Interfacial tension of demixed polymer solutions near the critical temperature: polystyrene+methylcyclohexane

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Interfacial tension between demixed solutions of polystyrene+methylcyclohexane has been measured near the critical temperature as a function of temperature using polystyrenes with molecular weights $9000 \sim 1.26 \times 10^6$. The critical exponent for the interfacial tension was determined to be about 1.30 for the lower molecular weight systems. However, for higher molecular weights the exponent could not be obtained because the system departed from critical behaviour. Magnitudes of the interfacial tension were proportional to about $N^{-0.44}$, where N is the polymerization index. Experimental results were compared with the recently-proposed theories and found to be in qualitative agreement. The tricritical theory of polymer solutions was also compared with the experimental results.

Keywords Interfacial tension; polymer solution; critical temperature; critical behaviour; polymerization index; molecular weight dependence; tricritical theory

INTRODUCTION

Critical phenomena in polymer solutions have recently attracted a great deal of attention. Coexistence curves have been measured by some authors[1-3] to examine the universality of the critical exponent β. The value for β is known to agree with that for low molecular weight substances and for magnetic materials. However, for other exponents, universality has not yet been well established.

Measurement of interfacial tension provides another exponent, μ, which can be tested for universality and investigated for scaling relationships.

The properties of critical amplitudes are also not well known. For polymers, molecular weight dependence is especially important, and this has been in question since Debye proposed the theory of critical opalescence for polymer solutions in 1959[4].

Interfacial or surface tension, however, has been studied for a long time, and theories for polymer solutions have been presented[5-13]. Vrij[5] derived an equation for the interfacial tension between demixed solutions of symmetrical polymer systems using the Cahn–Hilliard theory[14]. They found qualitative agreement with experiments by Langhammer and Nestler[15]. Roe[6] has presented a theory of the interface between polymers and polymer solutions based on his own theory of non-uniform systems, derived by modifying the Flory–Huggins theory of solutions.

Previously we proposed a theory[7] also based on Cahn–Hilliard theory. These theories predict the molecular weight and the temperature dependence of interfacial tension in the region from the critical temperature to temperatures far away from it. Scaling approaches to interface properties have recently been made by Widom[16], Fisk and Widom[17], Ohta and Kawasaki[18] and by Rice[19].

Interfacial tension between polymer melts far from the critical point has been extensively measured[20]. However, interfacial tension data for polymer solutions are few, except the results of Langhammer and Nestler[15] and our data[21] for polystyrene–methylcyclohexane solutions with polystyrene molecular weight 37000.

Properties near the critical temperature (i.e. the critical exponents, critical amplitudes and dependence of interfacial tension on molecular weight and temperature) are not yet known. Investigation of them would enable us to test the universality of the critical exponents and also to examine recent theories.

Here, we have measured interfacial tension for solutions of polystyrene-methylcyclohexane from the critical solution temperature to slightly below it, using different polystyrene molecular weights.

THEORETICAL

Moving from the critical temperature, T_c, to slightly below it we can distinguish certain regions.

(1) *Critical region*

This is the region in which the critical exponents are defined. De Gennes[22] derived the Ginsburg criterion which gives the width of the region $T_c - T$ wherein critical fluctuations cannot be neglected. This is written as:

$$T_c - T \propto \theta N^{-1/2} \qquad (1)$$

for a polymer–solvent system, where θ is the Flory θ-temperature and N is the polymerization index. This condition suggests that the higher the molecular weight the narrower the critical region. Determination of the critical exponents becomes difficult experimentally as the molecular weight is raised. Dobashi *et al.*[3] have

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investigated the molecular weight dependence of the width of the critical region.

The critical exponent, μ, for interfacial tension (hereafter abbreviated *IFT*) is defined as:

$$\sigma=\sigma_0(T_c-T)^{\mu} \tag{2}$$

From scaling arguments we obtain[16]:

$$\sigma \sim kT/\xi^{(d-1)} \tag{3}$$

where k is the Boltzmann constant; d is the number of spatial dimensions; and ξ is the correlation length which scales as:

$$\xi=\xi_0(T_c-T)^{-\nu} \tag{4}$$

where ν is another critical exponent describing the divergence of the correlation length near the critical point. Therefore, from equations (2)–(4) we obtain:

$$\mu=(d-1)\nu \tag{5}$$

When the theoretical value $\nu=0.630$[23] which is a result from renormalization group theory is assigned, $\mu=1.260$ is obtained for the three-dimensional case.

In mean-field type theories[7,8] (called square gradient theory by Widom[16]) *IFT* for a polymer–solvent system near the critical temperature depends on temperature and molecular weight:

$$\sigma \sim N^{-1/4}(T_c-T)^{3/2} \tag{6}$$

which gives $\mu=1.5$, and for interfacial thickness L:

$$L \sim N^{1/4}(T_c-T)^{-1/2} \tag{7}$$

thus $\nu=1/2$ when L is identified with ξ.

The molecular weight dependence of the critical amplitudes—the factors in front of (T_c-T)—is also of interest. De Gennes[24] pointed out that the correlation length, ξ, should not be proportional to $N^{1/2}$ as given by Debye, but to $N^{1/4}$. Chu[25] investigated the molecular weight dependence of ξ_0 by light scattering to obtain $\xi_0^2 \propto N^{0.57}$. Vrij and Esker[26] derived from their theory of critical opalescence that:

$$\xi_0^2=2\langle R_g{}^2\rangle\varphi_c \tag{8}$$

where R_g is the radius of gyration of the polymer coil and φ_c is the critical concentration. Equations (7) and (8) both predict that $\xi \propto N^{1/4}$.

Using the scaling law, we can show that equation (3) holds including the N-dependence of the critical amplitudes[27]. Then, assuming the following equation for ξ with large N,

$$\xi \propto N^{a}(T_c-T)^{-\nu} \tag{9}$$

we obtain an equation for *IFT*:

$$\sigma \sim N^{-2a}(T_c-T)^{2\nu} \tag{10}$$

(*2*) *Region* R $\sim$ L

Interfacial thickness, L, becomes smaller as temperature is lowered from the critical point. At a certain temperature, T', it becomes comparable with the polymer coil dimension, R. A crossover phenomenon may then be expected. This is similar to critical phenomena in thin films[28]. If we identify L with ξ and adopt equation (7), we obtain using $R \sim L$:

$$T_c-T' \sim N^{-1/2} \tag{11}$$

where $R \sim N^{1/2}$ is assumed. This condition is the same as the Ginsburg criterion (equation 1) and also limits the width of the critical region.

In this crossover region our theory[7] predicts a first order transition from a diffuse interface to a sharp one. When it takes place, polymer chains at the interface collapse along the direction perpendicular to the interface. This prediction is also similar to that of de Gennes' adsorption theory[29].

(*3*) *Region* R $\gg$ L

If we go further into the region where $R \gg L$, another type of universality appears—namely scaling properties obtained from the magnetic analogue.

Daoud and Jannink[30] have presented a theory which gives a temperature–concentration diagram for polymer solutions. According to their theory, the concentrated phase of a demixed polymer solution corresponds to the semi-dilute and tricritical region. In this region the correlation length is independent of molecular weight and is described by:

$$\xi \sim C^{-1} \tag{12}$$

where C is the polymer concentration. Therefore, using the relation $\sigma \sim kT/\xi^2$, we have:

$$\sigma \sim kTC^2 \tag{13}$$

where we assign to C the concentration of the polymer-rich phase, proposed by de Gennes[31]. In this region C may be expressed by:

$$C \propto (\theta-T) \tag{14}$$

Therefore, we have:

$$\sigma \sim kT(T-\theta)^2 \tag{15}$$

EXPERIMENTAL

Materials

Polystyrene samples (Pressure Chemical Co.) had molecular weights $M_w=9\,000, 17\,500, 37\,000, 110\,000$ and $233\,000$. One further sample (Toyo Soda) had $M_w=1.26\times10^6$ (*Table 1*).

Samples were purified by repeated precipitation by benzene and methanol and dried in a vacuum oven for a few days. Methylcyclohexane (spectroscopic grade, Tokyo Kasei Kogyo Co.) was purified by fractional distillation.

Methods

Interfacial tension was measured by a sessible bubble method; the apparatus is shown in *Figure 1*.

The solution in the glass vessel was magnetically stirred

Table 1 Sample molecular weights

Sample	M_w	M_w/M_n
Pressure Chemical	9000	1.06
	17500	1.06
	1.1×10^5	1.06
	2.33×10^5	1.06
Toyo Soda	1.26×10^6	1.05

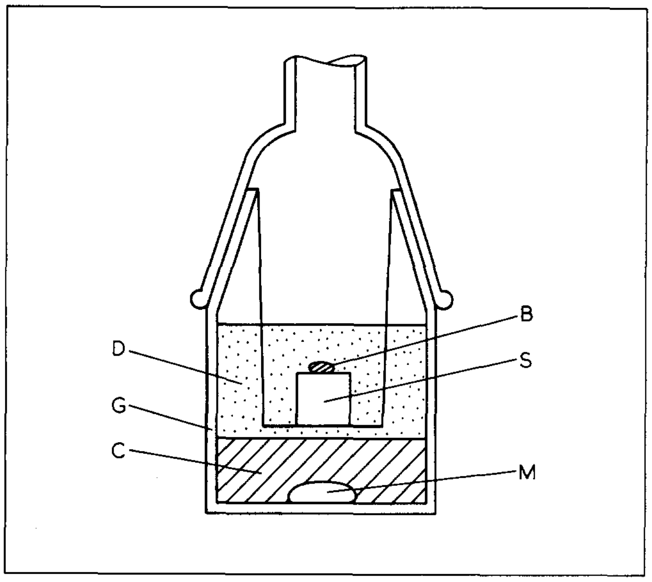

Figure 1 Apparatus for measuring interfacial tension: (B) bubble of the concentrated phase; (D) dilute phase; (M) magnetic stirrer; (G) glass vessel

for about 15 min at a given temperature. Dispersed droplets of the polymer-rich phase were then allowed to settle and accumulate on the cylinder (S) hanging in the solvent-rich phase to form an observable bubble. When the shape of the bubble changed no further with time, its height h and equatorical radius r were measured using a microscope. The interfacial tension σ was calculated from Porter's equation[32]:

$$\sigma/\Delta\rho g = h^2(0.5000 - 0.3047h/r + 1.219h^3/r^3)$$

where $\Delta\rho$ is the difference in density between the demixed phases, and g ($=980.7$ cm s^{-2}) is the acceleration due to gravity. Bubble size was kept within the range $0.1 < h/r < 0.5$. For $h/r > 0.5$ the value of $\sigma/\Delta\rho g$ calculated from the above equation is dependent on bubble size.

The density difference $\Delta\rho$ was measured with a float which was set within the solutions to penetrate the interface. $\Delta\rho$ was calculated by measuring the change in position when a weight on the float was changed.

The volume ratio of the demixed two phases was also measured to obtain coexistence curves. For $M_w = 1.26 \times 10^6$, $\Delta\rho$ was calculated from the coexistence curve obtained by the use of a refractometer.

Temperatures used for the measurements were $0.15° \sim 0.5°\mathrm{C} \leqslant T_c - T \leqslant 5° \sim 7°\mathrm{C}$ for density difference experiments and $0.3° \sim 0.5°\mathrm{C} \leqslant T_c - T \leqslant 5° \sim 7°\mathrm{C}$ for *IFT.* Temperatures were controlled within $\pm 0.01°\mathrm{C}$ or $\pm 0.005°\mathrm{C}$.

The critical exponent, β, was determined by least-squares figgint of the data for $\log(\Delta T/T_c) < -2.1(M_w = 9\,000)$; $-2.2(M_w = 17\,500)$; $-1.7(M_w = (M_w = 37\,000)$; $-1.9(M_w = 110\,000)$; $-1.8(M_w = 2.33 \times 10^5)$; $-1.7(M_w = 1.26 \times 10^6)$.

The critical exponent, μ, was determined by least-squares fitting of the data for $\log(\Delta T/T_c) < -2.2$ $(M_w = 9\,000)$; $-2.2(M_w = 17\,500)$; $-2.4(M_w = 37\,000)$.

The density difference $\Delta\rho$ was determined to within $\pm 3.0 \times 10^{-4}$ g cm^{-3} and the interfacial tension to within $\pm 5.0 \sim 7.0 \times 10^{-4}$ dyn cm^{-1}.

RESULTS

Critical concentrations φ_c (vol. fractions) and critical temperatures (T_c) are listed in *Table 2.*

Figure 2 shows a typical phase diagram for $M_w = 110\,000$. The Flory θ-temperature was determined to be 69.76°C from the Schultz–Flory plot in *Figure 3*; the value obtained agrees well with other reported results[33].

The molecular weight dependence of the critical concentration is shown in *Figure 4* together with the data of Dobashi *et al.*[3] for the same system. The plot is almost linear over the entire range of molecular weights but seems to become steeper at high molecular weights. The value of the slope obtained using data for all molecular weights is -0.40 compared with -0.44 when data for molecular weights 9 000 and 17 500 are omitted.

The relation between *IFTσ* and ΔT for various molecular weights is shown in *Figure 5.* The higher the

Table 2 Critical concentration ϕ_c and critical temperature T_c

M_w	T_c (K)	ϕ_c (g/ml)
9000	281.20	0.212
17 500	296.32	0.169
37 000	309.65	0.131
110 000	323.24	0.091
2.33×10^5	329.92	0.061
1.26×10^6	336.97	0.0289

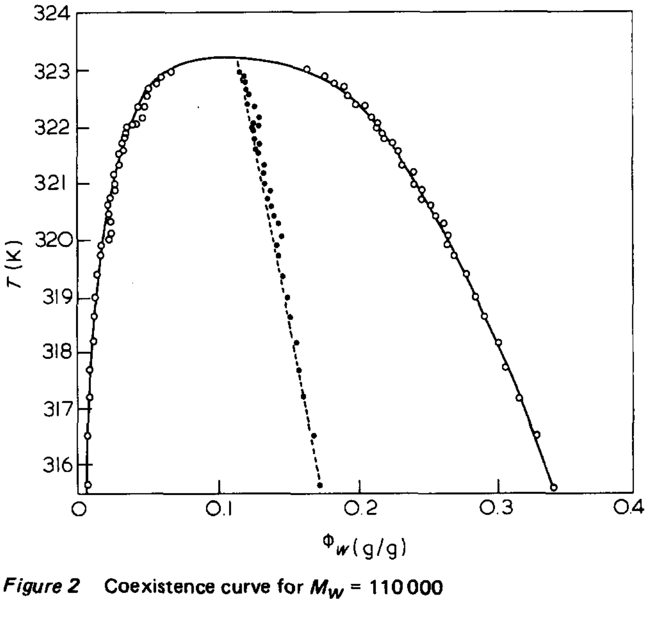

Figure 2 Coexistence curve for $M_w = 110\,000$

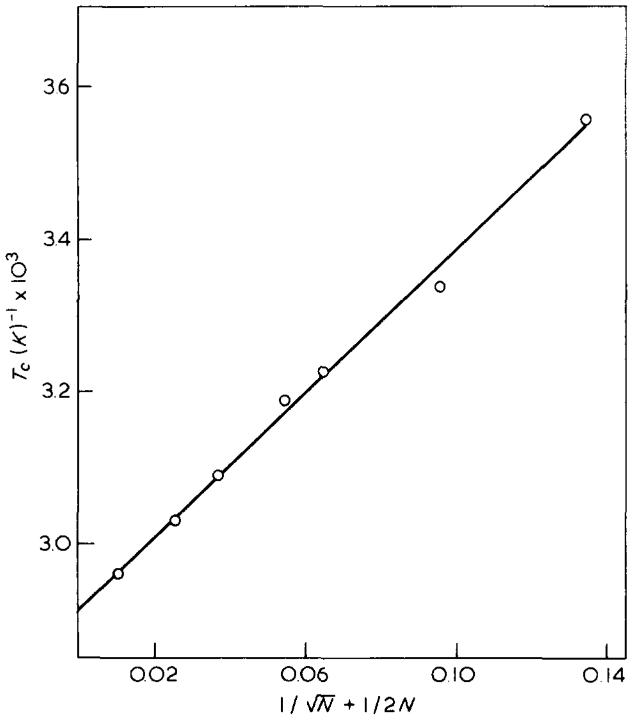

Figure 3 Schultz–Flory plot. $N = M_w/146$

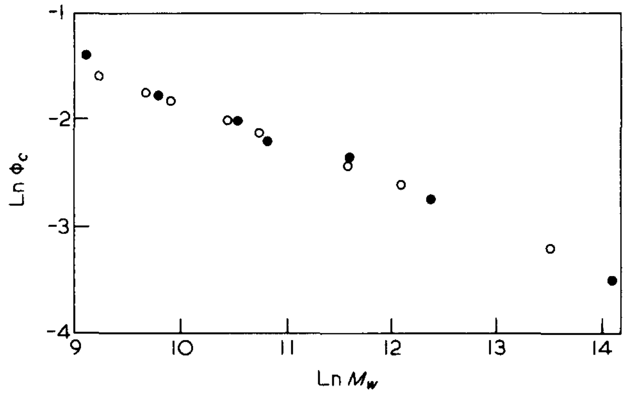

Figure 4 Molecular weight dependence of the critical concentrations, ϕ_c, for polystyrene in methylcyclohexane. Full circles present work; and open circles Dobashi *et al.*[3]

molecular weight the smaller the *IFT* (at the same ΔT) and the magnitudes of *IFT* increased as the temperature is lowered from the critical point. For $M_w = 17\,500$ and $37\,000$ a rather abrupt change in *IFT* can be seen near the critical temperature (see below).

Figure 6 shows plots of log $\Delta\rho$ vs. log ΔT. The plots are almost straight lines over the whole temperature region measured. Critical exponent, β, and the critical amplitudes, $\Delta\rho_0$, defined by

$$\Delta\rho = \Delta\rho_0(\Delta T/T_c)^{\beta} \qquad (16)$$

are obtained from these plots for all molecular weights. Results are listed in *Table 3*. The values of β obtained are almost the same for all the molecular weights.

The critical exponent, μ, and the amplitudes σ_0 for *IFT* defined by

$$\sigma = \sigma_0(\Delta T/T_c)^{\mu} \qquad (17)$$

are listed in *Table 4*. These values were obtained in the same manner as for $\Delta\rho$. For the higher molecular weights, it was not possible to obtain these values (see Discussion).

DISCUSSION

Critical exponents and amplitudes

Exponent β is obtained to be 0.34~0.35, in agreement with results reported by Nakata *et al.*[1]

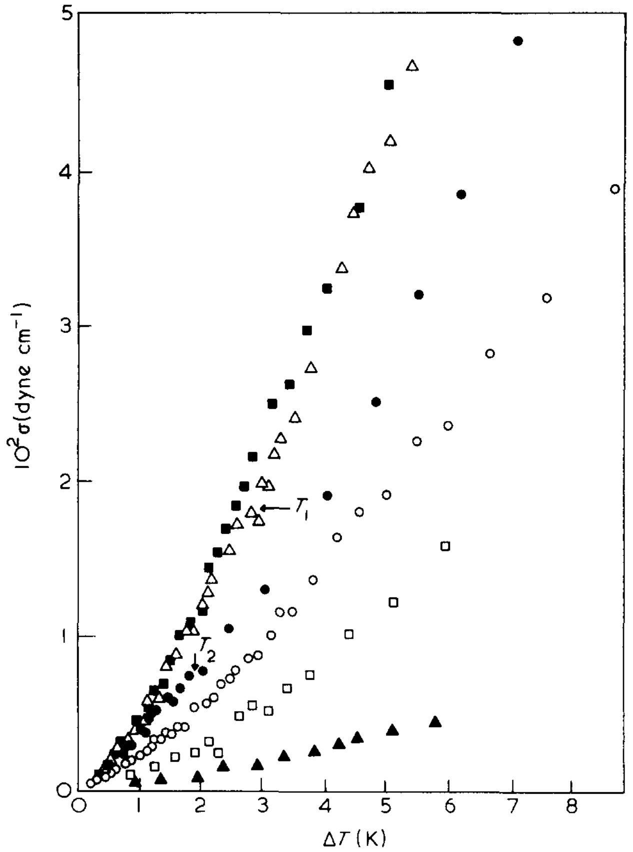

Figure 5 Interfacial tension σ as a function of $\Delta T = T_c - T$. ■, $M_w = 9000$; △, $M_w = 17\,500$; ●, $M_w = 37\,000$; ○, $M_w = 110\,000$; □, $M_w = 2.33 \times 10^5$; ▲, $M_w = 1.26 \times 10^6$

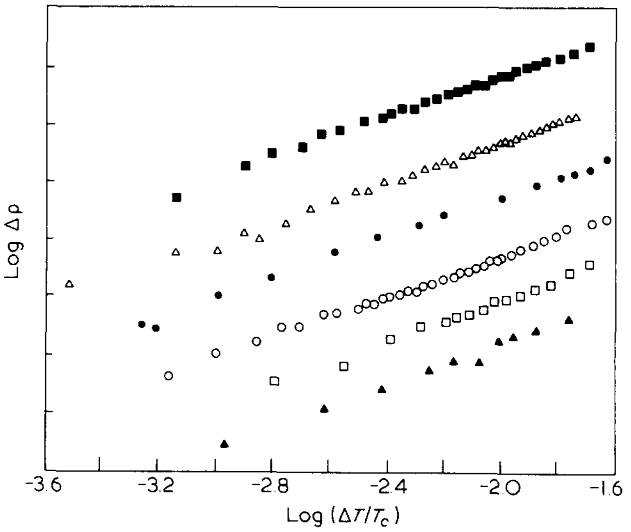

Figure 6 Log $\Delta\rho$ vs. log$(\Delta T/T_c)$: ■, $M_w = 9000$; △, $M_w = 17\,500$; ●, $M_w = 37\,000$; ○, $M_w = 110\,000$; □, $M_w = 2.33 \times 10^5$; ▲, $M_w = 1.26 \times 10^6$

Table 3 Critical amplitudes $\Delta\rho_0$ and critical exponent β for the density difference

M_w	$\Delta\rho_0$ (g/ml)	β
9000	0.463	0.35
17500	0.410	0.34
37000	0.385	0.35
1.1×10^5	0.294	0.34
2.33×10^5	0.227	0.34
1.26×10^6	0.080	0.34

Table 4 Critical amplitudes σ_0 and critical exponent μ for the interfacial tension

M_w	σ_0 (dyn/cm)	μ
9000	9.77	1.35
17500	8.49	1.31
37000	3.23	1.17
1.1×10^5	–	–
2.33×10^5	–	–
1.26×10^6	–	–

Figure 7 shows plots of log σ vs. $\log(\Delta T/T_c)$ for all the molecular weights measured. As seen from this Figure, the plots are almost straight lines for $M_w = 9\,000$, 17 500 and 37 000 but are not for $M_w \geq 110\,000$. In the latter case, the slopes for the plots change substantially near the critical temperatures, indicating that the systems have already deviated from critical behaviour. Thus, for $M_w = 110\,000$, 2.33×10^5 and 1.26×10^6 the critical exponent μ and the amplitudes σ_0 cannot be obtained.

The values $1.17 \sim 1.35$ for μ are close to 1.39, obtained for cyclohexane–aniline by Atack and Rice[34] and also close to that given by the Guggenheim equation, $\mu = 11/9 = 1.22$; the value of 1.26 calculated from renormalization group theory is also very close. This shows that the universality of the critical exponents is confirmed not only by β but also by μ.

The molecular weight dependence of the critical concentration obtained from *Figure 4*, $\varphi_c \propto N^{-0.40 \sim -0.44}$, indicates a deviation from the $\varphi_c \propto N^{-1/2}$ relationship derived from Flory–Huggins theory. Data recently reported by Dobashi *et al.*[3] for the same system are also plotted in *Figure 4*. Our results are almost the same as theirs; thus, at least for this system contradiction of the Flory–Huggins theory is evident. Using Flory–Huggins theory, Dobashi *et al.*[3] also determined an equation for the free energy from coexistence curves, and obtained the molecular weight dependence of the observed discontinuity in specific heat, ΔC, at the critical point:

$$\Delta C = (3T_c/V_m)(\partial^3 G/\partial\varphi^2 \partial T)^2/(\partial^4 G/\partial\varphi^4) \qquad (18)$$

where G is free energy and φ is volume fraction of polymer and V_m is the molar volume of the mixtures; ΔC is thus proportional to $N^{-0.40}$, while Flory–Huggins theory predicts that ΔC is proportional to $N^{-1/2}$; this discrepancy is closely related to that of the critical concentration.

From the molecular weight dependence of the critical amplitudes, $\Delta\rho_0$, the following relation is obtained:

$$\Delta\rho_0 \propto N^{-0.34} \qquad (19)$$

Dobashi *et al.*[3] also found that $\Delta\varphi$ is proportional to $N^{-0.23}$ where $\Delta\varphi$ is difference in concentration between the coexisting two phases; the value -0.23 is close to $-1/4$ which is given by Flory–Huggins theory but disagrees with our result; however, this disagreement is not serious because our plot of $\ln \Delta\rho_0$ vs. $\ln N$ is not so straight and the value of -0.34 is not exact.

The molecular weight dependence of *IFT* at various $\Delta T/T_c$ is shown in *Figure 8*. As stated above, the higher molecular weights systems deviate from critical behaviour; thus, the figure does not show the molecular weight dependence of the critical amplitude exactly in these systems.

However, if ΔT is small enough, σ at the same $\Delta T/T_c$ should be approximately proportional to σ_0. Therefore, we may expect that the slope in *Figure 8* at small $\Delta T/T_c$ is not far from that of the critical amplitude. Since a power dependence on N is expected at high molecular weights, we omit data on $M_w = 9000$ and obtain

$$\sigma \propto N^{-0.42 \sim -0.45} \qquad (20)$$

for the smallest $\Delta T/T_c (= -3.0)$.

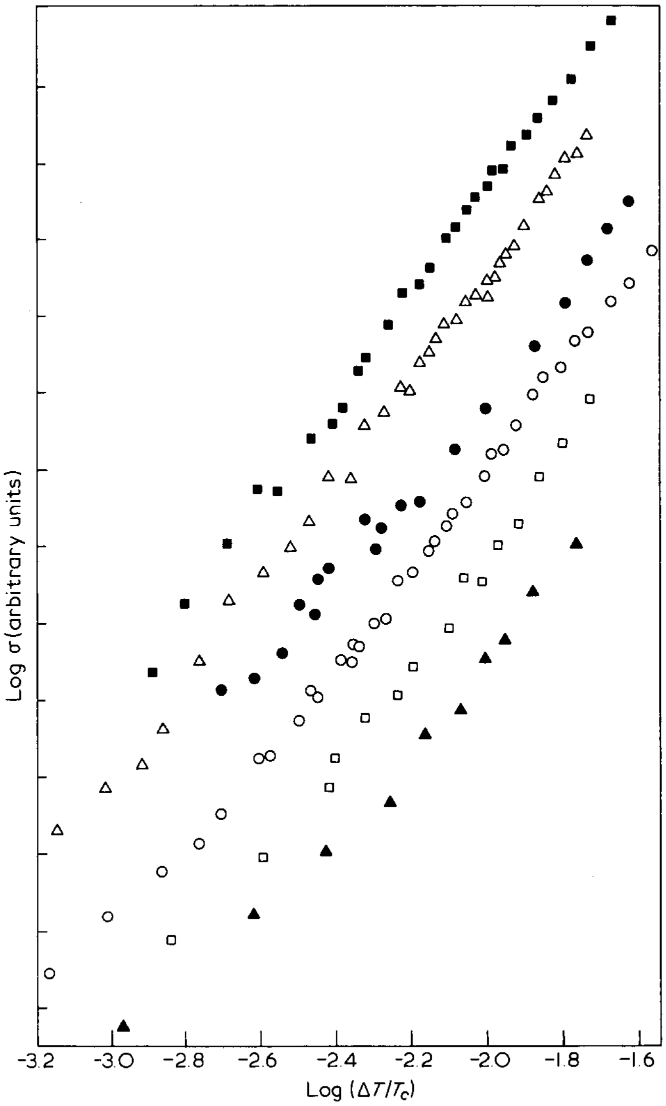

Figure 7 Log σ vs. $\log(\Delta T/T_c)$. ■, $M_w = 9000$; △, $M_w = 17\,500$; ●, $M_w = 37\,000$; ○, $M_w = 110\,000$; □, $M_w = 2.33 \times 10^5$; ▲, $M_w = 1.26 \times 10^6$

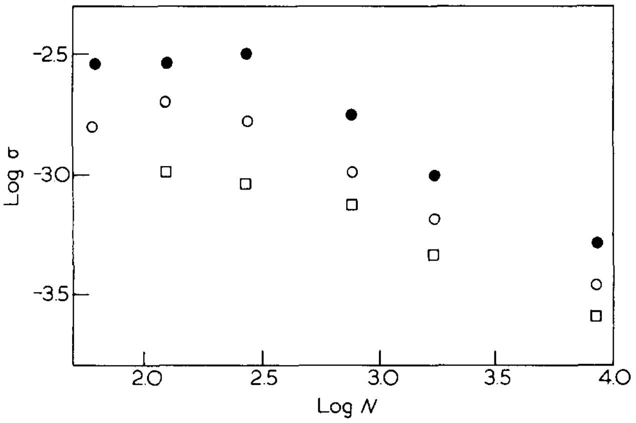

Figure 8 Molecular weight dependence of the interfacial tension near the critical temperature compared at the same $\log(\Delta T/T_C)$ (= −2.6 (●); −2.8 (○), and −3.0 (□))

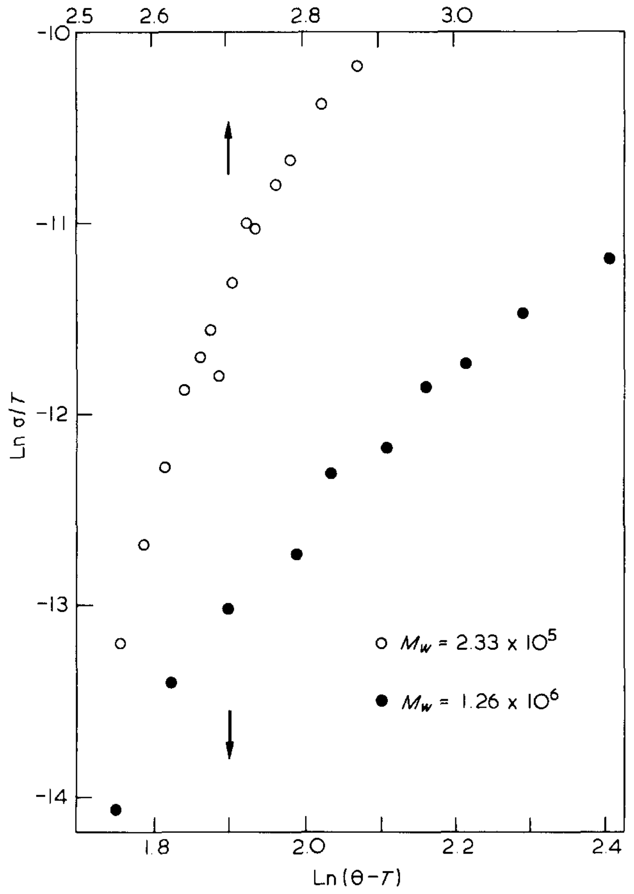

Figure 9 $\mathrm{Ln}(\sigma/T)$ vs. $\ln(\theta - T)$ plots for high molecular weights

The value thus obtained should be compared with −0.57 which is the power for the molecular weight dependence of the inversely-squared correlation length obtained by Chu[25] since equation (10) holds. The two values are close, and the disagreement may be due to the fact that equation (20) does not express the molecular weight dependence of the critical amplitude or that the molecular weight is not high enough. Both values (−0.44 and −0.57) substantially deviate from the mean field prediction, $\sigma \propto N^{-1/4}$.

Region from R ~ L *to* R ≫ L

In *Figure 5* we can see that the cruves for $M_w = 9000 \sim 110000$ are superimposed on each other near T_c and separate at slightly below T_c (at about T_1 for $M_w = 17\,500$ and T_2 for $M_w = 37\,000$). The plots in *Figure 7* also show deviations from linearity at $\Delta T/T_c$ corresponding to T_1 or T_2.

These sudden changes in slopes of the curves suggest a discontinuity in $\partial\sigma/\partial T$, i.e. the first order transition predicted by our theory. The non-linearity (*Figure 7*) of the higher molecular weights ($M_w = 233\,000$ and $1\,260\,000$) suggests that a change has already taken place at smaller ΔT than that of the experimental range.

According to the theory, a first order transition from a diffuse interface to a sharp one occurs with the change in polymer coil dimensions, becoming closer to T_c as the molecular weight increases, in accordance with the present result. This feature also supports the cross-over condition $R \sim L$. However, the sudden changes in slopes are so slight that we cannot be certain whether they have physical significance or are due to experimental scatter. Further experiments are needed to establish the validity of the transition.

Figure 9 shows plots of $\ln(\sigma/T)$ vs. $\ln(\theta - T)$ and *Figure 10* shows $\ln(\sigma/T)$ vs. $\ln C$, where C is concentration of polymer-rich phase. According to the equations (13) and (15), the slopes of these plots should approach 2 as the temperature is lowered from the critical point. However, as observed, these plots are not straight lines in the measured temperature range. If we draw straight lines in the final region within the measured range, we obtain slopes of 5.9 (*Figure 9*) and 3.6 (*Figure 10*) for $M_w = 2.33 \times 10^5$; and 3.2 (*Figure 9*), 3.2 (*Figure 10*) for $M_w = 1.26 \times 10^6$.

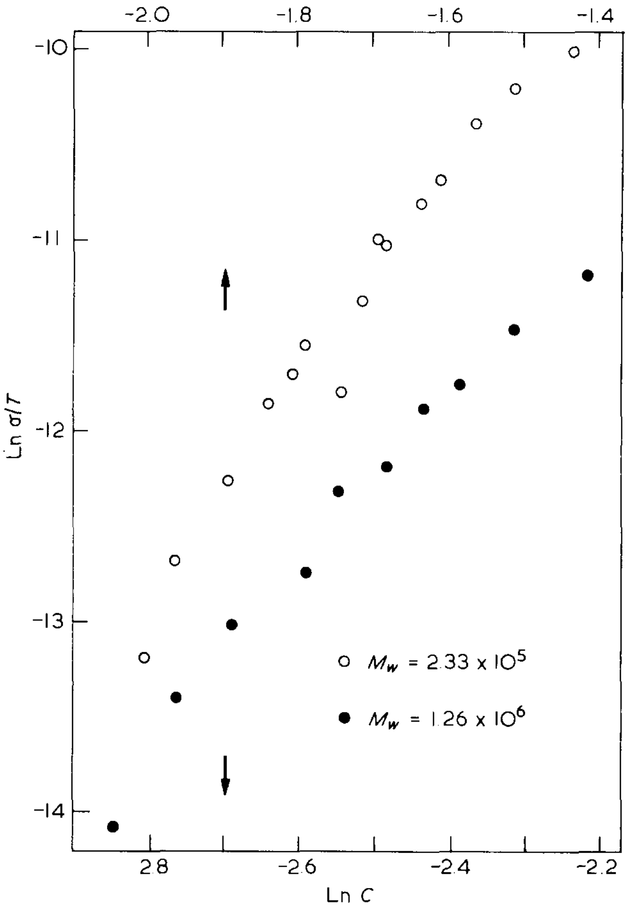

Figure 10 $\mathrm{Ln}(\sigma/T)$ vs. $\ln C$ plots for high molecular weights

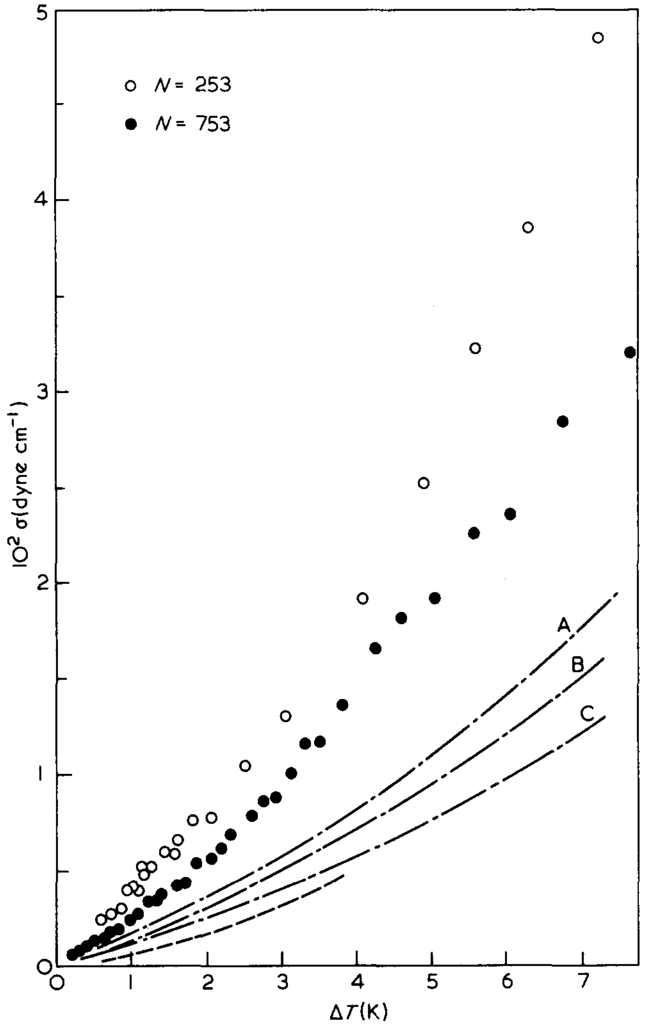

Figure 11 Comparison between experimental (○, ●) and theoretical[6,7]. — · — ·, Numerical results from Roe's theory[6]: (A) $N = 200$; (B) $N = 500$; (C) $N = 1000$. — — — Calculated from equations (21) and (22) for $N = 253$

All these values are larger than predicted theoretically but become smaller as molecular weight increases.

Reasons for the deviations are not clear, but it may be that the molecular weights are not high enough or the temperatures not far enough from the critical values to obtain the exponent. At any rate, it is clear that equation (12) does not hold in the measured molecular weight or temperature range.

COMPARISON OF *IFT* THEORIES

Numerical results obtained from Roe's theory[6] are plotted in *Figure 11* for a polystyrene–cyclohexane solution with $N = 200, 500$ and 1000 as a function of ΔT. N is the number of segments ($M_w/N = 146$) in a polymer molecule. The theory agrees well with experiment in order of magnitude, but gives values nearly half the corresponding experimental ones. However, according to our theory[7] the *IFT* of a polymer solution near its critical point, T_c, is expressed by:

$$\sigma = \sigma_0(\Delta T/T_c)^{3/2} \tag{21}$$

where

$$\sigma_0 = (2/3)\varphi_c{}^{1/2} kTc(\langle r^2\rangle_0/M)^{1/2}(M/N)^{1/2}$$

$$(1 + N^{-1/2} + N^{-1})^{1/2}/\omega$$

Here, k is the Boltzmann constant, $\langle r^2\rangle_0$ is the mean-square unperturbed chain dimension of a polymer coil, M is the molecular weight of polymer, ω is the volume of the solvent (assumed equal to that of segment) and φ_c is the critical concentration of polymer solution (vol fraction). When $kT\chi$ depends on temperature, equation (21) is rewritten:

$$\sigma_0' = \sigma_0[1 + 2(1 + N^{-1/2})^{-2}(\psi - 1/2)]^{3/2} \tag{22}$$

Using $\psi = 0.613$ from the Schultz–Flory plot, $(\langle r^2\rangle_0/M)^{1/2} = 6.6 \times 10^{-9}$ cm, $\omega = 136$ cm^3/mol and $M/N = 146$ and the experimental results for φ_c and T_c, we obtain from equations (21) and (22) the front factors σ_0 (dyn/cm) to be 5.75 ($M = 9000$); 5.38 ($M = 17\,500$); and 4.94 ($M = 37\,000$). The experimental *IFT* values are one figure larger than the corresponding experimental ones as shown in *Figure 11*. However, the calculated front factors agree well with experiment.

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