PHYSICAL REVIEW E VOLUME 54, NUMBER 3 SEPTEMBER 1996

# Entropically driven segregation in blends of branched and linear polymers

D. G. Walton* and A. M. Mayes†
*Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

(Received 22 December 1995; revised manuscript received 12 April 1996)

A self-consistent mean-field treatment of branched polymer additives in a linear polymer matrix is developed in order to study the effect of chain architecture on surface segregation. With branched additives, connectivity between side chains and an increased number of chain ends results in near-surface concentration profiles that differ both qualitatively and quantitatively from those seen with linear chain additives. A much larger degree of segregation with branched additives is observed when compared with linear additives of equivalent molecular weight. [S1063-651X(96)03509-X]

PACS number(s): 87.15.−v, 83.80.Es, 31.15.Ne, 81.65.Ya

Surface segregation is a phenomenon common to all material classes. In metallic alloys, the segregation of minority components to exposed surfaces can improve or diminish corrosion resistance. Likewise, dopant segregation to the surface of silicon can dramatically alter its local electronic properties. The fracture strength of inorganic glasses can similarly be affected by the surface localization of metal cations that modify the density of the surface region relative to the bulk. Typically, such segregation phenomena are driven by an associated reduction in the system enthalpy, e.g., by lowering the number of unfavorable bulk contacts or the number of unsaturated bonds residing at the surface. An exception is the case of polymer melts, for which configurational entropy can serve as a significant additional driving force for surface segregation.

In bulk polymer melts, the spatial conformation of a polymer chain is typically well represented by Gaussian statistics, with each monomer segment being roughly equivalent to a step in a three-dimensional random walk. The presence of a surface introduces a reflecting boundary condition that lowers the number of total configurations available to the chain and hence the entropy of the system. To minimize the number of reflections required at the material boundary, chain ends preferentially segregate to the surface of a monodisperse polymer melt, in the absence of strong interactions [1–3]. Preferential segregation of the lower molecular weight component is similarly predicted [4] and observed [5–7] in bimodal polymer blends of identical chemical structure. From a commercial standpoint, such entropically driven segregation could be useful for designing polymer surfaces rich in an energetically unfavorable component. In particular, the preparation of hydrophilic surfaces through selective segregation would have a wide range of applications from reducing static charge buildup in textile and microelectronics applications of plastics to improving resistance to protein adsorption in biomedical and marine applications. Unfortunately, entropic effects on segregation tend to be small and are therefore often dominated by enthalpic contributions to the surface free energy. This was demonstrated by Elman *et al.* [8] for the case of chain end segregation. Their study of functionally terminated polystyrenes showed a large surface excess of chain ends for materials terminated with low-energy fluorocarbon groups, but a surface depletion of ends for systems terminated with high-energy carboxylic acid groups. In bimodal blends, entropically driven segregation of the lower molecular weight species is similarly predicted [4] and observed [5–7] to be small, typically a few percent over the bulk concentration.

The ability to place high-energy groups at a surface through configurational entropy considerations alone would thus appear to require more complicated molecular architectures. In this study, a mean-field model is developed to examine entropically driven segregation in blends of branched and linear polymers of identical chemical nature. For highly branched polymers, the large number of chain ends may amplify selective segregation by significantly reducing the number of required reflections at the surface.

This problem was initially examined experimentally in blends of chemically similar (although not identical) polyolefins [9] where one component was more branched than the other. It was found that the more branched component segregated to the surface. Comparable results were found with polyolefin diblock copolymers [10] where the block with the more branched component was observed to reside at the surface. In these polyolefin systems, the branched components have smaller statistical segment lengths and are consequently more ‘‘flexible’’ than the linear components. Fredrickson and co-workers [11,12] predicted, using analytical self-consistent mean-field (SCF) and functional theories, that the more flexible component should segregate to the surface due to entropic effects. However, by Monte Carlo simulations, other groups [13,14] have predicted that the ‘‘stiffer’’ linear component segregates preferentially due to better packing at the surface and that enthalpic differences between the components must be invoked in order to theoretically capture the observed experimental results. It was recently shown that when bond angle restrictions are imposed, lattice SCF models also predict surface segregation of the stiffer component [15]. However, lattice models are still thought to be less suitable for describing packing effects at the surface or in the bulk than off-lattice methods that more accurately account for local segmental arrangements. Here we do not attempt to address packing influences but instead focus on the contribu-

---

*Electronic address: dwalton@monosparc.mit.edu
†Author to whom correspondence should be addressed. Electronic address: amayes@monosparc.mit.edu

tion of *configurational* entropy to surface segregation in athermal blends of branched and linear polymers with similar statistical segment lengths and packing characteristics. We then compare the magnitude of this effect with enthalpic differences between the components.

For this treatment, we initially omit all enthalpic interactions in the system and look only at the configurational entropic contribution to the segregation of various low molecular weight branched architectures in blends with a higher molecular weight linear matrix. We employ a self-consistent mean-field theory based on the method presented by Fleer *et al.* [16] for polymer adsorption. In this theory, all interactions in the system are averaged into a mean field that varies only in the direction perpendicular to the surface. We define a potential $U(z)=U'(z)$, where $z$ is the layer number in the system, with $z=1$ corresponding to the surface layer, and $U'(z)$ is the hard-core potential that is independent of segment type and is purely entropic in nature [16]. The volume fraction of a polymeric species is then given by

$$\phi_i(z)=(\phi_i^b/N_i)\sum_s G(z,s|e_j), \tag{1}$$

where $\phi_i^b$ and $N_i$ are the bulk volume fraction and number of units per chain, respectively, of component $i$, and $G(z,s|e_j)$ is the segmental weighting factor defined as the probability of finding segment $s$ in layer $z$, given that the chain ends $e_j$ may be located anywhere in the system. The segmental weighting factor is related, through a recursion relationship, to the potential $U(z)$ and is detailed in [16]. After an initial guess at the potential, the volume fraction of each species is calculated and, subject to the constraint that the volume fractions of all species sum to unity, the solution to the set of equations (1) is found self-consistently. All calculations were run on a hexagonal lattice, although variation of the lattice type to cubic shows no significant effect on the results.

For all of the branched architectures studied [see Fig. 1(a)], there are $B$ branches (and consequently $B$ chain ends), each of length $l$ (including the branch point, i.e., the location on the backbone at which the branches are attached) and $B-3$ branch connections, each of length $d$ (including the two adjacent branch points), such that the total number of branched additive units may be written as

$$N_A=Bl+(B-3)(d-2)-2 \tag{2}$$

for $B\geqslant 3$.

Figure 2 shows typical additive concentration profiles for blends of polymeric additives in a 1000-unit linear matrix ($N_M=1000$) with an additive bulk volume fraction $\phi_A^b=0.1$. The concentration profiles of a branched additive with $B=10$ branches, each of length $l=10$, and spaced at intervals $d=5$ along the backbone [$N_A=119$ units, after Eq. (2)] and a branched additive with $l=10$, $d=15$, and $B=7$ branches ($N_A=120$ units) are contrasted with a linear chain additive of molecular weight $N_A=119$. Although a surface excess of the additive is observed for all cases, the shapes of the profiles differ considerably. Whereas the concentration of the linear additive falls away monotonically from the surface, the branched additives exhibit a crest in the first few layers. This characteristic, also predicted by Wu and Fredrickson [12], is seen in most of the branched polymer architectures studied, disappearing only as the number of branches becomes small, as the branch lengths become either very large or approach a single unit or when the distance between branches becomes extremely long compared to the branch length. In other words, as a branched architecture begins to resemble a linear chain, this behavior is suppressed. The location of the crest is controlled by the branch length and moves away from the surface as the branch length increases.

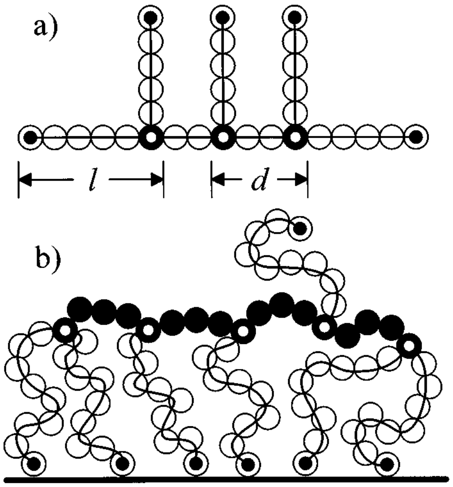

FIG. 1. (a) Schematic of a branched polymer architecture with $B=5$ branches, each of length $l=6$, and two branch connections, each of length $d=4$, corresponding to a molecular weight, after Eq. (2), of $N_A=32$ units. (b) Diagram of an adsorbed branched polymer with $l=10$, $d=5$, and $B=7$ branches ($N_A=80$ units), blended with a higher molecular weight linear polymer, showing the origin of the crest seen in the concentration profile (Fig. 2). For clarity, branch segments and branch-connection segments are depicted as white- and black-filled circles, respectively. Chain ends are shown as white circles with black dots and branch points are shown as black circles with white dots.

In order to understand the form of the branched additive concentration profile, the contribution of each segment type to the overall volume fraction was examined. Figures 3(a)

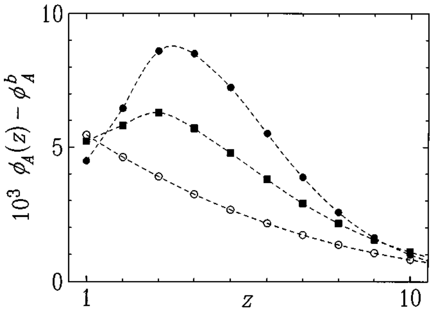

FIG. 2. Concentration profile of linear (○, $N_A=119$) and branched additives in a linear matrix of $N_M=1000$ units, with bulk composition $\phi_A^b=0.1$. ● and ■ correspond to branched architectures with $l=10$, $d=5$, and $B=10$ branches ($N_A=119$ units) and $l=10$, $d=15$, and $B=7$ branches ($N_A=120$ units), respectively. The branched additive profiles show crests characteristic of most branched architectures. All profiles show the exponential decay away from the surface commonly seen in segregated systems (for branched additives, this decay is seen after the crest).

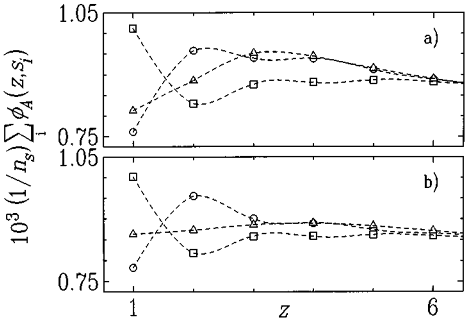

FIG. 3. Segment concentration profiles for branched additives with (a) $l=10$, $d=5$, and $B=10$ branches ($N_A=119$ units) and (b) $l=10$, $d=15$, and $B=7$ branches ($N_A=120$ units) in a linear matrix of $N_M=1000$ units with a bulk composition $\phi_A^b=0.1$. Shown is the volume fraction of segment type $s$, averaged over the $n_s$ segments of that type per molecule. ○, □, and △ correspond to the averaged segmental volume fractions of the branch points, chain ends, and midpoints of the branch connections, respectively.

and 3(b) show the averaged segmental concentration profiles for the chain ends, the branch points, and the midpoint along the branch connections for the same blends of branched and linear polymers presented in Fig. 2. Both branched architectures clearly show that the majority of the chain ends are located at the surface with a corresponding depletion of the branch points. This result is seen in all branched architectures studied. In Fig. 3(b), where the distance between the branches is larger than the branch lengths, we find that the midpoints of the branch connections are fairly evenly distributed among all the layers, with only a slight enhancement at $z=4$, and the overall additive concentration profile (see Fig. 2) exhibits only a small crest. In Fig. 3(a), where the branches are more closely spaced, however, these midpoints are highly localized next to the branch points, one to two layers deeper into the system. This localization is manifested as a large crest (see Fig. 2) and is depicted schematically in Fig. 1(b).

For low molecular weights and small bulk volume fractions, the surface layer composition of the branched additive is found to be lower than, but close to, that of a linear additive with identical molecular weight in a comparable blend with a higher molecular weight linear polymer matrix. At a critical value of the additive molecular weight, however, a crossover occurs, above which the surface layer concentration of the branched additive is found to be higher than its linear counterpart. For systems with equivalent additive and matrix molecular weights, such as that of Yethiraj [14], this crossover phenomenon is also observed. Specifically, for the branched architecture studied by Yethiraj ($l=2$, $d=3$, $B=8$ branches, and $N_A=N_M=19$) we find that there is a higher surface concentration of the *linear* component, as he predicts. For that system, however, we see a crossover with molecular weight at $B=11$ branches ($N_A=N_M=28$).

While the surface layer of a blend containing a branched additive may or may not exhibit a larger additive volume fraction when compared to a blend containing an equivalent molecular weight linear additive, the near-surface region of the branched additive *always* shows a larger additive surface excess $\Gamma_A$, given by

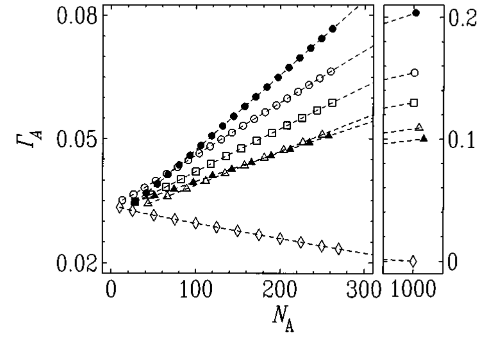

FIG. 4. Surface excess of linear (◇) and branched additives as a function of additive molecular weight with a constant matrix molecular weight of $N_M=1000$ units and a bulk composition $\phi_A^b=0.1$. ○, □, and △ correspond to branched architectures with $d=10$ and $l=5$, 10, and 15, respectively. ● and ▲ represent branched architectures with $l=10$ and $d=5$ and 15, respectively. Note that for a linear polymer blend with $N_A=N_M=1000$, $\Gamma_A=0$ since both components are identical and there is no preferential segregation of either. For blends of branched and linear polymers, however, there is a large surface excess of the branched species when $N_A=N_M=1000$.

$$\Gamma_A=\sum_z\,[\phi_A(z)-\phi_A^b], \tag{3}$$

where $z$ is the distance from the surface and $\phi_A^b$ is the additive volume fraction in the bulk. As shown in Fig. 4, over the molecular weight regime pictured, the surface excess of a linear additive decreases linearly as a function of additive molecular weight. By contrast, for branched additives the opposite trend is observed and the surface excess *increases* almost linearly with molecular weight over the regime shown, decreasing only as the molecular weight of the branched additive becomes much greater than the linear polymer in which it is blended, i.e., when the linear polymer becomes the low molecular weight additive and the branched polymer becomes the high molecular weight matrix.

Because the degree of surface excess is directly related to the form of the additive concentration profile, those branched architectures exhibiting a crest show large surface excesses. The factors that control the size of the crest therefore have a direct effect on the surface excess, such that a range of branch lengths and spacings exist where the crest, and consequently the degree of surface excess, is largest. The results shown in Fig. 4 also indicate that the segregation of a branched additive is roughly analogous to the segregation of each of its branches, independent of their connectivity. As a consequence, the backbone is dragged towards the surface, resulting in a crest in the additive concentration profile and a large excess in the near-surface region.

The size of the near-surface region in blends of branched and linear polymers is found to scale with the radius of gyration, as shown previously for linear polymer blends [4]. Consequently, for branched additives, the near-surface region is slightly more narrow than for linear additives since the radius of gyration of branched polymers is less than that of equivalent molecular weight linear chains.

The surface energy $\gamma$ can be trivially extracted from data already presented since [16]

$$\gamma a/kT=\Gamma_A(1/N_M-1/N_A)-\sum_z U(z)/kT, \tag{4}$$

where $a$ is the area per site. We find that for the molecular weight regime tested, the surface energy of systems with branched additives follows the scaling $\gamma \propto N_A^{-1}$, as seen for linear additives [4], and is found to be smaller for all branched polymer architectures than linear polymers of equivalent molecular weight. For a large number of branches the surface energy also scales as $\gamma \propto B^{-1}$, indicating that the surface energy reduction is related to the number of chain ends. This supports the hypothesis [4,17] that chain ends drive the segregation process.

In order to include enthalpic interactions in our analysis, we redefine the potential such that

$$\begin{aligned} U_A(z)&=U'(z)+kT[\chi_{AS}\delta(z-1)+\chi\langle\phi_M(z)-\phi_M^b\rangle],\\ U_M(z)&=U'(z)+kT\chi\langle\phi_A(z)-\phi_A^b\rangle, \end{aligned} \tag{5}$$

where $U'(z)$ is the hard-core potential, as before, $\chi_{iS}$ is the interaction parameter between component $i$ and the wall (here we set a *repulsion* between the additive and the wall and make the wall neutral to the matrix such that $\chi_{AS}>0$ and $\chi_{MS}=0$), and $\chi$ is the additive-matrix interaction parameter. The $\delta$ function multiplying the wall-additive interaction parameter ensures that its contribution affects only segments in the $z=1$ (i.e., the surface) layer and $\langle f(z)\rangle$ is defined as an average of the function $f(z)$ over all neighboring sites. By incorporating this potential, the self-consistent solution can be found as before.

Figure 5 compares the magnitude of the enthalpic and configurational entropic contributions to the surface segregation in these systems. It shows a critical additive molecular weight above which there is a net excess and below which there is a net depletion of the additive in the near-surface region. It can be seen that even with a surface that repels the additive, there is a range of $\chi_{AS}$ values for which there is an excess of the additive at the surface, regardless of whether or not the additive and matrix are compatible. Also, this region is larger for branched than for linear additives.

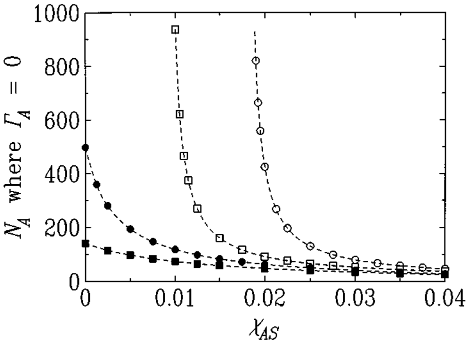

FIG. 5. Critical additive molecular weight above which the additive is depleted from and below which the additive is enhanced in the near-surface region as a function of the wall-additive interaction parameter $\chi_{AS}$ with the wall-matrix interaction parameter $\chi_{MS}=0$. Shown are results for compatible blends of linear (■) and branched (●) additives in a linear matrix of molecular weight $N_M=1000$ with bulk composition $\phi_A^b=0.1$ and an additive-matrix interaction parameter $\chi=-0.01$. Results for incompatible blends of linear (□) and branched (○) additives in a similar matrix with the same bulk composition and an additive-matrix interaction parameter $\chi=0.01$ are also presented. Results show that branched additives exhibit a larger range of wall-additive interaction parameters and molecular weights over which an excess of the additive exists at the surface.

In this paper we have examined the dependence of chain architecture, molecular weight, and number of branches (or chain ends) on the segregation of the branched species in blends of branched and linear polymers. By using a self-consistent mean-field theory with no enthalpic interactions, we have shown that in a linear polymer matrix, configurational entropy causes branched additives to segregate more readily to the near-surface region than linear additives of equivalent molecular weights. We also see that the incorporation of enthalpic differences between the components and a wall that repels the additive still allows for the segregation of the additive due to configurational entropy reasons, allowing for the possibility of segregating an enthalpically unfavorable additive to the surface by entropic means. We have also found that in these blends, the degree of segregation is aided by the fact that each branched chain behaves roughly as a collection of unconnected, short linear chains. Unlike oligomeric additives, however, the short side chains of a branched additive are connected to a backbone, which helps anchor the molecule to the matrix through entanglements. These results collectively suggest that entropically induced segregation by branching may be a viable route to creating thermodynamically stable and physically robust hydrophilic polymer surfaces.

This work was funded in part by the National Science Foundation, Grant No. DMR9357602.

[1] D. N. Theodorou, Macromolecules **21**, 1422 (1988).

[2] R. G. Winkler, T. Matsuda, and D. Y. Yoon, J. Chem. Phys. **98**, 729 (1993).

[3] S. Affrossman, M. Hartshorne, R. Jerome, R. A. Pethrick, S. Petitjean, and M. Rei Vilar, Macromolecules **26**, 6251 (1993).

[4] A. Hariharan, S. K. Kumar, and T. P. Russell, Macromolecules **23**, 3584 (1990).

[5] T. F. Schaub, G. J. Kellogg, A. M. Mayes, R. Kulasekere, J. F. Ankner, and H. Kaiser, Macromolecules **29**, 3982 (1996).

[6] P. P. Hong, F. J. Boerio, and S. D. Smith, Macromolecules **27**, 596 (1994).

[7] I. Hopkinson, F. T. Kiff, R. W. Richards, S. Affrossman, M. Hartshorne, R. A. Pethrick, H. Munro, and J. R. P. Webster, Macromolecules **28**, 627 (1995).

[8] J. F. Elman, B. D. Johs, T. E. Long, and J. T. Koberstein, Macromolecules **27**, 5341 (1994).

[9] U. Steiner, J. Klein, E. Eiser, A. Budkowski, and L. J. Fetters, Science **258**, 1126 (1992).

[10] M. Sikka, N. Singh, A. Karim, and F. S. Bates, Phys. Rev. Lett. **70**, 307 (1993).

[11] G. H. Fredrickson and J. P. Donley, J. Chem. Phys. **97**, 8941 (1992); D. T. Wu and G. H. Fredrickson, *ibid.* (to be published).

[12] D. T. Wu and G. H. Fredrickson, Macromolecules (to be published).

[13] A. Yethiraj, S. K. Kumar, A. Hariharan, and K. S. Schweizer, J. Chem. Phys. **100**, 4691 (1994); S. K. Kumar, A. Yethiraj, K. S. Schweizer, and F. A. M. Leermakers, *ibid.* **103**, 10 332 (1995).

[14] A. Yethiraj, Phys. Rev. Lett. **74**, 2018 (1995).

[15] C. C. van der Linden, F. A. M. Leermakers, and G. J. Fleer, Macromolecules **29**, 1172 (1996).

[16] G. J. Fleer, M. A. Cohen Stuart, J. M. H. M. Scheutjens, T. Cosgrove, and B. Vincent, *Polymers at Interfaces* (Chapman & Hall, London, 1993).

[17] P.-G. de Gennes, in *Physics of Polymer Surfaces and Interfaces*, edited by I. C. Sanchez (Butterworth-Heinemann, Stoneham, 1992).