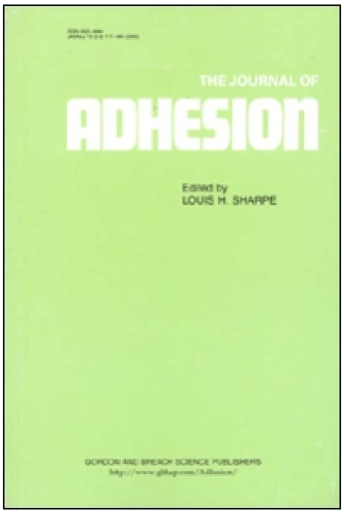

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Temperature Dependence of Interfacial Tension of Polymer Melts

Takuhei Nose[a]; Tomoyuki Kasemura[b]
[a] Department of Polymer Chemistry, Tokyo Insitute of Technology, Tokyo, Japan [b] Gifu University, Gifu-city, Gifu, Japan

To cite this Article Nose, Takuhei and Kasemura, Tomoyuki(1996) 'Temperature Dependence of Interfacial Tension of Polymer Melts', The Journal of Adhesion, 59: 1, 207 — 216
To link to this Article: DOI: 10.1080/00218469608011089
URL: http://dx.doi.org/10.1080/00218469608011089

J. Adhesion, 1996, Vol. 59, pp. 207–216
Reprints available directly from the publisher
Photocopying permitted by license only

Temperature Dependence of Interfacial Tension of Polymer Melts*

TAKUHEI NOSE**

Tokyo Insitute of Technology, Department of Polymer Chemistry,
2-12-1 Ookayama, Meguro-ku, Tokyo 152, Japan

and

TOMOYUKI KASEMURA

Gifu University, Yanagido, Gifu-city, Gifu, Japan

(In final form February 2, 1996)

A unique behavior of interfacial tension of polymer melts is that, in an ordinary temperature region of strong segregation, the entropy effect of chain molecules on the composition-gradient term in the free energy at the interface can make the interfacial tension increase with increasing temperature. To confirm this role of the entropy, interfacial tension of polystyrene/poly(dimethylsloxane) was measured as a function of temperature, and was found to increase with increasing temperature. Using temperature dependence of the segment-segment interaction parameter, which was evaluated from experimental coexistence curves, it was shown that the entropy effect was responsible for this positive temperature dependence of the interfacial tension. The experimental result was also discussed on the basis of scaled expressions of interfacial tension as a function of segregation strength covering weak, strong, and very strong segregation regimes.

KEY WORDS: Entropy effect; positive temperature dependence of interfacial free energy of polymer/polymer melts; segregation regimes; polystyrene/poly(dimethysiloxane) mixtures; coexistence curve; segment-segment interaction parameter.

INTRODUCTION

It is theoretically predicted that there are three temperature regimes for interfacial tension of polymer melts according to the segregation strength[1,2]. In Regime I of weak segregation near the critical point, the interfacial tension appears and increases as temperature goes away from the critical point. Regime I is specified by $\chi \sim 2/N$, where χ is the Flory-Huggins interaction parameter and N is the degree of polymerization. In the strong-segregation regime, Regime II, where $2/N < \chi < 1$, the interfacial tension is proportional to $T\chi^{1/2}$, while in Regime III of very strong segregation, where $\chi > 1$, it is proportional to $T\chi$, with T being the absolute temperature. The regime unique to polymeric systems is Regime II, where the interfacial

---

*Presented at the International Adhesion Symposium, IAS'94 Japan, at the 30th Anniversary Meeting of the Adhesion Society of Japan, Yokohama, Japan, November 6–10, 1994.

**Corresponding author.

tension can increase with increasing temperature even if the polymer blend has an upper critical solution temperature (UCST). We focus our attention on this theoretical prediction, and try to confirm it experimentally.

In this study, we selected polystyrene(PS)/poly(dimethylsiloxane) (PDMS) systems to measure the interfacial tension as a function of temperature. It has been reported by Kitazaki[3] that the PS/PDMS system exhibits a positive temperature dependence of interfacial tension. On the other hand, coexistence curves of PS/PDMS mixtures with different molecullar weights has been measured to evaluate the interaction parameter, χ, as functions of temperature and molecular weight[4]. The value of χ is indispensable as an indicator of the segregation strength, and will be utilized in data analysis and discussion in the present study.

THEORETICAL BACKGROUND

Adopting the square-gradient theory for the free energy of a non-uniform system, the interfacial tension γ is given by[5]

$$\gamma = \int_{-\infty}^{\infty} [\Delta f(\phi) + \kappa(\partial\phi/\partial z)^2] dz/\upsilon_0 \tag{1}$$

Here, Δf is the local free energy per site as a function of concentration, ϕ, in volume fraction, at the position z with the z-axis taken to be perpendicular to the interface, κ is the coefficient of square-gradient term, and v_0 is the site volume. Starting with Eq. (1), one can finally obtain the following approximate expressions for interfacial tension, γ, and the interfacial thickness, L.[1]

$$\gamma = \kappa_r^{1/2}(-S_{\max})^{1/2}(\Delta\phi)^2/(2\sqrt{2}\upsilon_0) \tag{2}$$

and

$$L = 2\sqrt{2}\kappa_r^{1/2}(-S_{\max})^{-1/2} \tag{3}$$

with

$$S = (\partial^2\Delta f/\partial\phi^2) \tag{4}$$

where κ_r and $S_{\max}$ are representative values of κ and the second-derivative S of Δf, respectively, and $\Delta\phi$ is the difference in ϕ between coexisting phases. For a binary polymer blend, S and κ are given as[6]

$$S/kT = \frac{1}{N_1\phi_1} + \frac{1}{N_2\phi_2} - 2\chi \tag{5}$$

$$\begin{aligned}\kappa &= \kappa_s + \kappa_e \\ &= kT\chi\lambda^2/2 + kT(l_1^2/\phi_1 + l_2^2/\phi_2)/36\end{aligned} \tag{6}$$

Here, the subscripts 1 and 2 denote the constitutional polymers 1 annd 2, respectively, l is the Kuhn-segment length, and λ represents the range of segment-segment interactions.

Hereafter, let us suppose a symmetrical system with $N_1 = N_2 = N$ and $l_1 = l_2 = l$, for simplicity. Then, the critical point locates at $\chi = 2/N = \chi_{\mathrm{cm}}$. $S_{\max}$ and κ_r are given from Eqs. (5) and (6) by putting $\phi_i = 1/2$ as

$$S_{\max} = 2kT(\chi_{\mathrm{cm}} - \chi) \tag{7}$$

$$\kappa_r = kT(\chi\lambda^2/2 + l^2/9) \tag{8}$$

Regime I (weak segregation; near critical, $\chi \sim \chi_{\mathrm{cm}} = 2/N$)

In this regime, $\kappa_r \approx kTl^2/9$, and $\Delta\phi \sim (\chi/\chi_{\mathrm{cm}} - 1)^{1/2}$. Then, γ and L can be approximately given from Eqs. (2) and (3) as

$$\gamma \sim kT(l/\upsilon_0)N^{-1/2}(\chi/\chi_{\mathrm{cm}} - 1)^{3/2} \tag{9}$$

$$L \sim lN^{1/2}(\chi/\chi_{\mathrm{cm}} - 1)^{-1/2} \tag{10}$$

In reality, very near the critical point, the mixture becomes more miscible because of large concentration fluctuations, resulting in χ_c at the real critical point being larger than χ_{cm}, and a different critical exponent, μ, from that given by the mean field theory such as the present treatment. Namely,

$$\gamma = \gamma_0(\chi/\chi_c - 1)^{\mu} \tag{11}$$

where μ is about 1.26,[7] and γ_0 is the critical amplitude.

Regime II (strong segregation, $2/N < \chi < 1$)

Since the segregation strength is strong, one can put $-S_{\max} = 2kT\chi$ and $\Delta\phi \cong 1$, but the entropy term in κ_r still dominates over the energy term, *i.e.*, $\kappa_r = kTl^2/9$. Therefore, Eqs. (2) and (3) yield Eqs. (12) and (13) for this regime.

$$\gamma \sim (kTl^2)^{1/2}(kT\chi)^{1/2}/\upsilon_0) = (kT/\upsilon_0)l\chi^{1/2} \sim (kT\chi/\upsilon_0)L \tag{12}$$

$$L \sim (kTl^2)^{1/2}(kT\chi)^{-1/2} = l\chi^{-1/2} \tag{13}$$

The entropy term, kTl^2, can possibly give rise to the positive temperature dependence of γ even when the blend has an upper critical solution temperature, *i.e.*, even when χ decreases with increasing temperature. This is a behavior unique to the polymeric system. Even in case of strong segregation, in the sense that $\chi \gg \chi_{\mathrm{cm}}$, the entropy of polymer chains is still active, leading to the increase of L as temperature increases even with the interaction energy, $kT\chi$, being constant. This gives rise to the increase of γ. A more explicit expression of γ with the numerical pre-factor for Regime II was derived by Helfand and Tagami[8] to be.

$$\gamma = (kT/\upsilon_0)l\chi^{1/2}/\sqrt{6} \tag{14}$$

Regime III (very strong segregation, $\chi > 1$)

In this regime, the energy term dominates over the entropy term, so that, $\kappa_r = kT\chi\lambda/2$. Since $-S_{\max} = 2kT\chi$ and $\Delta\phi \cong 1$, Eqs. (2) and (3) lead to

$$\gamma = (kT/\upsilon_0)\lambda\chi/2\sqrt{2} \sim (kT\chi/\upsilon_0)Ln \tag{15}$$

$$L = \sqrt{2}\lambda \tag{16}$$

Scaled Expressions

Asymptotic expressions in the three regimes are summarized in the following scaled form for mixtures with no strong asymmetry of polymeric index:

$$\frac{\gamma}{\gamma^*} = \frac{\sqrt{2}}{3}\varepsilon_{\chi m}^{3/2} \quad \chi \sim \chi_{\mathrm{cm}} \quad \text{(Regime I)} \tag{17}$$

$$= \frac{1}{\sqrt{6}}\varepsilon_{\chi m}^{-1/2} \quad 1 > \chi > \chi_{\mathrm{cm}} \quad \text{(Regime II)} \tag{18}$$

$$= \frac{1}{2\sqrt{2}}(\lambda/l)\chi_{\mathrm{cm}}^{1/2} \quad 1 < \chi \quad \text{(Regime III)} \tag{19}$$

with

$$\gamma^* = (kT\chi/\upsilon_0)l\chi_{\mathrm{cm}}^{-1/2} \tag{20}$$

$$\varepsilon_{\chi m} = \frac{\chi}{\chi_{\mathrm{cm}}} - 1 \tag{21}$$

$$\chi_{\mathrm{cm}} = \frac{1}{2}(N_1^{-1/2} + N_2^{-1/2})^2 \tag{22}$$

Here, the numerical pre-factor of Eq. (17) was derived by analytical calculation of the square-gradient theory[6,9]. The scaled expressions of the interfacial tension as a function of segregation strength are illustrated in Figure 1.

EXPERIMENTAL

Poly(dimethylsiloxane) (PDMS) was a product of Shin-etsu Co. Ltd., of $M_w = 1 \times 10^5$(PDMS − 2), which was roughly fractionated to eliminate low-molecular-weight fractions. Weight-average molecular weight, M_w, and polydispersity index, M_w/M_n, of the fractionated PDMS(PDMS − 1) were 2.3×10^5 and 2, respectively. Polystyrene was a product of Toso Co., with $M_w = 3.79 \times 10^4$ and

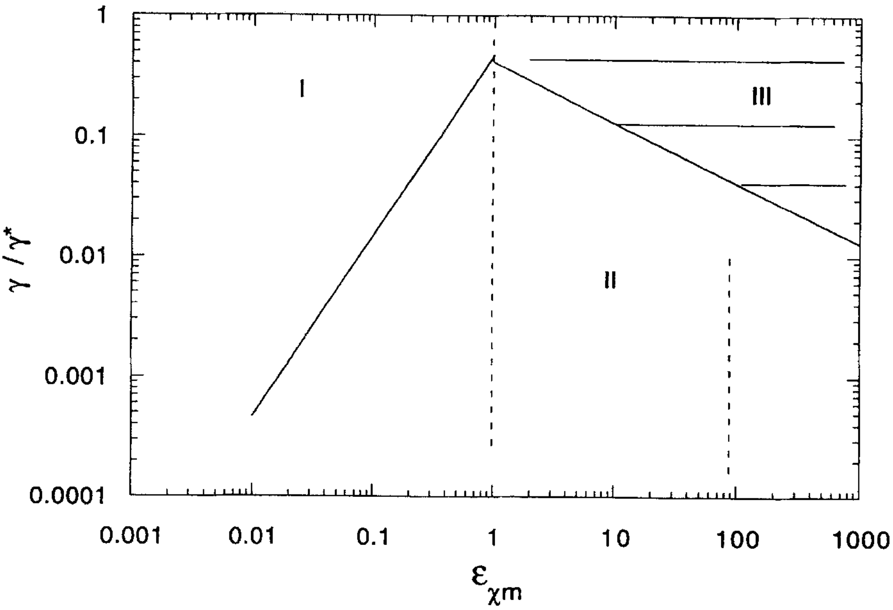

FIGURE 1 Presentation of interfacial tension as a function of segregation strength in a scaled form with the mean-field predictions (eqs 17–19) for asymptotic behavior of respective segregation regimes. Regime I: $\chi \sim \chi_{cm}$; Regime II: $1 > \chi > \chi_{cm}$; Regime III; $\chi > 1$.

$M_w/M_n = 1.01$. Interfacial tension, γ, was measured by the sessile-drop method. Values of $\gamma/g\Delta\rho$, where g is the gravity constant and $\Delta\rho$ is the density difference, were calculated from the profile of the sessile drop with Porter's equation.[10] Details of the sessile-drop method have been described elsewhere.[11] The density difference, $\Delta\rho$, was evaluated from the densities of PS and PDMS, assuming complete demixing, *i.e.*, it was assumed that the two phases making the interface were pure PS and PDMS. Density of PS and PDMS were measured as a function of temperature by a specially-designed pycnometer.

RESULTS AND DISCUSSION

Experimental results of γ are presented in Figure 2, showing a positive temperature dependence of γ, which is expressed by $\gamma/(\mathrm{mN\,m^{-1}}) = 3.48 + 0.00654T/K$ and $5.00 + 0.00250T/K$ for PDMS−1 and −2, respectively. The data of Kitazaki *et al.*[3] for PS($M_w = 3 \times 10^4$) /PDMS ($M_w = 1.8 \times 10^4$ were also plotted for comparison.

The positive temperature dependence of γ for PS/PDMS melts has been confirmed. Coexistence curves of PS/PDMS blends with low molecular weights are shown in Figure 3,[4] which are of the UCST type. Estimated χ-parameters from these phase diagrams are presented as χ/V_0-$1/T$ plots in Figure 4, along with those for higher molecular weight PS/PDMS blends.[4] Here, V_0 is the molar site volume, *i.e.*,

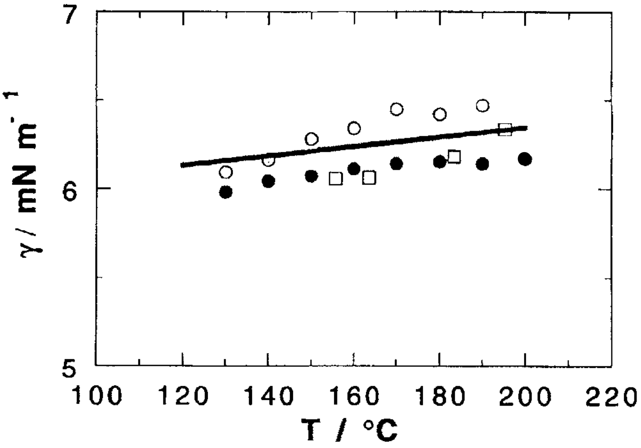

FIGURE 2 Temperature dependence of interfacial tension of PS/PDMS. (○)PDMS-1; (●)PDMS-2; (□) Kitazaki *et al.*[3]; (—) theoretical curve of Eq. (24)

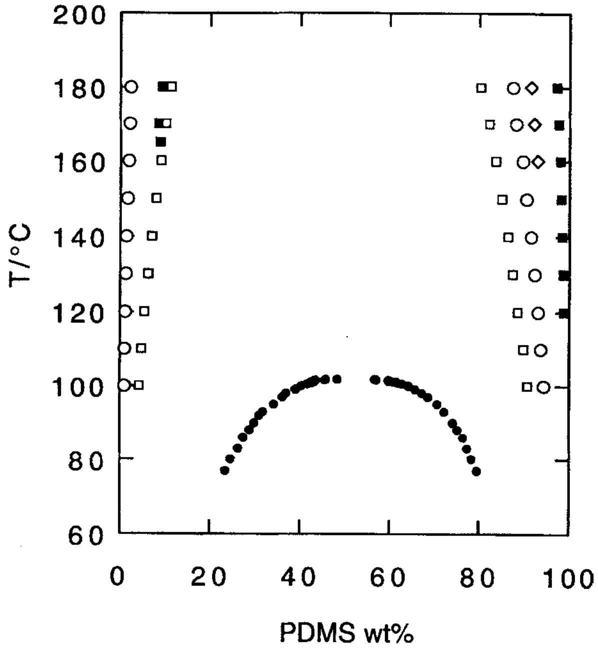

FIGURE 3 Coexistence curves of PS/PDMS blends with different molecular weights: (●) PS6/PDMS5; (□) PS6/PDMS14; (○) PS6/PDMS37; (◇) PS6/PDMS-1; (■) PS22/PDMS5. Molecular weight (Mw). PS6,600; PS22,2200; PDMS5,460; PDMS14,1400; PDMS37, 3700.

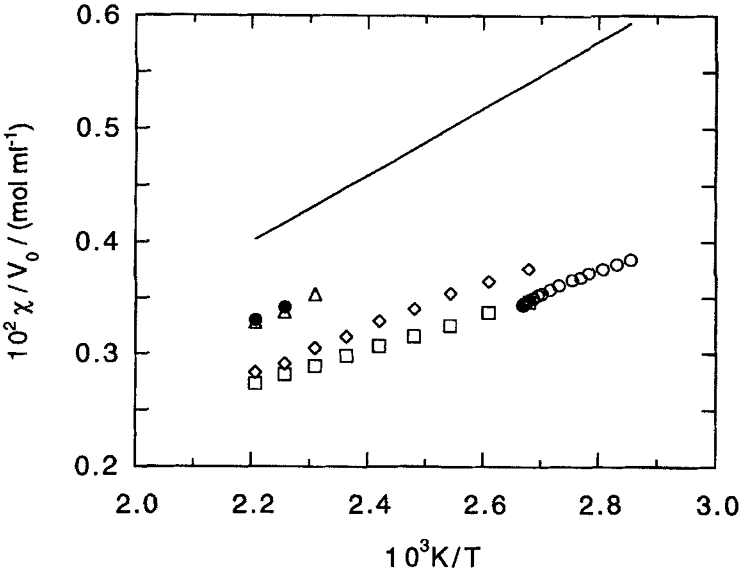

FIGURE 4 Temperature dependence of χ-parameters: (○) PS6/PDMS5; (□) PS6/PDMS14; (◇) PS6/PDMS37; (△) PS6/PDMS-1; (●) PS22/PDMS5; (—) high molecular-weight PS/PDMS (Eq. (23)). Molecular weights are shown in the caption of Figure 3.

$V_0 = \upsilon_0 N_A$ with N_A being the Avogadro constant. χ/V_0 for higher molecular weight was obtained by an extrapolation of those of lower molecular weights, which is expressed by[4]

$$\chi/V_0/(\text{mol ml}^{-1}) = 2.94/T - 0.00247 \tag{23}$$

The decrease of χ/V_0 with temperature directly indicates the increase of miscibility (UCST-type phase behavior) irrespective of molecular weight. The value of the χ/V_0 parameter for high-molecular-weight blends ranges from $4 \times 10^{-3} - 5 \times 10^{-3}$ mol ml^{-1} in the present temperature region, which is much larger than $\chi_{cm}/V_0 = (2/N)/V_0$ of the present blends. Note that NV_0 represents the molar volume of polymers. Consequently, the system is in the region of strong segregation, Regime II, and the complete demixing assumed in the experimental analysis is supported. The positive temperature dependence of γ of PS/PDMS implies that the interfacial tension of the polymer-melt interface can increase with increasing temperature even in case of increasing miscibility with temperature.

For more quantitative comparison with the theoretical prediction, Eq. (4) was rewritten in terms of the unperturbed end-to-end distance, r_0, for a chain of molecular weight, M, specific volume, v_p, molar site volume, V_0, and the gas constant, R, as

$$\gamma = [RT(r_0^2/M)/v_p]^{1/2}(RT\chi/V_0)^{1/2}/\sqrt{6} \tag{24}$$

Values of $r_0^2/M/v_p$ were calculated from data in the literature[12] to be $r_0^2/M/v_p = 0.00423\{1-0.0001(\mathrm{t}/°\mathrm{C}-140)\}$ nm^2 mol ml^{-1}. The interaction free energy density, $RT\chi/V_0$ (Eq. (23), decreases gradually, while the entropy term, $Rr_0^2/M/v_p$, is almost constant with increasing temperature. Using these equations, γ was calculated by Eq. (24) to be shown in Figure 2. The calculated values well describe the positive temperature dependence, which was a result of the entropy effect, *i.e.*, the presence of T in the entropy term, kTl^2/v_0, in the coefficient of square-gradient free energy density.

More quantitatively, the temperature dependence, $\partial\ln\gamma/\partial\ln T$, is given as the sum of contributions of κ_s and S:

$$\frac{\partial\ln\gamma}{\partial\ln T}=\frac{1}{2}\left(\frac{\partial\ln(\kappa_s/V_0)}{\partial\ln T}+\frac{\partial\ln(-S_{\max}/V_0)}{\partial\ln T}\right) \tag{25}$$

with

$$\frac{\partial\ln(\kappa_s/V_0)}{\partial\ln T}=1-\frac{\partial\ln(l^2/V_0)}{\partial\ln T} \tag{26}$$

$$\frac{\partial\ln(-S_{\max}/V_0}{\partial\ln T}=\frac{\partial\ln(T\chi/V_0)}{\partial\ln T}=f_s/(T\chi/V_0) \tag{27}$$

Here, f_s is the entropy term in the free energy density, $RT\chi/V_0$, *i.e.*, if the relation $T\chi/V_0=B+AT$ holds as Eq. (23), it follows that $f_s=AT$. In the present case, therefore, respective contributions at 450K are;

1 (entropy effect in κ_s) 1

$\partial\ln(l^2/V_0)/\partial\ln T$ -0.004

$f_s/(T\chi/V_0)$ -0.608

Consequently, the calculated value of $\partial\ln\gamma/\partial\ln T$ is $(1-0.004-0.608)/2\cong-.19$. Experimental values of $\partial\ln\gamma/\partial\ln T$ are 0.46 and 0.18_4 for PDMS−1 and PDMS−2, respectively. It is determined by a delicate balance of those contributions whether the sign of $\partial\ln\gamma/\partial\ln T$ is positive or negative. Ordinary polymer blends of the UCST-type may have a large entropy contribution in the segment-segment interaction free energy density, *i.e.*, $f_s/(T\chi/V_0)>1$. This may be responsible for the fact that the positive temperature dependence of γ is not frequently observed.

Scaled Plots

The experimental data were plotted in the scaled form in Figure 5, along with those of oligomer blends of PS/PDMS[13]. The present data were located in Regime II, scaled properly, and well described by the theoretical asymptotic behavior. The oligomer blend is weakly segregated, having the critical point around 102°C (see Figure 3). Because of large concentration fluctuations near the critical point, γ follows the power law of Eq.(11) with $\mu=1.27$,[13] and deviated away from the mean-field behaviour.

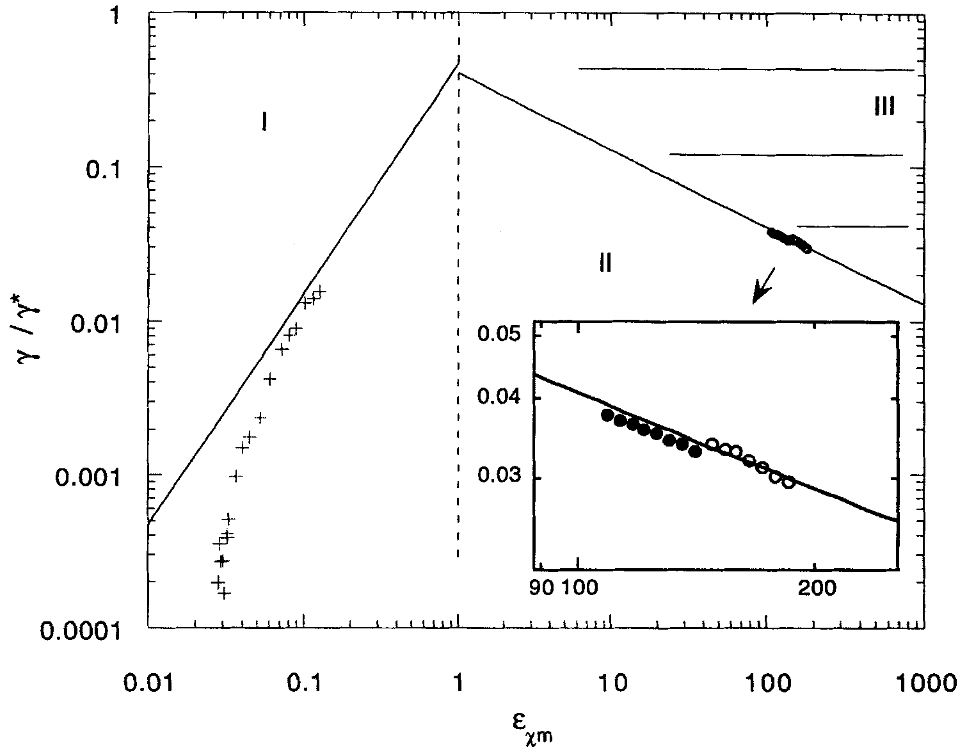

FIGURE 5 Scaled plots of interfacial tension against segregation strength $\varepsilon_{\chi m}$. (○) PS/PDMS-1; (●) PS/PDMS-2; (×) PS6/PDMS5.

CONCLUSIONS

It has been experimentally confirmed that the interfacial tension of phase-separated PDMS/PS blends increases with increasing temperature, while the coexistence curves exhibit the upper critical solution temperature. This positive temperature dependence of interfacial tension has been demonstrated to imply that in the strong segregation regime, where $2/N < \chi < 1$, the interfacial tension can increase with increasing temperature due to the entropy effect of chain molecules at the interface even if the polymer blend becomes more miscible as the temperature increases.

References

1. T. Nose, *J. Jpn. Soc. Colour Mater.* (in Japanese), **64**, 729 (1991).
2. G. H. Fredrickson, *Physics of Polymer Surfaces and Interfaces*, I. C. Sanchez, Ed. (Butterworth-Heinemann, UK, 1992), Chap.1.
3. Y. Kitazaki, T. Hata, *Polym. Preprint Jpn*, **18**, 478 (1969).
4. T. Nose, *Polymer*, **36**, 2243 (1995).
5. J. W. Cahn, J. E. Hilliard, *J. Chem. Phys.*, **28**, 258 (1958).
6. T. Nose, *Polymer J.*, **8**, 96 (1976).

7. B. Widom, *J. Chem. Phys.*, **43**, 3892 (1965).
8. E. Helfand, Y. Tagami, *J. Chem. Phys.*, **56**, 3592 (1971).
9. J. E. Joanny, L. Leibler, *J. Phys.(Paris)*, **39**, 951 (1978).
10. A. W. Porter, *Phil. Mag.*, **15**, 163 (1933).
11. T. Kasemura, T. Hata, *Kobunshi Ronbunshu*, **33**, 192 (1976).
12. *Polymer Handbook*, 3rd Ed., J. Brandrup, E. H. Immergut, Eds. (John Wiley & Sons, Inc., New York, 1989), VII/33.
13. T. Nose, *Macromolecules*, **28**, 3702 (1995).