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Interfacial Tension of Oligostyrene/Oligo(dimethylsiloxane) near the Critical Point

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ABSTRACT: Interfacial tension γ of an oligomer blend, oligostyrene ($M_w = 600$) and oligo(dimethylsiloxane) ($M_w = 460$), was measured by the sessile-drop method. The interfacial tension near the critical point could be fitted to $\gamma = \gamma_0 \epsilon_{1/T}^{\mu}$, where $\epsilon_{1/T}$ is the reduced temperature distant $\epsilon_{1/T}$ ($=T_c/T - 1$) from the critical point T_c. The critical exponent μ was determined to be 1.27, which was exactly of the Ising type, showing an importance of critical fluctuations. The critical amplitude γ_0 was 5.05 mN m^{-1}. The critical amplitude of the mean-field type theory was calculated with the interaction parameter χ evaluated from the coexistence curve. The theoretical prediction was reasonably consistent with the experimental result, taking into account that the critical behavior was of the Ising type.

Introduction

The importance of interfacial tension between polymer melts or coexisting phases of phase-separated polymer blends is increasingly being recognized in studies of multicomponent polymeric systems as a fundamental property. Considerable efforts have been devoted to the theoretical understanding of the interfacial tension of liquid–liquid interfaces of various polymeric systems, including polymer solutions.[1] Most experimental studies, however, have been limited to the interface of completely-immiscible polymer blends of industrial significance.[2] Few of the experimental studies were directed toward an understanding of partially-miscible polymeric systems,[3–11] in particular, to polymer blends. Most of the experimental studies of partially-miscible systems were of the critical behavior of the interfacial tension in polymer solutions[3–8] and polymer blend solutions.[9] Recently, Wagner and Wolf[11] have investigated the interfacial tension of polymer blends and their solutions in terms of the phase behavior of miscibility.

The interfacial tension of the liquid–liquid interface is primarily controlled by the segregation strength, i.e., miscibility. In polymer blends, temperature and molecular-weight dependences of the interfacial tension vary with the segregation strength.[12,13] Here, the segregation strength is characterized by the distance from the critical solution point, more specifically by the interaction parameter χ as $\chi \geq \chi_c$ (weak segregation), $1 > \chi \gg \chi_c$ (strong segregation), and $\chi > 1$ (very strong segregation), where χ_c is the value at the critical point. Therefore, studies of the interfacial tension of partially-miscible polymer blends as a function of the segregation strength are indispensable for better understanding of the interfacial tension of polymer liquid mixtures.

However, the experimental approach to this problem is difficult in general. One of the difficulties is obtaining macroscopic phases coexisting in equilibrium because of the high viscosity of the system. To make the macroscopic coexisting phases is essential for accurate interfacial tension measurement. It should be noted here that these same considerations apply to coexistence curve measurements. The coexistence curve is obviously important in discussing interfacial tension as a function of the segregation strength, and furthermore the density difference between coexisting phases is usually needed for interfacial tension measurements. Another experimental difficulty arises from the fact that most polymer pairs are immiscible, and very few polymer mixtures have the critical point at experimentally accessible temperatures.

Oligomer blends can solve these difficulties. Although they are not true polymer blends, the interfacial tension of oligomer blends can provide information about the interface and miscibility of polymer blends. This is a particular significance of studies of interfacial tension using oligomer blends.

In this study, interfacial tension near the critical point was measured for an oligomer blend, for which the coexistence curve near the critical point was precisely determined in our previous study.[14] Critical behavior of the interfacial tension is an issue for partially-miscible polymer blends at the weak segregation limit. To our knowledge, this is the first measurement of the interfacial tension of oligomer blends near the critical point. The system used was an oligostyrene/oligo(dimethylsiloxane) (OS/ODMS) blend with degrees of polymerization for both of about 6. In the following sections, after a brief review of the theoretical background, we describe details of the experimental method, followed by a presentation of the results and discussion. The critical exponent for the interfacial tension was evaluated to confirm that it is of the Ising type for oligomer blends. The magnitude of the interfacial tension, i.e., the critical amplitude, is discussed, comparing it with the prediction of mean-field theory.

Theoretical Background

Critical behavior is generally characterized by the critical exponents for static and dynamic properties.[15] Interfacial tension γ near the critical point, for instance, is expressed as

$$\gamma \propto \epsilon_T^{\mu} \tag{1}$$

where ϵ_T is the reduced temperature distance, which is defined as ($T/T_c - 1$) with the critical temperature T_c, and μ is the critical exponent. The mean-field theory breaks down near the critical point owing to large concentration fluctuations. Scaling laws give relationships among the critical exponents for various physical quantities. According to Widom's scaling for a three-

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dimensional system,[16]

$$\mu = 2\nu \tag{2}$$

Here, the exponent ν is for the correlation length $\xi \sim \epsilon_T^{-\nu}$. The exponent $\nu = 0.63$ for three-dimensional fluid systems, so $\mu = 1.26$. The *non*-mean-field critical behavior in such systems is often referred to as Ising-type behavior.

On the other hand, the mean-field theory predicts

$$\mu = \gamma/2 + 2\beta \tag{3}$$

with the critical exponents γ and β related to the susceptibility and the coexistence curve, respectively.[16] Therefore, in the mean-field theory, $\mu = 1.5$ because $\gamma = 1$ and $\beta = 0.5$.[15] Critical behavior of polymer blends with high molecular weight is expected to be of the mean-field type except very near the critical point.[17]

In the framework of the mean-field theory, adopting the square-gradient theory,[13] the interfacial tension near the critical point for a polymer blend is given as[18]

$$\gamma = \frac{2}{3}\frac{kT_{\mathrm{cm}}\chi_{\mathrm{cm}}\bar{l}}{v_0}\frac{\epsilon_{\chi\mathrm{m}}^{\ 3/2}}{(P_1^{\ -1/2} + P_2^{\ -1/2})f_{\mathrm{asy}}^{\ 2}} \tag{4}$$

with

$$\epsilon_{\chi\mathrm{m}} = \frac{\chi}{\chi_{\mathrm{cm}}} - 1 \tag{5}$$

$$\chi_{\mathrm{cm}} = \frac{1}{2}(P_1^{\ -1/2} + P_2^{\ -1/2})^2 \tag{6}$$

$$f_{\mathrm{asy}}^{\ 2} = \frac{1}{2}\left[\left(\frac{P_2}{P_1}\right)^{1/4} + \left(\frac{P_1}{P_2}\right)^{1/4}\right] \tag{7}$$

$$\bar{l}^2 = \left[\left(\frac{R_1^{\ 2}}{P_1}\right)P_1^{\ 1/2} + \left(\frac{R_2^{\ 2}}{P_2}\right)P_2^{\ 1/2}\right]/(P_1^{\ 1/2} + P_2^{\ 1/2}) \tag{8}$$

Here, k is the Boltzmann constant, v_0 is the site volume, χ is the interaction parameter per site between polymer 1 and polymer 2, and χ_{cm} represents χ at the mean-field critical point T_{cm}. P_1 and P_2 are the polymeric indices. The factor f_{asy} represents the asymmetry of the polymeric index. R_1^2 and R_2^2 are the mean-square end-to-end distance of polymer chains, so that l is an average Kuhn segment length l ($\equiv R_i^2/P_i$). An alternative expression of eq 4 is

$$\gamma = \frac{2}{3}\frac{kT_{\mathrm{cm}}}{v_0}\frac{\bar{l}}{(P_1P_2)^{1/4}}\epsilon_{\chi\mathrm{m}}^{\ 3/2} \tag{9}$$

Joanny and Leibler derived an equation equivalent to eq 9.[19] The χ-paramter is usually given as a function of temperature by

$$\chi = A + B/T \tag{10}$$

with constants A and B. Therefore, instead of ϵ_T defined above, the following parameter $\epsilon_{1/T}$ is often used in polymer systems.

$$\epsilon_{1/T} = T_c/T - 1 \tag{11}$$

The ϵ_χ defined as

$$\epsilon_\chi = \chi/\chi_c - 1 \tag{12}$$

is related to $\epsilon_{1/T}$ by eq 10 as

$$\epsilon_\chi = \frac{B}{T_c\chi_c}\epsilon_{1/T}, \quad \epsilon_{\chi\mathrm{m}} = \frac{B}{T_{\mathrm{cm}}\chi_{\mathrm{cm}}}\epsilon_{1/T\mathrm{m}} \tag{13}$$

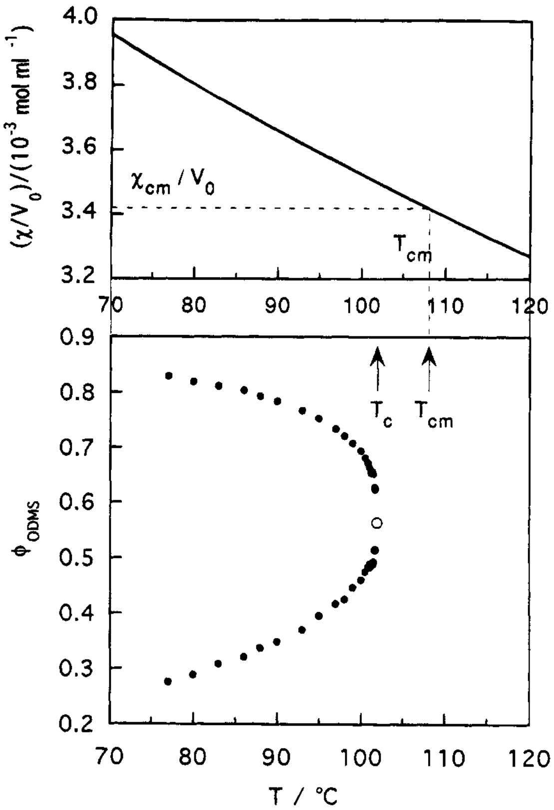

Figure 1. Coexistence curve of the critical blend of OS/ODMS with the χ-parameter. ϕ_{ODMS}, volume fraction of ODMS. V_0, molar site volume. T_{cm}, mean-field critical temperature, χ_{cm}, mean-field critical χ-parameter. ●, coexistence curve; ○, the critical point.

Experimental Section

Materials and Samples. Oligo(dimethylsiloxane) (ODMS) was a product of Shin-etsu Co., Ltd. Number-average molecular weight, M_n, determined by vapor pressure osmometry was 460. It was substantially the pentamer with narrow molecular-weight distribution, which was confirmed by size-exclusion chromatography. Oligostyrene (OS) was a product of Pressure Chemical Co. with $M_w = 600$ and $M_w/M_n < 1.10$. The coexistence curve for the mixture of ODMS/OS with the critical composition is shown in Figure 1, along with the estimated χ-parameter as a function of temperature.[14] The blend for interfacial tension measurements was of the critical composition Wt = 0.50 (0.55_7 in volume fraction).

Interfacial Tension Measurements. The interfacial tension of the phase-separated mixture was measured by the sessile-drop method.[20] The apparatus was specially designed for the present purpose, schematically illustrated in Figure 2. A drop of one of the coexisting phases was formed on a plate in a sample glass cell and was illuminated by an expanded laser beam. The drop image was focused on the detector of a CCD camera, and its size and shape were measured by image analysis. The blended sample sealed in the glass cell was first homogeneously mixed above the critical point and then cooled down to the desired temperature. As the phase separation proceeded, the segregated OS-rich phase sank due to its higher density and accumulated on the plate to form a drop in the ODMS-rich upper phase. It took about 30 min to 2 h, depending upon the temperature, to have clearly-separated coexisting phases and a sharp profile of the drop. After that time, no change in the composition of the coexisting phases was detected by a sensitive differential refractometer, and no substantial change of the drop profile was detectable. It should

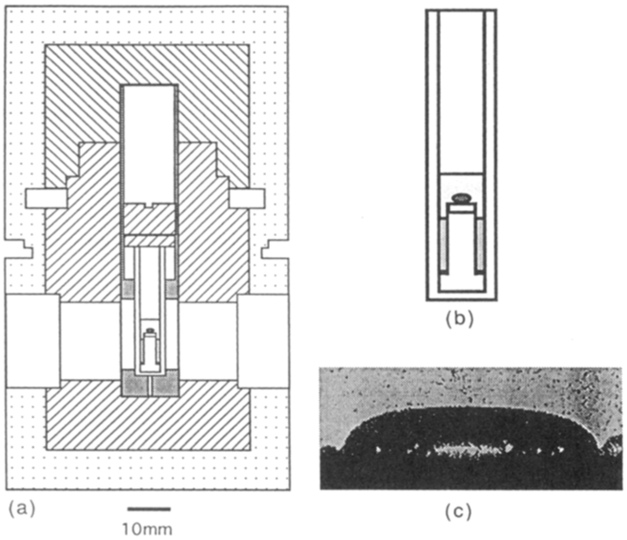

Figure 2. Schematic presentation of an apparatus of the sessile-drop method: (a) sample holder with thermostat, (b) sample cell, and (c) an example of the drop image taken at 93 °C by a CCD camera.

be noted that the total composition before phase separation was carefully adjusted to the critical composition. In a pure binary mixture, compositions of coexisting phases, and therefore the interfacial behavior, are never dependent on the total composition of the mixture. However, for polymer blends molecular-weight polydispersity is unavoidable, which gives rise to a dependence of the coexistence curve on the total composition. This was the case in the present blends.[14] Temperature was controlled to within ±0.05 °C.

The value of $\gamma/g\Delta\varrho$, with g and $\Delta\varrho$ being the gravity constant and density difference between coexisting phases, respectively, was evaluated from the size and shape of the drop either by the Porter equation[21] or by direct fitting of the drop profile computed by the Laplace equation:[20] With the apex h of the drop measured from the maximum radius r (see Figure 3a), the Porter equation is

$$\gamma/g\Delta\varrho = h^2[0.500 - 0.3047(h/r) + 1.219(h/r)^3]$$

which is valid for $0.1 < h/r < 0.5$. The Laplace equation is written as

$$\frac{1}{r_1} + \frac{1}{r_2} = \left(\frac{g\Delta\varrho}{\gamma}\right)y + \frac{2}{b}$$

The radii of curvature r_1 and r_2 are expressed by the first and second derivatives of y with respect to x, where x and y are the coordinates of horizontal and vertical axes, respectively (see Figure 3a). The origin was taken at the top of the drop. b corresponds to the radius of curvature at the top of the drop ($y = 0$). The fitting was made by taking $\gamma/g\Delta\varrho$ and b as parameters to determine the value of $\gamma/g\Delta\varrho$. The drop size was around 1 mm at the maximum radius r. The ratio h/r was larger than 0.5 at $T > 83$ °C, while it was between 0.1 and 0.5 at $T > 83$ °C. Figure 3b shows an example of the drop profile measured by image analysis with the fitting of the Laplace equation.

Interfacial tension γ was calculated from the values of $\gamma/g\Delta\varrho$ with density difference $\Delta\varrho$ obtained from the independently-measured coexistence curve of Figure 1.[14] $\Delta\varrho$ was evaluated from the composition difference ΔW (the coexisting curve) with the densities of pure OPDMS and OS by ignoring the excess volume ΔV_m of mixing. Since the density difference between pure ODMS and PS was rather large, about 0.258 g mL^{-1} at 100 °C, errors in the evaluation of $\Delta\varrho$ from ΔW measurements with the assumption of $\Delta V_m = 0$ would be about 1%, or a few percent even near the critical point,[14] and minor in the total error in γ-evaluation. The major part of the error in γ-evaluation came from errors in the drop profile measurements including experimental reproducibility. Estimated error in γ-evaluation arising from the error in measuring the drop profile from a CCD-camera picture increased from ±5% to ±20% with temperature approaching the critical point T_c, depending on the size and shape, h and h/r. The values of h near T_c were much smaller than those at lower temperatures away from T_c. Taking the experimental reproducibility into account, the expected total error was estimated to range from ±10% to ±30% in the present experimental conditions, which will be illustrated by error bars in the data plots hereafter.

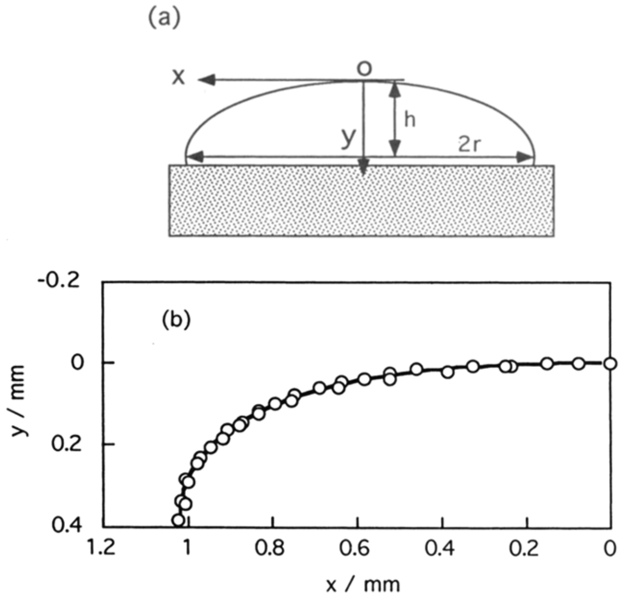

Figure 3. (a) Axes and coordinates for the Porter equation and the Laplace equation, and (b) an example of the fitting of the Laplace equation to a drop profile at 93 °C. In b: ○, measured profile; —, the fitting curve.

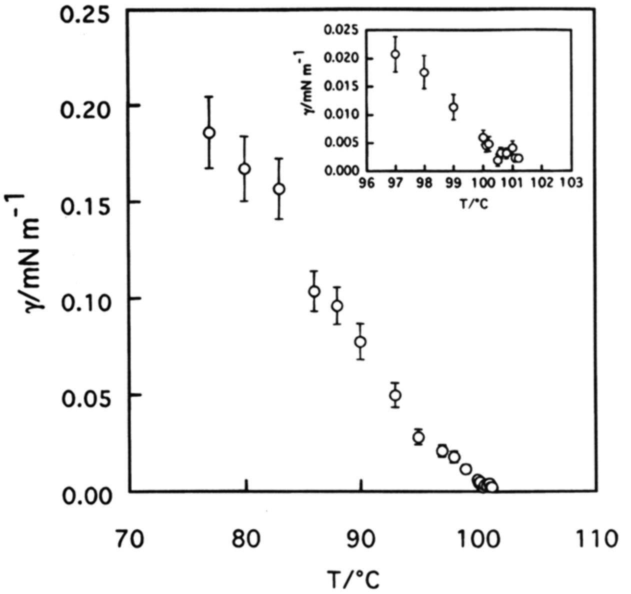

Figure 4. Temperature dependence of interfacial tension γ.

Results and Discussion

Interfacial Tension and Critical Exponent. The temperature dependence of the interfacial tension is shown in Figure 4. The interfacial tension appears at the critical temperature T_c, increases with decreasing temperature, and becomes on the order of 0.01 mN m^{-1} (1 mN m^{-1} = 1 dyn cm^{-1}) at temperatures about 5 °C away from T_c. To evaluate the critical exponent μ of the equation

$$\gamma = \gamma_0 \epsilon_{1/T}^{\mu} \qquad (14)$$

γ was plotted against $\epsilon_{1/T}$ in a log–log scale as shown in Figure 5. Here, T_c was taken to be 101.92 °C as previously determined from the coexistence curve.[14] The exponent μ and the critical amplitude γ_0 were obtained by the least-squares fitting for the data of $T \geq 90$ °C ($\epsilon_{1/T} \leq 0.033$) to be

$$\mu = 1.27, \quad \gamma_0 = 5.05 \text{ mN m}^{-1}$$

The critical exponent μ is of the Ising type, showing an importance of fluctuations near the critical point. It is likely because the degree of polymerization of the present system was very low.[21] This is consistent with the fact that the critical exponent β for the coexistence curve of this blend was $\beta = 0.33_6$ of the Ising type.[14] Looking at the γ–$\epsilon_{1/T}$ plots in Figure 5 very closely, one can see that the plots at $\epsilon_{1/T} > 0.033$ slightly deviate upward from the power-law line for the vicinity of the critical point. This seems to show the crossover from the Ising-type to mean-field type behavior.

Comparison with the Mean-Field Theory. The mean-field expression, eq 9, is rewritten as

$$\gamma = \frac{2kN_A T_{cm}}{3} \frac{\bar{\varrho}^{1/2}}{(\nu_1 \nu_2 M_1 M_2)^{1/4}} \overline{\left(\frac{R^2}{M}\right)}^{1/2} \epsilon_{\chi m}^{3/2} \qquad (15)$$

by replacing the average Kuhn-segment length l by an expression in terms of the mean-square end-to-end distance R^2 divided by molecular weight M.

$$\bar{l}^2 = \overline{\left(\frac{R^2}{M}\right)} \overline{M_0} \qquad (16)$$

with

$$\overline{\left(\frac{R^2}{M}\right)} = \frac{\left(\frac{R_1^2}{M_1}\right) p_1^{1/2} M_{01} + \left(\frac{R_2^2}{M_2}\right) p_2^{1/2} M_{02}}{p_1^{1/2} M_{01} + p_2^{1/2} M_{02}} \qquad (17)$$

$$\overline{M_0} = \frac{P_1^{1/2} M_{01} + P_2^{1/2} M_{02}}{P_1^{1/2} + P_2^{1/2}} \qquad (18)$$

Here, N_A is the Avogadro constant, M_0 is the molecular weight of a monomer, ν is the specific volume of polymers, $\bar{\varrho} = \overline{M_0}/V_0$ and $V_0 = v_0 N_A$. In the previous paper,[14] the χ-parameter of this blend was evaluated such that the Flory–Huggins type mean-field theory reproduced the experimental $\Delta\phi$ of the coexistence curve at $T \leq 93$ °C excluding the vicinity of the critical point, where $\Delta\phi$ was the difference in composition between coexisting phases. The obtained χ-values were shown in Figure 1 and can be expressed by[14]

$$\chi/V_0 \text{ (mol mL}^{-1}) = 1.849 \text{ K}/T - 0.00143 \qquad (19)$$

Inserting the value of χ_{cm} evaluated by eq 6 into eq 19, the mean-field critical temperature T_{cm} is estimated to be 381.37 K.[14] (It should be noted that quantities χ/V_0 and $P_i V_0$ are independent of the choice of the site size V_0, while χ and P_i depend on V_0.) Using $\overline{(R^2/M)}^{1/2} = 0.0670$ nm mol$^{-1/2}$ g$^{1/2}$ and $\varrho = 0.903$ g mL^{-1} with $T_{cm} = 381.37$ K, the numerical value of the front factor, i.e., the critical amplitude of eq 15, was calculated. The value of $(R^2/M)^{1/2}$ is coincidentally the same for both polystyrene and poly(dimethylsiloxane).[22] The result is

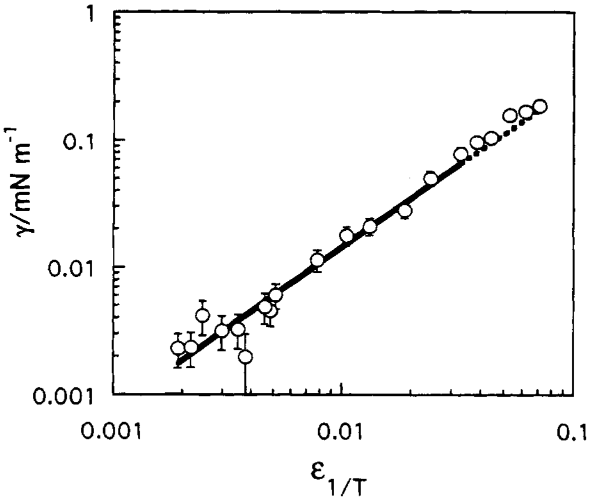

Figure 5. log–log plots of interfacial tension γ against $\epsilon_{1/T}$ ($=T_c/T - 1$). ○, experimental; solid line, the power-law fitting with $\mu = 1.27$ for $\epsilon_{1/T} < 0.033$; dotted line, extrapolation of the solid line to a larger $\epsilon_{1/T}$ range of $\epsilon_{1/T} > 0.033$.

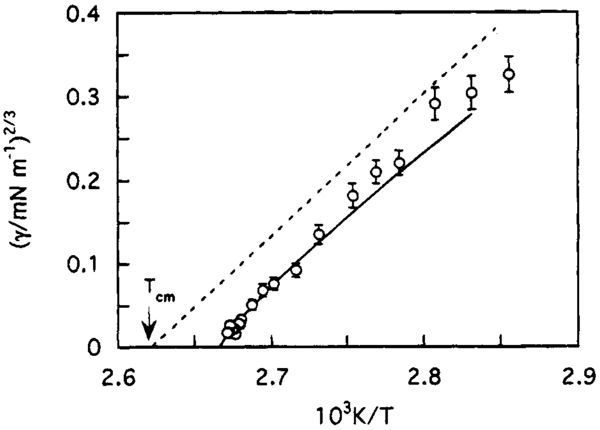

Figure 6. Comparison of γ with the mean-field theory. ○, experimental; —, eq 14 with $\mu = 1.27$ and $\gamma_0 = 5.05$ mN m^{-1}; (– – –), the mean-field theory of eq 21.

$$\gamma/(\text{mN m}^{-1}) = 5.56 \epsilon_{\chi m}^{3/2} \qquad (20)$$

Equation 19 leads to $B/\chi_{cm} = 541$ and can translate the χ-scale $\epsilon_{\chi m}$ to the $1/T$-scale $\epsilon_{1/T,m}$ by using eq 13. Equation 20 is transformed to

$$\gamma/(\text{mN m}^{-1}) = 9.40 \epsilon_{1/T,m}^{3/2} \qquad (21)$$

The mean-field critical amplitude γ_{0m} is 9.40 mN m^{-1}. The mean-field prediction thus obtained is shown in Figure 6 in order to compare with the experimental result. As the temperature decreases departing from T_c, the experimental interfacial tension appears to approach the mean-field calculation, presumably exhibiting the crossover from Ising-type to mean-field type behavior. The theory predicts the mean-field type behavior quite reasonably.

The quantitative agreement is, however, somewhat accidental, since there exists uncertainty in the evaluation of the mean-field prediction arising from the following factors. One is the evaluation of T_{cm}. The determination of T_{cm} was expedient and did not have sufficient theoretical and experimental bases. Another is the applicability of the theory to oligomer blends. The theory was developed for a blend of flexible long-chain polymers, where a Gaussian chain was assumed and the segment-interaction term in the coefficient of the square-gradient term of the free energy was neglected. These conditions are not relevant for short-chain oligomers. If the interaction term remains, the coefficient κ of the gradient term as a function of the composition ϕ is expressed as[12,13,18]

$$\kappa = \chi\lambda^2/2 + l^2/[36\phi(1 - \phi)] \qquad (22)$$

for a symmetrical blend of polymerization index P. The first term, which is usually ignored, represents the contribution of segment interaction. λ is the length of the segment-interaction range and may be of the same order of Kuhn segment length l. The second term is based on the Gaussian segment distribution. Equation 22 leads to the following more exact expression of the length L in the equation of interfacial tension near the critical point.[14]

$$L^2 = 9\lambda^2/P + l^2 \qquad (23)$$

Namely, l in eqs 4 and 9 should be replaced by L in the more exact expression. If the chain is long enough, i.e., P is large, L is reduced to be l as is assumed in the treatment in the theoretical background. In the case of small P as in the present case, however, the first term is not always negligible. Furthermore, relevancy of the second term based on the Gaussian distribution of the segment density is questionable in quantitative evaluation.

In a blend in strong segregation, low molecular-weight fractions can be adsorbed at the interface, resulting in the reduction of the interfacial tension.[23] In a weak segregation near the critical point, the adsorption effect must be minor and may be negligible in the present system with a reasonably narrow distribution of molecular weight.

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