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# Using Copolymer Mixtures To Compatibilize Immiscible Homopolymer Blends

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ABSTRACT: Using a theoretical model, we compare the relative effectiveness of single-component compatibilizers and binary copolymer mixtures in lowering the interfacial tension ($\gamma$) between immiscible homopolymers. The most dramatic effects are seen for mixtures of diblock and comb copolymers, where the mixture can reduce the interfacial tension to zero, even though neither component by itself can produce this effect. Combinations of different comb copolymers are also effective in reducing $\gamma$ to values lower than those achieved by either component alone. In the case of symmetric diblocks, the mixture is more effective at lowering $\gamma$ than the individual components if the molecular weights of the two copolymers are not significantly different. In general, we find that polydispersity has a beneficial effect on the compatibilizing activity of the diblocks. The results provide guidelines for designing the optimal additives for reducing interfacial tension.

## Introduction

The addition of a small amount of copolymer compatibilizer to a mixture of immiscible homopolymers can significantly alter the behavior of the system.[1] These chains effectively act as high molecular weight surfactants: they localize at the interface between the immiscible polymers and lower the interfacial tension, $\gamma$, between the incompatible components. An especially favorable situation arises when the compatibilizers drive the interfacial tension to very low values or to zero: there is no longer a substantial energetic penalty for creating interfaces, and the compatibilizers disperse the homopolymers into small domains. Consequently, the degree of adhesion between the different domains and the mechanical properties of the material are greatly enhanced.

Considerable attention has been focused on the compatibilizing activity of diblock copolymers;[2] however, diblock copolymers are relatively expensive to synthesize. Thus, it is of particular interest to determine the interfacial behavior of other copolymer architectures. In previous studies,[3−5] we adopted the model developed by Leibler[6] for the compatibilizing activity of diblocks and extended the theory to comb copolymers.[7] Through these studies, we isolated conditions under which comb copolymers are more efficient than diblocks at reducing the interfacial tension. These studies provide guidelines for enhancing the compatibilizing activity of combs by tailoring the architecture of the chain.[3−5]

In this paper, we determine if additional improvements in compatibilizing activity can be achieved by mixing different copolymers and using the mixture as a compatibilizing agent. Specifically, we examine (1) a mixture of diblock copolymers of different molecular weights, (2) a mixture of diblock and comb copolymers, and (3) a mixture of different comb copolymers. Our most dramatic finding is that the diblock−comb mixture can drive the interfacial tension to zero, even though the individual components cannot produce such a reduction in $\gamma$. In the case of the different combs, we again find that the mixture is more effective at lowering $\gamma$ than either component. For the mixture of diblocks, we pinpoint the conditions where mixing diblocks of different molecular weights proves beneficial.

The paper is organized as follows. We first formulate the theory for the interfacial behavior of a mixture of copolymers. Using this formalism, we determine the interfacial tension in the various systems. These findings are analyzed in the Results section. In the Conclusions, we highlight the implications of our findings.

## Model

We consider a blend that contains a volume fraction $\phi_A$ of homopolymer A and $\phi_B$ of homopolymer B. In this paper, $\phi_A = \phi_B$. The energetic interaction between the A and B monomers is characterized by the Flory−Huggins parameter $\chi$. We restrict our attention to the case where $\chi$ is relatively high. Here, the interface between the A−rich and B−rich phases is sharp and can be approximated by a flat plane.[6]

To this blend, we add a mixture of AB copolymers. The volume fraction of the copolymer mixture is relatively low and is given by $\phi_{bulk}$. The mixture contains two distinct copolymer components, the molecular weights of the different components are given by $N_1 = N_A^1 + N_B^1$ and $N_2 = N_A^2 + N_B^2$ (where $N_A^i$ and $N_B^i$ are the molecular weights of the respective blocks, and the symbol $i$ equals 1 or 2), and the chains have the same or different architectures. (Note that in calculations below, $N_A^i$ and $N_B^i$ denote the molecular weights of the respective blocks in the case where both types of monomers have the same size. If this is not the case, then $N_A^i$ and $N_B^i$ are generally the number of spherically symmetric units that form the blocks.) The composition of each component is given by $f_i = N_A^i/(N_A^i + N_B^i)$, which is the fraction of A monomers in the molecule of type $i$. The composition of the mixture is characterized by the relative volume fraction of the copolymers in the bulk, $q_i = \phi_i/\phi_{bulk}$, and $\sum_i q_i = 1$, where $i = 1,2$ denotes the type of the copolymer molecule.

Below, we first describe the theory for a mixture of two copolymers of different molecular weights. We then apply this formalism to examine the behavior of a mixture of two diblock copolymers, a mixture of diblock and comb copolymers, and a mixture of two comb copolymers.

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For low values of $\phi_{\rm bulk}$, the volume fractions of the respective copolymers, having molecular weights $N_1$ and $N_2$, in the B-rich phase of the bulk can be approximated as[6]

$$\phi_i = \phi_+^i = q_i\phi_{\rm bulk}/[\phi_{\rm B} + \phi_{\rm A}\exp\{\chi(N_{\rm A}^i - N_{\rm B}^i)\}] \quad (1)$$

The corresponding chemical potential of the copolymer in the bulk is given by

$$\mu_{\rm bulk}^i = \ln(\phi_i/N_i) + \chi N_i f_i + 1 \quad (2)$$

The amount of copolymer at the interface can be determined by equating the chemical potentials of the chains in the bulk and at the interface, or

$$\mu_{\rm bulk}^i = \mu_{\rm film}^i, \qquad i = 1,2 \quad (3)$$

and the chemical potential at the interface is given by

$$\mu_{\rm film}^i = \delta F_{\rm film}/\delta Q_i|_{s={\rm const}} \quad (4)$$

Here, $S$ is the area of the interface, and $Q_i$ is the number of copolymer molecules of type $i$ at the interface. All characteristic lengths are expressed in the units of the monomer size $a$, which is assumed to be the same for both the A and B monomers, and all energetic values are expressed in units of $kT$.

The free energy of the interfacial layer or film can be written as the sum of the interfacial energy, the stretching energy of the blocks, and the translational entropy of the chains at the interface:

$$F_{\rm film} = \gamma_0 S + (Q_1 + Q_2)F_{\rm str} + Q_1\ln(Q_1/S) + Q_2\ln(Q_2/S) \quad (5)$$

where $\gamma_0 = (\chi/6)^{1/2}$ is the interfacial tension of the pure A−B homopolymer interface.[8] The stretching energy (per molecule) of a copolymer at the interface is

$$F_{\rm str} = F_{\rm A} + F_{\rm B} \quad (6)$$

where $F_{\rm A}$ and $F_{\rm B}$ are the stretching energies for the respective blocks. Given the values $F_{\rm A}$ and $F_{\rm B}$, we can obtain the chemical potential of the film through eqs 4−6 and calculate the amount of copolymer at the interface. We can also calculate the interfacial tension:

$$\gamma = (\partial F_{\rm film})/(\partial S)|_{Q_i={\rm const}} \quad (7)$$

As previously demonstrated[3] and as shown below (with corrections involving the translational entropy terms), the interfacial tension can also be written as

$$\gamma = \gamma_0 - 2\frac{F_{\rm str}}{\sigma} \quad (8)$$

where $\sigma = S/(Q_1 + Q_2)$ is the average area per copolymer molecule at the interface.

In this study, we make the following assumptions:[3] (1) The volume fraction of copolymer in the bulk is sufficiently high that the chains form a brush at the interface. (2) We assume that the brush is “dry” on both sides of interface. That is, the homopolymers do not penetrate into the copolymer layer. (3) The copolymers are symmetric. We focus on the symmetric case because it was previously shown[4] that in 50/50 homopolymer mixture, 50/50 copolymers are more effective than other compositions in reducing the interfacial tension. It was also shown[3] that in the case of symmetric copolymers, micelle formation does not occur until the interfacial tension is reduced to 0. These assumptions were discussed in detail in refs 3 and 4, where we compared the results of the analytical theory and the SCF calculations and found good agreement between two approaches. This demonstrates that our assumptions are reasonable.

In formulating explicit expressions for the chemical potential and stretching energy, we expand on our previous results and now include the ln $N$ term in the chemical potential, eq 2, which was neglected in prior studies.[3,6] We also include the terms associated with the translational entropy of the molecules at the interface in the expression for the total free energy, eq 5, since the translational entropy can play an essential role in the properties of the mixture. Below, we consider three different cases.

**Mixture of Diblock Copolymers of Two Different Molecular Weights.** In this section, we consider the mixture of diblock copolymers of two different molecular weights, $N_1$ and $N_2 > N_1$. We characterize the composition of the copolymer mixture by the relative volume fraction of the longer diblock copolymer in the bulk, $q_{\rm b} \equiv q_2$. The composition of the copolymer layer at the interface is characterized by the number fraction of the longer diblock copolymer in the layer:

$$q = Q_2/(Q_1 + Q_2) \quad (9)$$

where $Q_i$ represents the total number of the molecules of type $i$ at the interface. Note, that $q \neq q_{\rm b}$.

The stretching energy per chain within the mixed interfacial layer for $f_i = 0.5$ can be written in the form[9]

$$F_{\rm str} = F_{\rm A} + F_{\rm B} = \pi^2 N_1(1 + \alpha q^3)/8\sigma^2 \quad (10)$$

where $\sigma = S/(Q_1 + Q_2)$ is the average area per chain at the interface and $\alpha = (N_2 - N_1)/N_1$ is the relative difference in the lengths of the long and short diblock copolymers. Note that eq 10 is written for a brush with a parabolic density profile rather than a steplike density profile. The difference between the expressions for the stretching energy in these two models is in the coefficients: it is $\pi^2/8$ for the parabolic case and 3/2 for the steplike case. Hence, the chemical potentials of the species at the interface are

$$\mu_{\rm film}^1 = 3\pi^2 N_1/8\sigma^2 + \ln((1 - q)/\sigma) + 1$$
$$\mu_{\rm film}^2 = 3\pi^2 N_1(1 + \alpha q^2)/8\sigma^2 + \ln(q/\sigma) + 1 \quad (11)$$

Equating $\mu_{\rm bulk}^i = \mu_{\rm film}^i$, we obtain a system of two equations for the two unknown variables, $\sigma$ and $q$:

$$\phi_1 = N_1\frac{1 - q}{\sigma}\exp\left\{3\pi^2\frac{N_1}{8\sigma^2} - \chi N_1 f_1\right\}$$
$$\phi_2 = N_2\frac{q}{\sigma}\exp\left\{3\pi^2\frac{N_1}{8\sigma^2}(1 + \alpha q^2) - \chi N_2 f_2\right\} \quad (12)$$

From eq 12 we can solve for $\sigma(q)$:

$$\sigma = \left( \frac{3\pi^2 N_1 \alpha q^2}{8\left[\ln\left(\frac{\phi_2}{\phi_1}\frac{N_1}{N_2}\frac{1-q}{q}\right) + \chi(N_2 f_2 - N_1 f_1)\right]} \right)^{1/2} \quad (13)$$

Substituting this expression for $\sigma(q)$ into eq 12, we obtain a single equation for $q$, which we solve numerically.

From eqs 12 and 13, we then calculate the interfacial tension:

$$\gamma = \gamma_0 - \pi^2 N_1(1 + \alpha q^3)/4\sigma^3 - 1/\sigma = \gamma_0 - 2F_{\rm str}/\sigma - 1/\sigma \quad (14)$$

Note that we can neglect the term $1/\sigma$ in the expression for the interfacial tension, eq 14, since it is relatively small in comparison with the stretching energy term.

**Mixture of Diblock and Comb Copolymers.** In this section, we consider a mixture of comb copolymers of molecular weight $N_{\rm c} = N_1$ and diblock copolymers of molecular weight $N_{\rm d} = N_2$, and we characterize the mixture by the parameter $q_{\rm diblock} \equiv q_{\rm b}$, which is the relative volume fraction of the diblock copolymer in the bulk. The number of teeth in the comb is $n$, and the composition of each copolymer is given by the parameter $f_i = N_{\rm A}^i/N_{\rm i}$, $i$ = d,c. As above, we set $f_i = 0.5$. In considering the comb and diblock copolymers at the interface, we again describe the interfacial layer as brushes "grafted" to both sides of the interface. Unlike the case of the diblock mixture, the brushes formed from the "backbone" and "teeth" of the combs are not symmetric, due to the difference in the backbone and tooth architecture. We consider the A-brush to be composed of $Q_{\rm d}$ number of A-blocks of length $N_{\rm A}^2 = N_{\rm d}f_{\rm d}$ and $nQ_{\rm c}$ number of A-teeth of length $N_{\rm A}^1 = (N_{\rm c}f_{\rm c})/n$ (see Figure 1a). We only consider the situation where $N_{\rm A}^2 > N_{\rm A}^1$, because this mixture will display particularly interesting features. In the opposite case $N_{\rm A}^2 < N_{\rm A}^1$, the influence of combs with long and multiple teeth is more dominant than the effect of the diblock copolymers.[3] Here, we investigate the effect of varying the relative number fraction of the longer A-block in the A-brush:

$$q \equiv q_{\rm A} = \frac{Q_{\rm d}}{Q_{\rm d} + nQ_{\rm c}} \quad (15)$$

where $Q_i$ is the number of molecules of each type at the interface.

The B-brush can be described in a similar way, with the assumption that the B portion of the backbone between the teeth is sufficiently long that it can be described by Gaussian statistics. Then, we simply cut the section of backbone between adjacent teeth into two equal parts.[3] In this way, the B-brush is formed by $Q_{\rm d}$ number of B-blocks of the length $N_{\rm B}^2 = N_{\rm d}(1 - f_{\rm d})$ and $2nQ_{\rm c}$ number of B-chains of the length $N_{\rm B}^1 = N_{\rm c}(1 - f_{\rm c})/(2n)$ (Figure 1b). (Here, "chain" does not mean an entire copolymer molecule, but refers to a section of the copolymer. For B's in the comb, "chain" refers to a section of backbone, as described above. For A's in the combs, "chain" refers to a tooth. And for the diblocks, "chain" refers to the individual blocks.) For the B-brush we have

$$q_{\rm B} = \frac{Q_{\rm d}}{Q_{\rm d} + 2nQ_{\rm c}} = \frac{q}{2 - q} \quad (16)$$

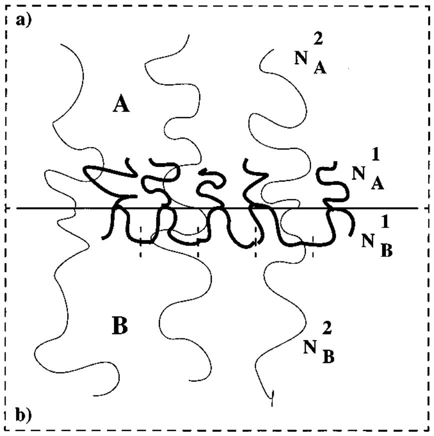

**Figure 1.** Schematic picture of the interfacial layer formed by the mixture of comb and diblock copolymers: (a) A-side; (b) B-side.

The total free energy of stretching (per chain), eq 6, can now be written in the form

$$F_{\rm str} = \frac{\pi^2}{8}\left[\frac{(Q_{\rm d} + nQ_{\rm c})(1 + \alpha_{\rm A} q_{\rm A}{}^3)N_{\rm A}^1}{(Q_{\rm c} + Q_{\rm d})\sigma_{\rm A}{}^2} + \frac{(Q_{\rm d} + 2nQ_{\rm c})(1 + \alpha_{\rm B} q_{\rm B}{}^3)N_{\rm B}^1}{(Q_{\rm c} + Q_{\rm d})\sigma_{\rm B}{}^2}\right] \quad (17)$$

where $\sigma_{\rm A} = S/(nQ_{\rm c} + Q_{\rm d})$ and $\sigma_{\rm B} = S/(2nQ_{\rm c} + Q_{\rm d})$ are the respective average areas per chain in the A- and B-brushes. The parameters $\alpha_{\rm A} = (N_{\rm A}^2 - N_{\rm A}^1)/N_{\rm A}^1$ and $\alpha_{\rm B} = (N_{\rm B}^2 - N_{\rm B}^1)/N_{\rm B}^1$ define the relative difference in the chain lengths in the A- and B-brushes, respectively.

We calculate the chemical potentials of the species at the interface in a similar way as before:

$$\mu_{\rm film}^1 = 3\pi^2\frac{nN_{\rm A}^1}{8\sigma_{\rm A}{}^2}(1 + (2 - q)^2) + \ln\left(\frac{1 - q}{n\sigma_{\rm A}}\right) + 1$$

$$\mu_{\rm film}^2 = 3\pi^2\frac{N_{\rm A}^1}{8\sigma_{\rm A}{}^2}\left(1 + \alpha_{\rm A}q^2 + \frac{1}{2}((2 - q)^2 + \alpha_{\rm B}q^2)\right) + \ln\left(\frac{q}{\sigma_{\rm A}}\right) + 1 \quad (18)$$

By equating $\mu_{\rm bulk}^i = \mu_{\rm film}^i$, we obtain a system of two equations for two unknown variables, $\sigma_{\rm A}$ and $q$:

$$\phi_1 = N_1\frac{1 - q}{n\sigma_{\rm A}}\exp\left\{3\pi^2\frac{nN_{\rm A}^1}{8\sigma_{\rm A}{}^2}(1 + (2 - q)^2) - \chi N_1 f_1\right\}$$

$$\phi_2 = N_2\frac{q}{\sigma_{\rm A}}\exp\left\{3\pi^2\frac{N_{\rm A}^1}{8\sigma_{\rm A}{}^2}\left(1 + \alpha_{\rm A}q^2 + \frac{1}{2}((2 - q)^2 + \alpha_{\rm B}q^2)\right) - \chi N_2 f_2\right\} \quad (19)$$

Again, we solve these equations numerically and present the results in the form of plots, which we discuss below.

From eqs 7 and 17, we then calculate the interfacial tension:

$$\gamma = \gamma_0 - \frac{\pi^2 N_1}{4{\sigma_A}^3}\left[\frac{f_1}{n}(1 + \alpha_A q^3) + \frac{1 - f_1}{2n}((2 - q)^3 + \alpha_B q^3)\right] - \frac{q}{\sigma_A} - \frac{1 - q}{n\sigma_A} = \gamma_0 - 2\frac{F_{str}}{\sigma} - \frac{q}{\sigma_A} - \frac{1 - q}{n\sigma_A} \quad (20)$$

where $\sigma = S/(Q_d + Q_c)$ is the average area per block copolymer molecule at the interface.

## Results

**Mixture of Diblock Copolymers of Different Molecular Weights.** We begin by calculating the interfacial tension, $\gamma$, of a mixture of diblock copolymers of two different molecular weights, $N_1 = 100$ and $N_2 = 150$. Figure 2 shows the dependence of $\gamma$ on the volume fraction of the mixed copolymer in the bulk, $\phi_{bulk}$. Curve 1 represents a mixture composed almost entirely of the short diblocks ($N_1 = 100$), and curve 6 represents the opposite limit, a mixture composed essentially of long diblocks ($N_2 = 150$). A comparison of these curves shows that at a fixed $\phi_{bulk}$, the higher molecular weight diblock (curve 6) is more efficient at lowering the interfacial tension than the lower molecular weight component (curve 1). In carrying out our calculations, our aim is to find the most "efficient" additive. We say that one additive is more efficient than another if a smaller amount is needed to achieve a desired reduction in the interfacial tension.

Mixtures of the two components, at different relative volume fractions of the longer copolymer, $q_b$, yield interfacial tensions in the range between the two limiting curves. When $\phi_{bulk}$ is held fixed, a gradual decrease in $\gamma$ is observed with an increase in the relative volume fraction of the longer component in the bulk, $q_b$. This effect is also illustrated by the solid curve in Figure 3, which shows a "cross-section" of Figure 2 at $\phi_{bulk} = 0.1$. Since the longer component is more efficient, the higher the amount of long copolymer in the mixture, the lower the interfacial tension.

To understand the contribution from each component in decreasing the interfacial tension, we introduce the dependence $\gamma(q_b)$ for the individual long (dashed curve) and short (dash–dotted curve) copolymers (see Figure 3). Specifically, the dashed curve represents the reduction in interfacial tension produced just by a volume fraction $q_b\phi_{bulk}$ of long copolymer, and the dash–dotted curve represents the reduction in $\gamma$ brought about solely by a volume fraction $(1 - q_b)\phi_{bulk}$ of the short copolymer. Note that the solid curve is the result of the *mixture* of $q_b\phi_{bulk}$ long copolymers *and* $(1 - q_b)\phi_{bulk}$ short copolymers in the bulk. It is seen that the solid and dashed curves lie very close together, displaying the significant effect of the longer block copolymer.

Figure 4 shows that the discrepancy between two curves diminishes when the molecular weight of the longer component is increased ($N_2 = 200$). This implies that the longer component plays the dominant role, and at an appreciable difference in the molecular weights, it controls the interfacial tension. The pronounced effect of the long copolymers is due to the fact that the chemical potential of the long chains in the bulk is higher than that of the short chains. Consequently, more of the long chains are localized at the interface than the short copolymers. Indeed, as seen from Figure 5, the number fraction of the long component at the interface, $q$, is very high even at very small values of $q_b$, and is higher at higher values of $N_2$.

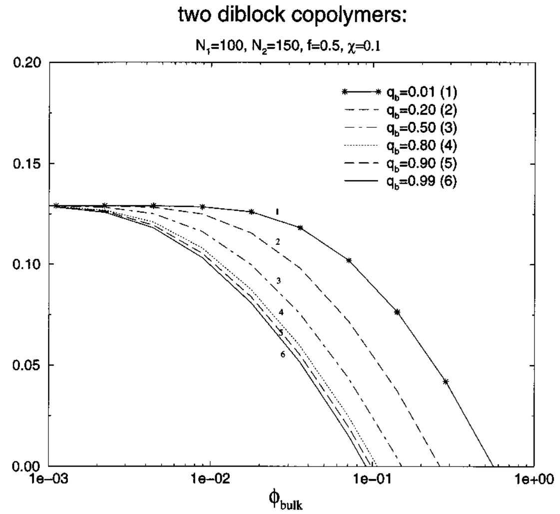

**Figure 2.** Behavior of $\gamma(\phi_{bulk})$ for the mixture of two diblock copolymers of molecular weights $N_1 = 100$ and $N_2 = 150$. The relative volume fraction of the longer component in the bulk, $q_b$, is noted on the plot.

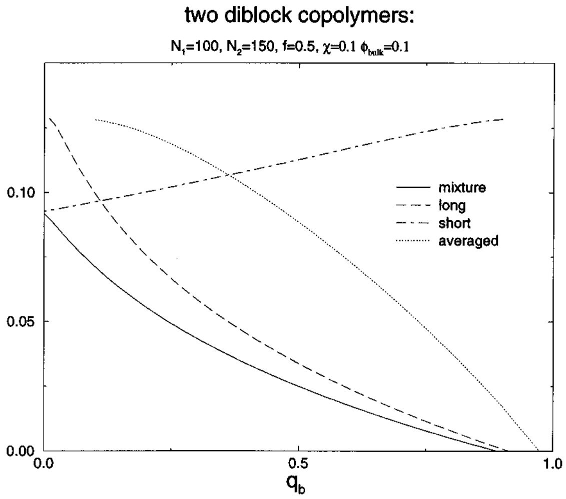

**Figure 3.** Dependence of $\gamma$ on $q_b$, the relative volume fraction of the longer component in the bulk, for the mixture of two diblock copolymers of molecular weights $N_1 = 100$ and $N_2 = 150$ (solid line), individual long copolymers (dashed line), individual short copolymers (dash–dotted line), and diblock copolymers of averaged molecular weight (dotted line). Here, $\phi_{bulk} = 0.1$.

We also compare the properties of the above mixture to the behavior of diblock copolymers that have a molecular weight equal to the average of the molecular weights of the two components (Figure 3, dotted curve):

$$\bar{N} = \frac{n_1 N_1 + n_2 N_2}{n_1 + n_2} \quad (21)$$

where $n_i$ are the numbers of molecules of type $i$ in the bulk. It follows from Figure 3 that the interfacial tension produced by the mixed copolymers (solid curve) is lower than that produced by copolymers of the averaged molecular weights (dotted curve). From this study, we demonstrate that the polydispersity of the compatibilizing agents can play a positive role in the reduction of the interfacial tension. At wide polydispersity, we expect, however, that the longer components dominate the behavior of the system, while the rest of the mixture acts as relatively inert components.

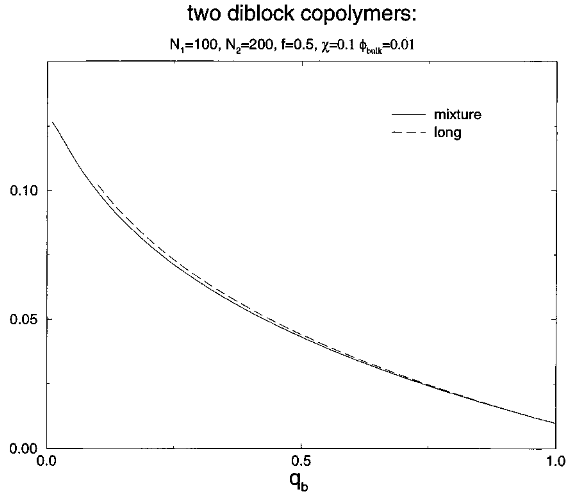

**Figure 4.** Dependence of $\gamma$ on $q_b$, the relative volume fraction of the longer component in the bulk, for the mixture of two diblock copolymers of molecular weights $N_1 = 100$ and $N_2 = 200$ (solid curve) and individual diblock copolymers of length $N_2 = 200$ (dashed curve) at $\phi_{bulk} = 0.01$.

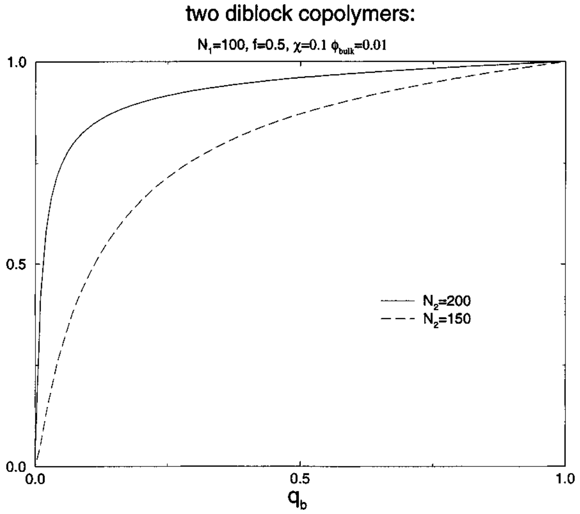

**Figure 5.** Dependence of $q$, the number fraction of long chains at the interface, on $q_b$, the relative volume fraction of the longer component in the bulk, for the mixture of two diblock copolymers of molecular weights $N_1 = 100$ and $N_2 = 150$ (dashed curve) and $N_1 = 100$ and $N_2 = 200$ (solid curve) at $\phi_{bulk} = 0.01$.

**Mixture of Diblock and Comb Copolymers.** We also examine the compatibilizing properties of a mixture of diblock and comb copolymers. When there is a large difference between the molecular weights of the diblocks and combs, we expect that the longer copolymer will dominate the behavior of the system and control the interfacial tension, in analogy with the binary mixture of diblock copolymers. Consequently, we do not consider this limit; our interest is focused on a mixture of copolymers with comparable molecular weights, or, more precisely, with comparable interfacial activities.

For the mixture of diblock and comb copolymers, we set the molecular weight of the diblock at $N_d = 200$ and vary the molecular weight of the comb from $N_c = 200$ to $N_c = 400$. The number of teeth within the combs is fixed at $n = 5$ and the composition of the copolymers is set at $f_c = f_d = 0.5$. Figure 6 shows the dependence of the interfacial tension, $\gamma$, on the relative volume fraction of diblock copolymers in the mixture, $q_{diblock}$, at $\phi_{bulk} = 0.01$. The fraction of diblock in the mixture increases from 0 to 1 along the horizontal axis. As follows from Figure 6, the pure diblock copolymers ($q_{diblock} = 1$) lower the interfacial tension better than any of the pure comb copolymers ($q_{diblock} = 0$). In all cases, addition of diblock copolymers to the mixture results in the lowering of the interfacial tension with respect to the pure comb copolymer case ($q_{diblock} = 0$).

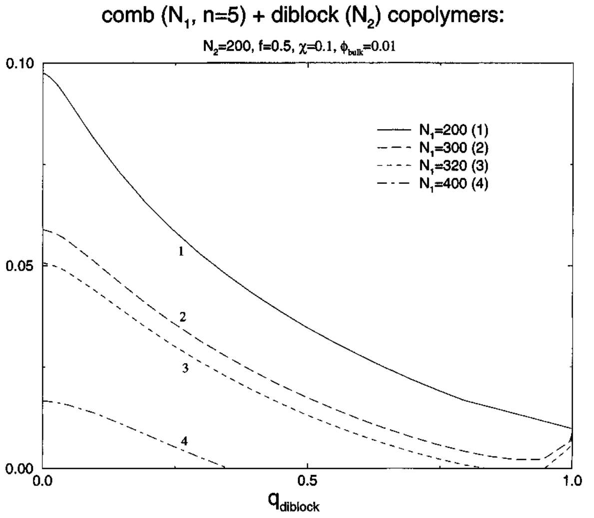

**Figure 6.** Dependence of $\gamma$ on $q_{diblock}$, the relative volume fraction of diblock copolymer in the bulk, for the mixture of diblock and comb copolymers of molecular weights $N_c = 200$ (curve 1), 300 (curve 2), 320 (curve 3), 400 (curve 4), $n = 5$, and $N_d = 200$. Here, $\phi_{bulk} = 0.01$.

When the molecular weight of the comb with multiple teeth (here, $n = 5$) is equal to the molecular weight of the diblock copolymer (curve 1), the interfacial tension produced by the pure comb ($q_{diblock} = 0$) is significantly higher than the interfacial tension produced by the same amount of diblock copolymer ($q_{diblock} = 1$). Curve 1 shows that increasing the fraction of diblock in the mixture causes a monotonic decrease in $\gamma$.

Increasing the molecular weight of the comb copolymers increases their efficiency in reducing the interfacial tension. In addition, at $N_c = 300$, 320, and 400, the curves (2−4 in Figure 6) exhibit a pronounced minimum, which indicates that the mixture is more efficient in reducing $\gamma$ than either of the pure components. In fact, curve 4 shows that while the individual components cannot reduce the interfacial tension to 0, there is a wide composition range where the mixture drives $\gamma$ to 0 (provided that $\phi_{bulk}$ is held fixed).[9]

The above effect is a result of a segregation of short blocks from the combs and long blocks from the diblock copolymers to the interfacial layer.[10] As shown in ref 10, the grafted layer formed by chains of two different lengths can be viewed as two sublayers: an "inner" layer (closer to the interface), where the ends of the short chains are localized, and an "outer" layer (farther from the interface), where the ends of the long chains are localized. The stretching energy of the short chains does not depend on the length of the long chains, and at an appreciable difference in the molecular weights of the chains, the two sublayers do not affect each other. Hence, the equilibrium amount of each copolymer at the interface can roughly be estimated as a balance between the chemical potentials of the species in the bulk and in the individual sublayers. In this way, chains do not compete for space at the interface, and the interfacial layer is more crowded than in the case of either of the pure components. Consequently, the interfacial tension is lower than that for the limiting cases of the pure components.

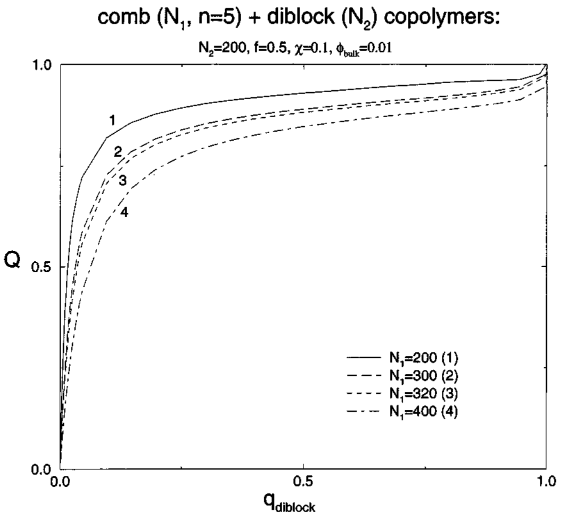

**Figure 7.** Dependence of $Q$, the number fraction of diblock molecules at the interface, on $q_{\text{diblock}}$, the relative volume fraction of diblock copolymer in the bulk, for the mixture of diblock and comb copolymers of molecular weights $N_c = 200$ (curve 1), 300 (curve 2), 320 (curve 3), 400 (curve 4), $n = 5$, and $N_d = 200$. Here, $\phi_{\text{bulk}} = 0.01$.

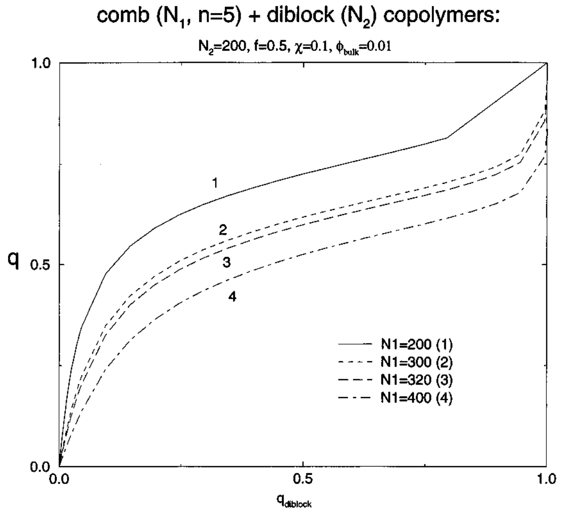

**Figure 8.** Dependence of $q$, the number fraction of long chains in the A-brush at the interface, on $q_{\text{diblock}}$, the relative volume fraction of diblock copolymer in the bulk, for the mixture of diblock and comb copolymers of molecular weights $N_c = 200$ (curve 1), 300 (curve 2), 320 (curve 3), 400 (curve 4), $n = 5$ and $N_d = 200$. Again, $\phi_{\text{bulk}} = 0.01$.

Another way to understand this phenomenon is to consider diblocks and combs that have the same compatibilizing activity. Note that in curve 4 of Figure 6, the $\gamma$'s at the pure comb and pure diblock cases are approximately equal. When these components are mixed, the diblocks can easily penetrate the interfacial layer formed by the combs. Consequently, the number of chains at the interface is relatively high (compared to the respective pure cases). The presence of a large number of interfacial chains contributes to further reduction in $\gamma$ and gives rise to the minima in the curves.

This mixing is also favorable in the case of the two diblock copolymers of different molecular weights, but in this mixture, the lower molecular weight copolymer has a much lower chemical potential in the bulk, and it contributes very little to the decrease in the interfacial tension. Indeed, as it was shown in Figure 5, the number fraction of short molecules at the interface is very small; i.e. short diblocks are almost totally excluded from the interfacial layer. With combs, the effect is quite different. We let $Q$ be the relative number fraction of diblock molecules in the mixed interfacial layer given by

$$Q = \frac{Q_d}{Q_d + Q_c} = \frac{1}{1 + (1 - q)/(nq)} \tag{22}$$

Although the number fraction of diblock *molecules*, $Q$, relative to the comb *molecules* is very high (see Figure 7), the number fractions of long *chains* (=diblock) and short *chains* (=teeth or parts of backbone in comb) in the interfacial layer are comparable over a wide range of $q_b$ (see Figure 8). Thus, both types of *chains* contribute to a decrease in interfacial tension. (For a mixture of two diblock copolymers, similar results could conceivably be obtained if somehow the shorter components would be driven to the interface in sufficient amounts.)

For both mixtures, comb + diblock and two diblocks, a minimum in the curve $\gamma(q_b)$ does not occur when the individual components yield significantly different values of $\gamma$. As was shown for the mixture of comb and diblock copolymers, $\gamma(q_{\text{diblock}})$ has a minimum only when the efficiencies of two components are comparable, i.e. when both sublayers contribute to the interfacial tension.

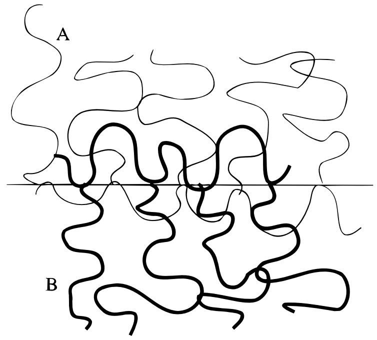

**Figure 9.** Schematic picture of the interfacial layer formed by two combs.

**Mixture of Two Comb Copolymers.** In this section, we consider the mixture of two comb copolymers of the same molecular weight and number of teeth, with the only difference being in the architectures: we assume that the one comb copolymer has a B-backbone and A-teeth, while the other has an A-backbone and B-teeth. When the volume fraction of copolymer in the bulk is fixed, the efficiency of either of these copolymers is the same; nevertheless the efficiency of the mixture should be different. Our hypothesis is that the mixture is more favorable because these combs can interpenetrate and thereby allow the teeth and backbones to segregate to the appropriate sides of the A/B boundary (see Figure 9). Here, the B-backbones occupy the "inner" layer, while the B-teeth are localized in the "outer" layer (and the same is true for the A-backbones and A-teeth). Thus, the different copolymers do not block each other from the interface, and more chains will localize at the interface than in the single-component case. The validity of this hypothesis can be seen from Figure 10, which shows that indeed the interfacial tension produced by the mixture of combs is lower than that produced by the either component.

## Conclusions

In this paper, we considered binary mixtures of different AB copolymers and determined the effective-

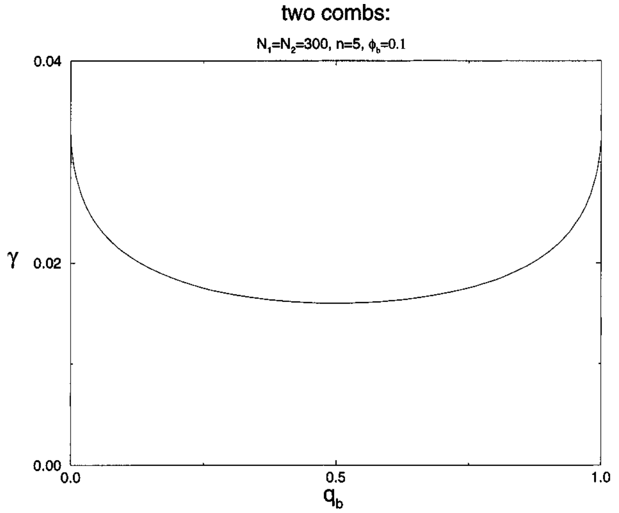

**Figure 10.** Dependence of $\gamma$ on $q_b$, the relative volume fraction of one of the combs in the bulk, for the mixture of two comb copolymers of molecular weights $N_1 = 200$, $n = 5$, and $N_2 = 200$, $\phi_{\text{bulk}} = 0.01$.

ness of the mixtures in lowering the interfacial tension. A significant finding is that mixtures of diblock and comb copolymers can reduce the interfacial tension to zero, even though neither component by itself can produce this effect. This phenomenon is attributable to the relatively high molecular weights of the chains and the differences in architecture. At high molecular weights, the copolymers are rather insoluble in the bulk and are thus driven to the interface. Due to the differences in architecture, the chemically identical segments do not compete for space at the interface and therefore do not exclude each other from this layer. As a consequence, the interface is more heavily saturated with copolymers and $\gamma$ is significantly more reduced than in either of the single-component situations.

The differences in architecture also prove advantageous for the mixture of comb copolymers. Again, the mixture yields a greater number of chains at the interface than either of the individual components.

In the case of symmetric diblocks, the mixture is more effective at lowering $\gamma$ than the individual components if the molecular weights of the two copolymers are not significantly different. If one copolymer is substantially longer than the other, this component will control the reduction in interfacial tension. The mixture, however, is better at lowering $\gamma$ than diblocks whose molecular weights are an average of the two components. Thus, we can conclude that polydispersity has a beneficial effect on the compatibilizing activity of diblock copolymers.

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