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Segregation of Low Molecular Weight Symmetric Diblock Copolymers at the Interface of High Molecular Weight Homopolymers

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ABSTRACT: Elastic recoil detection was used to study the segregation of low molecular weight symmetric diblock copolymers of polystyrene (PS) and poly(methyl methacrylate) (PMMA) to the interface of PS and PMMA homopolymers. Copolymer chains composed of 292 and of 262 segments were used. The PS and PMMA homopolymers were composed of 18 000 and 13 000 segments, respectively. At the concentrations studied, Σ_i^{-1}, the excess number of copolymer chains per unit area at the interface of the homopolymers, varied linearly with, ϕ_c, the volume fraction of copolymer chains in the bulk. The solubility of the copolymer chains was found to be slightly higher in the PMMA phase than in the PS phase. The results are compared with predictions based on modifications of mean field arguments of Leibler. The predicted dependence for the situation in which the density of copolymer chains at the interface is low is in good agreement with the experimental data. The predictions are based on assumptions that both the excluded volume interactions that lead to swelling of the copolymers at the interface and the elastic entropy contributions that limit the swelling of the copolymers are not important. An estimate of the Flory interaction parameter that was made based on the data and the theory is in good agreement with the value determined from small-angle neutron scattering of the PS/PMMA system. Finally, we estimated the reduction in interfacial tension that results when the copolymer chains segregate to the interface. It is consistent with surface tension data on similar systems.

Introduction

The mixing of two homopolymers is characterized by a low combinatorial entropy of mixing. Consequently, most polymer pairs are immiscible. Immiscible polymer mixtures are characterized by narrow interfaces and exhibit poor mechanical properties. For chains of infinite molecular weight, Helfand and Tagami[1,2] have shown that the width, D, of an interface between two immiscible polymers varies as $\chi^{-1/2}$

$$D = 2a/(6\chi)^{1/2} \tag{1}$$

where a is a statistical segment length and χ is the Flory–Huggins interaction parameter. The interfacial tension of the system was shown to vary as $\chi^{1/2}$

$$\gamma_0 = a\rho k_B T(\chi/6)^{1/2} \tag{2}$$

where ρ is the density, k_B is the Boltzmann constant, and T is the temperature. Since diblock copolymers behave like classical surfactants, there is great current interest in using them to modify the interfacial properties of materials. Blending small quantities of an appropriate diblock copolymer with a binary homopolymer mixture can be used to produce high-performance plastics with appreciably improved mechanical properties.[3] The copolymer chains migrate to the interface between the two polymers and orient such that each block extends into the homopolymer phase with which its energetic interactions are favorable. This reduces the total free energy of the system.[4]

The presence of the copolymers at the interface reduces the interfacial tension of the mixture. The Gibbs adsorption equation shows how the interfacial tension is reduced when adsorption to an interface occurs. Under conditions of constant temperature and pressure, the change in interfacial tension that results when there is an excess of species i of a homopolymer/copolymer mixture at an interface may be given by

$$d\gamma = -\sum_i \Sigma_i^{-1}\, d\mu_i \tag{3a}$$

where Σ_i^{-1} is the excess number of chains of species i per unit area that adsorb at the interface. μ_i is the chemical potential of species i. Since it is possible to choose a Gibbs dividing surface such that the excess of the homopolymer chains at an interface is zero, the reduction in interfacial tension may be written

$$d\gamma = -\Sigma_c^{-1}\, d\mu_c \tag{3b}$$

The subscript c refers to the copolymer chains. Each block of the copolymer forms entanglements with the homopolymer with which the energetic interactions are favorable. This improves the fracture toughness of the interface.[5,6] Neutron reflectivity studies[7,8] show that the presence of the copolymer chains also broadens the interfacial region between the homopolymers. This follows from the fact that the junctions of the chains are confined to a narrow interfacial region between the homopolymer phases. If this region is broadened, then there is less of an entropy penalty associated with confinement of the chains. These processes mentioned in the foregoing discussion contribute to the overall improvement of the mechanical properties of the mixture appreciably.

Theories constructed to describe the interfacial segregation of diblock copolymers have been developed by Leibler,[9] Hong and Noolandi,[3] and Shull and Kramer.[10] Early experiments that were designed to understand this process yielded limited data since they were restricted to determining surface tension of low molecular weight polymers.[11] A direct determination of the copolymer profiles in the copolymer/homopolymer system is much more advantageous. It enables a quantitative comparison

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with theoretical predictions. The first experimental study that attempted to quantify the segregation of copolymer chains to an interface was the work of Shull et al.[12] They studied a highly incompatible asymmetric diblock system of PS/poly(vinylpyridine). The work presented here concerns the use of elastic recoil detection (ERD),[13-16] to study the segregation of low molecular weight symmetric copolymer chains of polystyrene (PS) and poly(methyl methacrylate) (PMMA) to the interfaces of high molecular weight PS and PMMA homopolymers. The experimental results are discussed in light of mean field theory.

Experimental Section

The polystyrene homopolymer ($M_w = 1.8 \times 10^6$ and $M_w/M_n < 1.05$) was purchased from Pressure Chemical Laboratories and used without further purification. The PMMA ($M_w = 1.3 \times 10^6$ and $M_w/M_n < 1.05$) homopolymer and the symmetric diblock copolymers were purchased from Polymer Laboratories. The PMMA was used as received. Two different diblock copolymers of PS and PMMA were used. Both copolymers were purified with cyclohexane in order to remove any undissolved PS homopolymer. One of the copolymers was composed of 292 segments, denoted as P(d-S-b-d-MMA) and was completely deuterated. The volume fraction of PS was 0.51. In the case of the other copolymer of 262 segments, denoted P(d-S-b-MMA), only the PS segment was deuterated. The fraction of PS was 0.48. The molecular weight distribution of both copolymers were $M_w/M_n < 1.05$.

Films of PMMA or mixtures of PMMA with a diblock copolymer (a few percent or less) were spin coated onto a silicon substrate where the resultant film thickness was ~4000 Å. A separate film of PS (or PS mixed with a few percent or less of the copolymer) were spin coated onto a glass slide where the film was ~3000 Å. This film was then removed from the slide by floating it off onto a bath of distilled water. It was then picked up on top of the polymer-coated wafer in order to produce a bilayer sample. In some cases a trilayer was made. Here a layer of the copolymer was transferred on top of the PMMA-coated substrate and then a PS layer was transferred on top of the bilayer in order to produce a trilayer. The samples were annealed at 162 °C and at 170 °C in an ultraclean high-vacuum system for days in some cases.

ERD was then used to determine the volume fraction versus depth profile of the copolymers in the sample.[13] In the ERD experiment, incident helium ions (E_0 = 2.8 MeV) recoil protons and deuterons in the sample. These particles, after passing through a foil, which was placed there to prevent any forward scattered helium nuclei from being detected, were detected by use of a silicon surface barrier detector. One obtains from this experiment a spectrum of yield, number of particles scattered with energy E_d, $Y(E_d)$, versus energy E_d. Figure 1 shows a profile of yield versus energy of a sample in which the P(d-S-b-d-MMA) copolymer chains had segregated to the interface of the two homopolymer films. Note that the profile of protons from the homopolymers is located at lower energies. The front of that profile, at $E_d \approx 1000$ keV, is the front edge of the PS film. At an energy of E_d = 700 keV is the back edge of the PMMA film. At an energy of approximately E_d = 850 keV, there is a depletion of protons. This is due to the presence of the deuterated copolymer chains at the interface of the films. Located at higher energies, 1200 keV, is a profile of the deuterated copolymers. This profile can be converted to one of volume fraction, $\phi(x)$, versus depth, x, of the copolymer chains. A detailed account of ERD and the conversion process may be found in ref 13. Figure 2 shows $\phi(x)$ as a function of depth, x, for the P(d-S-b-d) copolymer that was annealed at 170 °C for 3 days.

At the concentrations used in this experiment, we did not at any time observe the segregation of copolymer chains to the free surface, as was observed by Shull and Kramer in the PS/PVP system.[10] It is not clear, however, that one should observe this behavior in this system. The observation of a surface segregation is consistent with the formation of micelles in the bulk. In the PS/PVP system the outer region of the micelles, the corona, is composed only of deuterated PS (d-PS) chains. The d-PS chains have a lower surface energy than that of the normal PS chains. Therefore, the free energy of the system is minimized if the micelles migrate to the free surface. This was not observed in the PS/PMMA system. It is not clear, however, that we should observe the formation of micelles considering that small-angle neutron-scattering experiments show that the 292-segment copolymer system is weakly segregated at 170 °C. The measurements also showed that the 262-segment copolymer was disordered at this temperature.[17]

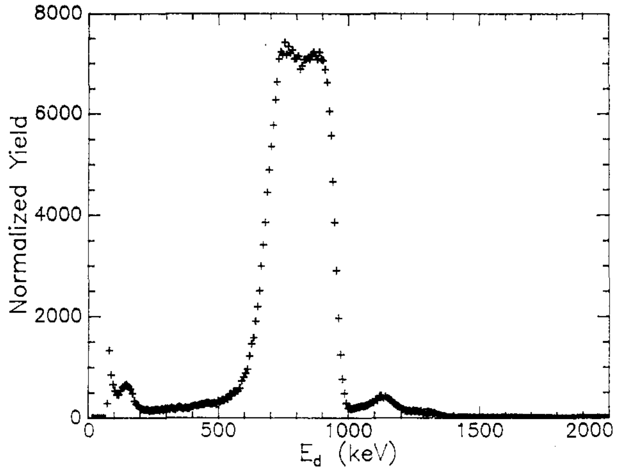

Figure 1. Typical ERD spectrum of yield versus energy of P(d-S-b-d-MMA) block copolymer chains that segregated to the interface of the PS and PMMA homopolymers. The profile that lies in the energy range between 600 and 1000 keV is the hydrogen from the homopolymers and the other profile, which lies between 1000 and 1400 keV, is that of the deuterium from the copolymer chains.

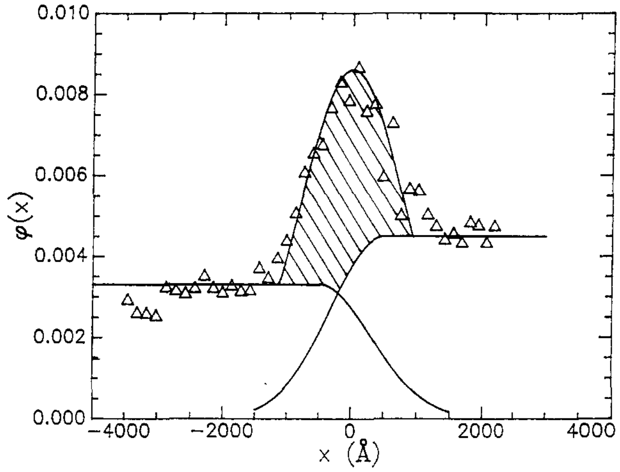

Figure 2. Profile of volume fraction versus depth of P(d-S-b-MMA) copolymer chains in the copolymer/homopolymer system. The shaded region is $\phi^*(0)$, the interface excess. The actual position of the profile has been shifted so that the origin represents the interface of the PS and PMMA homopolymers. The PS phase is located at $x < 0$. The volume fraction of copolymer chains in this phase is $\phi_c^{PS} = 0.0033$. The PMMA phase is located at $x > 0$ and the volume fraction of P(d-S-b-MMA) chains is $\phi_c^{PMMA} = 0.0044$. This sample was annealed at 162 °C for 100 h.

The shaded region in Figure 2 represents an interface excess of the copolymer chains, $\phi_c^*(0)$, where

$$\phi_c^*(0) = \int_{-\infty}^{+\infty} (\phi_c(x) - \phi_c^{PS} - \phi_c^{PMMA}) dx \tag{4}$$

Because of the limited detector resolution (1000 Å), the actual width of the interface is broadened considerably. The solid lines are therefore the density profiles of the copolymer segments in the interfacial region and in the PS and PMMA phases that have been broadened as a result of the limited detector resolution. Consequently, no details of the interface are learned. Only a surface excess is extracted from the experiment (cf. eq 4). The

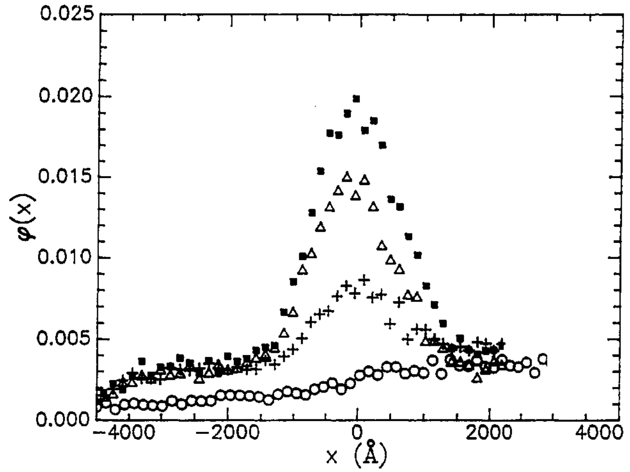

Figure 3. A demonstration of the increase in interfacial segregation of P(d-S-b-MMA) copolymer chains with the increase in bulk volume fraction of these chains. Initially these samples contained volume fractions of 0.014 (squares), 0.009 (triangles), 0.006 (+), and 0.003 (○). The samples were annealed for 100 h at 162 °C.

data in Figure 3 show that as the volume fraction of copolymer chains, P(d-S-b-MMA), increased, the degree of interfacial segregation increased. Of course, one expects saturation to occur at larger volume fractions.

Results and Discussion

It is clear from the data in Figures 1 and 2 that the copolymer chains segregate to the interfacial region between the PS and PMMA homopolymer phases at elevated temperatures and that some of the copolymer chains remain in the bulk. An overall decrease in the free energy of the system results from the interfacial segregation because the number of unfavorable interactions between the incompatible homopolymer chains in the interfacial region is decreased. Theory[4] has shown that the accompanying decrease in the combinatorial entropy of mixing and the loss of conformational entropy of the copolymers at the interface are not large enough to offset the decrease in enthalpic energy. In general, at sufficiently low concentrations (or more importantly at low copolymer chemical potentials), the copolymer chains in the bulk segregate to the interface.

In general, at concentrations above the critical micelle concentration (cmc), the chains aggregate in the bulk to form micelles. This reduces appreciably the number of copolymer chains that are able to migrate to the interface. In some cases, it is possible for micelles to form after the interface is saturated with copolymer chains.

In the mean field theory of Leibler,[9] the junctions of the copolymer chains are imagined to be located within a narrow interfacial region of thickness d. d is independent of P_i; the number of monomers per homopolymer chain of species i and N_i is the number of monomers of species i per copolymer chain. The blocks of the copolymer chains extend into the phases in which the energetic interactions are favorable. The chains extend a distance L_i ($d \ll L_i$) into phase i to form what Leibler referred to as "brushes". At equilibrium, $\mu_{\rm inf}$, the chemical potential of the chains in this interfacial region is equal to $\mu_{\rm c}$, the chemical potential of chains in the bulk. This determines the equilibrium number of copolymer chains, Q, that reside in the interfacial region.

The total free energy of the interfacial region with the copolymer chains present was approximated by[9]

$$F_{\rm tot} = \gamma_0 A + Q[g_{\rm A}(\Sigma) + g_{\rm B}(\Sigma)] \qquad (5)$$

where A is the total area of the interface, $g_i(\Sigma)$ is the free energy per copolymer chain. For chains at an interface, $g_i(\Sigma)$ has three contributions

$$\frac{g_i(\Sigma)}{k_{\rm B}T} = \ln\,(N_i/\rho a\Sigma) + \frac{1}{2}L_i\Sigma\rho\frac{1}{P}(1 - N_i/L_i\rho\Sigma)\ln\,(1 - N_i/L_i\rho\Sigma) + \frac{3}{2}\frac{L_i^{\,2}\rho a}{N_i} \qquad (6)$$

The first two terms describe the entropy of mixing between the copolymer and homopolymer chains and contribute to the swelling of the chains. The first term reflects the fact the chains are confined to two dimensions. The second term is the familiar Flory–Huggins expression with the $1/P$ excluded volume contribution. The last term is an elastic energy term that limits swelling. It is associated with the fact that the chains are slightly stretched beyond the ideal chain conformations. Equation 6 differs from the form Leibler used in ref 9 in two respects. Leibler replaced the density, ρ, with a^{-3}, where a is a statistical segment length and approximated the second term by $(^1/_2)(N_i^2/P_i)\rho L_i$.

Two main limits were addressed by the theory. In one limit, the dry brush limit, the interfacial region is nearly saturated by the copolymer chains and the homopolymer chains do not penetrate the interfacial copolymer layer appreciably. This occurs when the chemical potential of the copolymer chains is large. The above conditions are satisfied when $N_i < P_i^{3/2}$ and $\Sigma < N_i^{1/2}a^2$ (the density of chains at the interface is high). In this situation the free energy per chain at the interface could be approximated by the third term in eq 6, $g_i/k_{\rm B}T \approx (^3/_2)L_i^2/N_i a^2$.

The second case is the so-called wet brush case. Here the copolymer chains are long and the density of copolymer chains at the interface is small yet large enough that the chains can interact, $P_i^{1/2} < \Sigma/a^2 < N_i^{2/3}/P_i$. At equilibrium, the free energy per chain in the interfacial region is correctly given by eq 6 and

$$\frac{g_i(\Sigma)}{k_{\rm B}T} \cong \ln\,(N_i/\rho a\sigma) + G_i\Sigma_i^{-2/3} \qquad (7)$$

where $G_i = [(162)^{1/3}/4]N/(aP\rho)^{2/3}$ (i = PS, PMMA). The equilibrium value for L_i is given by

$$L_i \cong \frac{N}{(6\rho P)^{1/3}}\left(\frac{a^2}{\Sigma}\right)^{1/3} \qquad (8)$$

In the special case where the copolymers are symmetric, $\mu_{\rm inf}$ ($\mu_{\rm inf} = \partial F_{\rm tot}/\partial Q$ (at constant A)), the chemical potential of the copolymers in the interfacial region is given by[9]

$$\frac{\mu_{\rm inf}}{k_{\rm B}T} \cong 2 + 2\ln\frac{N}{\rho a\Sigma} + \frac{5}{3}(G_{\rm PS} + G_{\rm PMMA})\Sigma^{-2/3} \qquad (9)$$

Here N is $1/2N_{\rm c}$, the total number of segments per copolymer chain. It should be pointed out that the form given by Leibler in ref 9 omits the logarithmic term shown in our eq 7.

The chemical potential of the copolymer chains in the bulk can be obtained from the Flory–Huggins free energy of mixing

$$\frac{\mu_{\rm c}}{k_{\rm B}T} \cong \ln\phi_{\rm c}^{\,i} + 1 + \chi N \qquad (10)$$

The superscript i refers to the PS or PMMA phase. The validity of this equation is based on the fact that the volume fraction of copolymers in the bulk is very low. In the derivation it was implicitly assumed that the copolymer chains were distributed uniformly throughout the system.

It ignored the formation of micelles in the system. Based on the calculations of Leibler,[9] Witmore and Noolandi,[18] and Shull and Kramer,[10] the formation of micelles should occur at copolymer concentrations that are 1 order of magnitude higher than those initially blended with the homopolymers during sample preparation. As discussed at the end of the Experimental Section, there is no evidence that micelles were formed in this system. On the basis of eqs 9 and 10, the dependence of Σ^{-1} on the volume fraction of copolymers in phase i, $\phi_c{}^i$, is

$$2 + 2\ln\frac{N}{\rho a\Sigma} + \frac{5}{3}(G_{\mathrm{PS}} + G_{\mathrm{PMMA}})\Sigma^{-2/3} = \ln\phi_c{}^i + 1 + \chi N \tag{11}$$

The interfacial tension may be calculated by noting that it is defined as the change in free energy that results when the interfacial area is increased, $\gamma = \partial F_{\mathrm{tot}}/\partial A$ (at constant Q). Consequently

$$\gamma = \gamma_0 = \frac{2}{\Sigma} + \frac{2}{3}(G_{\mathrm{PS}} + G_{\mathrm{PMMA}})\Sigma^{-5/2} \tag{12}$$

The foregoing discussion applies to situations in which the density of copolymer chains at the interface is sufficiently large that the chains can interact and stretch. A realistic situation arises where density of the copolymer chains at the interface is very small and the chains are unable to interact. Here it is reasonable to expect that the copolymers are not stretched and therefore assume their ideal conformations.

Leibler treated this case where incorporated presence of a solvent is included. The analysis here follows exactly the same procedure. The copolymer chains do not interact because of the large dilution effect due to the penetration of the homopolymer chains. Here one can approximate the free energy per chain, g_i, by the first term in eq 6. This implicitly assumes that the volume fraction of homopolymer chains in the interfacial region is close to unity. It follows that

$$\frac{1}{\Sigma} = \frac{\rho a}{N}\phi_c{}^i e^{\chi N} \tag{13}$$

The superscript i refers to the PS or PMMA phase. The reduction in interfacial tension may be calculated to be

$$\gamma = \gamma_0 - \frac{k_{\mathrm{B}}T}{\Sigma} \tag{14}$$

If one incorporates the second term in eq 6 to reflect the fact that the degree of mixing between the copolymer and homopolymer chains is important, yet still assuming that the chains are ideal, then

$$\frac{g_i}{k_{\mathrm{B}}T} = \ln\frac{N}{\rho a\Sigma} + \frac{1}{2}\frac{N^{1/2}\rho a\Sigma}{P}\left(1 - \frac{N^{1/2}}{\rho a\Sigma}\right)\ln\left(1 - \frac{N^{1/2}}{\rho a\Sigma}\right) \tag{15}$$

It follows that the chemical potential of the copolymer chains at the interface is

$$\frac{\mu_{\mathrm{inf}}}{k_{\mathrm{B}}T} = 2\ln\frac{N}{\rho a\Sigma} + 2 - \frac{N}{P}\left[\ln\left(1 - \frac{N^{1/2}}{\rho a\Sigma}\right) + 1\right] \tag{16}$$

By equating eq 10 to eq 16, a relationship between Σ and $\phi_c{}^i$ is obtained:

$$\ln\phi_c{}^i + 1 + \chi N = 2\ln\frac{N}{\rho a\Sigma} + 2 - \frac{N}{P}\left[\ln\left(1 - \frac{N^{1/2}}{\rho a\Sigma}\right) + 1\right] \tag{17}$$

A comparison between the predictions and the experimental data may now be made. Figure 4a shows a plot of $1/\Sigma$ as a function of the volume fraction of copolymer chains in the PS phase. $1/\Sigma$ is calculated from the interface excess $\phi_c{}^*(0)$ by the relation

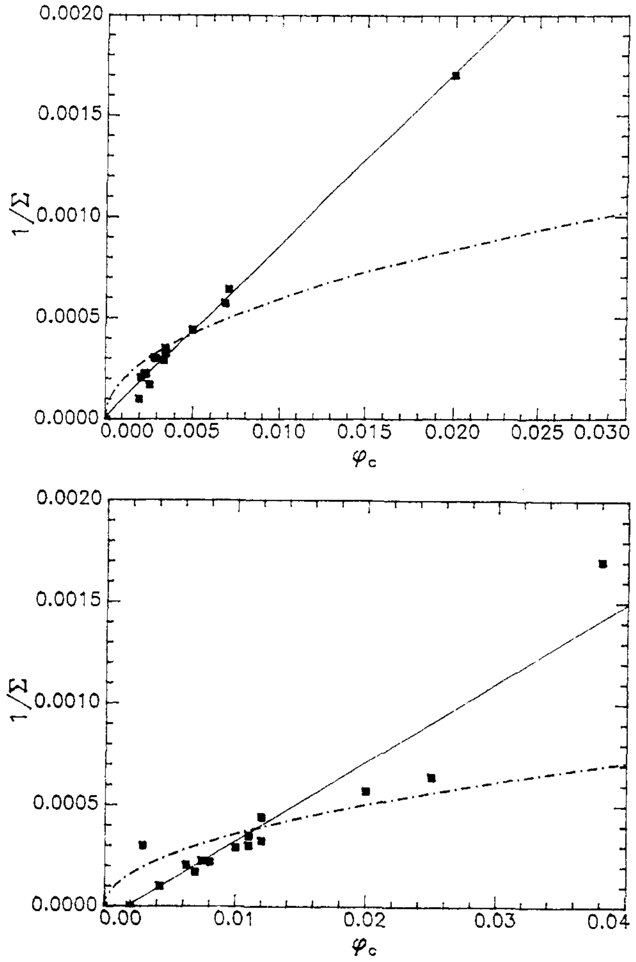

Figure 4. (a, top) Density of copolymer chains as a function of ϕ_c in the PS phase. (b, bottom) Density of copolymer chains as a function of ϕ_c in the PMMA phase.

$$1/\Sigma = \phi^*(0)\rho/N \tag{18}$$

While virtually all the data shown here are for the 262-segment copolymer, both the 262- and 292-segment copolymers exhibited the same degree of segregation. The straight line is a least-squares analysis of the data. A value of $\chi = 0.039$ was extracted. The broken line was computed by using eq 11. χ was used as an adjustable parameter. The straight line is clearly a better fit to the data. Similar plots are shown in Figure 4b, where the interface excess is plotted in terms of the volume fraction of copolymer chains in the PMMA phase. A value of $\chi = 0.031$ was used to compute the straight line and eq 11 was used to compute the curve. The slightly smaller χ parameter obtained for the copolymer chains in the PMMA phase is consistent with the fact that the PMMA segment of the copolymer is slightly larger than the PS segment. The value of χ is extremely sensitive to N; recall $1/\Sigma \sim e^{-\chi N}$. The analysis assumed that both PS and PMMA segments were exactly equal in length. The straight line appears to give a somewhat more reasonable description of the data. The values of χ used in the equations to compute the predictions are not unreasonable. Small-angle neutron-scattering measurements (SANS) show that $\chi = 0.038$ for this system at this temperature.[17] Comparisons were also made with the predictions of eq 17. We also found that eq 13 gave a better description of the data.

Figure 5 shows the reduction in interfacial tension as a function of ϕ_c. This result was obtained by using the

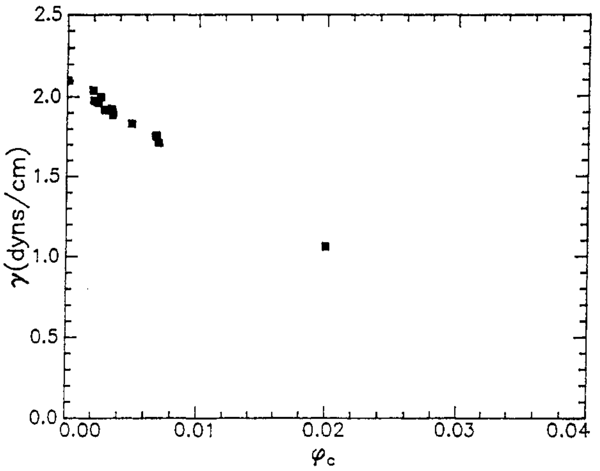

Figure 5. Reduction in the interfacial tension as a function of the volume fraction of copolymer. The decrease in interfacial tension results from the segregation of the copolymer chains to the interface.

experimental data, $1/\Sigma$ versus ϕ_c, and eq 14. By use of eq 2, with $\chi = 0.039$, a value of $\gamma_0 = 2.07$ dyn/cm was determined. This is in good agreement with the values quoted by Anastasiadis et al.[11] and by Wu.[19] The data in Figure 5 show that, with the addition of 1% copolymer, the interfacial tension is reduced by 25%. This result is quite reasonable in light of the available surface tension data on block copolymer homopolymer mixtures.

Conclusion

It has been shown that the interface excess, Σ^{-1}, varies linearly with ϕ_c. These results are well described by a theory that assumes that the density of chains at the interface is small and the interfacial region is interpenetrated appreciably by the long homopolymer chains. It also suggests that for the experimental situation addressed in this paper the excluded volume interactions that cause the copolymer chains at the interface to swell are insignificant. In addition, it suggests that the copolymer chains at the interface are evidently unperturbed. The elastic entropy contributions to g_i are also not important. These results are not surprising since the number of copolymer chains at the interface is very small. In fact, the experimental data in Figure 4 suggest that the separation between the copolymers at the interface is much larger than the dimensions of the radius of gyration of a single copolymer chain. Therefore the chains are unable to interact. Finally, the values of χ extracted from the data and the predicted reduction of interfacial tension are in good agreement with independent experiments.

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