Interfacial tension of demixed polymer solutions over a wide range of reduced temperature

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Interfacial tensions were measured for solutions of polystyrene–methylcyclohexane, polystyrene–heptamethylnonane and poly(dimethyl siloxane)–phenylethyl ether to investigate the behaviour of the interfacial tension from the critical point to a region far away from it. In the polystyrene–heptamethylnonane system, measurements were performed until the concentration of the polymer rich phase became about 70 ~ 80%. The molecular weight dependence of the interfacial tension was stronger away from the critical temperature than near to it. Data for polystyrene solutions with different solvents were connected by a scaling law. Recent scaling theories were compared with the results for poly(dimethyl siloxane) solution.

Keywords Interfacial tension; polymer solution; phase separation; molecular weight dependence; polystyrene; poly(dimethyl siloxane)

INTRODUCTION

Interfacial tension between demixed polymer solutions of polymer mixtures has not been widely investigated despite theoretical studies[1-9]. Investigations have been restricted to the temperature range far from the critical point except for the studies of Langhammer and Nestler[10] and by the authors[11,12]. We have previously reported the behaviour of interfacial tension between demixed polymer solutions near the critical temperature[12]. Here, the interfacial tension is studied over a wide range of temperature, including the region far from the critical point.

The behaviour of the interfacial tension, σ, of a demixed polymer solution is shown schematically in *Figure 1*. There are three qualitatively different regions. Region I lies near the critical temperature and is characterized as follows: the distance from the critical temperature is small enough for the interfacial thickness L to be much larger than the polymer coil dimension R; the molecular weight dependence of interfacial tension is very weak, e.g. $\sigma \propto N^{-1/4}$, where N is the polymerization index, according to mean-field theories[3,4]. This molecular weight dependence was confirmed qualitatively in the previous study[12]. As the temperature is lowered from the critical temperature, the interfacial thickness L becomes small and is soon comparable to the polymer coil dimensions; strong dependence on molecular weight then appears, i.e., the higher the molecular weight the smaller the interfacial tension. This feature characterizes region II. When the temperature is lowered further to region III, L becomes very small and the polymer-rich phase of the solution approaches the state of a polymer melt as the phase separation proceeds. Thus, as the system departs from the critical temperature, its interfacial tension becomes gradually independent of molecular weight. If molecular weights are so high that the critical temperatures for the solutions approach the θ temperature, the molecular weight dependence is different from that described above and will be independent of molecular weight over the complete temperature region.

Here, we clarify these features for moderately high molecular weights. We have measured interfacial tensions for solutions of polystyrene–methylcyclohexane, polystyrene–heptamethyl nonane and poly(dimethyl siloxane)-phenylethyl ether. Data for polystyrene solutions with different solvents are related by an adequate scale transformation.

EXPERIMENTAL

Materials

Polystyrene samples (Pressure Chemical Co.) had molecular weights $M_w = 9000$, 17 500, 50 000 and 110 000;

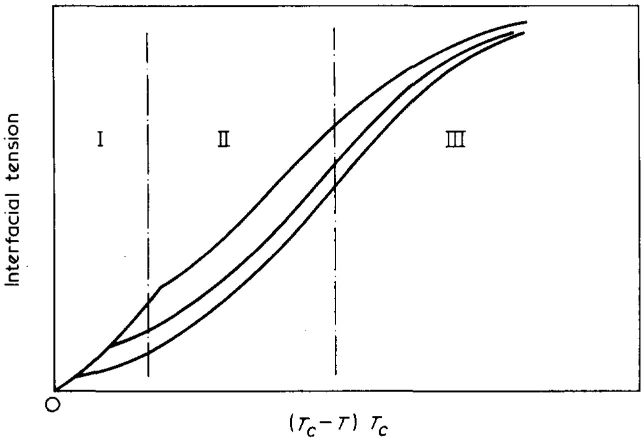

Figure 1 Qualitative behaviour of interfacial tension over a wide range of temperature. Each curve corresponds to a different molecular weight

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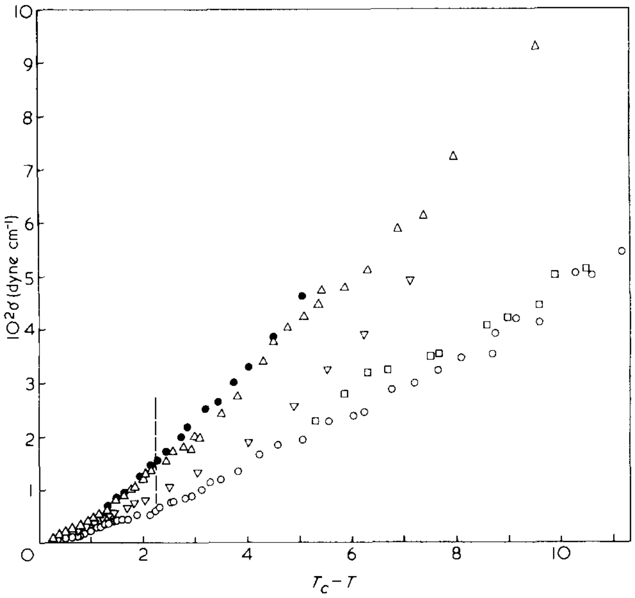

Figure 2 Interfacial tension of polystyrene–methylcyclohexane for M_W: ●, 9000; △, 17500; △, 37000; □, 50000; ○, 110000

M_w/M_n were less than 1.06. Purification was by repeated precipitation of a benzene solution into methanol followed by drying in a vacuum oven for a few days.

Poly(dimethyl siloxane) was prepared from Shin-etsu Silicone (Shin-etsu Kagaku Company) by fractionating from a dilute benzene solution using methanol as a precipitant; the molecular weight, from intrinsic viscosity measurement, was $M_w = 100\,000$.

Methylcyclohexane, heptamethyl nonane and phenylethyl ether solvents were purified by fractional distillation.

Methods

For polystyrene solutions with critical temperatures near room temperature, solution viscosity became extremely large as temperature was lowered from the critical point and it took a long time to establish equilibrium. Measurements thus became almost impossible, and measurements of interfacial tension far from the critical point had to be carried out at temperatures at least higher than the glass transition temperature.

For this reason, we used two solvents for polystyrene: near T_c, methylcyclohexane (MCH) was used, while far from T_c, heptamethyl nonane (HMN) (θ-temperature $>200°$C) was used.

Interfacial tension was measured by a sessible bubble method, described elsewhere[12].

The density difference $\Delta\rho$ between the two demixed phases was calculated from coexistence curves obtained by the use of a refractometer for polystyrene–MCH system.

For the polystyrene–HMN system, $\Delta\rho$ was calculated from the volume ratios of the two demixed phases with the concentration of a dilute phase estimated from the cloud point curve.

For the poly(dimethyl siloxane) solution, $\Delta\rho$ was measured with a float, set in the solution to penetrate the interface; $\Delta\rho$ was then calculated from a change in position of the float relative to the interface when a weight on it was changed. Coexistence curves obtained with a refractometer were also found for this system.

Temperature ranges were $T_c - T \leqslant 10°$C for polystyrene—MCH where T_c ranges from 8° to 50°C; for polystyrene–HMN 100°∼180°C; and $1°\text{C} \leqslant T_c - T \leqslant 30°$C for the poly(dimethyl siloxane)–phenylethyl ether (PEE) system, where T_c is about 70°C.

Temperature fluctuations were less than ±0.03°C for polystyrene–MCH. $\Delta\rho$ and σ were determined within an accuracy of $\pm 3.0 \times 10^{-4}$ g cm^{-3} and $\pm 0.05 \sim 0.07 \times 10^{-2}$ dyn cm^{-1} in this system. Temperature fluctuations were less than ±0.03°C for poly(dimethyl siloxane)–PEE and ±0.1°C for the polystyrene–HMN system.

RESULTS

The interfacial tension of the polystyrene–MCH solution is shown in *Figure 2* as a function of temperature–distance from the critical point. Previous data are also shown[12].

Figure 3 shows that interfacial tension for polystyrene–HMN varies almost linearly with temperature and the slopes of the plots for $M_w = 9000$ and 17 500 are steeper than those for $M_w = 50\,000$ and 110 000.

Figure 4 shows the concentrations of the polymer rich phase for the polystyrene–HMN system as a function of temperature.

Figure 5 shows the coexistence curve for poly(dimethyl siloxane)–PEE. The critical temperature T_c was determined to be 68.84°C from the temperature dependence of $\Delta\rho$; the critical concentration φ_c was determined from this curve to be 0.105 (wt fraction). The interfacial tension for this system is shown in *Figure 6* as a function of $T_c - T$. As temperature is lowered, interfacial tension rapidly increases and does not level off over this temperature range.

DISCUSSION

From the critical temperature to slightly below it

Transition from the region I to the region II is seen in *Figure 2*. The threshold is shown by the broken line. The crossover condition is given by $R \sim L$ as mentioned

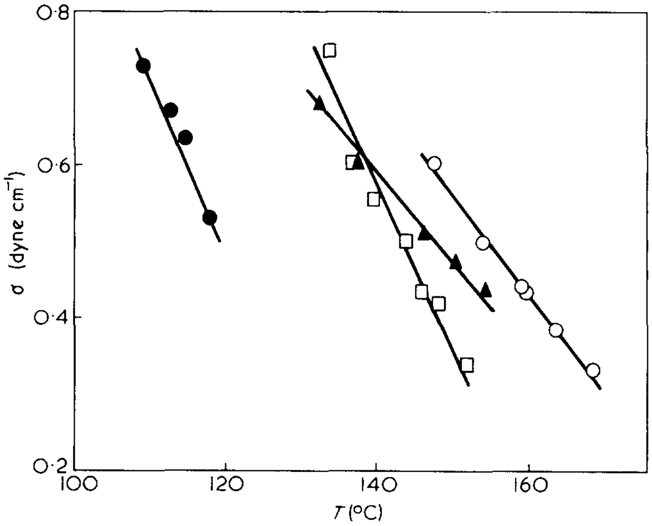

Figure 3 Interfacial tension of polystyrene–heptamethylnonane for M_W: ●, 9000; ▲, 17500; □, 50000; ○, 110000

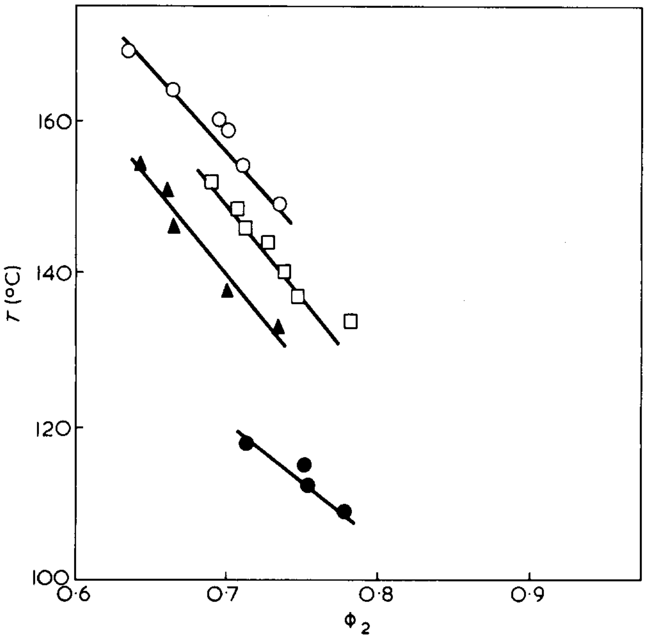

Figure 4 Concentration of the polymer-rich phase in the polystyrene–heptamethylnonane system for M_w: ●, 9000; ▲, 17 500; □, 50 000; ○, 110 000

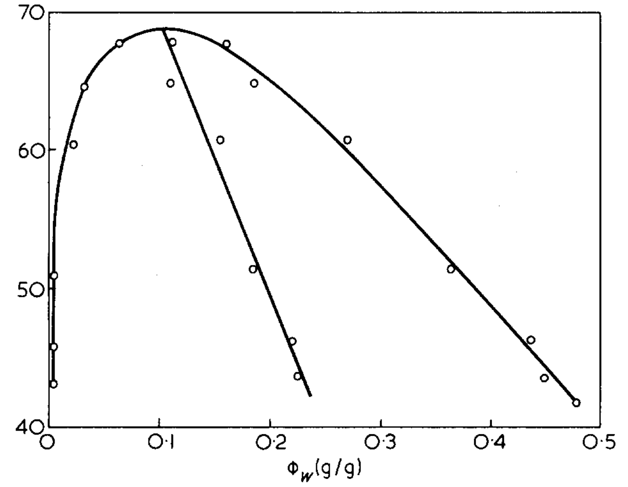

Figure 5 Coexistence curve for the poly(dimethyl siloxane)–phenylethyl ether system; ϕ_W is the weight fraction of polymer

previously, where R is the polymer coil dimension, and the crossover temperature T' satisfies the condition:

$$T_c - T' \sim N^{-1/2} \qquad (1)$$

where $R \sim N^{1/2}$ and $L \sim N^{1/4}$ are assumed[12]. Thus, deviation from region I behaviour occurs at temperatures progressively closer to T_c as the molecular weight is raised, (broken line, *Figure 2*). For $M_w = 9000$ and 17 500 the curves almost overlap, and this may be attributed to the fact that both systems exhibit region I behaviour over this range.

Molecular weight dependence of interfacial tensions for regions I and II are shown in *Figure 7*. In region II the molecular weight dependence is stronger than in the region I, as expected from theory.

Comparison among the three systems using reduced quantities

To compare the results for the three systems polystyrene–MCH, polystyrene–HMN and poly(dimethyl siloxane)–PEE the values of interfacial tension and distance from the critical temperature must be measured in appropriate units.

We took the interaction parameter χ as a measure of the distance from the critical point. Since χ denotes the

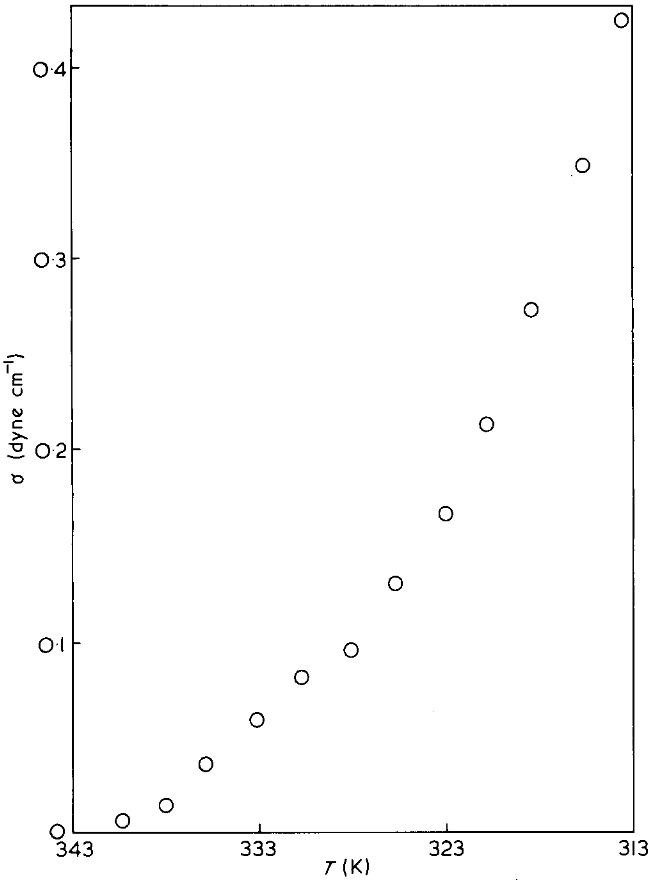

Figure 6 Interfacial tension of the poly(dimethyl siloxane)–phenylethyl ether system

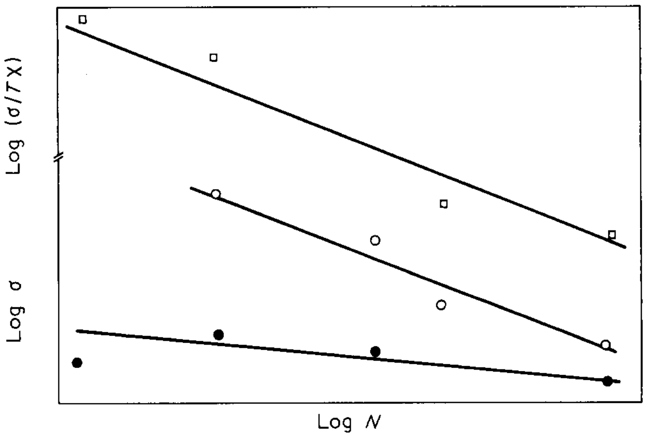

Figure 7 Molecular weight dependence of the interfacial tensions in arbitrary units. $T_c - T = 0.48$ (●) and 7 (○) for the polystyrene–methylcyclohexane system with $N = M_w/146$; $(\chi - \chi_c)/\chi_c = 0.78$ for the polystyrene–heptamethyl nonane system (□) with $N = M_w/126$

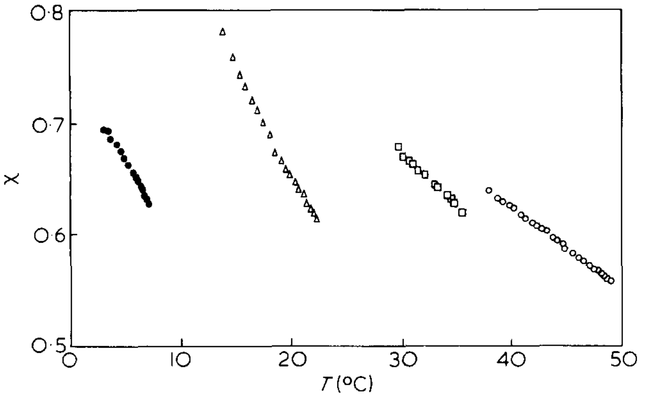

Figure 8 χ–*T* relation for polystyrene–methylcyclohexane with M_w: ●, 9000; △, 17500; □, 50000; ○, 110000

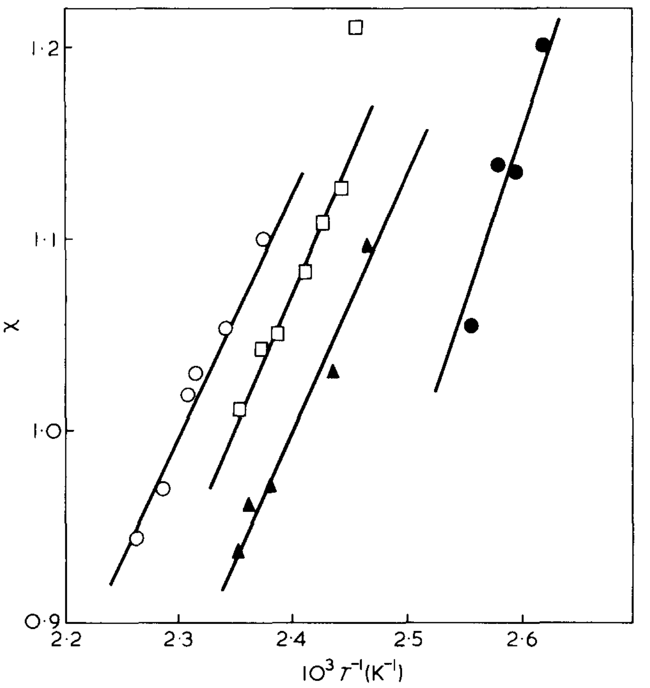

Figure 9 χ–*T* relation for polystyrene–heptamethyl nonane with M_w: ●, 9000; △, 17500; □, 50000; ○, 110000

polymer–solvent interaction, Δu, in the Flory–Huggins theory:

$$\chi = \Delta u / kT \qquad (2)$$

therefore, $\Delta u \propto T\chi$ and values of the interfacial tension will be scaled by $T\chi$.

The χ–T relations for polystyrene solutions are shown in *Figures 8* and *9*. χ was evaluated from coexistence curves by the Flory–Huggins theory as follows.

The theory usually gives χ as a function of the concentrations φ', φ'' of the two existing phases, temperature, and the polymerization index, N. We write χ as a function of $\Delta\varphi(\equiv \varphi' - \varphi'')$, the concentration difference between the coexisting phases and insert the experimental values of $\Delta\varphi$ to fit the critical points. The molar volume ratio of the polymer and the solvent is taken as N.

We determined χ by this method for polystyrene–MCH and poly(dimethyl siloxane)–PEE.

For polystyrene–HMN χ was evaluated in the same way as above for $M_w = 9000$. When $M_w = 17\,500$, $50\,000$ and $110\,000$ we calculated χ from Flory–Huggins theory setting the concentrations of the dilute phase equal to 0 since these were negligible. Values thus obtained are substantially dependent on molecular weight, which is not predicted from the Flory–Huggins theory. In spite of this, we used the χ values as measuring units.

Figure 10 shows the values of $\sigma/T\chi$ plotted against $(\chi - \chi_c)/\chi_c$ for all molecular weights measured, where χ_c is the value of χ at the critical temperature. The following conclusions can be reached from this plot:

(1) polystyrene solutions with different solvents (MCH or HMN) show a tendency to connect almost smoothly and this suggests that our scale is adequate;

(2) however, the curve for the poly(dimethyl siloxane) solution is different from those for polystyrene solutions, suggesting that the scale does not work well for different polymers;

(3) the dependence of interfacial tension on $(\chi - \chi_c)/\chi_c$ and on molecular weight is still strong, indicating that we are still in region II, even though the polymer-rich phase is highly concentrated (70~80%); region III will lie at polymer concentrations higher than 90%.

The molecular weight dependence of the interfacial tension for polystyrene–HMN is shown in *Figure 7*. The slope for this system is almost equal to that for polystyrene–MCH slightly below the critical temperature ($T_c - T = 7$), also indicating that the two systems are in region II.

Poly(dimethyl siloxane)–PEE over a wide range of temperatures

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 poly(dimethyl siloxane)–PEE.

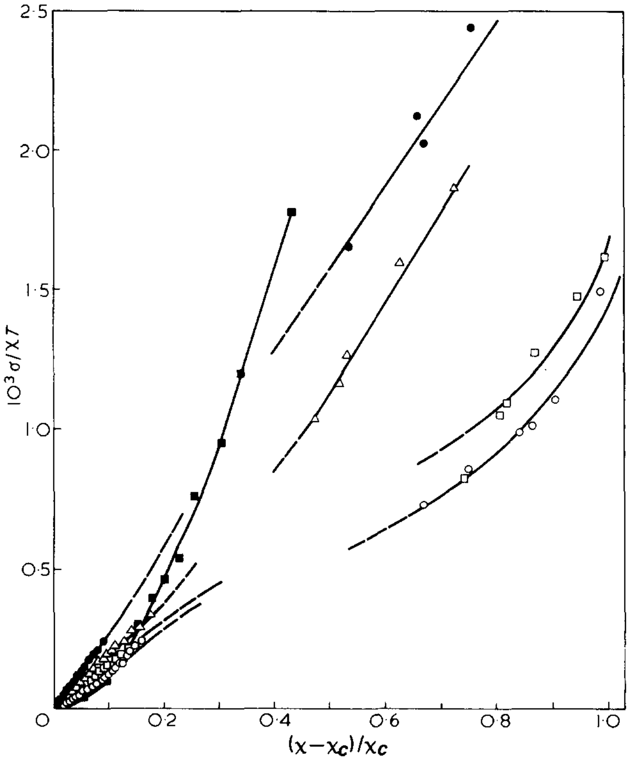

Figure 10 Comparison using reduced quantities: polystyrene solutions with M_w: ●, 9000; △, 17500; □, 50000; ○, 110000. ■, Poly(dimethyl siloxane)–phenylethyl ether system

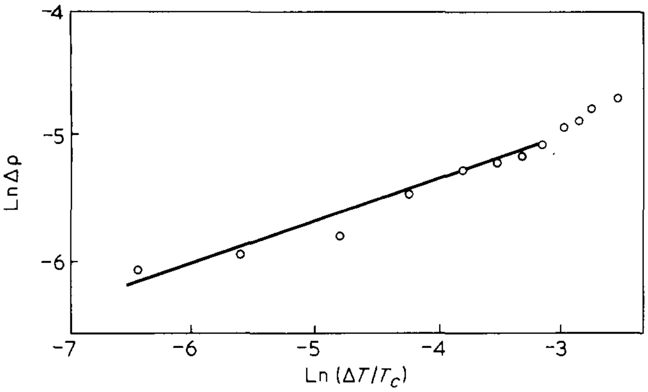

Figure 11 Ln $\Delta\rho$ vs. $\ln(\Delta T/T_c)$ plots for the poly(dimethyl siloxane)–phenylethyl ether system

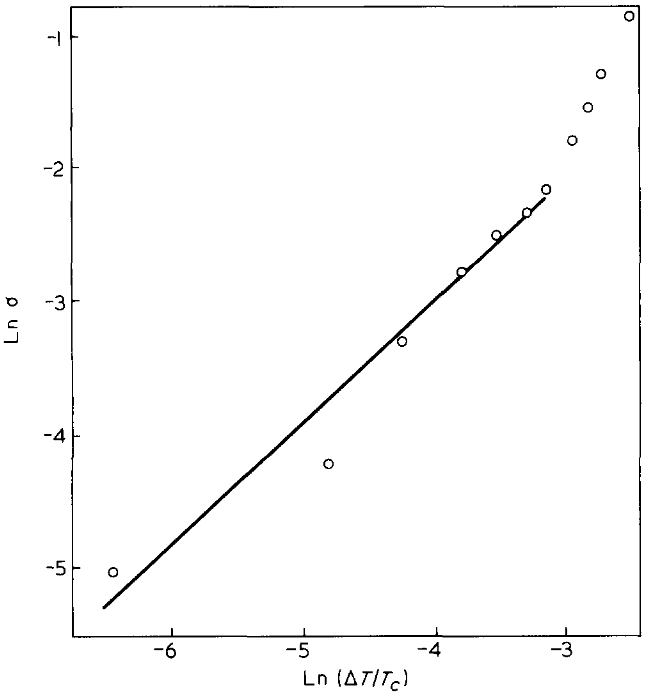

Figure 12 Ln σ vs. $\ln(\Delta T/T_c)$ plots for the poly(dimethyl siloxane)–phenylethyl ether system

Sufficiently near the critical temperature the plots give values of $\Delta\rho_0$, β, σ_0 and μ defined by:

$$\Delta\rho = \Delta\rho_0(T_c - T)^{\beta} \tag{3}$$

$$\sigma = \sigma_0(T_c - T)^{\mu} \tag{4}$$

The plots in *Figure 11* are almost straight near T_c. The value of β is close to the universal value, and we may regard the value obtained as the critical one. The slope becomes steeper at lower temperatures, as found by Dobashi *et al.*[13]. Its value in the lower temperature region is about 0.56. It should be noted that the deviation from single exponent behaviour is due to two effects: i.e. corrections due to higher order terms of $\Delta T/T_c$ and a reduction in the effects of the critical fluctuations. The latter is estimated by the Ginsburg criterion which succeeds in giving the width of the critical region where mean field theory fails. The value obtained in the lower temperature region is close to the mean field value of 0.5, and the result may be attributed to the fact that the critical fluctuations are reduced and the system has become describable by mean field theory. However, as mentioned above, the deviation occurs because of complicated effects and the value of ~ 0.5 is somewhat fortuitous.

However, the plots in *Figure 12* show a large deviation from linearity, suggesting that the system is already outside the critical region with respect to σ. If a straight line is drawn, as shown in *Figure 12*, the value of μ is about 0.9, a long way from the universal value ($=1.26$). This feature also appeared for polystyrene–methylcyclohexane when $M_w \geqslant 110\,000$[12]. It is suggested that the deviation from the critical region occurs at temperatures closer to T_c in case of the interfacial tension than in case of $\Delta\rho$.

Daoud and Jannink[14] recently proposed a theory which gives a temperature–concentration diagram for polymer solutions. According to their theory, a polymer-rich phase in a demixed polymer solution corresponds to the semi-dilute and tricritical region. In this region the correlation length ξ is given by $\xi \sim C^{-1}$, where C is the polymer concentration. Therefore, using $\sigma \sim kT/\xi^2$, the interfacial tension is given by:

$$\sigma \sim kTC^2 \tag{5}$$

where the concentration of a polymer-rich phase is C as proposed by de Gennes[15]. *Figure 13* shows plots of $\ln \sigma/T$ vs. $\ln C$, the slope of which should be equal to 2, according to equation (5). However, the slope approaches 3.4, deviating significantly from the theoretical value. The same plots were drawn for polystyrene–

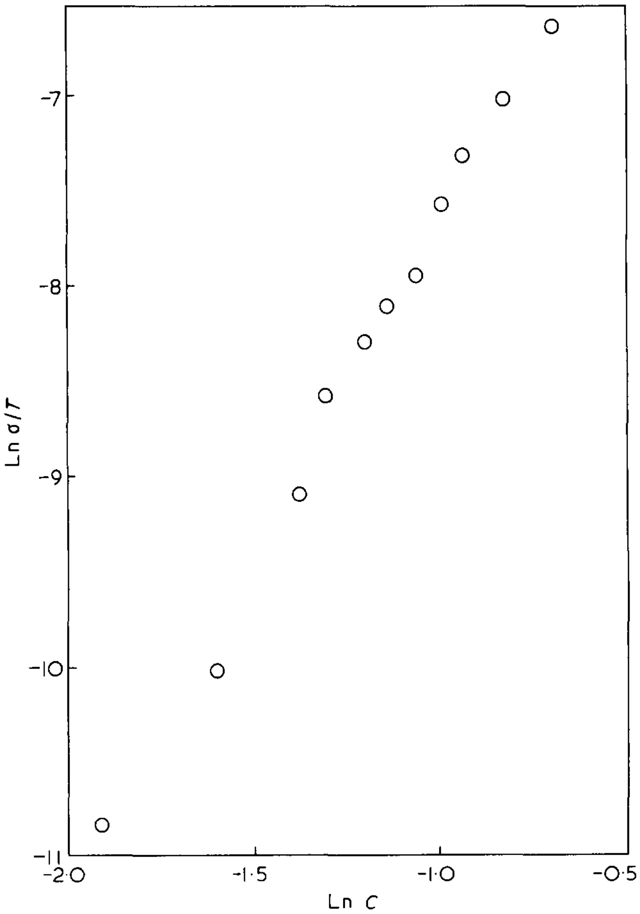

Figure 13 Ln σ/T vs. ln C plots for the poly(dimethyl siloxane)–phenylethyl ether system

methylcyclohexane in the previous study[12] and the values of the slopes were found to be about $3.2 \sim 3.4$ in the measured range of temperature and molecular weights ($M_w = 2.33 \times 10^5$ and 1.26×10^6).

Reasons for these deviations are not yet clear. Probably the molecular weights were not high enough or the temperatures were not far enough from the θ temperature for the exponent to be obtained.

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