Macromolecules **2003,** *36,* 771−781

Optimal Chain Architectures for the Molecular Design of Functional Polymer Surfaces

Patricia Anne V. O'Rourke-Muisener and Jeffrey T. Koberstein*,†

Department of Chemical Engineering, Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06269

Sanat Kumar

Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802

Received November 13, 2001

ABSTRACT: The Scheutjens−Fleer self-consistent mean-field theory is used to calculate the surface segregation of various chemical functional moieties located on functional polymers of different architectures. Our results demonstrate the importance of the number and location of functional groups and their surface preference relative to polymer backbone segments in determining surface segregation. In general, we conclude that adjacency of similar functional groups is the most effective means for enhancing surface segregation of functional groups and that having two functional groups of similar character is always preferable to having two functional groups of opposite character, the Pushmi-Pullyu architecture, where one group prefers the surface while the other is repelled from it. The calculations demonstrate that the optimal architecture for producing a low-energy release surface is a functional polymer with adjacent low-energy functional groups located at one chain end. In this situation, both enthalpic and entropic factors serve to drive chain ends to the surface. In contrast, high-energy adhesive surfaces are best obtained by placing adjacent high-energy functional groups at the center of the polymer chain. High-energy groups situated at the middle of the chain locate preferentially in the second lattice layer, from which they can migrate readily to the surface when it is contacted with any other high surface energy medium.

Introduction

Strategies for polymer surface modification are an important element in many different technologies including paints, coatings, adhesives, lubricants, and polymer blends. Achieving the desired surface properties is usually dependent upon the ability to locate particular functional groups at the surface. When release properties are the goal, for example, a common approach to surface modification is the inclusion of low-energy fluorocarbon or silicone components that lower the surface tension. High-energy functional groups are often incorporated into the polymer structure when adhesive properties are desired. Early surface tension measurements on block and graft copolymers prepared from two monomers of different surface energy provide clear evidence that the distribution of various functional groups along the polymer chain has a marked influence on their surface properties.[1,2] Surface tension is much lower for the block copolymers where lower-energy repeat units are less constrained and freer to adsorb preferentially at the air−polymer interface. Chain architecture is expected to have a similarly potent influence on the surface properties of functional polymers. An important goal of our research, therefore, is to gain a molecular-based understanding of how the distribution and nature of functional groups attached along a polymer chain can be used to design the surface properties of a functional polymer. In this sense, we broadly define a functional group as any chemical unit that imparts a particular desired property to the surface.

Functional polymers must be considered as heterogeneous materials, particularly with respect to their surface properties, and are therefore susceptible to surface segregation phenomena. That is, a functional group that has a lower surface energy than its polymer backbone will segregate to the surface in order to decrease the overall surface energy and free energy of the system. The degree of segregation is determined by a balance between the free energy gain associated with the surface tension reduction and the free energy cost of relocating the functional groups to the surface. Surface segregation is a general phenomenon for miscible and immiscible multicomponent systems and has been studied for polymer blends,[3,4] copolymers,[5] polymer solutions,[6] and end-functional homopolymers.[7]

End-functional polymers serve as a convenient model system for understanding the general behavior of functional polymer surface properties. Surface tension measurements[8] on functionally terminated poly(dimethylsiloxane) indicated that end groups with low surface energy relative to the chain backbone were selectively adsorbed at the polymer−air interface. Conversely, end groups with higher surface energy relative to the chain backbone were depleted from the surface. X-ray photoelectron spectroscopy measurements[9] confirmed the depletion of higher surface energy end groups from the surface and showed that the depletion zone was nanometers in thickness, comparable to the chain dimensions.

Neutron reflectometry experiments were performed on three end-functional polystyrenes: a "neutral" control specimen prepared by proton termination, a "repulsive" end group system terminated with high surface energy carboxylic acid end groups, and an "attractive" end group system containing low surface energy fluorocar-

---

* To whom correspondence should be addressed.

† Present address: Department of Chemical Engineering, MC4721, Columbia University, 500 West 120th Street, New York, NY 10027.

10.1021/ma011969q CCC: $25.00 © 2003 American Chemical Society
Published on Web 01/04/2003

bon chain ends.[7] The fluorinated end groups were absorbed at the surface, and the carboxylic acid end groups were depleted from the surface. For the "neutral" end group system, the *sec*-butyl initiator fragments located at the opposite chain end segregated preferentially to the air interface since they were the lowest surface energy constituent of the polymer.

Several groups have examined the effects of fluorinated end groups on the surface composition and properties of different model systems, in particular polystyrene and poly(ethylene oxide).[10−14] Angle-dependent X-ray photoelectron spectroscopy studies of ω-fluorinated polystyrenes demonstrated a surface excess of the low-energy fluorosilane end groups,[15] and contact angle measurements revealed that the degree of end group surface enrichment decreased with increasing molecular weight.[16]

Theodorou[17,18] applied the mean-field self-consistent lattice theory of Scheutjens and Fleer[19] to the case of copolymers with arbitrary architecture in order to study the behavior of a polymer chain with an "attractive" end group. It was found that selective adsorption of the lower energy end groups in the topmost lattice layer was accompanied by depletion in deeper layers, the latter result arising from chain connectivity. The tendency of the attractive end groups to absorb on the surface became more pronounced with increasing chain length.

In previous work, we used a similar lattice model to study end group partitioning in α,ω-functional polymers.[20] The theory successfully reproduced experimental surface tension data for several α,ω-functional poly(dimethylsiloxanes).[8] End group segregation was primarily controlled by surface energy differences between the chain ends and repeat units; entropic effects were found to be negligible for most practical cases. The entropic driving force for end group segregation was shown to be of the order of $^1/_2 k_B T$ and to lead to a slight surface excess of nonfunctional chain ends at the surface, in agreement with previous theoretical results.[18,21]

The goal of this paper is to answer a number of remaining questions regarding the surface properties of functional polymers. An extension of Theodorou's formalism[17] is applied to theoretically probe how the location, number, and type of functional groups placed along a polymer chain influence the composition and distribution of functional groups at a surface. The dependence of surface properties on the chain length and the surface energy difference between functional groups and the chain backbone is also examined. The information obtained through this study provides a framework for the molecular design of functional polymer surfaces with properties that are optimized for a particular application.

Theoretical Background

The framework for the calculations is the self-consistent mean-field lattice theory originally developed by Scheutjens and Fleer[19] to study adsorption in polymer solutions. A similar approach was utilized by Hariharan et al.[22,23] to study the surface properties of polydisperse polymer melts and binary polymer blends, Theodorou[17,18] to study the behavior of copolymers of arbitrary architecture near a hard surface, and our own group to investigate the surface properties of α,ω-functional polymers.[20]

The functional polymer is placed on a cubic lattice confined within two impenetrable walls that are sufficiently separated to provide a bulklike region in the center of the film. The lattice is incompressible with each lattice site occupied by a single chain segment. Normally the lattice volume is set equal to the volume of the polymer repeat unit; however, it is more convenient in the present case to equate it to the volume of the functional group. The number of total chain segments, or normalized chain length, r, is then the total volume of the chain divided by the volume of the functional group

$$r = \frac{Zv_r + Nv_{\text{ref}}}{v_{\text{ref}}} \tag{1}$$

where Z is the number of repeat units of volume v_r, v_{ref} is the reference volume for a lattice site which is set equal to volume of the functional group, and N is the total number of functional groups per polymer chain.

Surface segregation is governed by a balance between the resultant surface energy reduction and the required change in chemical potential associated with segregation of the functional group. The magnitude of the latter effect is related to the bulk interaction parameter, χ, between a functional group and the chain backbone. We neglect bulk interactions in the calculations but show in the Appendix that bulk interactions simply increase the degree of surface segregation but do not alter the qualitative nature of surface segregation behavior.

The surface interaction parameter is related to the difference in adsorption energies of the functional group and a repeat unit segment

$$\chi_s = \frac{U_s^1 - U_s^2}{k_B T} = \frac{(\gamma_1 - \gamma_2)a}{k_B T} \tag{2}$$

where k_B is Boltzmann's constant, T is temperature, and U_s^i is the change in energy associated with moving a segment of type i from the pure bulk to the surface. The latter adsorption energy is equal to the surface tension, γ_i, multiplied by the surface area per lattice site, which for a cubic lattice is $a = v_{\text{ref}}^{2/3}$. The surface interaction parameter is defined so that a positive value indicates that a functional group is repelled from the surface (repulsive or high surface energy functional group), while a negative value implies that functional groups are preferentially absorbed at the surface (attractive or low surface energy functional group).

The equations utilized in the self-consistent-field treatment are outlined in the Appendix. The parameters needed for these calculations are the number and location of the functional groups, the polymer chain length, and surface interaction parameters, χ_s. The output of the calculations is the functional group concentration for each lattice layer.

Results and Discussion

Basic Features of End-Functional Polymer Surfaces. The characteristic features of all functional polymer surfaces that we have studied are qualitatively similar and can be conveniently illustrated by reviewing the surface properties of α-functional polymers. To make this review more relevant, we first consider the range of surface interaction parameter values that might be practically encountered in real systems. χ_s values reported in the literature range from −1.5 for an end fluorinated polystyrene[12] to 0.61 for carboxyl-terminated

PDMS.[20] General discussions are therefore confined to a range of reasonably expected χ_s values defined by $-4 \le \chi_s \le 4$. To simplify discussion, we adopt the convention of referring to a functional group as "attractive" when it has a lower surface tension than that of the polymer backbone ($\chi_s < 0$) and it adsorbs preferentially at the surface and as "repulsive" when it has a higher surface tension than the chain backbone ($\chi_s > 0$) and is depleted from the surface.

The molecular configurations anticipated from lattice model calculations for functional and nonfunctional polymers at an air–polymer interface are qualitatively illustrated in Figure 1. The darker cubes represent a cubic lattice site occupied by an end group while the lighter cubes are lattice sites occupied by the chain repeat units. The end groups on the nonfunctional polymers (Figure 1b) are distributed randomly throughout the cubic lattice. Attractive end groups on the α-functional polymer (Figure 1a) are enriched at the surface and depleted in subsequent layers with the end group concentration gradually rising to the bulk end group concentration. Repulsive end groups (Figure 1c) are depleted in the top lattice layer and enriched in deeper layers with the end group concentration gradually decaying to the bulk value.

Predicted surface concentration depth profiles for α-functional polymers with chain length $r = 11$ are presented in Figure 2, where $\phi_{f,i}$ is the volume fraction of functional groups in lattice layer i. Results are shown for three cases: attractive end groups, "neutral" end groups ($\chi_s = 0$), and repulsive end groups. The concentration depth profiles for attractive functional groups (Figure 2a) exhibit two regions of behavior. End groups are enriched at the surface, but the zone of excess is only one lattice layer deep. The magnitude of enrichment increases as χ_s becomes more negative. A gradient of functional group depletion begins in the second lattice layer and continues to a depth that corresponds roughly to the chain length. Maximum depletion is observed in the second lattice layer, and the degree of depletion decreases gradually with increasing depth.

The profile for neutral end groups (Figure 2b) is qualitatively similar to that for the attractive end group, although the degree of enrichment and depletion are much smaller. When $\chi_s = 0$, the enthalpic driving force for end group segregation vanishes, but an entropic driving force favoring end group surface segregation leads to a small surface excess of end groups. Chain backbone units placed at an interface suffer a loss of entropy because configurational paths that penetrate the interface are disallowed. In a cubic lattice, a propagating chain has five paths to follow; however, the chain cannot follow the path that is normal to the surface. The loss of one out of five possible trajectories causes a net entropic change of $k_B\ln(1/5)$ or a free energy penalty of about $0.5k_BT$ for chain backbone units to locate at a surface.[18,20,21] End groups do not suffer this entropy loss and are therefore driven preferentially to the surface, even in the absence of surface energy effects (i.e., when $\chi_s = 0$).

The concentration depth profiles for repulsive end groups (Figure 2c) also show two regions of behavior: depletion in the first lattice layer and enrichment for deeper layers with the magnitude of enrichment decreasing with depth. The magnitude of surface depletion increases with increasing χ_s.

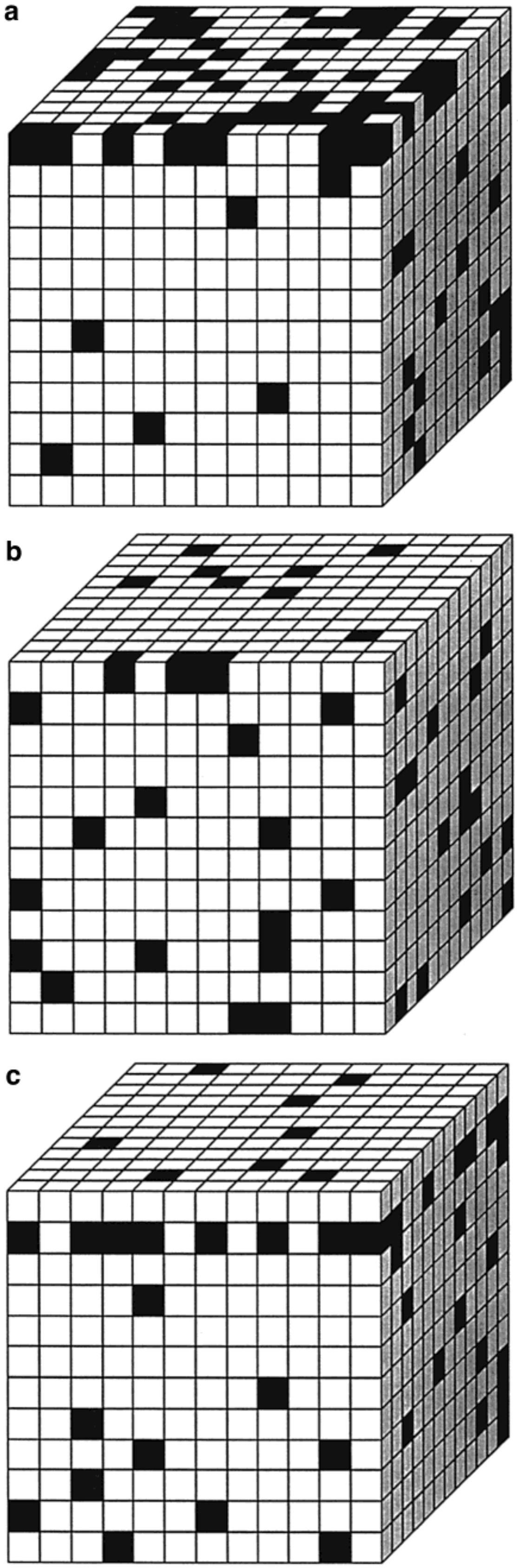

Figure 1. Schematic representation of functional polymer chains configured on a cubic lattice. The darker cubes indicate a lattice site occupied by a functional end group, and the lighter cubes are occupied by polymer chain segments. Part a illustrates a chain with a low-energy attractive end group, part b depicts a nonfunctional polymer with neutral end groups, and part c shows the configuration of a polymer with high-energy repulsive end groups.

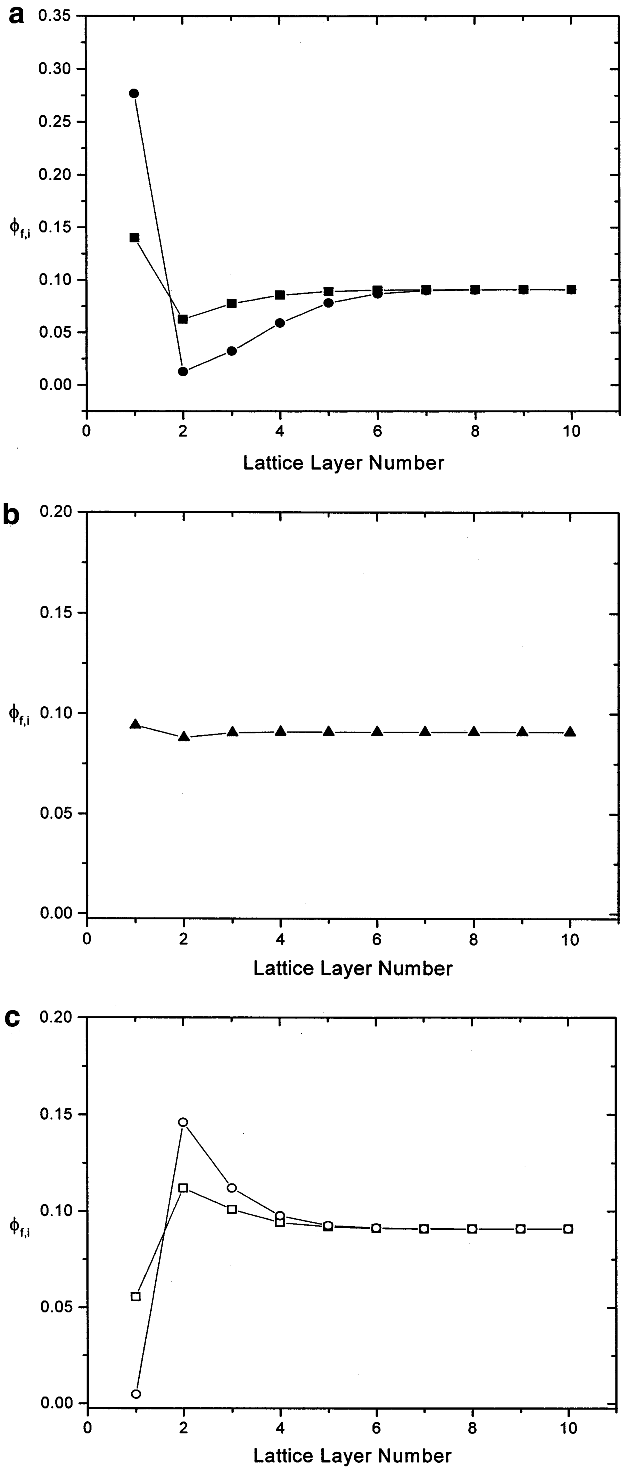

Figure 2. Functional group volume fraction for α-functional polymers with $r = 11$ as a function of the lattice layer number, i, for various values of the surface interaction parameter: (a) $\chi_s = -4$ (filled circles), -1 (filled squares); (b) 0 (filled triangles); (c) 1 (open squares), 4 (open circles).

The effects of chain length are illustrated in Figure 3. The depth of the initial zone of enrichment or depletion associated with the direct surface interaction is always confined to the first lattice layer, consistent with the concept of screening. Interactions between lattice sites are screened over distances larger than the screening length, equal to the statistical segment length for bulk polymers. Because the lattice size is roughly equivalent to the statistical segment length, screening is expected for distances greater than one lattice layer.

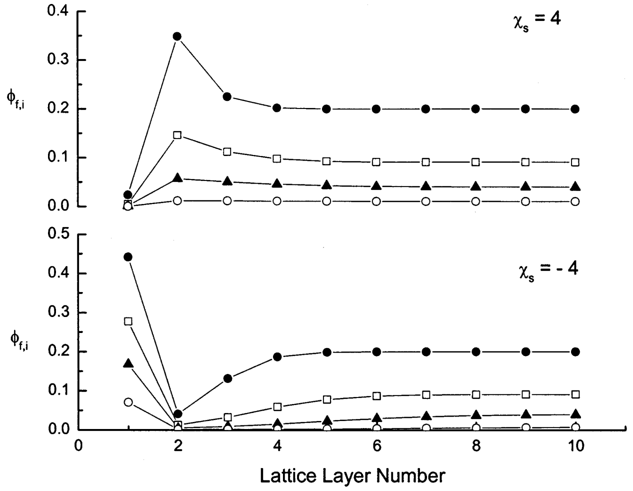

Figure 3. Functional group surface composition–depth profiles for α-functional polymers with $\chi_s = -4$ (bottom) and $\chi_s = 4$ (top) for four different values of r: $r = 5$ (filled circles), $r = 11$ (open squares), $r = 25$ (filled triangles), and $r = 101$ (open circles).

Table 1. Regression Parameters for Interpolation Formulas

chain length, r	$a_0(r)$	$a_1(r)$	$a_2(r)$
5	0.202 79	−0.048 10	0.001 92
7	0.146 94	−0.040 50	0.002 29
11	0.095 93	−0.031 57	0.002 39
15	0.071 76	−0.026 42	0.002 29
25	0.044 73	−0.019 62	0.002 01
51	0.023 12	−0.012 85	0.001 55
101	0.012 24	−0.008 51	0.001 15
201	0.006 39	−0.005 59	0.000 83

The depths of the depletion or enrichment gradients that follow scale with the chain dimensions, because chain connectivity dictates that the overall composition must equal that of the bulk when integrated over a depth corresponding to the size of an individual chain.

Theodorou[18] studied α-functional polymers with an attractive end group for χ_s values within the range $-5 \le \chi_s \le -33$. The reported reduced concentration depth profiles show essentially complete depletion in several lattice layers due to the extremely large χ_s values used and therefore differ significantly in appearance from the profiles presented here for much lower χ_s values.

Calculated end group surface volume fractions, $\phi_{f,1}$, for α-functional polymers are a function of chain length and surface interaction parameter, and this dependence can be conveniently expressed through the following interpolation formula[20]

$$\phi_{f,1} = a_0(r) + a_1(r)\chi_s + a_2(r)\chi_s^{\,2} \qquad (3)$$

wherein the chain-length-dependent regression coefficients are given in Table 1.

The surface tension can be calculated from the following group contribution relationship developed previously for α,ω-functional polymers using $\phi_{f,1}$ values estimated from (3)

$$\gamma = \gamma_f\phi_{f,1} + \gamma_r(1 - \phi_{f,1}) \qquad (4)$$

If not known, the surface energies of the functional group, γ_f, and repeat units, γ_r, required in (4) may be calculated by group contribution methods.

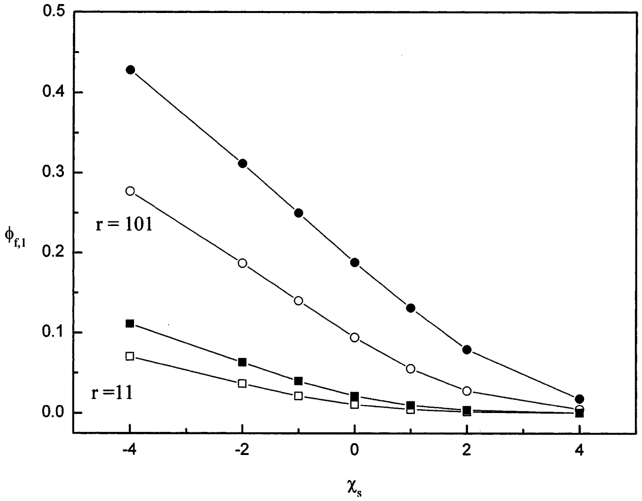

Figure 4. Dependence of functional group surface fraction on χ_s for two different chain lengths ($r = 101$, circles; $r = 11$, squares) and two different architectures: an α-functional polymer (filled circles or squares) and an α,ω-functional polymer (open circles or squares).

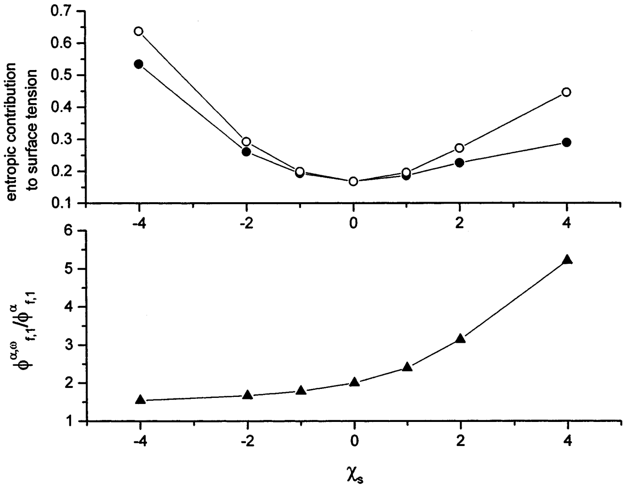

Figure 5. Influence of χ_s on the entropic contribution to surface tension for α-functional (filled circles) and α,ω-functional polymers (open circles) and the ratio of functional group surface concentrations (triangles) for the two architectures.

The influence of the number of functional groups on surface properties can be evidenced by comparing the behavior for the two functional polymers with the simplest chain architectures: α,ω-functional and α-functional polymers. The surface concentrations for α,ω-functional and α-functional polymers are compared directly in Figure 4 for two different chain lengths. The functional end group surface composition for the α,ω-functional polymer, $\phi^{\alpha,\omega}_{f,1}$, and the corresponding α-functional polymer, $\phi^{\alpha}_{f,1}$, generally do not differ by a factor of 2 (see also the ratio of surface compositions in Figure 5), as would be expected from stoichiometric considerations. Deviations from stoichiometric behavior occur because entropic and enthalpic effects become coupled for functional polymers as a result of chain connectivity. That is, surface segregation of end groups requires reorientation of the chain backbone and a commensurate loss in configurational entropy. Deviations from stoichiometric behavior increase with decrease in molecular weight as configurational constraints become more severe. Stoichimetric behavior is found in the limit of infinite molecular weight where configurational effects vanish and surface segregation behavior reduces to that of an ideal gas mixture.[22]

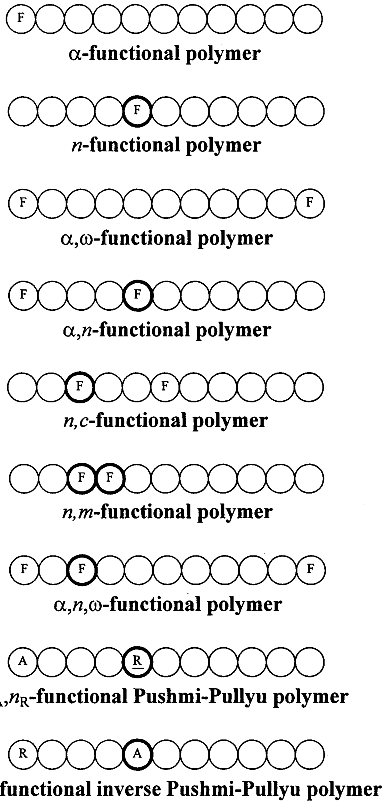

Figure 6. Functional polymer architectures. Circles represent polymer repeat units with the letter F indicating the position of a functional group (attractive functional groups are indicated by the letter A and repulsive groups are indicated by the letter R). Functional groups denoted with a bold circle are located at the *n*th or *m*th repeat unit along the chain.

The influence of the surface interaction parameter on configurational entropy effects is illustrated in Figure 5, which shows the relationship between the entropic contribution to surface tension and the ratio of surface functional group concentration for α-functional and α,ω-functional polymers. When χ_s is negative (i.e., attractive functional groups), the ratio of the surface concentrations of functional groups is less than 2 because the entropic contribution to surface tension is higher for the α,ω-functional polymer. When χ_s equals zero, the ratio of surface concentrations is exactly two because the entropic contribution to surface tension is the same for both the α,ω-functional and α-functional polymers. When χ_s is positive (i.e., repulsive functional groups), the ratio of surface concentrations is much greater than two because the entropic contribution to surface tension is again greater for the α,ω-functional polymer. In the case where high-energy reactive functional groups (i.e., repulsive functional groups) are desired at a surface, the effects of entropic constraints may be beneficial because they oppose the segregation of repulsive functional groups away from the interface and lead to a higher surface concentration.

Optimizing Functional Polymer Chain Architecture. The functional chain architectures depicted schematically in Figure 6 were studied in order to determine which architecture provided optimal surface properties for various applications. The architectures investigated include α-terminated and α,ω-terminated end-functional polymers, *n*-functional polymers where a functional group is located at the *n*th repeat unit along the backbone of the polymer chain, *n,c*-functional polymers with one functional group at the *n*th repeat unit and a second functional group at the center of the chain, polymers with functional groups located both at the chain ends and at the *n*th repeat unit along the chain backbone (α,n-functional and α,n,ω-functional polymers), polymers with adjacent functional groups located at sequential positions *n* and *m* along the chain backbone (*n,m*-functional polymers), and "Pushmi-Pullyu" polymers containing an attractive functional group of type A and a repulsive functional group of type R located along the same chain.

The two-headed llama named Pushmi-Pullyu featured in the Dr. Dolittle series of children's novels[24] provided the inspiration for designating the latter architecture. The two-headed llama provides a vivid visual illustration of how conflict and cooperativity affect the surface segregation problem. When the llama wants to move, a cooperative decision for one head to pull and the other head to push is required. Stagnation results when both heads attempt to push or pull at the same time. The intrinsic conflict or cooperation embodied in the Pushmi-Pullyu llama reflects the behavior of a functional polymer that contains both repulsive and attractive functional groups. The question to be addressed is whether the Pushmi-Pullyu mechanism can be employed to enhance the magnitude of functional group surface segregation in functional polymers.

Herein we will adopt the convention that group A is an attractive functional group with surface tension lower than that of the chain backbone (i.e., $\chi_s < 0$) and group R is a repulsive functional group with surface tension higher than that of the chain backbone (i.e., $\chi_s > 0$). The convention is applied by subscripting the position variable either with the letter A or R depending upon the type of group resident at that location. Pushmi-Pullyu polymers, for example, are either α_A,n_R-functional Pushmi-Pullyu polymers with a low-energy end group and a high-energy functional group located along the chain or α_R,n_A-functional inverse Pushmi-Pullyu polymers with a high-energy end group and a low-energy functional group located along the chain. When functional polymers contain both repulsive and attractive functional groups, a similar convention is applied to label volume fractions. For example, $\phi_{A,1}$ is the volume fraction of attractive functional groups in the first lattice layer and $\phi_{A,b}$ is the bulk average volume fraction of attractive groups.

Optimizing Chain Architecture for Release Properties. In applications where release properties are important, it is desirable to maximize the surface concentration of attractive functional groups, thereby minimizing the surface tension. The optimization of chain architecture for this case is straightforward: one chooses a chain architecture that provides the highest concentration of attractive functional groups within the first lattice layer.

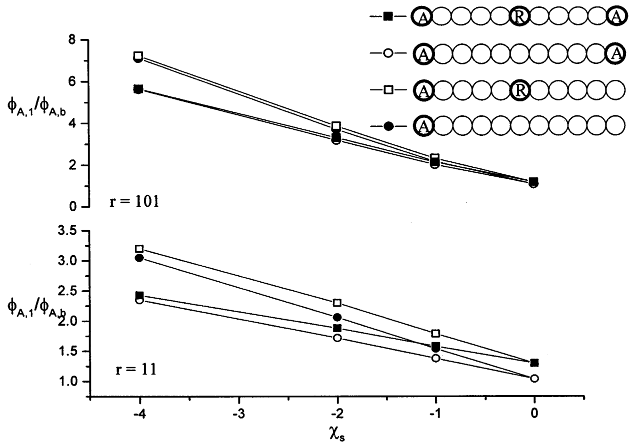

Figure 7. Effect of χ_s on the relative surface enrichment of attractive end groups for four different architectures: an α-functional polymer with one attractive end group (filled circles), an α,ω-functional polymer with two attractive end groups (open circles), an α_A,n_R-functional Pushmi-Pullyu polymer with one attractive end group and one repulsive functional group ($\chi_s = 4$) located at the center (i.e., $n = r/2$) of the polymer (open squares), and an α_A,n_R,ω_A-functional Pushmi-Pullyu polymer with two attractive end groups and one repulsive group ($\chi_s = 4$) located at the center of the polymer chain (filled squares). The inset illustrates each chain structure with A representing an attractive group and R representing a repulsive group.

The number and nature of attractive functional groups can greatly affect their surface concentration and thus the surface properties of the polymer. Figure 7 shows the relative enrichment of attractive functional end groups as a function of their surface interaction parameter for two chain lengths ($r = 11$ or $r = 101$) and four different chain architectures: an α-functional polymer with an attractive end group, an α_A,n_R-functional Pushmi-Pullyu polymer with one attractive end group and one repulsive group ($\chi_s = 4$) located at the center of the polymer (i.e., $n = r/2$), an α,ω-functional polymer with two attractive end groups, and an α_A,n_R,ω_A-functional Pushmi-Pullyu polymer with two attractive end groups and one repulsive group ($\chi_s = 4$) located at the center of the polymer chain. The relative surface enrichment defined as the surface concentration of attractive functional groups, $\phi_{A,1}$, divided by their bulk concentration, $\phi_{A,b}$. For all four architectures, the relative enrichment increases with chain length, even though the bulk concentration scales inversely with molecular weight. When a repulsive functional group is placed at the center of a chain with one attractive functional end group, both the surface concentration and relative enrichment of the attractive functional groups increase, thus validating the Pushmi-Pullyu mechanism for the α_A,n_R-functional Pushmi-Pullyu polymer. The α_A,n_R,ω_A-functional Pushmi-Pullyu architecture is also effective in enhancing the surface segregation of attractive functional groups for the polymers. Both Pushmi-Pullyu architectures bring about an increase in surface segregation when compared to the corresponding end-functional control polymers.

The surface concentration of attractive functional groups and the surface composition−depth profile are dependent upon the location of the attractive functional group along the chain backbone. The effect of location for a single attractive functional group is illustrated in Figure 8. The surface concentration of functional groups is highest when the functional group is placed at either chain end and lowest when it is located at the chain center. Location of attractive functional groups at the chain ends is optimal because both the enthalpic factors associated with surface tension reduction and entropic factors associated with configurational entropy losses favor segregation of the chain ends to the surface.

Figure 9 compares the surface concentration of attractive functional groups obtained for four architec-

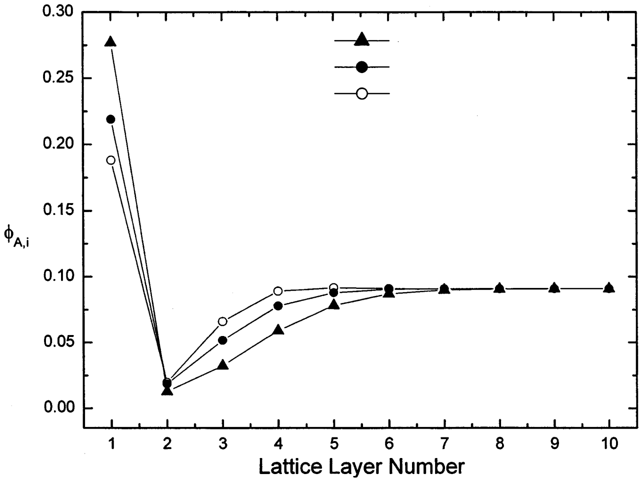

Figure 8. Surface composition−depth profiles for *n*-functional polymers with one attractive functional group for $\chi_s = -4$ and $r = 11$. $n = 1$ (filled triangles), $n = 3$ (filled circles), $n = 5$ (open circles). The inset illustrates each chain structure with A representing an attractive group.

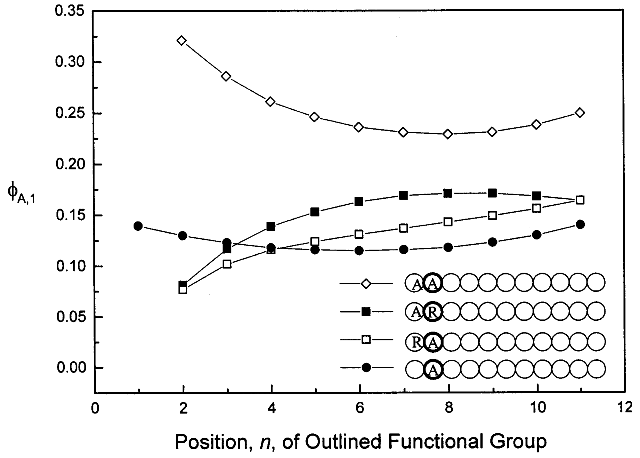

Figure 9. Surface volume fraction of attractive functional groups as a function of the position, *n*, of a midchain group (denoted by bold circles on the figure inset) for four different architectures with $r = 11$: α,n-functional polymer with two attractive functional groups (open diamonds); α_A,n_R-functional Pushmi-Pullyu polymer with an attractive functional end group and a repulsive functional group at position *n* (filled squares); α_R,n_A-functional inverse Pushmi-Pullyu polymer with a repulsive functional end group and an attractive functional group at position *n* (open squares); *n*-functional polymer with one attractive functional group at position *n* (filled circles). The attractive functional groups have $\chi_s = -1$, and the repulsive functional groups have $\chi_s = 4$. The inset illustrates each chain structure with A representing an attractive group and R representing a repulsive group.

tures: α,n-functional polymer with two attractive functional groups, α_A,n_R-functional Pushmi-Pullyu polymer with an attractive functional end group and a repulsive functional group located at position *n*, α_R,n_A-functional inverse Pushmi-Pullyu polymer with a repulsive functional end group and an attractive functional group located at position *n*, and *n*-functional polymer with one attractive functional group located at position *n*. The abscissa on the plot denotes the position, *n*, of the functional groups indicated by the bold circles in the figure inset.

Both the Pushmi-Pullyu and the inverse Pushmi-Pullyu architectures are more effective than the *n*-functional control when the two opposing functional groups are separated by more than 3−4 segments along the chain. When functional groups of opposing energies are well separated, the repulsive functional groups prefer to locate in the bulk and, in so doing, convey adjacently connected polymer chain segments away from the surface. Movement of the repulsive functional groups and connected chain segments away from the surface generates an additional convective driving force for polymer chain segments connected to attractive functional groups to segregate to the surface. Adjacency of opposing functional groups is detrimental, because adjacent repulsive functional groups are carried along when attractive functional groups adsorb at the surface and cause an elevation in the overall surface energy. The α_A,n_R-functional Pushmi-Pullyu architecture is generally more efficient than its inverse α_R,n_A-functional counterpart, because the favored location of low surface tension attractive functional groups is always at the chain end.

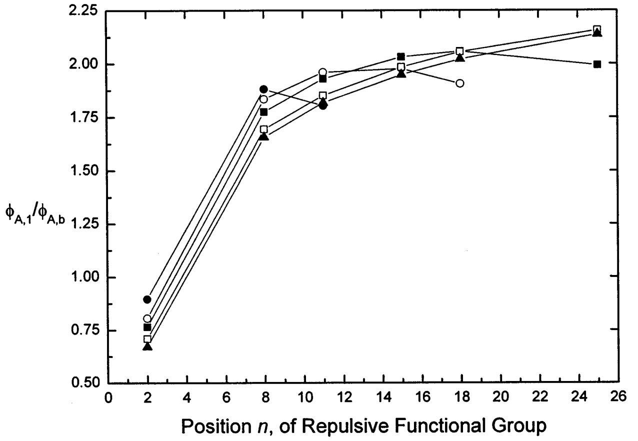

Figure 10. Relative enrichment of attractive functional groups as a function of the position, *n*, of repulsive functional group for α_A,n_R-functional Pushmi-Pullyu polymers with five different chain lengths: $r = 11$ (filled circles), 18 (open circles), 25 (filled squares), 51 (open squares), and 101 (filled triangles). The repulsive groups have $\chi_s = 4$, and the attractive groups have $\chi_s = -1$.

The optimal placement of the repulsive functional group for α_A,n_R-functional Pushmi-Pullyu polymers depends on molecular weight, as illustrated in Figure 10. There exists a maximum in the relative enrichment at a specific location of the repulsive functional group that differs for each chain length. For all chain lengths, the optimum position of the repulsive functional group is approximately 3*r*/4 when the attractive functional group is located at the α-terminus.

The Pushmi-Pullyu and inverse Pushmi-Pullyu architectures are more efficient at increasing the surface concentration of attractive functional groups than the α-functional architecture; however, when evaluating the effectiveness of various architectures, it is important to perform any comparisons at equal total number of functional groups. When this is done, it is clear that the optimal surface segregation for polymers containing two functional groups occurs when both functional groups are attractive, as shown in Figure 9. Regardless of the position of the second attractive functional group, the surface concentration of attractive functional groups for this architecture always exceeds that of any of the Pushmi-Pullyu architectures. A chain architecture wherein both attractive functional groups are adjacent to each other at one end of the polymer chain provides

Table 2. Comparison of Overall Surface Enrichment and Enrichment of Each Attractive Functional Group for Adjacent End-Functional Polymer Architectures[a]

	relative enrichment			
architecture	overall	1st group	2nd group	3rd group
A−P	2.60	2.60		
A−P−A	2.19	1.095	1.095	
A_2−P	3.73	1.89	1.84	
A_2−P−A	3.78	1.12	1.10	0.56
A_3−P	4.43	1.50	1.52	1.41

[a] The chain length, *r*, is 25, and the attractive functional groups, A, have a χ_s of −2.

for the highest degree of surface segregation and should exhibit the best overall release properties for a polymer containing two functional groups.

The effect of adjacency on the surface segregation of attractive functional groups is examined more thoroughly in Table 2. Surface segregation predictions are compared for four different chain architectures: an α,ω-functional polymer with two attractive functional end groups, A−P−A; a polymer with two adjacent attractive functional groups at one chain end, A_2−P; a polymer with two adjacent attractive functional groups at one chain end and a third attractive functional group at the other end, A_2−P−A; and a polymer with three adjacent attractive functional groups at one chain end, A_3−P. For all chain architectures considered in Table 2, the chain length, *r*, is set to 25, and the attractive functional groups are characterized by a value of $\chi_s = -2$. The table reports the relative enrichment of each individual functional group, defined by the concentration of each functional group in the first lattice layer divided by the bulk concentration of all functional groups, as well as the overall enrichment.

The A_3−P chain design exhibits the highest degree of surface partitioning for attractive functional groups. A comparison of the A_2−P and A−P−A architectures reveals that functional group adjacency enhances the segregation of attractive functional groups due to chain connectivity effects. That is, the A_2−P chain architecture is more effective at bringing attractive functional groups to the surface because it is more probable for an adjacent group to reside at the surface when the end group is already absorbed there. In fact, the data in Table 2 show that the surface composition of the second functional group is almost identical to that of the first group. This result suggests that the conditional probability for the second functional group to locate in the first lattice layer if the adjacent chain end is also located there is close to unity. In the case of the A_3−P polymer, the surface concentrations of all three attractive functional groups are nearly identical, illustrating the extreme effectiveness of adjacency in driving surface segregation.

The functional group concentrations in the first layer are nearly equivalent for the A_2−P and A_2−P−A architectures. The addition of the second functional end group in the A_2−P−A architecture is not effective due to the effects of configurational constraints discussed earlier for α,ω-functional polymers; only a minimal increase in the surface volume fraction is observed.

The data represented in Table 2 clearly show that functional group adjacency is the most effective architectural variant for promoting surface enrichment of attractive functional groups. For a fixed number of attractive functional groups, the optimal chain architecture for creating release surfaces is a polymer with all of the functional groups located adjacent to each other at the chain end.

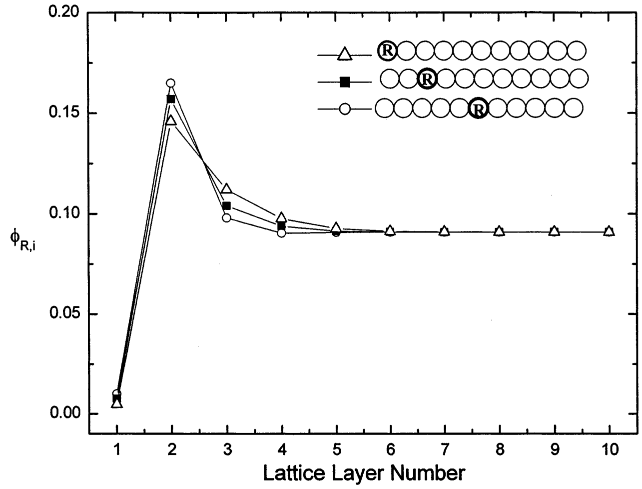

Figure 11. Volume fraction of repulsive functional groups with $\chi_s = 4$ as a function of the lattice layer number *i* for three different locations of the functional group along a *n*-functional polymer of length, $r = 11$. $n = 1$ (open triangles); $n = 3$ (filled squares); $n = 6$ (open circles).

Optimizing Chain Architecture for Adhesive Properties. It is not immediately obvious how to optimize chain architecture for applications requiring an adhesive or reactive surface, because the functional groups required to create these types of surfaces normally have higher surface energies than the polymer backbone and therefore are naturally depleted from the surface. In this case, the criteria for optimization depend on how the surface will be utilized. In practice, an adhesive or reactive surface will be placed against some other substrate. Upon contact with a substrate, the value of χ_s changes instantaneously, and the functional polymer interface reorganizes in an attempt to reach a new equilibrium with the substrate.

In previous experiments,[25,26] we have shown that the surface of functional polymers can reorganize in this fashion even in the glassy state. The importance of reorganization is that functional groups below the surface can still be active in terms of performance. Although repulsive functional groups are repelled from the first lattice layer, groups located in the second layer and perhaps even deeper can reorganize to relocate to the newly formed interface with the contacting substrate. Our preliminary results demonstrate that molecular motion over length scales equivalent to only one or two lattice layers is sufficient to bring about an almost complete reconstruction of the interface.

The fact that surfaces can reorganize provides the basis for a practical metric that can be applied to optimize polymer architecture for adhesive and reactive surfaces. Adhesive/reactive surface character can be optimized by maximizing the concentration of repulsive functional groups in the second lattice layer under the assumption that the polymer will reorganize when in contact with the substrate of interest. Since the concentration of repulsive groups in the first lattice layer is very low, we neglect this factor and use the concentration of repulsive groups in the second lattice layer herein to judge the efficacies of functional polymer architectures in fabricating adhesive and reactive polymer surfaces.

The influence of functional group location on the surface structure of *n*-functional polymers with repulsive functional groups is illustrated in Figure 11. The

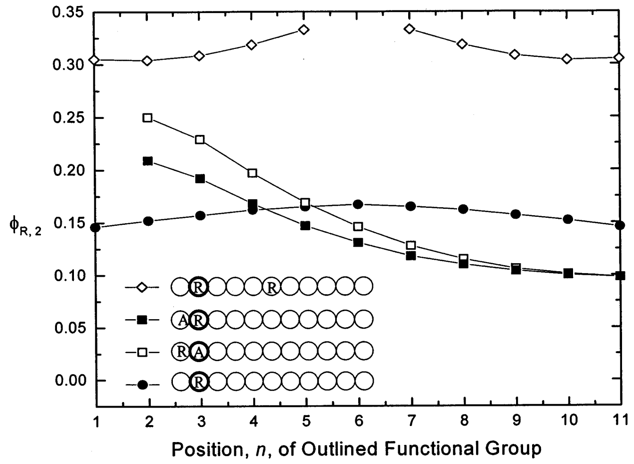

Figure 12. Volume fraction of repulsive functional groups within the second lattice as a function of the position, *n*, of a midchain group (denoted by bold circles on the figure inset) for four different architectures: an n_R,c_R-functional polymer with two repulsive functional groups (open diamonds); α_A,n_R-functional Pushmi-Pullyu polymer with an attractive functional end group and a repulsive functional group at position *n* (filled squares); α_R,n_A-functional inverse Pushmi-Pullyu polymer with a repulsive functional end group and an attractive functional group at position *n* (open squares); an *n*-functional polymer with one repulsive functional group (filled circles). The attractive functional groups have $\chi_s = -1$, and the repulsive functional groups have $\chi_s = 4$.

repulsive case is similar to the attractive case discussed previously in that two regions of behavior exist; however, the general trends are reversed. The functional group fraction in the first lattice layer is depleted from that in the bulk. For a given chain length, the depletion increases with χ_s. Following this depletion, there is an enhancement of repulsive functional groups in subsequent layers so as to conserve the total number of functional groups in the interfacial layer. The width of the interfacial layer scales with the chain length, and the surface interaction is confined to the first lattice layer. More complicated architectures with repulsive functional groups follow the same basic trends that are exhibited by the simpler end-functional polymers.

The optimal position for a single repulsive functional group on a polymer chain is at the center of the polymer chain, for which the repulsive functional group concentration is highest in the second layer. The strategy for creating optimal adhesive interfaces is thus exactly opposite that for creating release surfaces. Optimal adhesive surfaces are obtained by maximizing configurational constraints that act upon repulsive functional groups. The center-functional architecture, which we will refer to as a *c*-functional polymer, is most effective because that segment is more constrained from moving away from the interface.

Figure 12 compares the concentration of repulsive functional groups in the second lattice layer obtained for four architectures: a *n*,*c*-functional polymer with one repulsive functional group located at position *n* along the polymer backbone and a second repulsive functional group at the center of the polymer; an α_A,n_R-functional Pushmi-Pullyu architecture with a repulsive functional group located at position *n* and an attractive functional end group; an α_R,n_A-functional inverse Pushmi-Pullyu polymer with an attractive functional group at position *n* and a repulsive functional end group; a *n*-functional polymer control with one repulsive functional end group located at position *n*.

The Pushmi-Pullyu architectures are only more effective than the *n*-functional control when the opposing functional groups are adjacent on the chain or are near neighbors. In this case, the tendency for the neighboring attractive functional group to locate in the first lattice layer helps to carry the repulsive group to the second lattice layer. The inverse Pushmi-Pullyu architecture is more efficient in creating adhesive surfaces than the Pushmi-Pullyu architecture, just the opposite of what was found for release surfaces. If two functional groups are to be placed along the polymer chain, however, the most efficient architecture is the *n*,*c*-functional polymer with two repulsive groups. Adjacency of functional groups is the most effective means to optimize surface segregation for adhesive applications, similar to what was found for the case of optimizing release surfaces. In contrast, however, the optimal functional polymer architecture for creating adhesive surfaces is a functional polymer with adjacent repulsive functional groups located at the center of the polymer chain.

Summary

The effects of chain architecture on the surface properties and structure of functional polymers are investigated through self-consistent lattice model calculations. Functional group concentration depth profiles show similar qualitative behavior for all of the architectures studied. In the case of functional groups with surface tensions lower than the chain backbone, the depth profile exhibits functional group enrichment only for the first lattice layer. The second lattice shows maximum depletion of functional groups while the concentration in deeper layers gradually recovers to the bulk value over a distance that is roughly equivalent to the chain dimensions. Functional groups with surface tensions greater than that of the chain backbone are depleted from the first lattice layer and are in excess in the second lattice layer. The excess decays in deeper layers until the bulk concentration is recovered at a depth equivalent to the size of the polymer chain.

The lattice calculations are employed to explore the effectiveness of a variety of functional polymer architectures to produce surfaces with either release or adhesive properties. The optimal architecture for release applications is a functional polymer with several low surface energy functional groups located at one chain end. The optimal structure for an adhesive surface is obtained when high surface energy reactive functional groups are placed adjacently at the center of the polymer chain. Optimal architectures arise in functional polymers as a result of configurational constraints that are associated with the coupling of entropic and enthalpic contributions to the free energy.

Acknowledgment. This material is based upon work supported by, or in part by, the U.S. Army Research Office under Contract/Grant DAAD19-001-0104 and the National Science Foundation Polymer Program under Grant DMR-98-09687.

Appendix

The self-consistent lattice model determines the reduced free segment probabilities for the functional group, $p_{f,i}$, and the repeat unit segments, $p_{r,i}$, in each layer, *i*. The reduced free segment probability is defined as the probability that a particular segment in a conformation *c* locates in layer *i* with respect to the unconstrained bulk. The free segment probability for the functional group in the first layer is given by[17]

$$p_{\mathrm{f},1} = p_{\mathrm{r},1} \exp\left[(\chi_{\mathrm{s}} + \lambda_1\chi) + 2\chi\left(\lambda_0\phi_{\mathrm{f},1} + \lambda_1\phi_{\mathrm{f},2} - \frac{N}{r}\right)\right] \tag{A-1}$$

where $\phi_{j,i}$ is the volume fraction of component j in layer i, $\lambda_0 = {}^2/_3$ is the probability that segments are connected within the same layer and $\lambda_1 = {}^1/_6$ is the probability that segments are connected to a layer lying either above or below that layer i. For layers 2 through $M - 1$, the free segment probability is

$$p_{\mathrm{f},i} = p_{\mathrm{r},i} \exp\left[2\chi\left(\lambda_1\phi_{\mathrm{f},i-1} + \lambda_0\phi_{\mathrm{f},i} + \lambda_1\phi_{\mathrm{f},i+1} - \frac{N}{r}\right)\right] \quad 1 < i < M \tag{A-2}$$

The free segment probability for the center layer is

$$p_{\mathrm{f},M} = p_{\mathrm{r},M} \exp\left[2\chi\left(\lambda_1\phi_{\mathrm{f},M-1} + (\lambda_0 + \lambda_1)\phi_{\mathrm{f},M} - \frac{N}{r}\right)\right] \tag{A-3}$$

The volume fraction of repeat units and functional group in each layer are

$$\phi_{\mathrm{f},i}p_{\mathrm{f},i} = \frac{1}{r}\sum_{s=1}^{r}\delta_{\mathrm{f}(t(s))}p^{+}(i,s)\,p^{-}(i,r-s+1) \quad 1 \le i \le M \tag{A-4}$$

$$(1 - \phi_{\mathrm{f},i})p_{\mathrm{r},i} = \frac{1}{r}\sum_{s=1}^{r}\delta_{\mathrm{r}(t(s))}p^{+}(i,s)\,p^{-}(i,r-s+1) \quad 1 \le i \le M \tag{A-5}$$

Two end segment probabilities must be considered for asymmetric chain architectures. $p^{+}(i,s)$ is the probability that end segments of a subchain of s segments will lie in layer i taken in the positive direction, from the left chain end to the right. $p^{-}(i,s)$ is the end segment probability for an s-segment subchain in the negative direction, taken from the right chain end to the left. $p^{+}(i,s)$ and $p^{-}(i,s)$ are calculated from

$$p^{+}(i,s) = \sum_{j}\lambda_{j-i}\, p_{\mathrm{t}(s)i}p^{+}(j,s-1) \quad 2 \le s \le r \tag{A-6}$$

$$p^{-}(i,s) = \sum_{j}\lambda_{j-i}\, p_{\mathrm{t}(s)i}p^{-}(j,s-1) \quad 2 \le s \le r \tag{A-7}$$

where $p_{\mathrm{t}(s)i}$ is the free segment probability for a type s segment in layer i.

A total segment balance yields the relation

$$\phi_{a,i}p_{a,i} + (1 - \phi_{a,i})p_{b,i} = \frac{1}{r}\sum_{s=1}^{r}p^{+}(i,s)\,p^{-}(i,r-s+1) \quad 1 < i < M \tag{A-8}$$

Using the incompressibility constraint and eq A6, the total segment balance becomes

$$1 - \frac{1}{p_{\mathrm{a,i}}\mathrm{r}}\sum_{s=1}^{r}p^{+}(i,s)\,p^{-}(i,s) - \frac{1}{p_{\mathrm{b,i}}\mathrm{r}}\sum_{s=1}^{r}p^{+}(i,s)\,p^{-}(i,s) = 0 \tag{A-9}$$

This set of M simultaneous equations is solved with the IMSL subroutine, DNEQNF, starting with an initial guess for the free segment probability of the repeat unit ($p_{\mathrm{r}i}$ = 1.2, 1.1, 1, 1, 1, ...). Segment densities in every layer are then calculated using (A-6) and (A-7).

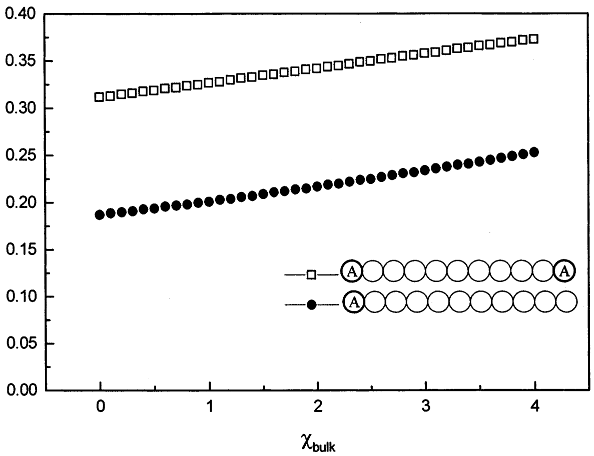

Figure 13. Volume fraction of attractive functional groups with $\chi_{\mathrm{s}} = -2$ in the first lattice layer vs the bulk interaction parameter, χ_{bulk}, for two different chain architectures: α-functional (filled circles) and α,ω-functional polymers (open squares).

For calculations with a finite bulk interaction parameter, χ, a zero-order continuation scheme in χ was implemented to solve for the free segment probabilities. Calculations for a given chain length and χ_{s} were started with the bulk interaction parameter set to zero and then proceeded to progressively increasing values of χ using the solution obtained in each case as an initial guess for the next one. A step size of $\Delta\chi = 0.1$ proved adequate for computations up to high values of χ.

The effects of including these bulk interactions on the degree of surface segregation for attractive functional groups are examined in Figure 13. As χ_{bulk} increases, the degree of surface segregation increases linearly for both α-functional and α,ω-functional polymer. The qualitative nature of surface segregation, however, is not altered when bulk interactions are included in the calculation.

References and Notes

(1) Rastogi, A. K.; St. Pierre, L. E. *J. Colloid Interface Sci.* **1969**, *31*, 168; *J. Colloid Interface Sci.* **1971**, *35*, 16.
(2) Wu, S. *Polymer Interfaces and Adhesion*, 1st ed.; Marcel Dekker: New York, 1982.
(3) Pan, D. H.; Prest, W. M. J. *J. Appl. Phys.* **1985**, *58*, 2861.
(4) Bhatia, Q. S.; Pan, D. H.; Koberstein, J. T. *Macromolecules* **1988**, *21*, 2166.
(5) Schmitt, R. L.; Gardella, J. A., Jr.; Magill, J. H.; Salvati, L., Jr. *Macromolecules* **1985**, *18*, 2675.
(6) Gaines, G. L., Jr. *J. Chem. Phys.* **1969**, *73*, 3143.
(7) Elman, J. F.; Johs, B. D.; Long, T. E.; Koberstein, J. T. *Macromolecules* **1994**, *27*, 5341.
(8) Jalbert, C.; Yilgor, I.; Gallagher, P.; Krukonis, V.; Koberstein, J. *Macromolecules* **1993**, *26*, 3069.
(9) Jalbert, C.; Balaji, R.; Bhatia, Q.; Salvati, L.; Yilgor, I.; Koberstein, J. *Macromolecules* **1994**, *27*, 2409.
(10) Hunt, M. O. J.; Belu, A. M.; Linton, R. W.; DeSimone, J. M. *Macromolecules* **1993**, *26*, 4854.
(11) Affrossman, S.; Hartshorne, M.; Kiff, T.; Pethrick, R. A.; Richards, R. W. *Macromolecules* **1994**, *27*, 1588.
(12) Hopkinson, I.; Kiff, F. T.; Richards, R. W.; Bucknall, D. G.; Clough, A. S. *Polymer* **1997**, *38*, 87.
(13) Schaub, T. F.; Kellogg, G. J.; Mayes, A. M.; Kulasekere, R.; Anker, J. F.; Kaiser, H. *Macromolecules* **1996**, *29*, 3982.

(14) Su, Z.; Wu, D.; Hsu, S. L.; McCarthy, T. J. *Macromolecules* **1997**, *30*, 840.

(15) O'Rourke Muisener, P. A. V.; Yuan, C.; Jalbert, C.; Baetzold, J.; Mason, R.; Wong, D.; Kim, Y. J.; Elman, J. F.; Koberstein, J. T.; Gunesin, B. *Macromolecules*, submitted for publication.

(16) Mason, R.; Jalbert, C.; O'Rourke Muisener, P. A. V.; Koberstein, J. T. *Adv. Colloids Interface Sci.*, in press.

(17) Theodorou, D. N. *Macromolecules* **1988**, *21*, 1411.

(18) Theodorou, D. N. *Macromolecules* **1988**, *21*, 1422.

(19) Scheutjens, J. M. M. H.; Fleer, G. J. *J. Phys. Chem.* **1979**, *83*, 1619.

(20) Jalbert, C.; Koberstein, J. T. ; Hariharan, A.; Kumar, S. K. *Macromolecules* **1997**, *30*, 4481.

(21) Kumar, S. K.; Vacatello, M.; Yoon, D. *Macromolecules* **1990**, *23*, 2189.

(22) Hariharan, A. H.; Kumar, S. K.; Russell, T. P. *Macromolecules* **1990**, *23*, 3584.

(23) Hariharan, A. H.; Kumar, S. K.; Russell, T. P. *Macromolecules* **1991**, *24*, 4909.

(24) Lofting, H. *Doctor Dolittle's Circus*; Lippincott: Philadelphia, 1952.

(25) Koberstein, J. T. *MRS Bull.* **1996**, *21*, 16.

(26) Jalbert, C. Ph.D. Dissertation, University of Connecticut, 1993.

MA011969Q