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Reduction of the Interfacial Tension of the Homopolymer−Homopolymer Interface by Addition of Diblock Copolymers near the Critical Solution Temperature

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ABSTRACT: The effects of a small amount of added A−B diblock copolymers on the interfacial tension of a homopolymer A/homopolymer B blend near the critical solution temperature have been studied. A simple theoretical consideration predicts that, as the temperature (T) changes away from the critical temperature, the interfacial tension (γ) increases and then decreases, exhibiting a maximum, if the polymeric index of the diblock copolymer is much larger than those of the homopolymers. The maximum is a result of a crossover from weak adsorption to strong adsorption of diblock copolymers onto the interface. This prediction has experimentally been confirmed for a demixed oligo(styrene)/oligo(dimethylsiloxane) blend with poly(styrene)-*block*-poly(dimethylsiloxane). The polymeric index of the block copolymer was about 18 times larger than those of homooligomers, and the concentration of added copolymer ranged from 0.01 to 0.8 wt %. The temperature of the maximum approaches the critical point with increasing copolymer concentration. An excess amount (Γ) of the copolymer at the interface was also evaluated by using the Gibbs adsorption equation. The concentration of the adsorbed copolymer was not so high, even where an appreciable reduction of interfacial tension was observed beyond the maximum of the $\gamma-T$ curve.

Introduction

The interfacial tension between coexisting phases of a demixed homopolymer A/B interface is reduced by addition of A−B block copolymer at the interface. This phenomenon has been paid much attention from both scientific and industrial points of view and has been studied theoretically and experimentally. Leibler[1,2] theoretically treated the homopolymer/homopolymer/copolymer system, including the vicinity of the critical point, on the basis of the random-phase approximation and pointed out that the effects on the interfacial tension reduction could be divided into dilution and adsorption effects. Noolandi and Hong[3,4] applied the self-consistent-field theory to this problem and evaluated the interfacial tension reduction in completely demixed homopolymer blends. Since their papers appeared, extensive studies on the interface of homopolymer/homopolymer/copolymer systems have been reported to refine the theories and to see the microscopic structures of copolymers at the interface using forward recoil spectroscopy or neutron reflectivity. However, direct measurements of the interfacial tension have been limited. A pioneering experimental work for the effect of added block copolymers on the polymer/polymer interfacial tension was done by Patterson et al.,[5] and later Gailard et al.[6] measured the interfacial-tension reduction for the polymer/polymer/monomer interface with the block copolymer. Anastadiadis et al.[7] measured the reduction of the interfacial tension of the polystyrene/1,2-polybutadiene interface with their block copolymer and obtained results that are consistent with the theory of Noolandi and Hong. Park and Roe[8] evaluated the interfacial tension for the homopolymer/homopolymer/block copolymer indirectly by analyzing the data of the phase separation kinetics.

The effect of diblock copolymers at the interface on the interfacial tension should depend on the segregation strength of the homopolymer blend. Near the critical solution temperature, the presence of diblock copolymers must give only a slight change to the interfacial tension,[1] whereas at stronger segregation away from the critical point, it must appreciably reduce the interfacial tension owing to pronounced adsorption of the copolymers at the interface. Therefore, it is expected that one can see a crossover from the weak to the strong reduction of the interfacial tension upon going away from the critical temperature, where the interfacial tension (γ) possibly exhibits a maximum in its temperature (T) dependence.

In this study,[9] we focus our attention on the above expectation. A simple theoretical consideration based on a mean-field treatment is made on the interfacial tension of a homopolymer/homopolymer/diblock copolymer system, where two dominant factors only are taken into account, localization entropy loss and segmental interaction energy gain with adsorption of the copolymers. The theory predicts the maximum of the $\gamma-T$ relation to be near the critical point for a blend containing a small amount of diblock copolymers with a much larger polymeric index than those of the homopolymers. To confirm this prediction experimentally, the interfacial tension near the critical point has been measured for a demixed oligo(styrene)/oligo(dimethylsiloxane) (OS/ODMS) blend with poly(styrene)-*block*-poly(dimethylsiloxane) (PS-*b*-PDMS) . In fact, we find the maximum and see the copolymer concentration dependence of the maximum temperature. An excess amount of adsorbed copolymer at the interface is also evaluated by the Gibbs adsorption equation.

Theoretical Consideration

Pure Blend System. First, suppose a symmetrical homopolymer/homopolymer blend near the critical point in the two-phase region. In the mean-field theory, the

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difference in the concentration ($\Delta\phi$) between the coexisting phases is given as

$$\Delta\phi = \sqrt{3}\epsilon_{\chi 0}^{\ 1/2} \tag{1}$$

Here, $\epsilon_{\chi 0}$ represents the distance from the critical point in terms of the Flory−Huggins interaction parameter (χ) and is defined by $\epsilon_{\chi 0} = \chi/\chi_{c0} - 1$, where the critical χ value (χ_{c0}) is $\chi_{c0} = 2/P$, with the polymeric index P. The interfacial tension (γ_0) and the interfacial thickness (L_0) for the interface between these coexisting phases near the critical point can be evaluated by the square-gradient theory of the mean-field approximation as follows:[10,11]

$$\gamma_0 = \frac{2}{3}\frac{kT}{\nu_0}\frac{l}{P^{1/2}}\epsilon_{\chi 0}^{\ 3/2} \tag{2}$$

$$L_0 = \frac{2}{3}lP^{1/2}\epsilon_{\chi 0}^{\ -1/2} \tag{3}$$

Effects of Diblock Copolymers. The block copolymer consisting of an A block connected to a B block, both blocks having the same polymeric index ($N/2$), is added to the homopolymer blend. The concentrations of the block copolymer in coexisting phases are denoted as ϕ_{3e}, which are the same in the two phases because of the symmetry of the system, while the homopolymers are assigned to components 1 and 2, respectively. The effects of the copolymer on the reduction of the interfacial tension can be separated into two effects, i.e., diluent effect and adsorption effect. The basic conditions supposed in the discussion hereafter are that the amount of copolymer added is very little, i.e., $\phi_{3e} \ll 1$, and that the adsorption is not very strong so that the copolymer concentration (ϕ_3) is sufficiently lower than unity even at the interface.

Diluent Effects. A ternary *symmetrical* polymer blend system with nonadsorbed diluent, which implies that ϕ_3 is the same throughout the system, can be regarded as a quasi-binary system so that the free-energy density ($f(q, \phi_i, \chi; \phi_{3e})$) of the system is simply related to that of a corresponding binary system, $f(q; \phi_i, \chi; 0)$, as

$$f(q; \phi_i, \chi; \phi_{3e}) = (1 - \phi_{3e})f(q, \Phi_i, (1 - \phi_{3e})\chi; 0) \tag{4}$$

where q is the wave number of composition fluctuations and $\Phi_i = \phi_i/(\phi_1 + \phi_2) = \phi_i/(1 - \phi_{3e})$ for $i = 1$ and 2. The relation of eq 4 leads to the transformations $\gamma \rightarrow (1 - \phi_{3e})\gamma$, $L \rightarrow L$, and $\Delta\phi \rightarrow (1 - \phi_{3e})\Delta\Phi$ at the same ϵ_χ by the diluent effect. Therefore, the critical point (χ_c) and the concentration difference ($\Delta\phi$) of homopolymer for the system with diluent are respectively

$$\chi_c = \frac{2}{P(1 - \phi_{3e})} \tag{5}$$

and

$$\Delta\phi = \sqrt{3}(1 - \phi_{3e})\epsilon_\chi^{\ 1/2} \tag{6}$$

with

$$\epsilon_\chi = \chi/\chi_c - 1 \tag{7}$$

The interfacial tension (γ_{00}) and the interfacial thickness (L_{00}) for the nonadsorbed system are expressed as

$$\gamma_{00} = \frac{2}{3}\frac{kT}{\nu_0}\frac{l(1 - \phi_{3e})}{P^{1/2}}\epsilon_\chi^{\ 3/2} \tag{8}$$

$$L_{00} = \frac{2}{3}lP^{1/2}\epsilon_\chi^{\ -1/2} \tag{9}$$

Therefore, in the present case where the concentration (ϕ_{3e}) of added copolymers is low enough, the diluent effect is very small, as long as the above scale of ϵ_χ is used. If one sees the effect at a fixed temperature, i.e., at a fixed value of χ, then the relative reduction $(\gamma_{00} - \gamma_0)/\gamma_0$ is quite large *very close to* the critical point due to the shift of the critical point (see eq 5).

Adsorption Effects. The adsorption of diblock copolymers has no effect on the bulk-phase properties such as χ_c and $\Delta\phi$, while the interfacial properties do change with adsorption. The interfacial tension of the homopolymer blend with the copolymer is expressed here as

$$\gamma = \gamma_{00} + \Delta\gamma_{00} \tag{10}$$

with reduction ($\Delta\gamma_{00}$) of interfacial tension being

$$\Delta\gamma = \gamma - \gamma_{00} \tag{11}$$

The reduction of interfacial tension is assumed to be primarily determined by the balance of the energy gain of the segment interaction due to the adsorption with entropy loss of copolymer localization to the interface. Then, following the treatment of Noolandi and Hong,[3] $\Delta\gamma_{00}$ is evaluated as follows. The free-energy change $(kT/\nu_0)\Delta f_{ad}$ by adsorption of copolymers with orientation at the interface is approximately expressed as

$$\Delta f_{ad} = \Delta f_s + \Delta f_e \tag{12}$$

$$\Delta f_s = \frac{\phi_3}{N}\ln \phi_3/\phi_{3e} - \frac{1}{N}(\phi_3 - \phi_{3e}) \tag{13}$$

$$\Delta f_e = \Delta e(\phi_3 - \phi_{3e}) \tag{14}$$

when adsorption is not very strong; i.e., the difference $\phi_3 - \phi_{3e}$ is sufficiently smaller than unity, as assumed in the present treatment. Here, $(k/\nu_0)\Delta f_s$ and $(kT/\nu_0)\Delta f_e$ are the entropy and energy changes with the copolymer adsorption, respectively. Δe is the energy change per segment when a copolymer chain is brought from the bulk phase to the interface. Then, one can approximately evaluate $\Delta\gamma_{00}$ due to the adsorption as

$$\Delta\gamma_{00} \cong \frac{kT}{\nu_0}\int_{-\infty}^{\infty}\Delta f_{ad}\,dz$$
$$\cong \frac{kT}{\nu_0}\overline{\Delta f}_{ad}D \tag{15}$$

where $\overline{\Delta f}_{ad}$ is the average Δf_{ad} at the interface and D is the thickness of the adsorbed layer. $\overline{\Delta f}_{ad}$ at equilibrium can reasonably be evaluated by the condition $\partial\Delta f_{ad}/\partial\phi_3 = 0$. This condition yields an expression of the average concentration (ϕ_3) at the interface as

$$\bar{\phi}_3 = \phi_{3e}\exp(-N\Delta e) \tag{16}$$

and then, from eq 15 with eqs 12−14, one has

$$\Delta\gamma_{00} \cong \frac{kT}{\nu_0} D\Delta\overline{f_{\mathrm{ad}}}(\bar{\phi}_3) = \frac{kT}{\nu_0} D\phi_{3\mathrm{e}}\{1 - N\Delta e - \exp(-N\Delta e)\}/N \qquad (17)$$

The amount of the adsorbed copolymer, Γ_3, in volume per unit area (see Appendix) can approximately be evaluated as

$$\Gamma_3 = \int_{-\infty}^{\infty}(\phi_3 - \phi_{3\mathrm{e}})\,\mathrm{d}z \cong (\bar{\phi}_3 - \phi_{3\mathrm{e}})D = \phi_{3\mathrm{e}}[\exp(-\mathrm{N}\Delta e) - 1]/D \qquad (18)$$

One can see from eqs 17 and 18 that the problem is now reduced to the evaluations of Δe and D.

Energy Change by Adsorption of Copolymers at the Interface. The situation of copolymers adsorbed at the interface is basically characterized by the dimension (R) of a copolymer chain, the interfacial thickness (L), and the composition gradient ($\Delta\phi/L$) of the interface. It is assumed here, because of the weak adsorption of copolymers ($\phi_3 \ll 1$), that the profile of segmental composition is essentially the same as that for the blend with no adsorption. Another assumption imposed here for simplicity is that the excess copolymers adsorbed at the interface are completely oriented such that the director connecting the centers of the A and B blocks is perpendicular to the interfacial plane. This is somewhat inconsistent with the weak adsorption and overestimates the energy change (Δe) with adsorption. However, it can describe the essence of the effect of adsorption qualitatively. Under these assumptions, one may evaluate Δe as follows.

If $L > R$, a whole copolymer falls within the interface having the composition gradient. Then, the Δe per segment is approximately given by $\Delta e \cong -\chi\delta\phi/2$. Here, $\delta\phi$ denotes the concentration difference between the positions of the A and B blocks and is roughly given by

$$\delta\phi = \frac{R}{2L}\Delta\phi \qquad (19)$$

Therefore, one has

$$\Delta e = -\frac{\chi}{4}\left(\frac{R}{L}\right)\Delta\phi \qquad (20)$$

On the other hand, if $L \ll R$, one has $\Delta e = -\chi\Delta\phi/2$, since most parts of the A block and B block are located in the A-rich phase and B-rich phase, respectively. Connecting this equation to eq 20 at $L = R$ smoothly, one can modify it as

$$\Delta e = -\frac{\chi}{2}\left\{1 - \frac{1}{2}\left(\frac{L}{R}\right)^{2\alpha}\right\}\Delta\phi \qquad (L < R) \qquad (21)$$

This modification implies that the N_L segment in the total segments of a copolymer chain is located at the interface with the composition gradient, while the residual ($N - N_L$) segments are in the bulk-phase compositions, with N_L/N being $N_{\mathrm{L}}/N = (L/R)^{2\alpha}$. The exponent ($\alpha$) may be between 0.5 and 1. In the case of the strong segregation limit, one can put $\Delta\phi = 1$ and $L \ll R$. Then, eq 21 is reduced to $\Delta e = -\chi/2$, and this equation for Δe with eqs 12−14 recovers the result of the Noolandi−Hong theory.[3]

Thickness (D) of the Adsorption Layer. Most of the junction points of the adsorbed copolymers must be located within the potential energy well at the interface, with its depth being represented by Δe. The width of the potential energy well is of the order of L for $L > R$ and is very narrow for $L < R$. Therefore, the D of the adsorption layer is assumed to be proportional to L, $D = C_D L$, for $L > R$, while $D = R$ for $L < R$. Connecting these two asymptotic expressions continuously at $L = R$, we here put $L \geq R$

$$D = C_D L\left(1 - \frac{R}{L}\right)^2 + R \qquad (22)$$

and $L < R$

$$D = R \qquad (23)$$

C_D is a constant of the order of unity.

Expressions of Interfacial Tension and Adsorption. Here, we define $\epsilon_\chi{}^*$ as ϵ_χ at $L = R$, which is written by (see eq 9)

$$\epsilon_\chi{}^* = \left(\frac{2}{3}lP^{1/2}/R\right)^2 = \left(\frac{2}{3}\right)^2 P/N = \frac{4}{9}\tilde{N}^{-1} \qquad (24)$$

with

$$\tilde{N} = N/P$$

and the relation $R = lN^{1/2}$ for a Gaussian chain is used since the present treatment ignores deformation of adsorbed chains. Then, putting $L = L_{00}$ with eq 9, one has

$$\frac{R}{L} = (\epsilon_\chi/\epsilon_\chi{}^*)^{1/2} = \frac{3}{2}\tilde{N}^{1/2}\epsilon_\chi{}^{1/2} \qquad (25)$$

From eqs 17 with eqs 6, 20−23, and 25, the reduced interfacial tension is expressed as

$$\tilde{\gamma} = \frac{\gamma_{00} + \Delta\gamma_{00}}{\gamma^*} = (1 - \phi_{3\mathrm{e}})\epsilon_\chi{}^{3/2} - \frac{3}{2}\tilde{D}\tilde{N}^{-1/2}F(X)\phi_{3\mathrm{e}} \qquad (26)$$

where the characteristic interfacial tension (γ^*) is defined by

$$\gamma^* = 2kTl/(3\nu_0 P^{1/2}) \qquad (27)$$

and the amount of adsorbed copolymer is given from eq 18 as

$$\bar{\Gamma}_R \equiv \frac{\Gamma_3}{R} = \tilde{D}G(X)\phi_{3\mathrm{e}} \qquad (28)$$

or

$$\bar{\Gamma}_D \equiv \frac{\Gamma_3}{D} = G(X)\phi_{3\mathrm{e}} \qquad (29)$$

Here, we put

$$F(X) = \exp(X) - X - 1 \qquad (30)$$

$$G(X) = \exp(X) - 1 \qquad (31)$$

$$X = -\Delta eN$$

and

$$\tilde{D} = D/R = D/(lN^{1/2}) \tag{32}$$

X and D are given as a function of ϵ as shown below:

for $\epsilon_\chi < \epsilon_\chi$* (or $\tilde{\chi} - 1 < 4/9\tilde{N}^{-1}$)

$$X = \frac{3\sqrt{3}}{4}(1 - \phi_{3e})\tilde{N}^{3/2}\epsilon_\chi \tag{33}$$

$$\tilde{D} = \epsilon_\chi^{-1/2}\left[\frac{2}{3}C_d\left(1 - \frac{9}{4}\tilde{N}\epsilon_\chi\right)^2\tilde{N}^{-1/2} + \epsilon_\chi^{1/2}\right] \tag{34}$$

for $\epsilon_\chi > \epsilon_\chi$* (or $\tilde{\chi} - 1 > 4/9\tilde{N}^{-1}$)

$$X = \frac{\sqrt{3}}{2}(1 - \phi_{3e})\tilde{N}\epsilon_\chi^{1/2}[2 - (9/4\tilde{N}\epsilon_\chi)^{-\alpha}] \tag{35}$$

$$\tilde{D} = 1 \tag{36}$$

The case where $\epsilon_\chi > \epsilon_\chi$*, i.e., $L < R$, is realized only when $\tilde{N} > 1$, because $\tilde{\chi} - 1 < 1$ near the critical. The reduced excess amount of copolymer, $\bar{\Gamma}_D$, indicates the concentration $\phi_3 - \phi_{3e}$ in the volume fraction of the adsorbed copolymer at the interfacial layer with thickness D, while the $\bar{\Gamma}_R$ is the concentration if the adsorbed copolymers were forced to be pressed and confined in the interfacial layer of thickness R.

Numerical Results of the Theoretical Equations. The reduced interfacial tension ($\tilde{\gamma}$) and the reduced adsorption ($\bar{\Gamma}$) are given as functions of ϵ_χ, $\tilde{N}$, and ϕ_{3e}. Figures 1−3 represent calculated $\tilde{\gamma}$ and $\bar{\Gamma}$ against ϵ_χ with various copolymer concentrations (ϕ_{3e}) for $\tilde{N} = 0.1$, 1, and 18, respectively. Here, we put $C_D = 0.2$ and $a = 0.5$. The qualitative results of $\tilde{\gamma}$ and $\bar{\Gamma}$ vs ϵ_χ were insensitive to the values of these parameters. When $\tilde{N} \leq 1$, one finds only a very small reduction of $\tilde{\gamma}$ and a very small adsorption with the addition of copolymers over a whole range of $\epsilon_\chi < 0.15$. In the cases of $\tilde{N} \leq 1$, L is always larger than the copolymer chain dimension R in the present range of $\epsilon\chi$, where $\epsilon\chi < \epsilon\chi$*. On the contrary, when $\tilde{N} \gg 1$, as shown in Figure 3a, the presence of small amount of copolymers gives a pronounced reduction of $\tilde{\gamma}$ appreciably away from the critical point, while a weak effect is predicted very near the critical. Consequently, $\tilde{\gamma}$ against ϵ_χ has a maximum. The maximum position ($\epsilon_{\chi_{\max}}$) depends on the copolymer concentration, approaching the critical point as the copolymer concentration increases, and has no direct relation to the position (ϵ*) of $L = R$, which is independent of ϕ_{3e}. $\bar{\Gamma}$ of the copolymers (Figure 3b) exhibits the change with ϵ_χ corresponding to $\tilde{\gamma}$ behavior, being very small near the critical, and then increasing rapidly with increasing ϵ_χ. $\epsilon_{\chi_{\max}}$ appear after the upturn of $\bar{\Gamma}$ and are located around the same adsorption irrespective of ϕ_{3e}. It is also noteworthy that the magnitude of $\bar{\Gamma}$, in other words, $\bar{\phi}_3$ at the interface, is still very small near $\epsilon_{\chi_{\max}}$. In the ϵ_χ range of the present calculations, ϕ_3 at the interface is low enough to satisfy the assumption in the present theoretical treatment.

Near the critical point, which implies that $\chi \cong 2/P$, the segregation strength of the copolymer with $\tilde{N} \leq 1$ is very weak, i.e., $N\chi \leq 1$, whereas that of the copolymer with $\tilde{N} \gg 1$ is very strong, i.e., $N\chi \gg 1$. These characteristics in the segregation strength of the block copolymers yield the results shown in Figures 1−3.

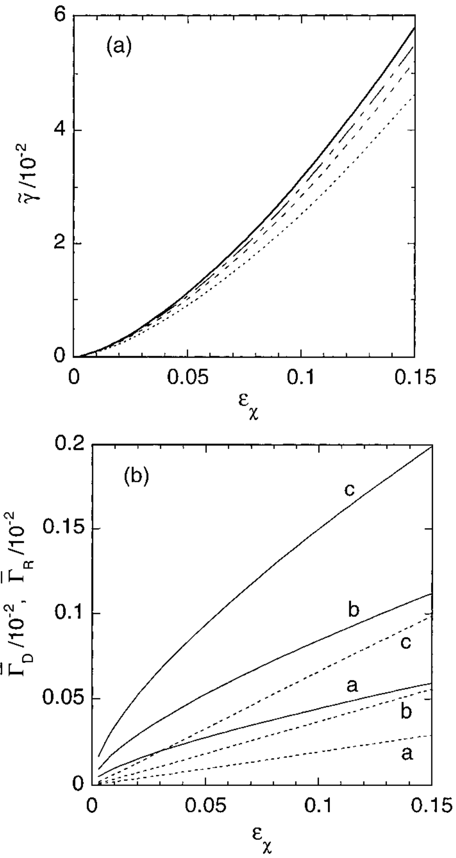

Figure 1. Scaled presentation of the theoretical curves of interfacial tension and adsorption of copolymer for $\tilde{N} = 0.1$ as a function of scaled temperature distance (ϵ_χ) from T_c at various ϕ_{co}. (a) Interfacial tension, ϕ_{co}: (—), 0%, (— - —) 5%; (— —) 10%; (- - -) 20%. (b) Adsorption. (—) $\bar{\Gamma}_R$, (- - -) $\bar{\Gamma}_D$. ϕ_{co}: (a) 5%; (b) 10%; (c) 20%.

Lastly, it is noted that the copolymer of $\tilde{N} \gg 1$ may become immiscible with the blend to precipitate and make the third phase and/or may form micelles in the bulk phase as ϕ_{3e} and/or ϵ_χ increase(s). In the present consideration, we suppose that the present ϕ_{3e} range is lower than the concentration at which these will start to take place and do not take them into account. This issue, i.e., which phenomenon, the maximum of γ, the precipitation, or micellization, occurs at a lower concentration than the others, will be discussed elsewhere.

Experimental Section

Materials and Samples. The blend was a mixture of oligo(dimethylsiloxane) (ODMS) and oligostyrene (OS), of which the coexistence curve and the interfacial tension near the critical point have been studied in our previous papers.[12,13] ODMS was a product of Shin-etsu Co. Ltd., with a number-average molecular weight (M_n) being 460. It was substantially the pentamer with a narrow molecular-weight distribution. OS was a product of Pressure Chemical Co., with a weight-average molecular weight $M_w = 600$ and $M_w/M_n < 1.10$. The mixture of ODMS/OS has an upper critical solution temperature at 101.92 °C, and the critical composition of ODMS is 0.50 in weight fraction (0.55_7 in volume fraction). The critical exponents for $\Delta\phi$ and γ are 0.33_6 and 1.27, respectively, exhibiting three-dimensional-Ising critical behavior. The added diblock copolymer was poly(styrene)(PS)-*block*-poly(dimethylsiloxane)-(PDMS), which was polymerized anionically. The molecular weights of the PS and PDMS blocks were 5700 and 4200, respectively, and M_w/M_n was 1.23.

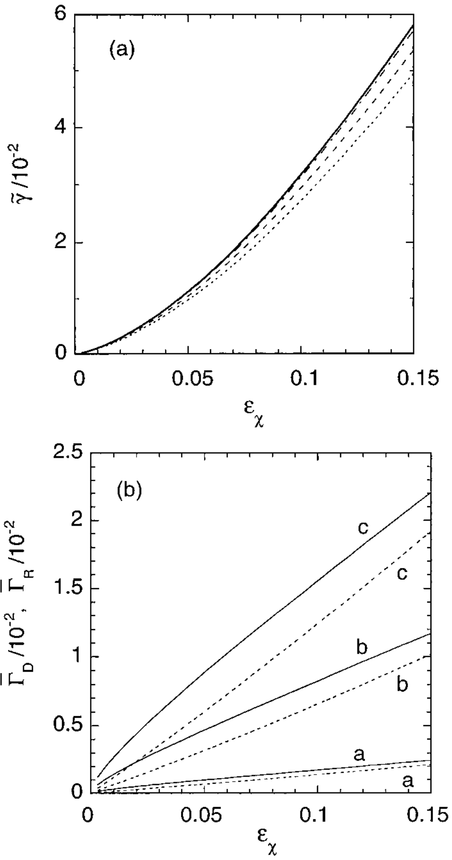

Figure 2. Scaled presentation of the theoretical curves of interfacial tension and adsorption of copolymer for $\tilde{N} = 1$ as a function of scaled temperature distance (ϵ_χ) from T_c at various ϕ_{co}. (a) Interfacial tension. ϕ_{co}: (—) 0%, (– - –) 1%; (– –) 5%; (- - -) 10%. (b) Adsorption. (—) $\bar{\Gamma}_R$,(- - -) $\bar{\Gamma}_D$. ϕ_{co}: (a) 1%; (b) 5%; (c) 10%.

The composition of OS/ODMS of the blended samples was fixed at the critical composition, and the concentration (ϕ_{co}) of added PS-*b*-PDMS in the blend ranged from 0.05 to 0.8 wt %, which are practically equivalent to those of vol % because the system is approximately symmetrical.

Interfacial Tension Measurements. The interfacial tension of the phase-separated mixture was measured in the same way as in the previous study[13] using the sessile-drop method. The apparatus was a specially designed one. A drop of one of the coexisting phases was formed on a plate in a sample glass cell. Its image was focused on the detector of a CCD camera, and its size and profile were measured by image analysis. The blended sample with a desired amount of the copolymer was sealed in the glass cell and was homogeneously mixed above the critical temperature. Then, it was cooled to the temperature of measurement. 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. Any third phase or precipitant owing to the addition of the copolymer was not visually detected. The temperature was controlled to within ±0.05 °C.

The value of $\gamma/g\Delta\rho$, with g and $\Delta\rho$ being the gravity constant and density difference between coexisting phases, respectively, was evaluated from the size and profile of the drop by fitting of the drop profile computed by the Laplace equation. γ was calculated from the values of $\gamma/g\Delta\rho$ with density difference $\Delta\rho$. $\Delta\rho$ was evaluated from the measured coexistence curve of the pure blend of OS/ODMS,[12] assuming that the addition of the copolymer gives substantially no effect on the coexistence curve because of its small amount. The details of the experiments and data analysis have been described in our previous paper.[13]

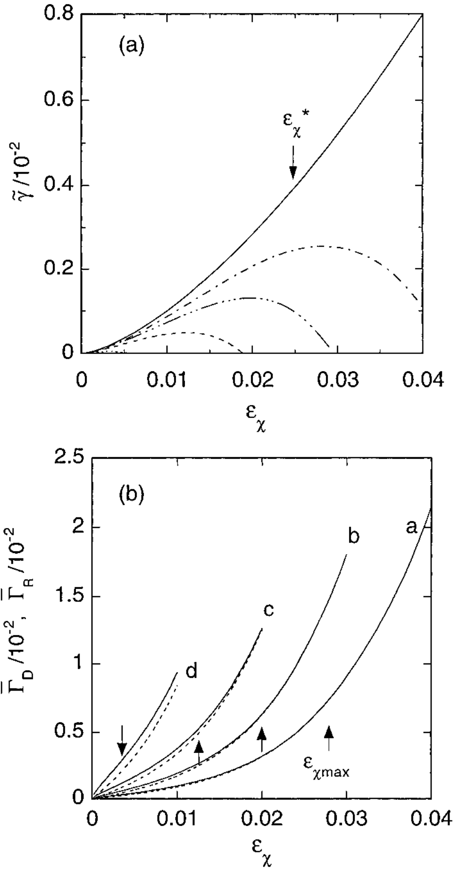

Figure 3. Scaled presentation of the theoretical curves of interfacial tension and adsorption of copolymer for $\tilde{N} = 18$ as a function of scaled temperature distance (ϵ_χ) from T_c at various ϕ_{co}. (a) Interfacial tension, ϕ_{co}: (—) 0%, (– - –) 0.05%; (– - - - –) 0.1%; (– –) 0.2%; (- - -) 0.5%; ϵ_χ*, ϵ_χ at $L = R$. (b) Adsorption (—) $\bar{\Gamma}_R$, (- - -) $\bar{\Gamma}_D$. ϕ_{co}: (a) 0.05%; (b) 0.1%; (c) 0.2%; (d) 0.5%. Arrows with $\epsilon_{\chi_{\max}}$, the position of ϵ_χ at the maximum of γ.

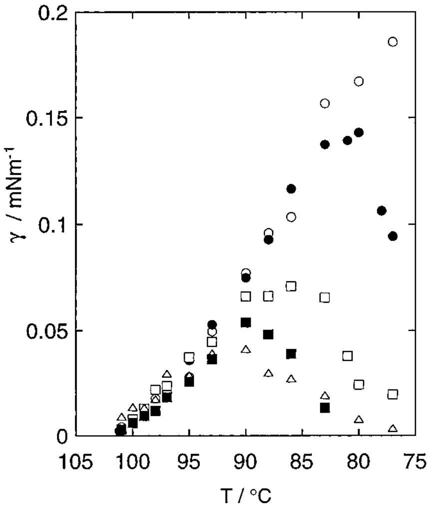

Figure 4. Temperature dependence of interfacial tension near the critical point for OS(M_w = 600)/ODMS(M_w = 460) with PS-*b*-PDMS (M_w = 9900). PS-*b*-PDMS concentration: (○) 0%; (●) 0.05%; (□) 0.16%; (■) 0.4%; (△) 0.8%.

Experimental Results

Figure 4 shows the temperature dependence of the interfacial tension near the critical point for various copolymer concentrations. The interfacial tensions of all the blends with the block copolymers disappear around the same temperature, the critical temperature, of the pure blend without the copolymers. This is consistent with the theoretical expectation (eq 5) and also supports the assumption in the data analysis that the coexistence curve is not appreciably affected by the presence of copolymers. The interfacial tension of the

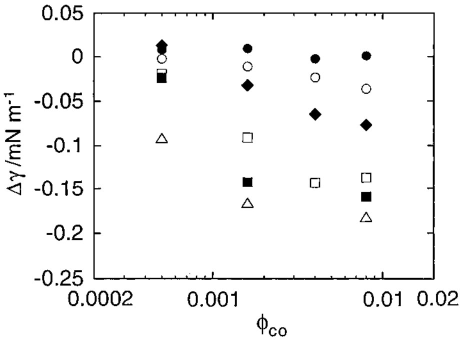

Figure 5. Reduction of interfacial tension of OS/ODMS with addition of PS-*b*-PDMS plotted against concentration of the block copolymer at various fixed temperatures in the semilogarithmic scale. (●) 95 °C; (○) 90 °C; (◆) 86 °C; (□) 83 °C; (■) 80 °C; (△) 77 °C.

pure blend increases monotonically with temperature, decreasing away from the critical point, whereas those of the systems with PS-*b*-PDMS increase first and then decrease with decreasing temperature, exhibiting the maximum. The temperature ($T_{\max}$) at the maximum increases, i.e., approaches the critical temperature, with increasing concentration of the copolymer.

In Figure 5 is plotted the reduction $\Delta\gamma = \gamma - \gamma_0$ of the interfacial tension by addition of the block copolymer against the logarithm of the concentration ($\phi_{\rm co}$) of added copolymer at various fixed temperatures. The interfacial tension decreases rapidly first and then seems to level off as $\phi_{\rm co}$ increases.

From the concentration dependence of γ, we calculated the excess copolymers ($\Gamma_{\rm co}$) adsorbed at the interface by using the Gibbs equation for isothermal adsorption (see Appendix)

$$\Gamma_{\rm co} = -\frac{v_0 N}{kT}\left(\frac{\partial \gamma}{\partial \ln \phi_{\rm co}}\right)_T \tag{37}$$

The gradient, $d\gamma/d \ln \phi_{\rm co}$, was evaluated around $\phi_{\rm co} = 0.001$. The obtained values of $\Gamma_{\rm co}$ are plotted against temperature in Figure 6. Also shown are values of the reduced adsorption $\bar{\Gamma}_R = \Gamma_{\rm co}/R$, with the end-to-end distance (R) of the copolymer being taken as $R = 6.7$ nm, evaluated by using $(R^2/M)^{1/2} = 0.067$ nm g$^{1/2}$ mol$^{-1/2}$.[14] The value of $(R^2/M)^{1/2}$ is coincidentally the same for both PS and PDMS. The adsorption is very low near the critical temperature down to about 95 °C and then increases sharply as the temperature decreases. $T_{\max}$ at $\phi_{\rm co} = 0.001$ is located around 84 °C, slightly lower than the temperature of upturn of $\bar{\Gamma}_R$. The value of $\bar{\Gamma}_R$ is rather low, about 0.05 around $T_{\max}$ and about 0.12 at the lowest temperature (80 °C) of the present experiments.

Discussion

The mixture studied experimentally here is approximately a symmetrical system and has the polymeric index ratio $\tilde{N} = 18$ so that the experimental results can be compared with those of the theoretical treatment shown in Figure 3. The experimental results verify the theory predicting the presence of the maximum in the temperature dependence of interfacial tension and the shift of the maximum with copolymer concentration change. A change of $\bar{\Gamma}_R$ with decreasing temperature (Figure 6) is also well reproduced by the numerical calculation in Figure 3b, although the theoretical value is fairly smaller than the experimental one. For a more quantitative comparison, the theoretically predicted $\epsilon_{\chi_{\max}}$ was calculated and the experimentally observed temperature of the maximum was transferred to $\epsilon_{\chi_{\max}}$ by using the χ vs temperature relation[12] obtained from the experimental coexistence curve. The results of $\epsilon_{\chi_{\max}}$ are shown as a function of $\phi_{\rm co}$ in Figure 7. The concentration dependence of the predicted $\epsilon_{\chi_{\max}}$ is reasonably comparative to the experimental result, though the absolute value of $\epsilon_{\chi_{\max}}$ is much lower.

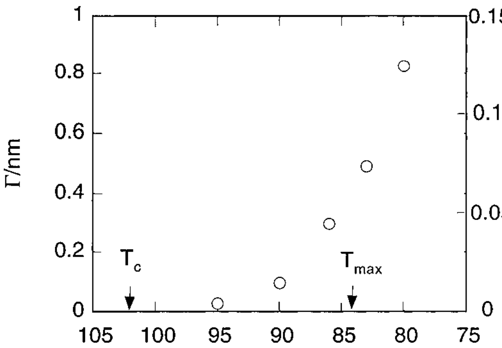

Figure 6. Temperature dependence of adsorption of the block copolymer at the interface of OS/ODMS blends with PS-*b*-PDMS around the concentration $\phi_{\rm co} = 0.001$. T_c, the critical temperature; $T_{\max}$, the temperature at the maximum of γ.

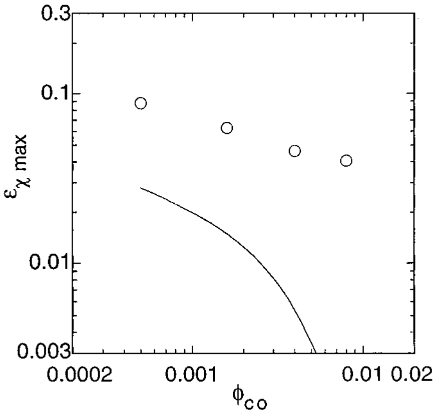

Figure 7. $\epsilon_{\chi_{\max}}$ and ϵ_χ at the interfacial maximum as a function of the copolymer concentration. $\phi_{\rm co}$: (○) experimental; (—) theoretical for $\tilde{N} = 18$.

The present theory reproduces well the experimental findings of γ and $\Gamma_{\rm co}$ qualitatively so that the essence of the maximum phenomenon of interfacial tension can be interpreted by the present theoretical consideration. However, the quantitative agreements in $\epsilon_{\chi_{\max}}$ and $\bar{\Gamma}_R$ are very poor. The discrepancy may primarily be due to the overestimation of Δe rising from the assumption of *perfect* orientation of adsorbed copolymers at the interface, as pointed out before. The overestimation of Δe results in a larger reduction of γ and, accordingly, a smaller $\epsilon_{\chi_{\max}}$ than the observed ones. As the result of that, the calculated $\bar{\Gamma}_R$ is smaller around $T_{\max}$ (or $\epsilon_{\chi_{\max}}$). Furthermore, the present theory is a very simplified one, taking almost no care of numerical factor, and is a mean-field theory ignoring large composition fluctuations near the critical point. There are other possible reasons for the quantitative disagreement, although they may be thought to be secondary.

Appendix

The Gibbs isothermal equation for the interfacial tension[15] is

$$\mathrm{d}\gamma_T = -\left(\sum_{i=1}^{i}\Gamma_i\,\mathrm{d}\mu_i\right) \tag{A-1}$$

$\mathrm{d}\gamma_T$ denotes an isothermal change of γ, μ_i is the chemical potential of component *i* per segment volume, and Γ_i is the adsorption of component *i* (so called by Gibbs) in volume per unit surface area. For the symmetrical system considered in the Theoretical Consideration section, the dividing surface of the Gibbs model[16] here is taken at the maximum of ϕ_3 (block copolymer surfactant), and then, under the assumption of incompressibility, one has

$$\Gamma_1 = \Gamma_2 = -\Gamma_3/2 \tag{A-2}$$

Therefore,

$$\mathrm{d}\gamma_T = -\Gamma_3\left(\mathrm{d}\mu_3 - \frac{1}{2}[\mathrm{d}\mu_1 + \mathrm{d}\mu_2]\right) \tag{A-3}$$

The free energy of mixing under random mixing with no order phase is written as

$$\Delta_{\mathrm{m}}f = (1/P)(\phi_1 \ln \phi_1 + \phi_2 \ln \phi_2) + (1/N)\phi_3 \ln \phi_3 + \chi(\phi_1\phi_2 + (1 - \phi_3)\phi_3/4) \tag{A-4}$$

which leads to

$$\frac{\Delta\mu_1 + \Delta\mu_2}{2} = \frac{\ln(\phi_1\phi_2)}{2P} + \phi_3\left(\frac{1}{P} - \frac{1}{N}\right) + \frac{\chi}{2}(1 - \phi_3 + {\phi_3}^2/2) - \chi\phi_1\phi_2 \tag{A-5}$$

$$\Delta\mu_3 = \frac{\ln \phi_3}{N} + (1 - \phi_3)\left(\frac{1}{N} - \frac{1}{P}\right) + \frac{\chi}{4}(1 - \phi_3)^2 - \chi\phi_1\phi_2 \tag{A-6}$$

Therefore, one has

$$\mathrm{d}\mu_3 - \frac{1}{2}[\mathrm{d}\mu_1 + \mathrm{d}\mu_2] = \left[\frac{1}{P(1 - \phi_3)} + \frac{1}{N\phi_3}\right]\mathrm{d}\phi_3 - \frac{1}{P}\mathrm{d}[\ln(\Phi_1\Phi_2)] \tag{A-7}$$

Then, eq A-3 yields

$$\left(\frac{\partial\gamma_T}{\partial\phi_3}\right)_T = -\frac{kT}{\nu_0}\left[\frac{1}{P(1 - \phi_3)} + \frac{1}{N\phi_3} - \frac{1}{P}\left(\frac{\partial[\ln(\Phi_1\Phi_2)]}{\partial\phi_3}\right)_T\right]\Gamma_3 \tag{A-8}$$

or

$$\Gamma_3 = -\frac{\nu_0 N}{kT}\left(\frac{\partial\gamma_T}{\partial \ln \phi_3}\right)_T\left[1 + \left\{\frac{1}{(1 - \phi_3)} - \left(\frac{\partial[\ln(\Phi_1\Phi_2)]}{\partial\phi_3}\right)_T\right\}\tilde{N}\phi_3\right]^{-1} \tag{A-9}$$

where eqs 5 and 7 are used. The term $\partial[\ln(\Phi_1\Phi_2)]/\partial\phi_3$ near the critical point can be evaluated by using eq 6 as follows:

$$\left(\frac{\partial[\ln(\Phi_1\Phi_2)]}{\partial\phi_3}\right)_T = \left(\frac{\partial[\ln\{1 - (\Delta\Phi)^2\}]}{\partial\phi_3}\right)_T = \frac{3(\epsilon_\chi + 1)}{(1 - \phi_3)(1 - 3\epsilon_\chi)} \tag{A-10}$$

Here, it should be noted that the differential under constant temperature (isothermal) implies that under constant χ. Using this equation (eq A-10), the following equation is obtained from eq A-9 for the vicinity of the critical point, i.e., for $\epsilon_\chi \ll 1$:

$$\Gamma_3 = -\frac{\nu_0 N}{kT}\left(\frac{\partial\gamma_T}{\partial \ln \phi_3}\right)_T\left[1 - \frac{2(1 + 3\epsilon_\chi)}{(1 - \phi_3)(1 - 3\epsilon_\chi)}\tilde{N}\phi_3\right]^{-1} \tag{A-11}$$

If the concentration of the copolymer is low enough, then the above equation is reduced to the following well-known Gibbs isothermal adsorption equation:

$$\Gamma_3 = -\frac{\nu_0 N}{kT}\left(\frac{\partial\gamma_T}{\partial \ln \phi_3}\right)_T \tag{A-12}$$

In the present case of $\tilde{N} = 18$, if ϕ_3 is taken to be 0.001, then the correction term in the bracket of eq A-11 is about 0.08 even at $\epsilon_\chi = 0.1$. Therefore, the correction term is less than 10%, and the calculated adsorption may be slightly underestimated, but it is not so bad in the present case to use the Gibbs equation, eq A-12. The experimental system in this study is not exactly symmetrical so that the experimentally obtained values of Γ_{co} involve some ambiguity from the asymmetry. However, this is not thought to be serious, because the slight asymmetry in the experimental system is that of the block composition in the copolymer, of which effect appears in the correction term of finite ϕ_3 through the intermolecular interaction involving the χ parameter.

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