T$ . The higher the molecular weight the smaller the interfacial tension; however the curves for the molecular weights  $5.0 \times 10^4$  and  $1.0 \times 10^5$  are almost superimposed on each other.

## DISCUSSION

### Phase diagram

The molecular weight dependence of the critical concentrations  $\phi_{pc}$  is shown in Figure 7. The slope of the plots is  $-0.46$ , but becomes steeper at high molecular weights. The value  $-0.46$  does not agree with the Flory-Huggins value of  $-1$  or the scaling prediction of  $-0.8$ . The reason for the discrepancy is not clear; a possible reason could be: where the solvent is not good enough or the molecular weight is not high enough, the excluded volume effect is not sufficiently large that the polymer coil dimension  $R$  is proportional to  $N^{3/5}$ ; if the chains are almost Gaussian on account of the weak excluded volume effect the critical concentration  $\phi_{pc}$  is proportional to  $N^{-1/2}$  as is seen from equation (5). The exponent  $-1/2$  is near the value  $-0.46$  obtained.

Figure 8 shows the molecular weight dependence of the density difference  $\Delta\rho$  compared at the same  $\Delta T$  value. Since  $\Delta\rho = (\rho_1 - \rho_2)(1 - \phi_{0c})\Delta\theta$  (where  $\rho_1$  and  $\rho_2$  are the

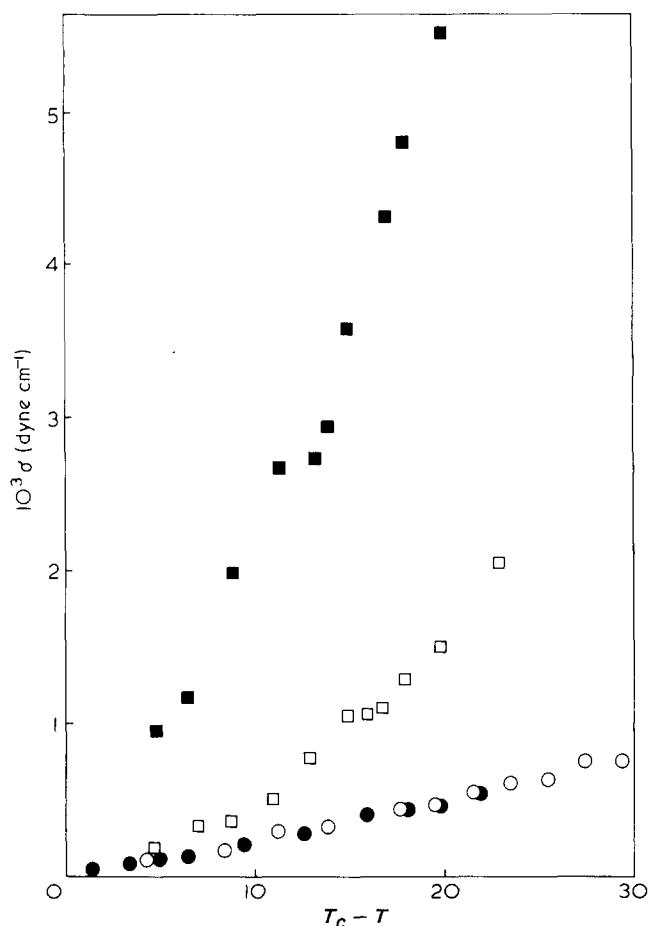


Figure 6 Interfacial tension as a function of  $T_c - T$ ; symbols as for Figure 5

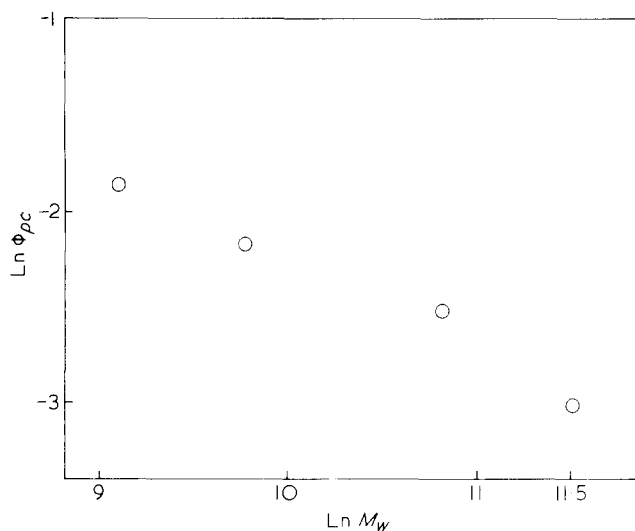


Figure 7 Molecular weight dependence of the critical concentration of the total polymer  $\phi_{pc}$ , where  $M_w$  is the molecular weight of polystyrene

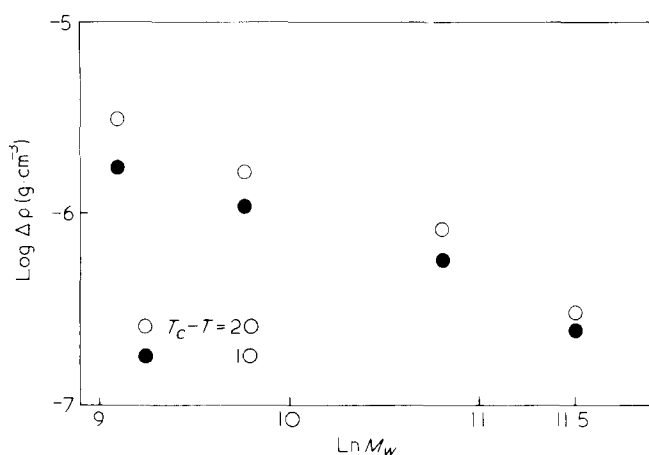


Figure 8 Molecular weight dependence of the density difference  $\Delta\rho$  between the two demixed phases

densities of the two polymers), then  $\Delta\rho$  is proportional to  $N^{-1}$  according to the Flory-Huggins theory (from equation (4)). However,  $\Delta\rho$  is proportional to  $N^{-0.4}$ ,  $N^{-0.6}$ , and the plots have the same features as that for  $\phi_{pc}$ , that is, the slope of the plots becomes steeper at high molecular weights. The molecular weight dependence of  $\Delta\rho$  is slightly weaker than that of  $\phi_{pc}$ , which means that the values of  $\Delta\rho/\phi_{pc}$  for different molecular weights plotted against  $T_c - T$  are almost superimposed on each other but not exactly so. The higher the molecular weight the larger the values of  $\Delta\rho/\phi_{pc}$  as is shown in Figure 9. The Flory-Huggins theory predicts that  $\phi_{pc}$  and  $\Delta\rho$  have the same  $N$  dependence. The molecular weight dependence appearing in the coexistence curves (Figure 5) is a result of the breakdown in the  $N$  dependence of the  $\phi_{pc}$  and  $\Delta\rho$  values.

### Interfacial tension

The order of magnitude of the interfacial tension lies between  $10^{-4}$  and  $10^{-3}$  dyn  $\text{cm}^{-1}$ , and almost agrees with the result obtained by Langhammer and Nestler<sup>6</sup>, which was  $10^{-4}$ – $10^{-2}$  dyn  $\text{cm}^{-1}$ . This value range is smaller than that for the polymer-solvent system we have previously reported<sup>2,3</sup>. In the present ternary system the two different polymers overlap with each other at the interface where a larger interfacial thickness compared with that in the polymer-solvent system is expected. This is predicted by the theory<sup>1</sup>, and results in lower values for the interfacial tension from the relation  $\sigma \approx kT/L^2$  ( $L$  = interface thickness)<sup>3</sup>.

Figure 10 shows the molecular weight dependence of the interfacial tension at the same  $\Delta T$ . The interfacial tension decreases with molecular weight, but its dependence on molecular weight becomes weaker as the molecular weight is raised. The theories described in the theoretical section qualitatively agree with the fact that the interfacial tension is a decreasing function of molecular weight. In order to compare the result quantitatively with the theoretical predictions  $m = -1.5$  or  $-1$ , we estimate the slope of the plots from the intermediate region of the molecular weight ( $17\,500 \lesssim M_w \lesssim 5.0 \times 10^4$ ). The value of the slope is about  $-1$ , which is the same

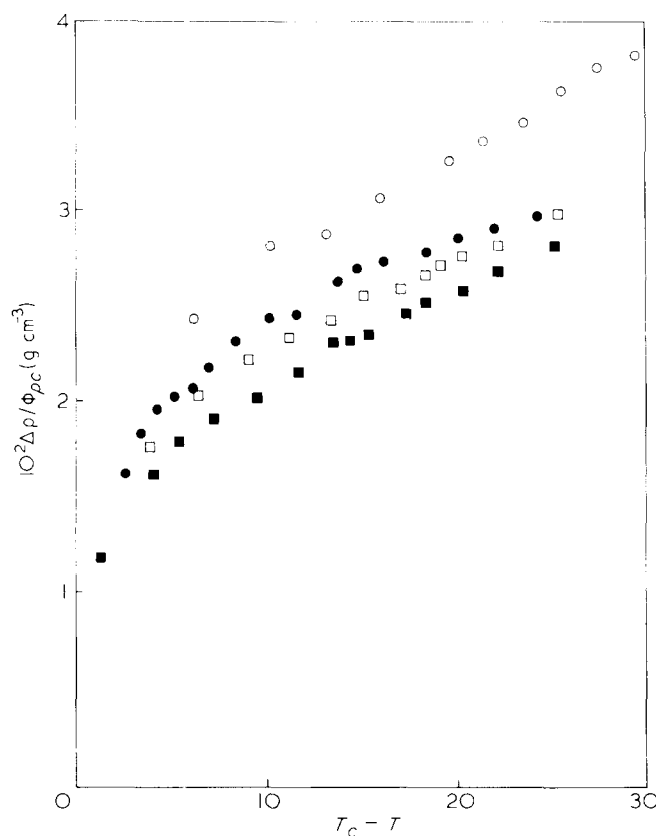


Figure 9 Density difference  $\Delta\rho$  scaled by the critical concentration  $\phi_{pc}$ ; symbols as for Figure 5

Table 2 Prefactors and exponents ( $\Delta\rho_0$ ,  $\beta$ ,  $\sigma_0$ ,  $\mu$ ,  $\sigma_{0cal}$  and  $\mu_{0cal}$ ) for various polystyrene  $M_w$  values

$M_w$ (polystyrene)	$\Delta\rho_0$ (g/ml)	$\beta$	$\sigma_0$ (dyne $\text{cm}^{-1}$ )	$\mu$	$\sigma_{0cal}$ (dyne $\text{cm}^{-1}$ )	$\mu_{0cal}$
9000	$9.1 \times 10^{-3}$	0.30	0.215	1.30	0.173	
17500	6.82	0.29	0.121	1.50	0.0897	
50000	5.49	0.30	0.0207	1.37	0.0379	1.50
$1.0 \times 10^5$	4.00	0.33	0.0126	1.18	0.0162	

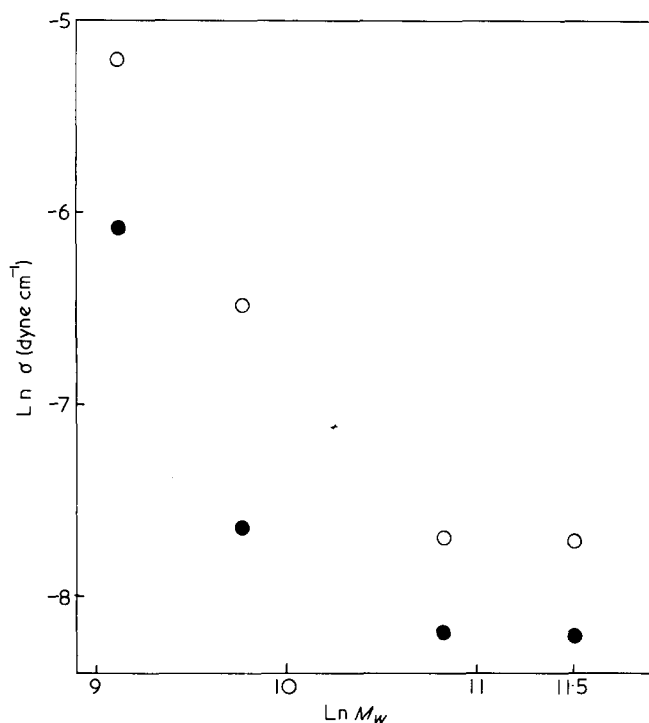


Figure 10 Molecular weight dependence of interfacial tension.  $T_c - T = 20$  (○),  $10$  (●)

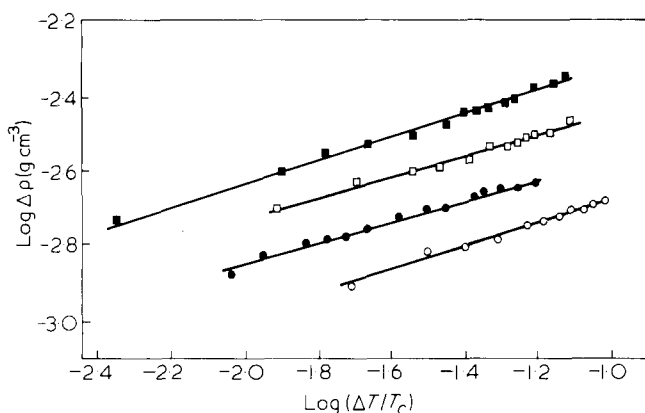


Figure 11 The plots of  $\ln \Delta\rho$  vs.  $\ln(\Delta T/T_c)$  for  $M_w$  (polystyrene) =  $1.0 \times 10^5$  (○),  $5.0 \times 10^4$  (●), 17 500 (□), and 9000 (■)

order of magnitude as the predictions, i.e.  $-1.5$  or  $-1$ .

Figures 11 and 12 show plots of  $\ln \Delta\rho$  vs.  $\ln(\Delta T/T_c)$  and  $\ln \sigma$  vs.  $\ln(\Delta T/T_c)$  for all the measured systems. These plots are almost straight lines; therefore, we may write  $\Delta\rho$  and  $\sigma$  as follows:

$$\Delta\rho = \Delta\rho_0(\Delta T/T_c)^\beta \quad (8)$$

$$\sigma = \sigma_0(\Delta T/T_c)^\mu \quad (9)$$

The exponents  $\beta$ ,  $\mu$  and the prefactors  $\Delta\rho_0$ ,  $\sigma_0$  are listed in Table 2, which were determined from all the plots in the measured region. Although the measured temperature regions were rather far from the critical temperature ( $T_c - T \approx 1.5$ – $4^\circ\text{C}$ ), the exponents obtained are  $0.29$ – $0.33$  for  $\beta$  and  $1.18$ – $1.50$  for  $\mu$ , which are almost equal to the values in the polymer-solvent system<sup>2,3</sup>, the ordinary binary mixture<sup>12</sup> or liquids<sup>13</sup>, and the universal values of  $\beta(=0.325)$  and  $\mu(=1.26)$ <sup>14</sup>. Therefore, although our estimate of the critical exponent is approximate, it is

suggested that the present pseudo-two-component system belongs to the same symmetry class as ordinary binary mixtures or liquids. In the polymer-solvent system no universal value was found for high molecular weights ( $M_w \geq 5.0 \times 10^4$ ) on account of the very narrow critical region<sup>3</sup>. In the present ternary system this feature is not seen; the critical region may not become narrower as the molecular weight is raised in contrast to the polymer-solvent system, but we cannot be sure as the measured range of molecular weight is not sufficiently wide.

The prefactor  $\sigma_0$  is written from equation (6) as follows:

$$\sigma_0 = (2/3\omega)N^{-1}kT_c(1 - \phi_{0c})(\langle r^2 \rangle_0/M)^{1/2} \quad (10)$$

Numerical results for  $\sigma_0$  calculated from this equation are also listed in Table 2, where  $M/N = 140$ ,  $(\langle r^2 \rangle_0/M)^{1/2} = 6.6 \times 10^{-9}$  cm,  $\omega = 2.31 \times 10^{-22}$  cm<sup>3</sup>, and the experimental values of  $\phi_{0c}$  in the volume fraction were used in the calculation. The values of  $M/N$  and  $\omega$  are the mean values for polystyrene and poly(dimethylsiloxane), respectively, determined by a previously described method<sup>2</sup>. The values of  $(\langle r^2 \rangle_0/M)^{1/2}$  are almost the same for the two polymers<sup>15</sup>. The calculated values of  $\sigma_0$  agree very well with experimental values. Therefore, the theory gives a qualitatively accurate description of the interfacial tension as a function of molecular weight near the critical temperature.

The theory<sup>1</sup> predicts a phase transition from a diffuse interface to a sharp one with an abrupt change in polymer coil dimension. In previous studies<sup>2,3</sup> we reported an anomaly found in the  $\sigma$ - $T$  relation. However, no anomaly is present in Figure 6 nor in Figure 12. Since the transition will occur when the interface thickness is comparable with the polymer coil dimension, the large interface thickness, as was previously suggested<sup>3</sup> will cause a lower transition temperature or no transition in low molecular weight<sup>1</sup>. Therefore, the transition may not be found in the measured temperature range.

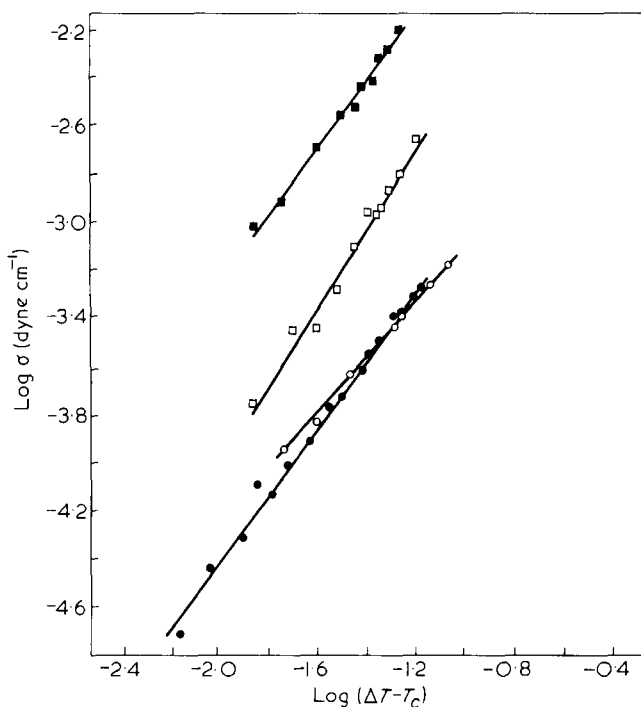


Figure 12 The plots of  $\ln \sigma$  vs.  $\ln(\Delta T/T_c)$  for  $M_w$  (polystyrene) =  $1.0 \times 10^5$  (○),  $5.0 \times 10^4$  (●), 17 500 (□), and 9000 (■)

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