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Interfacial Tension Reduction in Polystyrene/ Poly(dimethylsiloxane) Blends by the Addition of Poly(styrene-*b*-dimethylsiloxane)

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ABSTRACT: The effects of diblock copolymer addition on the interfacial tension of immiscible homopolymer blends are examined for the ternary system comprising polystyrene (PS), poly(dimethylsiloxane) (PDMS), and poly(styrene-*b*-dimethylsiloxane) [P(S-*b*-DMS)]. Interfacial tension is measured, as a function of the diblock copolymer concentration and the molecular weight of PDMS, using an automated pendant drop tensiometer. The interfacial tension of the blend initially decreases upon an increase in the copolymer concentration and then attains a constant value above a certain critical concentration. A maximum interfacial tension reduction of 82% is achieved at a critical concentration of 0.002% diblock copolymer. At a fixed PS molecular weight, the reduction in interfacial tension increases and the critical concentration decreases with an increase in the PDMS molecular weight. These results are compared to the predictions of Leibler's theory for copolymer brushes wherein the critical concentration can be attributed either to saturation of the interface (i.e., for the dry brush case) or to the onset of copolymer micelle formation (i.e., for the wet brush case). The degree of interfacial tension reduction is found to be dependent on the sample preparation procedure. When the copolymer is mixed into the PS phase, the amount of interfacial tension reduction is much less than the reduction when it is blended into the PDMS phase. This behavior suggests that the polymer blend interface may act as a kinetic trap that limits the attainment of global equilibrium in these systems.

Introduction

The most important parameter characterizing the interface in immiscible polymer blend systems is the interfacial tension. This parameter provides a direct interrogation of the thermodynamic state of the interface, since it is directly related to the free energy of the system. It is also of great practical interest, since it is known to influence the morphology of the blend. The size of the dispersed phase in immiscible blends, for example, is known to be directly proportional to the interfacial tension. Since optimal mechanical properties for polymer blends can be obtained only at a critical particle size, interfacial tension modification has emerged as an important method for property modification in polymer blends.

It is well-known that the localization of surfactants at water/oil interfaces can reduce the interfacial tension. Many previous studies have demonstrated that block copolymers play an analogous role when added to immiscible polymer blends. These works have provided experimental evidence for the interfacial excess of block copolymers[1] in ternary blend systems, as well as documenting the effectiveness of block copolymers[2-5] in reducing the interfacial tension of blends. The addition of block copolymers promotes a more stable and smaller particle size, and a narrower particle size distribution as well.[6-8] Therefore, block copolymers can also be regarded as efficient and useful emulsifying agents.

The technological importance and simple structure of diblock copolymers have motivated many recent theoretical studies[9-13] of their interfacial behavior. Most theories investigate the interfacial tension of homopolymers A and B in the presence of an A–B diblock copolymer. When the diblock copolymer is added into the system, the entropy of mixing of the block copolymer with the homopolymer favors a random distribution of the copolymer in the bulk. However, the unfavorable interaction of the A and B segments tends to drive the copolymer toward the interface. The localization of the copolymer at the interface, with the blocks extending into their respective homopolymer phases (i.e., block A in the homopolymer A phase and vice versa) not only minimizes the contacts between the unlike segments of the copolymer and homopolymer but also displaces the two homopolymers away from the interface, thereby decreasing the enthalpy of mixing between the homopolymers. Noolandi and Hong[9] considered the contributions to the free energy from all these effects and found that the enthalpy terms outweigh the entropy contribution. In other words, the copolymer chains are preferentially absorbed at the interface. As a result, there is less mixing of the homopolymers, and since the interaction energies of the A and B blocks of the copolymer are approximately the same in the bulk or at the interface, the interfacial tension is reduced.

Leibler[13] used a scaling argument to predict the interfacial tension reduction for a very immiscible A/B/A-*b*-B ternary blend system. He considered the copolymer chains at the interface as brushes, with one brush (block A) in homopolymer A, the other brush (block B) in homopolymer B, and the interface acting as a wall. The theory distinguishes two distinct brush regimes: wet brush and dry brush. The criteria differentiating the two regimes are the area per copolymer chain, σ, and the molecular weight ratio of a copolymer sequence to its corresponding homopolymer. For a relatively large interfacial area per chain (low grafting density) and relative low homopolymer molecular weight, a wet

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brush is obtained, where the homopolymer chains tend to penetrate into the copolymer brush. At the opposite extreme, that is when the chains are highly extended and densely packed, the brush resembles a neat block copolymer lamella and is referred to as a dry brush. Here there is little interpenetration of the brush and homopolymer matrix. The ability to distinguish whether a dry or wet brush exists is important in that the interfacial adhesion is dependent upon the degree of interpenetration across the interface.

The theory predicts that the reduction in interfacial tension, $\Delta\gamma$, should scale as a power of ln Φ_{cop}, where $\Phi_{\rm cop}$ is the volume fraction of the block copolymer in the homopolymer phase. In the wet brush case, the interfacial tension reduction is expected to increase with an increase in the molecular weights of the homopolymers and copolymer. In the dry brush regime, it is predicted to be independent of the homopolymer molecular weight and to increase with the block copolymer molecular weight. When the interface of very incompatible homopolymers (high χN, where χ is the Flory interaction parameter and N is the polymerization index of the copolymer) becomes saturated with the block copolymer, the interfacial tension is predicted to go to zero.

In practice, the interfacial tension reduction is often limited by the formation of copolymer micelles. As the copolymer concentration exceeds the critical micelle concentration, $\Phi_{\rm cmc}$, free copolymer chains tend to aggregate and form micelles, rather than migrate to the interface. Therefore, the interfacial tension remains almost constant above $\Phi_{\rm cmc}$. Experimental evidence for copolymer micelles in polymeric matrices has been provided by small-angle X-ray and neutron scattering measurements.[14,18] Theoretical studies[9,19,20] have shown that $\Phi_{\rm cmc}$ decreases with increasing incompatibility and with increasing molecular weights of the copolymer and homopolymers.

In this paper, we investigate the interfacial tension of a ternary system—polystyrene (PS), poly(dimethylsiloxane) (PDMS), and poly(styrene-*b*-dimethylsiloxane) [P(S-*b*-DMS)]—as a function of the copolymer concentation and the molecular weight of the homopolymer. The copolymer is added into either the PS or the PDMS phase in order to examine the effect of the homopolymer matrix on the interfacial tension reduction. These experimental data are compared to the predictions of the Leibler brush theory so as to better understand the molecular level origins of the interfacial tension reduction behavior.

Experimental Section

Materials. The homopolymers used in this study were polystyrene (PS) from Pressure Chemical Co. and poly(dimethylsiloxane) (PDMS) from Polysciences Inc. (PDMS4.5K) and Petrarch Systems Inc. (PDMS1.6K). Their characteristics are listed in Table 1. The molecular weight and polydispersity of PS were provided by Pressure Chemical Co. The molecular weights and polydispersities of PDMS homopolymers were measured using gel permeation chromatography (GPC) that was calibrated in polystyrene equivalents and referenced to a universal calibration curve provided through vapor phase osmometry measurements. The diblock copolymer, poly(styrene-*b*-dimethylsiloxane) (P(S-*b*-DMS)), was synthesized by standard anionic methods using *sec*-butyllithium as initiator and benzene as solvent. The molecular weight of the diblock copolymer, 13 000, and the polydispersity index, 1.15, were determined by size exclusion chromatography coupled with a low-angle laser light scattering detector. The weight fraction of PS in the copolymer is 50%, as determined by elemental anlaysis of the silicon and carbon concentrations.

The theoretical treatment by Noolandi and Hong[9] demonstrated that localization of the homopolymer at the interface is favored when the block copolymer molecular weight exceeds that of the homopolymers. For this purpose we have selected a system in which the block copolymer molecular weight exceeds that of all of the homopolymer constituents and for which there is a large repulsive interaction parameter between the copolymer sequences. Under these conditions, the solubility of the block copolymer within the homopolymer phases should be very low, satisfying an assumption inherent to the Leibler theory.[13]

The densities of the PDMS homopolymers were obtained from a digital density meter (Anton Paar Co., Model DMA60, with external cell DMA602). Linear correlations for the temperature dependence of the density were found as follows:

$$\varrho\ (\text{g/cm}^3) = 0.9575 - 0.0008T\ (^\circ\text{C}) \quad \text{for PDMS1.6K} \quad (1)$$

$$\varrho\ (\text{g/cm}^3) = 0.9807 - 0.0008T\ (^\circ\text{C}) \quad \text{for PDMS4.5K} \quad (2)$$

The density of the polystyrene homopolymer, PS4K, was calculated[21] to be 0.9968 g/cm^3 at 140 °C.

Sample Preparation. Since the density of PS is higher than that of PDMS, PS was used as the drop phase and PDMS, as the matrix for interfacial tension measurements. The diblock copolymer P(S-*b*-DMS) was added to either the drop phase [PS + P(S-*b*-DMS)]/PDMS or to the matrix phase PS/[PDMS + P(S-*b*-DMS)]. P(S-*b*-DMS) was mixed with PDMS by melt blending, while it was mixed with PS by solution blending (in THF) due to the high viscosity of PS. A microextruder with a vacuum line and a temperature controller was used to fill drop materials into glass pendant drop tensiometry capillaries. The material was heated at 180 °C under vacuum for 1 h and then was extruded into a capillary. The matrix material (PDMS) was placed inside a cuvette and degassed in a vacuum oven for 1 h prior to interfacial tension measurements.

Interfacial Tension Measurements. Interfacial tensions were measured by application of a modified pendant drop method employing digital imaging to determine the drop profile and robust shape analysis to compare this profile to the predicted shapes for asymmetric fluid drop profiles. Details regarding a similar apparatus and its utilization can be found elsewhere.[22] All interfacial tension (or surface tension) measurements were carried out at 140 °C (±1 °C), a temperature that is well above the glass transition tempertaures of the blend components. At this temperature, the blend components are highly immiscible, and the coexisting phases are assumed to have the density of the respective pure homopolymers for the purpose of the interfacial tension analysis. The pendant drop cell was purged with argon to prevent degradation of the polymers. The parameters describing the shape of the pendant drop were then determined by analysis of a digital image of the drop using a robust shape comparison algorithm. Interfacial tension values were subsequently calculated from these shape parameters and the known densities of the two homopolymer melts. Approximately 1 h was allowed to achieve thermal equilibrium, and then data were taken as a function of time until a stable interfacial tension (or surface tension) was obtained.

Results and Discussion

The interfacial tension measured for the binary homopolymer blend PS4K/PDMS4.5K, without added diblock copolymer, is 4.85 ± 0.05 dyne/cm at 140 °C (all interfacial tension measurements were made at this temperature). The value is high compared to those of moderately incompatible homopolymers [e.g., 1.7 dyne/cm for polystyrene/poly(methyl methacrylate],[23] indicating that the system is highly immiscible. The corresponding interfacial tension for the PS4K/PDMS1.6 K blend, 4.02 ± 0.09 dyne/cm, is lower than that of PS4K/PDMS4.5K, consistent with what is expected for a lower molecular weight homopolymer.[24]

When a nearly symmetric diblock copolymer P(S-*b*-DMS) ($f = N_{\rm PS}/N = 0.42$) is added into the PDMS4.5K homopolymer phase, the interfacial tension of the

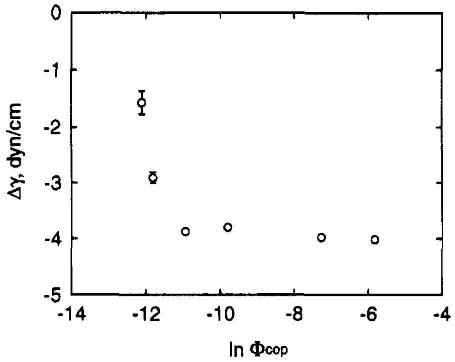

Figure 1. Interfacial tension reduction of PS4K/[PDMS4.5K + P(S-*b*-DMS)].

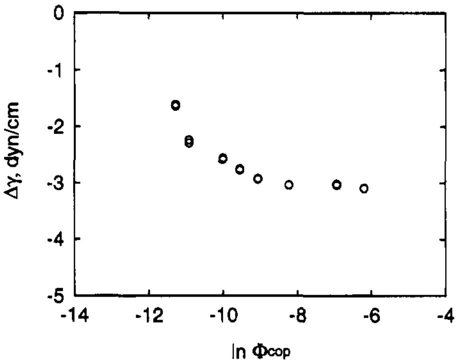

Figure 2. Interfacial tension reduction for PS4K/[PDMS1.6K + P(S-*b*-DMS)].

ternary system, PS4K/[PDMS4.5K + P(S-*b*-DMS)], decreases as a function of the copolymer concentration, as shown in Figure 1. The minimum interfacial tension of 0.90 dyne/cm (82% reduction) is achieved at a critical copolymer concentration of about 0.002%. Above the critical concentration, the interfacial tension remains almost constant. Figure 2 shows the interfacial tension reduction as a function of the copolymer concentration when the PDMS matrix is changed to PDMS1.6K. The reduction in interfacial tension is not as prominent as in the case of PDMS4.5K. The maximum reduction is 76% and it occurs at a much higher concentration of 0.03%.

The limited reduction in interfacial tension could be due either to saturation of the interface or to micelle formation by the diblock copolymers. At this point, it is interesting to compare these data with Leibler's brush theory[13] for ternary systems comprising an A-*b*-B diblock copolymer brush residing at the interphase between A and B homopolymers.

In the dry brush limit, the homopolymer does not penetrate the brush, and the interfacial monolayer resembles a block copolymer lamella. The interfacial tension reduction for a dry brush is therefore independent of the homopolymer molecular weights and is given by

$$\frac{\Delta\gamma}{\gamma_o} = \left(\frac{48^{1/2}}{9}\right)\left(\frac{\mu}{kT}\right)^{3/2} N^{-1/2}\chi^{-1/2} \qquad \textit{dry brush} \qquad (3)$$

where N is the total polymerization index of the copolymer, k is Boltzmann's constant, χ is the Flory interaction parameter, and γ_o is the interfacial tension between the immiscible homopolymers[26]

$$\gamma_o = \left(\frac{kT}{a^2}\right)\left(\frac{\chi}{6}\right)^{1/2} \qquad (4)$$

Table 1. Characteristics of the Homopolymers Studied

homopolymer	designation	M_n	M_w/M_n	P
polystyrene	PS4K	4000	1.06	38.5
poly(dimethylsiloxane)	PDMS4.5K	4500	1.36	61
poly(dimethylsiloxane)	PDMS1.6K	1600	1.12	22

where a is the statistical segment length. At equilibrium, the chemical potential of the copolymer in the interfacial film, μ, must equal that in both of the bulk phases, leading to the expression

$$\frac{\mu}{kT} = \ln \Phi_{\text{cop,A}} + \chi N_B = \ln \Phi_{\text{cop,B}} + \chi N_A \qquad (5)$$

where $\Phi_{\text{cop,A}}$ represents the volume fraction of block copolymer in the A homopolymer phase and the polymerization indices of the A and B block copolymer sequences are N_A and N_B, respectively. For a dry brush, the interfacial tension approaches zero at saturation such that $\Delta\gamma = \gamma_o$. Inserting this result into (3) yields an expression for the saturation concentration

$$\Phi_{\text{sat}} = \exp[(3/4^{2/3})(\chi N)^{1/3} - \chi N_i] \qquad \textit{dry brush} \quad (6)$$

The expression demonstrates that interfacial saturation cannot always be achieved. For example, for a symmetric block copolymer with $N = 200$, interfacial saturation cannot be obtained if χ is less than 0.02.

Another case for which interfacial saturation for the dry brush case is not attained is when the critical micelle concentration, Φ_{cmc}, is less than Φ_{sat}. The copolymer is then favored to form micelles in the bulk phases rather than saturate the interface. The critical micelle concentration is given by[13]

$$\Phi_{\text{cmc}} = \exp[\mu_{\text{cmc}}/kT - \chi N_A] \qquad (7)$$

where A denotes the shorter sequence and the chemical potential at the Φ_{cmc} is defined as

$$\mu_{\text{cmc}}/kT = (3/2)^{4/3} f^{4/9}(1.74 f^{-1/3} - 1)^{1/3}(\chi N)^{1/3} \qquad (8)$$

This result indicates that saturation can only be obtained for a dry brush (i.e., $\Phi_{\text{sat}} < \Phi_{\text{cmc}}$) when the symmetry factor, $f = N_A/N$, is greater than 0.31.

In the case of a wet brush, the homopolymers penetrate into the copolymer chains in the interfacial film, and saturation is never achieved. The interfacial tension reduction for a wet brush is therefore dependent upon the homopolymer chain lengths, P_A and P_B, as well as the block copolymer sequence lengths, N_A and N_B, and is given by

$$\frac{\Delta\gamma}{\gamma_o} = \left(\frac{256}{3125}\right)^{1/2}\left(\frac{\mu}{kT}\right)^{3/2}(N_A P_A{}^{-2/3} + N_B P_B{}^{-2/3})^{-3/2}\chi^{-1/2} \qquad \textit{wet brush} \quad (9)$$

The degrees of polymerization for the PS and PDMS sequences of the diblock copolymer are 63 and 88, respectively, and those of the homopolymer studied (i.e., P) are listed in Table 1. The interaction parameter between PDMS and PS at 140 °C (estimated from the experimental data reported by Galin et al.[25]) is $\chi = 0.23$.[21] A direct calculation[21] of the interaction parameter from the tabulated solubility parameter data yields a comparable value of 0.26 at 140 °C. The large repulsive interaction parameter for the blend is further indication that it is highly immiscible. With the above information, the interfacial tension reduction and critical concentrations can be calculated from Leibler's

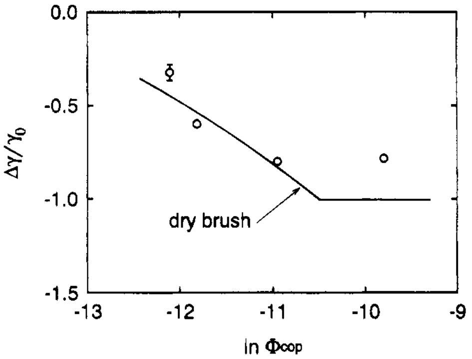

Figure 3. Comparison with the Leibler dry brush theory[13] for PS4K/[PDMS4.5K + P(S-*b*-DMS)].

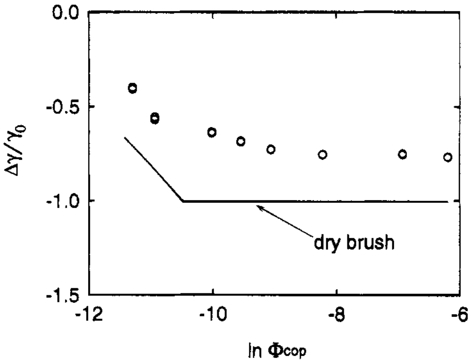

Figure 4. Comparison with the Leibler dry brush theory[13] for PS4K/[PDMS1.6K + P(S-*b*-DMS)].

theory.[13] A wet brush is expected when $N > 2P^{3/2}$, while a dry brush is expected when $P > N^{2/3}$

In the case of the PDMS4.5K ternary blend, the latter inequality holds and a dry brush is expected. A comparison between the dry brush theory and the experimental interfacial tension data for the PDMS4.5K blends is shown in Figure 3. Overall, the theory agrees well with the experimental data. The dry brush theory predicts that the saturation concentration is less than the critical micelle concentration for diblock copolymers with $f > 0.31$. The saturation concentration calculated from (6), 0.003%, is close to the experimental critical concentration, 0.002%, observed in Figure 3. In the brush theory, the dry brush layer is a pure copolymer layer. The interfacial tension will vanish as copolymer chains saturate the interface since the interfacial tension of copolymers is essentially zero. However, practically there is a finite interface between different blocks. In addition, complete exclusion of the homopolymers from the brush region seems unlikely. Therefore, there exists a finite interfacial tension above the apparent Φ_{sat} in Figure 3, although the decrease in the interfacial tension before the critical concentration agrees well with the theoretical prediction for a dry brush.

Figure 4 compares the dry brush theory to the data for the PDMS1.6K ternary blends. The apparent experimental critical concentration (0.03%) is much larger than both the predicted Φ_{cmc} of 0.004% (for the diblock in the PDMS1.6K homopolymer matrix) and the predicted saturation concentration of 0.003%. The theory overestimates the amount of interfacial tension reduction attained. That is, the interfacial tension observed is larger than that expected for a dry brush, suggesting that there is some penetration of the lower molecular weight PDMS1.6K homopolymer into the copolymer brush region. The interpenetration increases the unfavorable contacts between the PDMS and PS homopolymers, thereby increasing the interfacial tension.

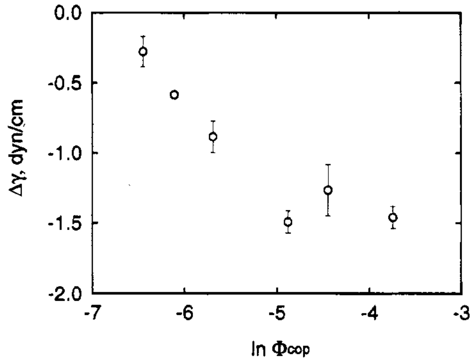

Figure 5. Interfacial tension reduction for [PS4K + P(S-*b*-DMS)]/PDMS4.5K.

If we examine the relative chain length criteria for the PDMS1.6K blend, we find that $P \cong N^{2/3}$ and $2P^{3/2} > N$. In this case, the brush is not in the limit of being wet, but is also not completely dry. It falls within the crossover region between the two limiting behaviors. Interfacial saturation may not be achieved, and the critical concentration may be associated with micelle formation of the block copolymer.

It was shown[27] that a system has to overcome a high potential energy barrier in order to form a micelle. Therefore, it was suggested that the apparent Φ_{cmc} determined by experiments might be controlled by the barrier rather than the thermodynamic potential of a micelle and might be much larger than the equilibrium Φ_{cmc} at infinite time. This behavior is consistent with our observation that the experimental critical concentration is larger than Φ_{cmc} for the PDMS1.6K blends.

The systems that have been discussed up to this point have been formulated by mixing the A-*b*-B diblock copolymer into only one of the homopolymer phases to provide two immiscible phases (e.g., A and B/A-*b*-B). That is, the block copolymer was added to the PDMS homopolymer phase and allowed to partition to the melt interphase with the PS homopolymer during the interfacial tension measurements. There is no study in the literature to compare the amount of interfacial tension reduction for the cases where the copolymer A-*b*-B is added into the homopolymer A phase and where it is mixed into the homopolymer B phase. Figure 5 shows the interfacial tension reduction for the system [PS4K + P(S-*b*-DMS)]/PDMS4.5K where the block copolymer has now been added to the PS phase. Surprisingly, the maximum reduction is only 29% compared to the 82% reduction obtained when the copolymer was added to the PDMS phase. The critical concentration, ~1%, is also much higher than that (0.002%) for the PS4K/[PDMS4.5K + P(S-*b*-DMS)] blends. In the case of the [PS4K + P(S-*b*-DMS]/PDMS1.6K blends, the amount of reduction is only 20% (Figure 6), compared to the 76% reduction found when the copolymer is added into the PDMS phase. The amount of interfacial tension reduction decreases when the molecular weight of the PDMS homopolymer decreases, as expected from the theories; however, there is a large difference in the interfacial tension results depending on which phase the copolymer is added to.

For the case when the copolymer is added in the PS matrix, it is possible to directly measure the critical micelle concentration of the copolymer in PS by performing surface tension measurements. For this purpose the drop material [PS4K + P(S-*b*-DMS)] was placed in an argon environment instead of the PDMS matrix. The surface tension of the drop was measured as a function of the copolymer concentration. The result is

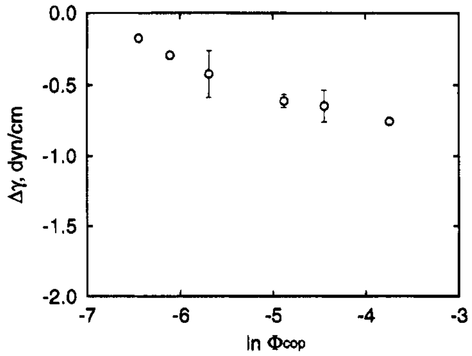

Figure 6. Interfacial tension reduction for [PS4K + P(S-*b*-DMS)]/PDMS1.6K.

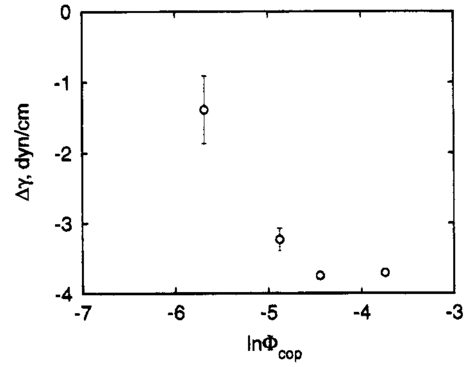

Figure 7. Surface tension reduction for PS4K + P(S-*b*-DMS).

shown in Figure 7. The surface tension of pure PS4K is 20.3 dyne/cm. Surface tension decreases as the copolymer concentration is increased until a plateau is reached at 1%.

It is well-known that low-energy additives can migrate to a surface and lower the surface tension.[28,29] The surface activity of the lower-energy block in a copolymer has been reported as well.[30] When an A-*b*-B diblock copolymer, where B has a lower surface energy than A, is blended with homopolymer A, the copolymer will migrate to the surface due to the unfavorable enthalpy of mixing of segments A and B and the lower surface energy of the B blocks. The localization of the B blocks at the surface results in a reduction of the surface energy. The surface tension of pure B blocks could be obtained if the surface is saturated with the diblock copolymer.

The surface tensions of PS and PDMS of infinite molecular weights are 30 and 14 dyne/cm at 140 °C, respectively.[23] In this case, a minimum surface tension of 14 dyne/cm is expected when the surface becomes saturated. The minimum surface tension obtained from the measurement was 16.6 dyne/cm, suggesting that saturation of the air–polymer interface is not attained and that observation of the plateau in the concentration dependence of surface tension is indicative of the formation of block copolymer micelles. The apparent critical micelle concentration for the block copolymer in the PS4K matrix is therefore 1%, comparable to the concentration for onset of the interfacial tension plateau in the ternary system [PS4K + P(S-*b*-DMS)]/PDMS4.5K (Figure 5). This result implies that the origin of both the limited interfacial tension reduction in the ternary system and the plateau in the surface tension may be attributed to micelle formation of the diblock copolymer in the PS phase.

Theory[20] predicts that the critical micelle concentration decreases as the homopolymer molecular weight increases. Based on this result, the origin of the level-off in interfacial tension for the [PS4K + P(S-*b*-DMS)]/PDMS1.6K blends (Figure 6) may also be attributed to copolymer micelle formation, although the trend is not so obvious as in Figure 5. This is an expected result for a wet brush; that is, the system is expected to reach the Φ_{cmc} before interfacial saturation is obtained.

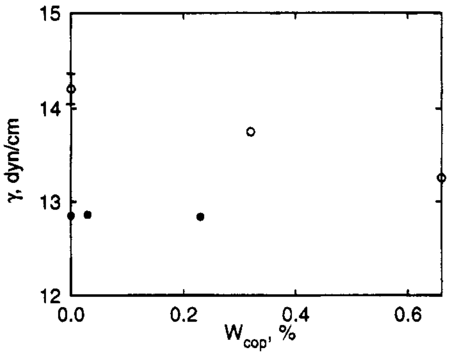

Figure 8. Surface tension of PDMS + P(S-*b*-DMS) for different PDMS molecular weights: (open circles) $M_n = 4500$; (filled circles) $M_n = 1600$.

The surface tensions of PDMS1.6K/P(S-*b*-DMS) and PDMS4.5K/P(S-*b*-DMS) blends as a function of the copolymer concentration are shown in Figure 8. The block copolymer does not show any surface activity in the former case. In the latter, the surface tension decreases very slowly with the copolymer concentration and there is no plateau region. The lack of surface activity of the P(S-*b*-DMS) diblock copolymer in the PDMS matrices is attributed to the higher surface energy of the PS blocks relative to the PDMS blocks. Initial attempts to determine the Φ_{cmc} for these systems by small angle X-ray scattering analysis were not successful.

The strong dependence of interfacial tension on the sample preparation procedure is an interesting phenomenon that has not been previously reported and one that merits further discussion. When added to the PS4K phase, the block copolymer produces a limiting interfacial tension reduction of about 29% at a critical composition of roughly 1%. This composition corresponds well to the Φ_{cmc} of 1% determined by surface tension measurements on the binary PS4K/copolymer blend. Both of these measurements were taken after the systems were allowed to equilibrate for long periods of time, when the experimental results had attained constant values. The correspondence of the critical concentrations and the apparent equilibration of the long time interfacial tension data, suggest that local equilibrium is achieved in the PS phase. On the other hand, a limiting interfacial tension reduction of 82% is attained at a critical concentration of only 0.002%, when the copolymer is added to the PDMS4.5K phase. Here again, local equilibrium appears to be obtained, since the results approach a constant value at long times, and since the critical concentration for at least one of the blends is similar to the predicted Φ_{sat}. The results imply, therefore, that while local equilibrium is attained, these ternary blends do not reach a true global equilibrium.

There are several factors which influence how the system may achieve a global equilibrium. The most obvious of these are kinetic factors associated with the diffusion of the block copolymer to the interface.[21] The diffusion of the block copolymer is clearly slower in the PS phase than in the PDMS phase, owing to the higher viscosity of PS. The fact that the interfacial tension reaches constant values at long times suggests, however, that this does not account for the nonequilibrium behavior. A second factor that presents itself in these data is the rather large apparent difference in the solubility of the copolymer in the two matrices. The copolymer solubility limit (apparent Φ_{cmc}) is about 1% in the PS4K matrix compared to 0.002%–0.03% in the PDMS matrices. This result is also unexpected from (7), since the copolymer is symmetric and the PS and PDMS matrices have similar molecular weights.

Although we do not fully understand this behavior at present, we would like to describe two plausible effects that may provide an explanation for this phenomenon. The first of these is the geometry of the experiment itself. The volume of the drop is considerably smaller than that of the matrix phase. When the copolymer is blended into the PS, it must travel first to the interface and then across it to saturate the PDMS matrix. Since the reservoir of copolymer in the PS phase is small, a high initial concentration of block copolymer may be required to provide enough material to saturate the PDMS matrix, and the actual final concentration of copolymer in the PS phase (i.e., at equilibrium) may be much smaller than the initial value. In the inverse experiment, when the copolymer is added to the matrix phase, the reservoir is relatively large, and the copolymer concentration may not be depleted significantly when some copolymer diffuses into the relatively small drop phase. This possibility can easily be examined either by changing the relative volumes of drop and matrix phases or by putting block copolymer into both phases. Experiments of this nature are in progress.

The second effect that may explain these results is the possibility that transport across the interface is hindered by some activation barrier, such that the two coexisting phases do not achieve a true equilibrium. That is, a copolymer adsorbed at the interface is energetically stable, and there may be an activation barrier toward movement away from the interface that effectively traps the copolymer at the interface. While additional experiments are clearly necessary to resolve the origin of this interesting behavior, these results clearly demonstrate, from a practical point of view, that care must be exercised in the formulation of commercial blends containing block copolymer compatibilizers, since the results may depend strongly upon the sequence of blending certain components and details of the overall blend preparation methodology.

Summary

The effect of a diblock copolymer on the interfacial tension of immiscible homopolymers is investigated for ternary blends of PS, PDMS, and P(S-*b*-DMS). The interfacial tension reduction arises from the localization of copolymer chains at the interface and increases as the copolymer concentration increases until a critical concentration is attained. When the copolymer was blended with the PDMS matrix, the amount of reduction increases with increasing molecular weight of the host. This is associated with the reduced entropy of mixing for the higher molecular weight, which drives the copolymer to the interface. In addition, shorter homopolymer chains have a higher chance to penetrate into the interfacial brush region. This leads to a wet brush regime, and the reduction in the interfacial tension decreases. When the interface is saturated with copolymer chains, zero interfacial tension is hypothetically achieved and this corresponds to the dry brush regime. The results for the higher molecular weight host suggest that a nearly dry brush is formed at the interface and that the concentration where interfacial tension is observed to attain a constant value is associated with saturation of the interface.

When the copolymer is mixed into the PS phase, the amount of interfacial tension reduction is much less than the reduction when it is blended into the PDMS phase, indicating that global equilibrium is not achieved in these systems. The limiting reduction is most likely due to micelle formation of copolymer chains in the bulk PS phase, since the critical concentration for the interfacial tension reduction is comparable to that observed for the surface tension reduction of PS/P(S-*b*-DMS) binary blends.

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