Contrasting the Compatibilizing Activity of Comb and Linear Copolymers

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ABSTRACT: Using Monte Carlo computer simulations, we compared the interfacial behavior of various comb and linear copolymers at a penetrable interface, which represents the boundary between two incompatible homopolymers, A and B. The backbone of the combs is composed of A sites (the majority of the species in the comb), while the teeth are composed of B sites. We varied the number and length of the teeth and found that combs with fewer, longer teeth can more readily localize at the interface than combs with multiple, short teeth. In addition, combs will more readily localize at the interface than comparable linear multiblocks. The findings highlight the importance of molecular architecture in determining the interfacial activity of copolymers. The results also provide guidelines for fabricating copolymers that act as the optimal compatibilizers between immiscible polymers.

Introduction

Copolymer "compatibilizers" are added to blends of immiscible polymers in order to improve the mechanical properties and structural integrity of the composite material. Specifically, the compatibilizing chains sit at the boundary between the incompatible polymers; here, they lower the interfacial tension and enhance the degree of adhesion between the different domains. Branched or comb copolymers are commonly used as compatibilizers in large-scale, industrial processes.[1] Although this practice is now well established, there have been few fundamental studies to probe the effect of comb architecture on the efficiency of the compatibilizing activity. In this paper, we use Monte Carlo computer simulations to determine how the number and length of side chains ("teeth") affect the interfacial behavior of comb copolymers. Using these simulations, we also compare the properties of the combs with the behavior of linear, multiblock copolymers. The latter have the same composition as the combs: they are formed by inserting the tooth components directly into the backbone of the chain. Through this comparison, we can further pinpoint the effect of molecular architecture on interfacial activity.

Below, we describe the details of the computer simulations we used to model both comb and multiblock copolymers at a penetrable interface. We then describe the findings that emerged from this study. An important implication of the results is that they provide guidelines for fabricating comb compatibilizers that yield enhanced adhesion between the incompatible polymeric phases.

Model

The simulation involves a three dimensional lattice that is 128 × 128 × 128 sites in size. Periodic boundary conditions are imposed along the x and y directions. Within this lattice, the copolymers are modeled as self-avoiding random walks. Each comb contains both A and B monomers or lattice sites. The backbone section is composed entirely of A monomers, and the length of this fragment is held fixed at 114 lattice sites. The side chains, or teeth, are composed of B sites. The length and number of teeth are varied; however, all teeth are uniform in length. The first and last tooth extend from bead numbers 7 and 107, respectively, in the backbone. (In other words, the outermost teeth are hung from sites that are 7 beads in from the ends of the backbone.) The remainder of the teeth are evenly distributed along the length of the backbone. We note that in all the examples studied here, the number of tooth (B) sites is always less than the number of backbone (A) sites.

To compare the behavior of a comb copolymer and the comparable linear chain, we fashioned the comb into a linear chain by "cutting" the teeth and inserting these fragments into the backbone (see Figure 1). For example, consider a comb with S teeth, each of which is n units of B in length. To generate the comparable linear copolymer, we first divided the inner 100 A backbone sites into S blocks of length m. (If 100 is not evenly divisible by S, then the blocks are all as close to m as possible.) The first 7 sites of the linear multiblock are the terminal A units, followed by n sites of B (one "inserted" tooth), then m sites of A, followed by n sites of B, and so on until the $2S$ blocks of A and B have all been incorporated into the backbone. The last 7 sites will again be the terminal A sites. For example, in the case where the comb has 5 teeth, each of length 7, the corresponding linear chain will have the formula $[A_7(B_7A_{20})_5A_7]$.

In the simulation, we consider a single comb (or multiblock) at the interface between two immiscible fluids or homopolymers. The z = 64 plane represents this penetrable interface. In particular, this plane separates the cube into two symmetric regions: the lower half of the box represents fluid or homopolymer A, while the upper half of the lattice represents the fluid or homopolymer B. We introduce the following one-body potentials to differentiate the two regions:

$$U_A(z) = \begin{cases} 0 & z < 64 \\ +\Delta_A & z > 64 \end{cases} \quad \text{and} \quad U_B(z) = \begin{cases} +\Delta_B & z < 64 \\ 0 & z > 64 \end{cases} \tag{1}$$

The parameters Δ_A and Δ_B represent the respective monomer–fluid interaction energies. For $\Delta_A, \Delta_B > 0$, the A monomers prefer the A region, while the B monomers prefer the B domain. We also include an intrachain interaction between the A and B monomers, Δ_{AB}, which allows us to model the repulsion between the species.

We use the "pivot" algorithm to move the chains about the lattice.[2] This algorithm is particularly efficient at

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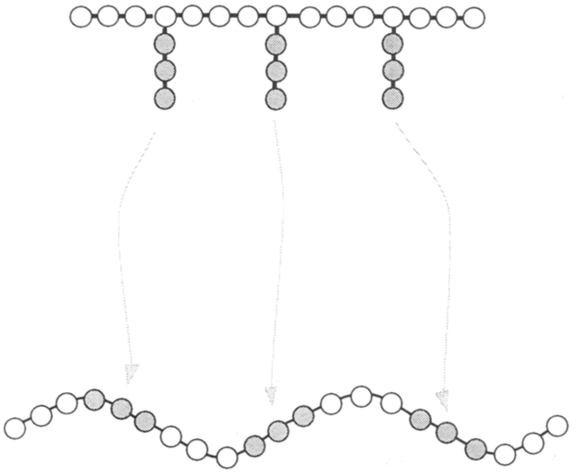


Figure 1. Model of the comb and linear copolymers used in the simulation. Both have the same composition of A (clear circles) and B (shaded circles) monomers. The linear polymer is generated by inserting the teeth (B monomers) into the backbone at regular intervals.

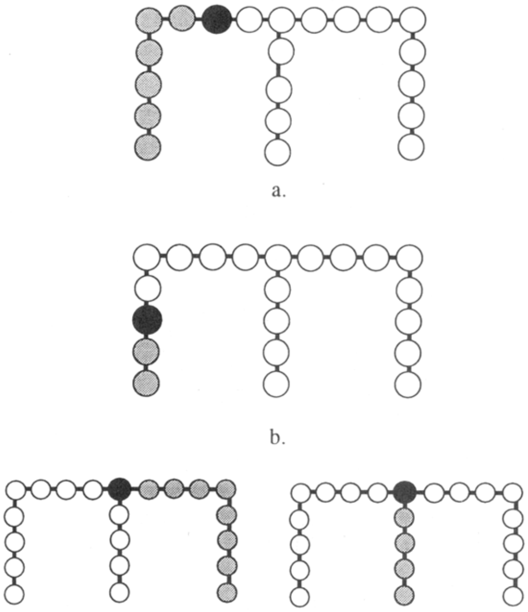
equilibrating the conformation of single polymer chains and was previously used to model the behavior of linear copolymers in bilayers[3] and at a single penetrable interface.[4] In addition, the pivot algorithm has been successfully used to describe the equilibrium properties of star polymers.[5]

The pivot algorithm, when applied to linear chains, consists of the following steps. A monomer on the chain is picked at random and designated as the pivot point. A random symmetry operation, such as a rotation or a reflection, is then applied to the segment of the chain subsequent to the pivot point, with the pivot point acting like the origin. On a linear polymer there are only two possible sections of the chain that can be pivoted about the pivot point. With the introduction of side chains or teeth, however, the situation is more complicated.

In a comb polymer, we must distinguish between three types of pivot points. The monomer that is designated as the pivot point will either be a site along the backbone, a tooth site, or a junction site (Figure 2). If the selected monomer is on the backbone of the comb, we pivot all the monomers to the left or right of this monomer (the direction is chosen at random) (Figure 2a). If the selected site is a tooth site, then we move only those monomers in the tooth that are below the pivot point (Figure 2b). Finally, if we pick a junction point, a choice is randomly made whether to pivot about the tooth or the backbone and, depending on our choice, we proceed as described above (Figure 2c). (If we choose to pivot about the backbone, we do not move the monomers that belong to the tooth connected to the junction site.)

The symmetry operations that can be performed on the chain depend on the type of lattice that is used in the simulation. For the cubic lattice, these operations correspond to the O_h symmetry group and consist of 48 possible operations. Once the move is performed, its acceptance is determined through the Metropolis algorithm,[6] where moves that reduce the energy of the system are accepted with unit probability. Moves that increase the energy of the system are only accepted with the probability $\exp(-\Delta E)$, where ΔE is the energy change associated with the move. (In our simulation, only nearest neighbors contribute to the energy of the system.) The condition of excluded volume is maintained by rejecting moves that allow the comb to cross itself.

The comb was initially started in a random self-avoiding configuration and then given $5N^2$ attempted pivots to equilibrate, where N is the total number of monomers in the comb. After the equilibration, results were averaged over 10^4 Monte Carlo steps, where each step involved $N \log N$ attempted pivots of the chain. To obtain the data in the plots below, four independent runs were executed for each case that we examined. Thus, each data point in our curves represents an average over four separate values.



a.

b.

c.

Figure 2. Comb polymers. The dark circles represent three possible types of pivot points for a comb copolymer: (a) a backbone site, (b) a tooth site, and (c) a junction site. The shaded circles represent the sites that are pivoted about the selected point.

Results and Discussion

Our specific aim was to isolate the structural and energetic conditions that drive the combs to localize at the interface. With this goal in mind, we first considered a comb with a fixed tooth length of 7 B sites and varied the number of teeth, S, from 2 to 7. For each of these structures, we also systematically varied the comb interaction energies. In particular, we set $\Delta_A = \Delta_B = \Delta_{AB} \equiv \Delta$ and varied the values of Δ from 0.08 to 0.32. This procedure was repeated for a comb with a tooth length of 14, i.e., the number of teeth were varied and, for each architecture, the value of Δ was systematically increased. The ensuing results allow us to probe the effect of tooth length, number of teeth, and interaction energy on the behavior of combs near the penetrable surface.

To characterize the properties of the various combs, we determined the density profiles of the polymers at the interface. Figure 3 shows such density profiles for several values of Δ in the case where the tooth length is 7 and there are 3 teeth. (In this and in subsequent figures, for purposes of clarity, we present only the density profiles for the backbone of the combs.) At low values of Δ, fragments of the teeth can penetrate into the incompatible A domain and backbone units are seen to diffuse into the unfavorable B phase. For these cases, the width of the profiles is relatively broad. It is apparent, however, that the width of the profiles decreases as the value of Δ increases. Thus, as the energetic penalty for having a monomer in an incompatible solvent becomes larger, the teeth are driven into the B region, while the backbone remains segregated in the A phase. As a result, the entire chain becomes more localized at the interface.

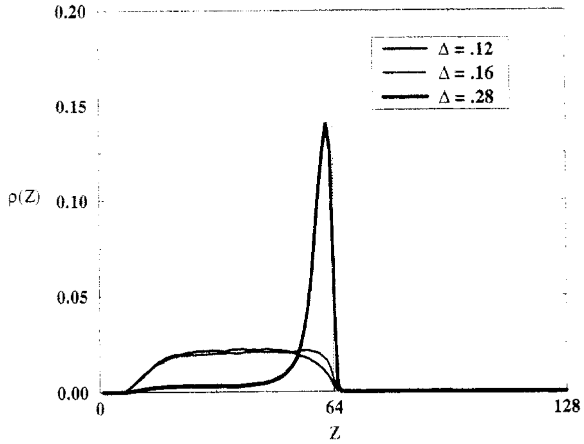


Figure 3. Normalized concentration profiles of the backbone of the comb for various values of Δ. We fixed the number of teeth at 3, and each tooth is 7 units long. Increasing Δ drives the comb to the interface, but at lower values of Δ the combs are delocalized.

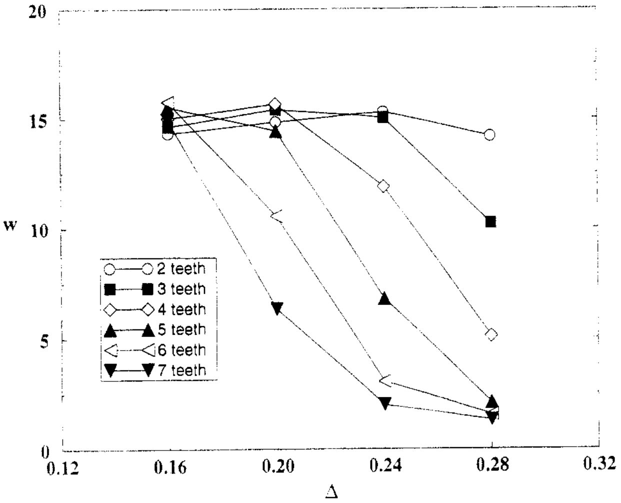


Figure 4. Width of the concentration profile, w, plotted as a function of Δ for combs with increasing numbers of teeth at a fixed tooth length of 7. Here and in subsequent plots of w vs Δ, the size of the error bars (the standard deviation of the four averaged values that make up each data point) is comparable to the size of the symbols used to designate the data points.

To quantify these observations, we calculated the width of the concentration profile of the backbone, w, where

$$w = [(\sum_{i=1}^{L}(z_i - \bar{z})^2\rho(z_i))]^{1/2} \tag{2}$$

The square brackets represent an average over time, and L is the z dimension of the lattice. The parameter $\bar{z}$ gives the average value of z_i for that particular comb, and $\rho(z_i)$ is the normalized density of the comb backbone at site z_i on the lattice:

$$\sum_{i=1}^{L}\rho(z_i) = 1 \tag{3}$$

Plots of w as a function of Δ are shown in Figure 4, not only for the case of 3 teeth, but also for $S = 2$ and 4–7. These figures highlight two important effects. First, as the previous qualitative discussion indicated, w decreases with an increase in Δ. Second, increasing the number of teeth decreases the value of Δ at which the combs localize at the interface. Increasing the number of teeth introduces more B sites and effectively increases the attraction between the comb and the B phase. Thus, the combs are more easily driven to the interface.

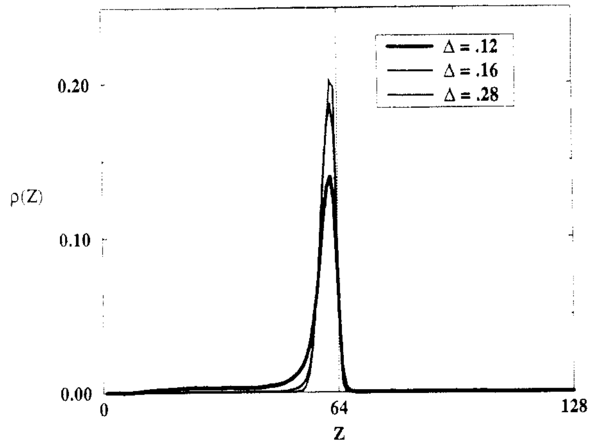


Figure 5. Normalized concentration profiles of the comb backbone for various values of Δ. Here, the number of teeth was fixed at 3, and each tooth is 14 units long. In this case, the comb is localized at the interface for all values of Δ.

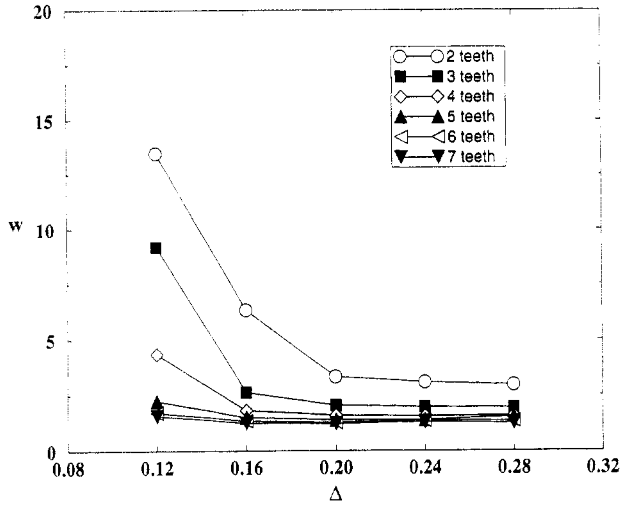


Figure 6. Widths of the concentration profiles, w, plotted as a function of Δ for varying numbers of teeth. The tooth length is fixed at 14 units.

The above plots where also calculated for the case where the tooth length was doubled to 14 lattice sites. Figure 5 shows the concentration profiles at various values of Δ for the case where $S = 3$. By comparing this figure with Figure 3, it is clear that the combs with the longer teeth (and thus more B sites) display narrower concentration profiles and, therefore, are more localized at the interface for the same value of Δ. Figure 6, which shows w versus Δ plots for the tooth length equals 14 examples, emphasizes the observation that these chains can readily localize at the interface. In fact, for values of $S \geq 3$ and $\Delta > 0.16$, these combs are always highly localized at the A/B boundary. Careful comparison of Figures 4 and 6 reveals a surprising result, which is highlighted in Figure 7. Here, we compare the behavior of two combs that contain the same number of B monomers, 4 teeth of length 7 and 2 teeth of length 14, at various values of Δ. The curves clearly show that the combs with the longer teeth display smaller values of w for all values of Δ. Thus, these chains can more readily localize at the interface than the case with the 4 shorter teeth. The same phenomenon is seen when we compare the behavior of a comb with 6 teeth of length 7 with a comb with 3 teeth of length 14 (see inset in Figure 7). (The curves finally coincide at the highest value of Δ, where both architectures are completely localized at the interface.) Thus, the localization of these AB combs is not just a function of the number of B's within the teeth.

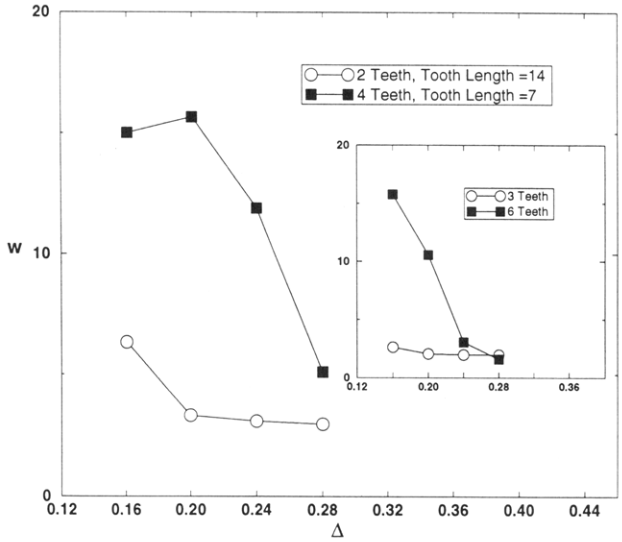


Figure 7. Comparison of the widths of the concentration profiles for combs having the same numbers of A and B monomers, but with different architectures. The combs with fewer, longer teeth more readily localize at the interface. The main graph shows the comparison between combs containing 2 teeth of length 14 ("2 × 14") and 4 teeth of length 7 ("4 × 7"). The inset shows the comparison between the "3 × 14" case and the "6 × 7" case.

The reason for the above behavior can be understood by examining Figure 8, which shows the typical equilibrium conformation for a comb with 6 teeth of length 7 (Figure 8a) and a comb with 3 teeth of length 14 (Figure 8b) when both are localized at the interface. In Figure 8a, the short backbone segments between the teeth are fairly stretched. Significant energy is needed to overcome this loss in conformational entropy. Figure 8b, however, shows that, in the case of fewer, longer teeth, the backbone segments between the teeth are sufficiently long that the conformational entropy of these blocks is not greatly reduced when the chain is localized at the interface. As a result, a smaller value of Δ is sufficient to drive the comb to the A/B boundary.

In addition to this entropic effect, an additional factor may contribute to the fact that higher energies are needed to localize the "6 × 7" case as opposed to the "3 × 14" example. Specifically, for low energies and shorter teeth, the teeth can be dragged away from the interface. Larger values of Δ increase the energetic penalty associated with such a move and, thereby, force the teeth to remain in the B phase. For longer teeth, however, even at lower Δ's such moves are energetically unfavorable (since this involves dragging a larger number of B's into the A phase). Thus, even at low Δ's, the combs with the longer teeth remain strongly localized at the interface.

Contrasting Combs and Multiblocks

In addition to comparing the properties of various combs, we also contrasted the properties of combs and multiblocks, which were constructed in the manner described in the "Model" section and illustrated in Figure 1. Note that both types of copolymers have identical compositions; only the architecture of the chains was varied. (Also recall that in all the examples in this paper, the number of A sites is greater than the number of B sites in the chains.) In the case where the tooth or B block length was set equal to 7 lattice sites, we found that the linear chains were delocalized for all the values of Δ we examined, in contrast to the behavior of comparable combs (see Figure 4). While this difference in behavior diminishes when the tooth or B block length is increased to 14, the effect still persists, as can be seen by comparing Figures 9 and 6.

Figure 8. Graphical representation of the effects of architecture on the ability of the comb to localize at the interface: (a, top) a comb with 6 teeth of 7 monomers each (note how the backbone is constrained at the interface); (b, bottom) a comb with 3 teeth of 14 monomers each (here the backbone is more "relaxed"). The value of Δ in (a) is 0.24 and 0.28 for (b).

A factor that contributes to this difference between multiblocks and combs can be understood by viewing

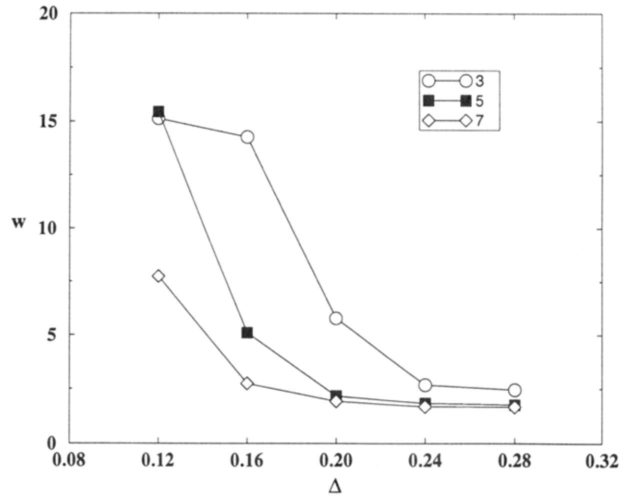


Figure 9. Widths of the concentration profiles for linear copolymers with the B block length fixed at 14 units as a function of Δ.

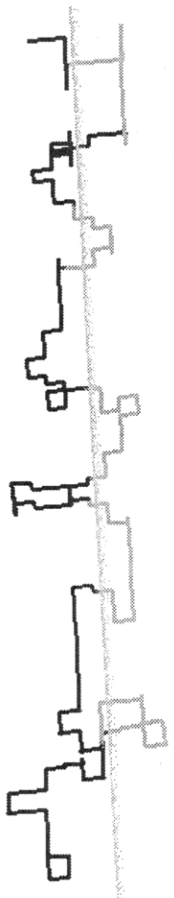


Figure 10. Snapshot from the simulation of a linear copolymer localized at the A/B interface. The darker line segments represent the A block while the lighter line segments represent the B blocks. The interface is denoted by the dotted line. Here the linear copolymer has 5 B blocks consisting of 14 monomers each. Δ = 0.24.

“snapshots” of typical conformations of multiblocks at the interface. As can be seen in Figure 10, the short B blocks form small loops that penetrate into the B phase. There is an appreciable entropic cost to forming such a constrained loop. Hence, sufficiently high Δ's are required to localize the linear chain. As the length of the B block is increased, the conformation of the chain is less constrained. Consequently, the behaviors of the tooth length and block length equals 14 examples are more similar.

Conclusions

We compared the localization of various combs and multiblock copolymers at a penetrable interface that modeled the boundary between immiscible homopolymers. This comparison allows us to establish guidelines for fabricating copolymers compatibilizers that will enhance the strength of the interface. In particular, the optimal compatibilizers should display two important characteristics. First, the chains should readily localize at the polymer/polymer interface. Second, the chains should form “effective crossings” through this boundary.[7] The term “effective crossings” implies that a chain weaves back and forth across the interface, intersecting this boundary at multiple points, and in so doing, forms large “stitches” that extend beyond the entanglement length of the homopolymers.[7] The latter condition ensures that the bulk polymer will entangle with the compatibilizer, thereby making chain “pull-out” more difficult.

Applying the above criteria to our simulation results, we can conclude that combs with fewer, longer teeth will display the optimal architecture for compatibilizing activity. These chains readily localize at the interface: only small values of Δ are needed to drive these combs to the A/B boundary. Furthermore, the intervening backbone segments form large loops that extend far into the A domain. The longer teeth also penetrate deeper into the B phase. These large excursions allow the bulk polymer to entangle with the AB copolymer, thus fulfilling the final condition noted above.

We are careful to add that while longer teeth are preferable, the total number of B monomers should remain less than or comparable to the number of A units. Increasing the number of B's beyond this value will drive the chains to become localized in the B phase.

Our results also reveal that comb copolymers, in general, form better compatibilizers than linear, multiblock chains of the same chemical composition. Taken together with our observations on the differences between the various combs, the findings highlight the importance of molecular architecture in controlling the interfacial activity of macromolecules. The results also illustrate how computer simulations can be used to establish design criteria for synthesizing copolymers that enhance the adhesion between immiscible polymers.

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