HIGHLIGHT

Molecular Design of Functional Polymer Surfaces

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Received 5 March 2004; Revised 5 May 2004; Accepted 8 May 2004
DOI: 10.1002/polb.20157

ABSTRACT: Three design principles are presented that allow for the molecular design of functional polymer surfaces: surface segregation, surface structure, and surface reorganization. These design principles are illustrated by a description of the behavior of model end-functional polymers that accurately reflect the general behavior of essentially all possible linear functional polymer architectures. Several applications of the design principles are described to show how they may be used to provide molecular engineering solutions for problems of practical interest. The applications include the optimization of functional polymer architectures for producing adhesive and release surfaces, the suppression of dewetting by the use of functional additives to lower the surface tension of a coating, and the creation of smart polymer surfaces with selective adhesion properties. © 2004 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 42: 2942–2956, 2004

Keywords: surfaces; interfaces; ESCA/XPS; functionalization of polymers

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INTRODUCTION

It is rare for both bulk and surface properties required for a particular polymer application to be obtained through a single polymer processing operation or with a single polymeric material. Today's polymers are complex formulations that may contain several different polymers, stabilization and processing additives, extenders, and fillers. Current polymer processing operations now routinely employ sophisticated concepts such as dynamic vulcanization, phase inversion, *in situ* grafting, and reactive blending to achieve bulk properties that fit the needs of virtually any application. The nature of the materials is simply too complex to allow for the simultaneous optimization of bulk and surface properties. Postprocessing modification of polymer surfaces has, therefore, become a common practice in the fabrication of many polymeric materials and products.

The overall goal of polymer surface modification is generally to bring about one of two objectives: to increase the potential for surface interactions (e.g., adhesion promotion) or to decrease the degree to which the surface interacts with a given material (e.g., release or antifouling applications). Although the methods of polymer surface modification are myriad and can be complex in nature, all surface modification strategies basically share the common goal of controlling the nature and number of chemical functional groups at the polymer surface. Here the term *functional group* is used generically to indicate any chemical moiety that brings about a desired function of a surface.

If a release surface is the goal of modification, the functional groups that are desired at the surface must have low forces of interaction, that is, only London dispersive interactions, and the choices for functional groups are basically limited to the following set:[1] —CF_3, $\text{—CF}_2\text{—}$, —CH_3, and $\text{—CH}_2\text{—}$. Such low-surface-tension groups naturally segregate to the surface or can be easily delivered there by the use of macromolecular surfactants or through processes such as plasma polymerization. Clever material designs that deliver these low-energy functional groups to the surface and stabilize them by self-assembly processes such as crystallization[2] or crosslinking[3] have produced superhydrophobic surfaces with water contact angles exceeding 150°.

Surface modification for adhesion promotion generally involves creating or delivering high-energy functional groups to the surface that have high interaction potentials or are reactive in nature. The incorporation of dipole–dipole or hydrogen-bonding forces across the interface can greatly augment the thermodynamic work of adhesion, and interfacial reactions lead to mechanical loss mechanisms that enhance adhesion. The number of methods for increasing polymer surface interactions are numerous and range dramatically in nature from brute-force oxidation methods, such as corona discharge or plasma treatments, to specific chemical modifications that use known organic reactions to produce specific functional groups of interest.[4] Interest in the latter types of treatments has grown commensurately with the sophistication of the applications. For example, recent trends in the design of biomaterial surfaces call for the ability to attach biological molecules such as peptide adhesion ligands[5] or growth factors[6] to surfaces in very precise concentrations. There are, however, a number of problems usually associated with the generation of high-energy functional groups on the surface of a typical low-energy polymer. Brute-force oxidation treatments do not provide for much control over the species formed or their surface density, and direct chemical modifications are difficult to confine to the surface and can produce relatively deep modification layers depending on how long the treatment is applied. Furthermore, because surfaces are driven thermodynamically to lower their surface energy, the high-energy surfaces created by modification techniques are often unstable and susceptible to reorganization processes in which surface functionality is rapidly lost.[7]

For almost 20 years, it has been an ongoing goal of our research laboratory to develop a set of fundamental principles that could be applied to design the structure and properties of functional polymer surfaces at the molecular or nanoscale level. The constraints involved with this task make it a daunting one. Ideally, a true design capability would allow for precise dosing of multiple functional groups of any kind simultaneously at a surface in a completely stable manner without significantly effects on the bulk properties. Fortunately, tremendous progress has been made in accomplishing this goal.[8] This brief review first summarizes three fundamental design principles that have emerged as important aspects in the molecular design of functional polymer surfaces. The fundamental design principles are described through a review of the surface properties of a number of model functional polymer systems with controlled architectures that have been carefully synthesized and characterized expressly for this purpose. The model systems employed are primarily end-functional polymers, but we have shown through theoretical modeling that the behavior of these simple model systems is characteristic of the behavior of essentially all functional polymers, regardless of their architecture. We illustrate the utility of the design principles by showing how they can be applied to develop molecular engineering solutions for several practical polymer surface applications.

PRINCIPLE I: SURFACE SEGREGATION

Functional polymers are by nature heterogeneous materials containing at least two constituents: the polymer backbone and the functional group of interest. If the goal of surface modification is to create a release surface, then the functional group usually has a lower surface energy than the polymer backbone, whereas the situation is reversed if adhesion promotion is the objective of surface modification. In virtually all cases of interest, the difference in the surface energies between the two constituents is appreciable. This situation results in the lower energy component being favored at the surface to minimize the overall free energy, as can be illustrated by an examination of the thermodynamic equilibrium condition for a multicomponent polymer in the presence of an air–polymer interface. This can be written in terms of a modified Gibbs–Duhem equation for a two-constituent system as follows:

$$d(n_r\mu_r) + d(n_f\mu_f) = -A d\gamma = A(\gamma_r - \gamma_f) d\phi_{s,f} \quad (1)$$

This simple equation illustrates that the degree to which one constituent segregates preferentially to the surface is determined by a balance of bulk and surface free energy changes. The two terms on the left side of the equation represent the bulk free energy penalty that is incurred if a constituent is removed from the bulk phase as a result of segregation to the surface. The subscripts r and f refer to the repeat unit (i.e., the polymer backbone) and the functional group, respectively; μ is the chemical potential, and n is the number of moles. The right-hand side of the equation represents the change in the interfacial free energy that occurs for the surface area (A) when the surface fraction of the functional group ($\phi_{S,f}$) is changed by a certain amount ($d\phi_{S,f}$). The interfacial tensions of the repeat unit and functional group are γ_r and γ_f, respectively. For an air–polymer interface, it is a common practice to speak of these two interfacial tensions as surface tensions. The driving force for functional group surface segregation is, therefore, proportional to the factor $A(\gamma_r - \gamma_f)$. When this factor is positive, the functional group has the lower surface tension and segregates preferentially to the surface; when the factor is negative, the polymer backbone has the lower surface tension, and functional groups are depleted from the surface. Surface segregation is a general phenomenon for all multicomponent polymer systems and has been the subject of many investigations. The reader is directed to the text by Jones and Richards[9] and our own previous work[10] for an in-depth discussion of surface segregation in polymer blends and to the monograph by Wu[4(a)] for a review of the surface properties of copolymers and other heterogeneous polymer systems. This review focuses on surface segregation in heterogeneous functional polymers containing one or more functional groups along the polymer chain.

Surface segregation for functional polymers is intrinsically different from that for polymer blends because of the effects of chain continuity.[8] Because the two constituents, the functional group and polymer repeat unit, are covalently bonded, entropic and enthalpic effects cannot be separated in the case of a functional polymer. The length scale for segregation in functional polymers is, therefore, restricted to the approximate size of the polymer chain.

Surface segregation in functional polymers can be illustrated by an examination of the surface properties of two model polymer systems based on poly(dimethylsiloxane) (PDMS) and polystyrene (PS). End-functional polymer architectures were initially chosen to represent the general case of functional polymers, and fortunately it has now been shown by lattice model calculations that essentially all functional polymer architectures behave in a similar fashion. The two polymer systems chosen for study have distinct advantages and disadvantages as model systems. In the first system, α,ω-aminopentyl-terminated poly(dimethylsiloxane) (APDMS) synthesis by an equilibration reaction essentially guarantees that both chain ends are terminated with a functional group but yields a most probable distribution of the molecular weights with a polydispersity index of about 2. For the study of this system, it was therefore necessary to demonstrate at the onset that segregation by molecular weight did not complicate the results. Experiments on samples fractionated by supercritical extraction showed that the surface tension was independent of the molecular weight distribution for the same number-average molecular weight, demonstrating convincingly that the surface segregation of low-molecular-weight species is not important in this system.[11] The second system, ω-fluorosilane-terminated polystyrene (PSF), is prepared by anionic synthesis and has a narrow molecular weight distribution, but the efficiency of the fluorosilane termination reaction is less than 100%, leading to a functionality typically in the range of 80–95%. The PSF model systems then are actually blends of a functional polymer and a small fraction of a nonfunctional polymer. Fortunately, the functional polymer acts as a surfactant in the nonfunctional polymer, and the adsorption isotherm for such high concentrations leads to results that effectively are the same as they would be for a pure functional polymer. Another complication of this system is that the second chain end is a *sec*-butyl group that is a residual fragment from the initiator. The *sec*-butyl groups segregate to the surface of a proton-terminated PS control[13] but do not significantly affect the properties of the PSF polymers.[14]

The functional amine end groups on the APDMS polymer have a higher surface tension than the PDMS backbone and are thus expected to be depleted from the surface. Angle-dependent X-ray photoelectron spectroscopy (ADXPS) has been used to illustrate this behavior,[15] as shown in Figure 1. ADXPS provides a weighted integral depth profile,[16] as discussed later in this review,

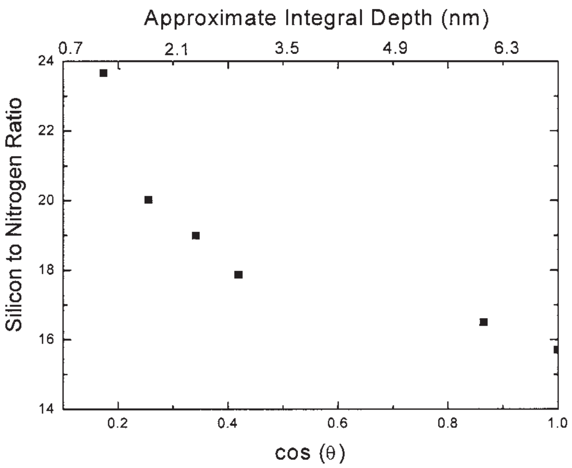

Figure 1. Ratio of atomic nitrogen to silicon as a function of the sine of θ (i.e., integral depth) determined by ADXPS for APDMS (number-average molecular weight = 960).

in which the photoelectron takeoff angle (θ) is related to the integral depth probed (d) by the relation $d \approx 3\ \lambda \cos \theta$. Because the photoelectron mean free path (λ) is about 2.5 nm, the technique probes depths in the range of approximately 1–8 nm. The takeoff angle, that is, the angle between a vector normal to the polymer surface and the direction of detected line-of-sight photoelectrons, is varied during the experiment to probe different integral depths. The Si2p photoelectrons are used to measure the silicon content and therefore to determine the concentration of the PDMS backbone, whereas the N1s photoelectrons reflect the nitrogen content and are used to calculate the concentration of amine end groups. The nitrogen-to-silicon atomic ratio increases at the surface, and this is indicative of a depletion of amine end groups at the surface. The gradient in the surface composition has a length scale similar to the overall size of the polymer chain.

The fluorosilane terminus on the ω-functional PS has a lower surface tension than the PS backbone and segregates preferentially to the air–polymer interface to lower the surface tension.[17] ADXPS was again applied to study the surface of PSF polymers,[18] but in this case, the fluorine 1s signal was used to monitor the surface composition of the fluorosilane end groups, and the carbon 1s signal was used to calculate the concentration of the PS backbone. The fluorine-to-carbon ratio reported in Figure 2 as a function of the integral depth (i.e., takeoff angle θ) shows clearly that the fluorosilane-functional groups segregate preferentially to the surface for this polymer system.

Experiments on the two model systems show that the surface segregation of functional groups is an important factor to consider for the design of a polymer surface. If the functional groups have a lower surface tension than the polymer backbone, the surface concentration of the functional groups will be higher than the bulk composition, and the surface tension will be lower than that expected from the overall composition. If the functional groups have a higher surface tension than the polymer backbone, they will be depleted from the surface, and the functional group concentration at the surface will be much lower than expected. Again, the surface tension will be lower that that expected from the overall composition. Surface segregation is, therefore, advantageous if the goal is to create a release surface of low surface tension, but it is problematic if the goal is to modify the surface with high-energy reactive functional groups.

PRINCIPLE II: STRUCTURE OF FUNCTIONAL POLYMER SURFACES

It is becoming increasingly important in many polymer applications to precisely control the areal density of functional groups located at a surface. The knowledge alone that surface segregation may be occurring is not sufficient to meet this requirement. A quantitative understanding of surface segregation and the molecular structure of the functional polymer surfaces is required to enable the *a priori* design of a surface with known concentrations of functional groups. Because our interest was born out of the need to engineer surface properties for real applications, we sought a fundamental framework that could account quantitatively for all observed behavior but that could also be applied without the need

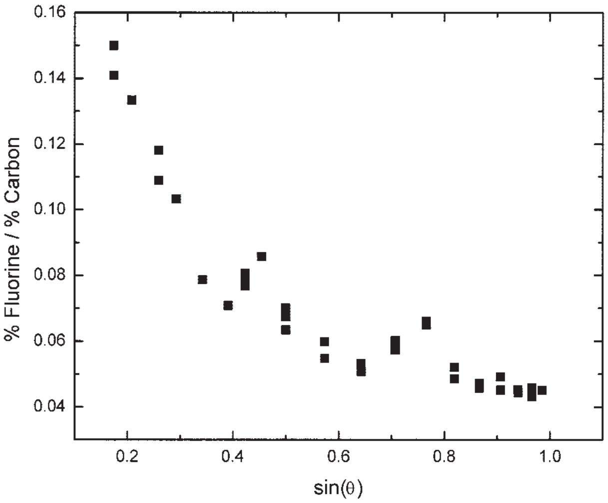

Figure 2. Ratio of atomic fluorine to carbon as a function of the sine of θ (i.e., integral depth) determined by ADXPS for PSF (number-average molecular weight = 5000).

for extensive experimentation to define a large number of material parameters. Fortunately, Theodorou[19] developed a relatively straightforward model for the surface structure of end-functional polymers and copolymers that meets these requirements. The theoretical framework for the model is the lattice treatment developed by Scheutjens and Fleer[20] to describe polymer adsorption. A similar theoretical framework was used by Kumar et al.,[21] and it was through a collaboration with his group that the lattice model was extended to calculate the surface properties of functional polymers of essentially all possible architectures.

The model requires the knowledge of only three parameters: the normalized chain length, equal to the volume of the functional polymer molecule divided by a reference volume (ν_{REF}); the Flory interaction parameter (χ) between the polymer repeat unit and functional group segments; and a surface interaction parameter (χ_{S}) reflecting the driving force for surface segregation defined in eq 1. To enable the estimation of the parameters without the need for experimentation, we can use the regular solution theory expression for χ:

$$\chi = \frac{\nu_{\mathrm{REF}}(\delta_{\mathrm{r}} - \delta_{\mathrm{f}})^2}{kT} \tag{2}$$

where k is Boltzmann's constant and I is temperature.

This expression is adopted because the required solubility parameters (δ_i) can be estimated directly from the structure of the polymer repeat unit or functional group by group-contribution methods.[22] In this fashion, the interaction parameter can be estimated without the need for any experimental parameters. χ dictates the magnitude of the bulk free energy cost, represented by the left-hand side of eq 1 and associated with the segregation of one constituent to the surface.

The reduction in the surface free energy associated with surface segregation is represented by the right-hand side of eq 1. The dimensionless form of this term (χ_{S}) is defined as follows:

$$\chi_{\mathrm{s}} = \frac{A(\gamma_{\mathrm{f}} - \gamma_{\mathrm{r}})}{kT} \tag{3}$$

In defining the surface interaction in this fashion, we adopt the convention that χ_{S} is negative when functional groups have the lower surface tension, that is, when functional groups are attracted to the surface, and is positive when the surface tension of the repeat unit is lower and functional groups are repelled from the surface. The surface area of a segment (A) is equal to $(\nu_{\mathrm{REF}})^{2/3}$ because a cubic lattice is assumed, and the surface tensions (γ_i) are again estimated by group-contribution methods[23] based on the chemical structures of the polymer repeat unit and functional group. The most difficult aspect of the modeling is the determination of ν_{REF}. There are basically two logical alternatives to use: the volume of the repeat unit and the volume of the functional group. Through experience, it has been learned that it is generally better to use the repeat unit volume as ν_{REF} because with this definition the chain stiffness and entropy are correctly accounted for. The choice of ν_{REF} can be problematic if it leads to a fractional number of functional groups, for example, if a large end group turns out to be equivalent to 1.5 segments, so at times one has to employ an approximated or compromised definition that best corresponds to the functional polymer chain under consideration.

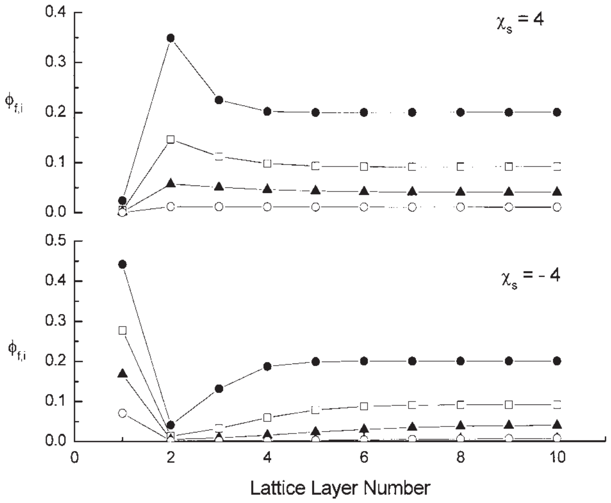

Figure 3. Functional end-group-concentration depth profiles predicted by the lattice model for α-functional polymers of various normalized chain lengths: (●) 5, (□) 11, (▲) 25, and (○) 101.

Lattice model calculations provide a prediction of the volume fraction of functional groups (ϕ_{f}) in each lattice layer. The surface structures predicted by the lattice model for end-functional polymers[24,25] are shown in Figure 3, in which the volume fraction of functional groups is plotted as a function of the depth in terms of the number of lattice layers. The lattice layer dimension is defined as the cube root of ν_{REF}, so that one lattice layer corresponds to a depth increase of approximately 1.0 nm. Several interesting features are evident in these concentration depth profiles. When χ_{S} is less than 0, the functional groups clearly segregate to the surface, but the region of excess is only one lattice layer thick. Below the region of surface excess is a depletion zone that scales roughly with the radius of gyration. The highest functional group concentration is in the first lattice layer, and the lowest concentration of functional groups is found in

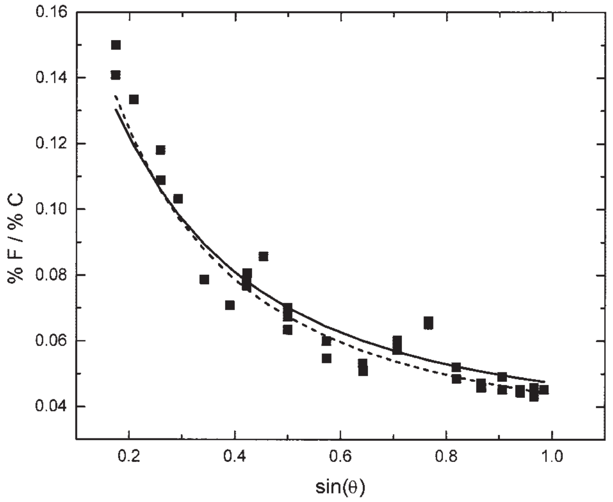

Figure 4. (■) Experimental and (—,- - -) calculated ADXPS depth profiles for PSF (number-average molecular weight = 5000).

the adjacent, second layer. The situation is just the opposite when χ_S is greater than 0. These trends qualitatively reflect the experimental X-ray photoelectron spectroscopy (XPS) results cited in the previous section devoted to principle I. Therefore, there are two characteristic length scales for functional polymers: the lattice dimension, equivalent in size to the polymer repeat unit, and the radius of gyration, characteristic of the size of the entire chain.

Experimental ADXPS data for fluorosilane-terminated PS are well represented by the lattice model, as shown in Figure 4. XPS is an integral technique in which the total photoelectron signal $S_j(\theta)$, associated with any particular atom j and θ, is related to the integral of photoelectrons generated at all depths x:

$$S_j(\theta) = K\int_0^\infty n_j(x)e^{-(x/\lambda \cos\theta)}\,dx \tag{4}$$

The concentration depth profile for atom j is $n_j(x)$, and K is a known constant. Theoretical integral concentration depth profiles are generated from the lattice calculation through the insertion of the calculated concentrations for each lattice layer, that is $n_j(x)$, into eq 4 and through summation over all lattice layers. The same degree of agreement between calculation and experiment illustrated in Figure 4 was obtained for essentially all cases studied when the necessary interaction parameters were estimated with eqs 2 and 3. A brute-force regression of the lattice model to the complete set of ADXPS data for PSF polymers of various molecular weights was used to obtain χ_S and χ values that best fit the entire ensemble of experimental data. These optimal values compared well with the values estimated by group-contribution methods when the appropriate ν_{REF} value was used.[18]

The lattice model can also be applied to calculate the surface tension of functional polymers, one of the most important properties describing the character of a polymer surface. Although the lattice model provides a rigorous route to calculating the surface tension, the surface tension can be estimated to a high degree of accuracy from knowledge of only the fraction of functional groups in the first lattice layer ($\phi_{f,1}$). If additivity by the surface area is assumed, the surface tension can be calculated in a group-contribution manner as follows:

$$\gamma = \gamma_f\phi_{f,1} + \gamma_r(1 - \phi_{f,1}) \tag{5}$$

This simple relationship successfully reproduces the molecular weight dependence of the surface tension for PDMS polymers with four different end groups, as shown in Figure 5. The χ_S values and constituent surface tensions were again calculated from group-contribution methods, and in this case, the effects of the bulk interactions were neglected. Equation 5 is an extremely useful means of calculating surface tensions because $\phi_{f,1}$ values calculated from the lattice model can be put in a tabular format along with interpolation formulas, so that it is not necessary to redo the calculation each time for a new polymer structure. We can calculate the value of the surface tension of an ω-functional[24] or α,ω-difunctional polymer[25] by simply looking up the tabulated value of $\phi_{f,1}$ for a given chain length and χ_S value and applying

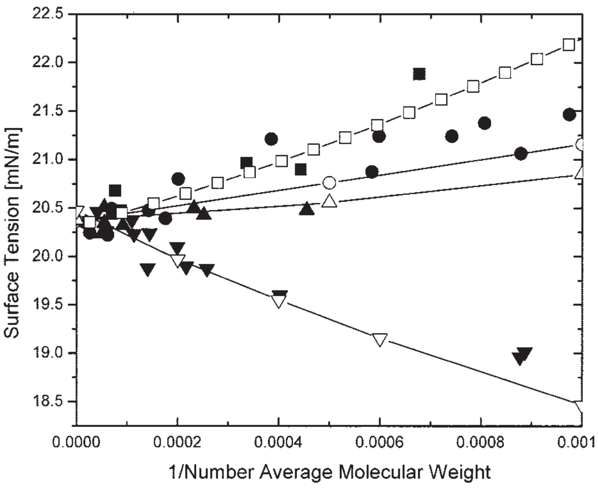

Figure 5. Comparison of (■,●,▲,▼) experimental and (□,○,△,▽,—) calculated surface tensions for α,ω-terminated PDMS: (■,□) carboxypropyl-terminated, (●,○) aminopropyl-terminated, (▲,△) hydroxypropyl-terminated, and (▼,▽) methyl-terminated.

eq 5 with surface tensions estimated by group-contribution methods.

The lattice model has been extended to treat essentially all possible functional chain architectures and to examine the effects of functional group adjacency and the inclusion of high- and low-energy functional groups on the same chain.[25] Although quantitative differences have been found for different architectures, all examined architectures exhibit surface structures that are qualitatively the same as those shown in Figure 3. Excellent agreement between experimental and theoretical ADXPS functional group concentration depth profiles has also been found for end-functional polycaprolactones,[26] end-functional polylactides[27] and center-functional polylactides.[27]

The success of the lattice model calculations and the approximations applied to developing simplified strategies for the estimation of the required material parameters provide an accurate means of calculating both the surface concentration of functional groups and the surface tension of functional polymers.

PRINCIPLE III: REORGANIZATION OF FUNCTIONAL POLYMER SURFACES

The third principle that is important to arriving at a quantitative molecular design for a functional polymer surface is the consideration of surface reorganization. Most polymers are fabricated in hydrophobic environments in which the interface is an air–polymer interface and it is appropriate to use surface tensions in eq 1. After fabrication, however, this air–polymer interface often comes into contact with other materials and is replaced by a material–polymer interface. In this case, it is appropriate to replace air–polymer surface tensions with material–polymer interfacial tensions in eq 1. The original structure favored at an air–polymer interface will no longer be stable, and the new interface will attempt to reorganize and re-equilibrate in response to its new environment. The reorganization of the surface structure is especially well documented for biomaterials,[28] in which the original hydrophobic air–polymer interface is replaced by an aqueous–polymer interface when the polymer is placed *in vivo*. Reorganization also occurs in hydrophobic environments after surface modification techniques are applied to increase the surface tension.[4(b)] Plasma treatments on polyolefins, for example, can initially increase the surface tension to allow for printing, but the stability of these surfaces is limited and these surfaces reorganize, reverting rapidly back to a relatively unmodified state with lower free energy.

Surface reorganization occurs when the polymer environment is changed, even if the polymer is in the glassy state, as illustrated by the water contact angle data for end-functional PS[8(a),29,30] presented in Figure 6. The fluorosilane-terminated polymer shows initially high water contact angles associated with the preferential surface segregation of fluorosilane end groups to create a hydrophobic surface. After exposure to water vapor in the glassy state, however, the surface reorganizes, and the water contact angles eventually fall to a value characteristic of the PS control sample. Fluorosilane end groups adsorbed initially at the surface move away from the surface and are replaced by PS units to minimize the energy of the new interface. For carboxylic acid terminated PS, the contact angle is initially the same as that of the PS control, and this indicates the absence of carboxylic acid groups at the surface. When exposed to water vapor well below the glass-transition temperature, the carboxylic acid groups are drawn to the new interface to lower the interfacial tension with water vapor. Eventually, enough carboxylic acid groups can be drawn to the surface (depending on the molecular weight) to render the surface of hydrophobic PS water-wettable. This example demonstrates that the end-functional model systems not only are interesting from an academic point of view but also constitute viable architectures for surface modification applications.

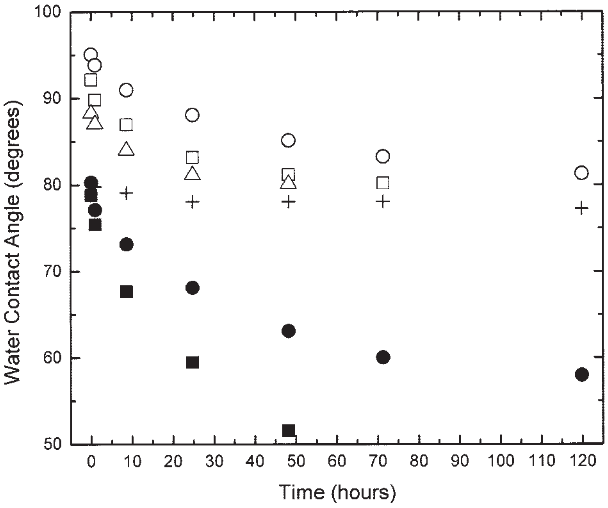

Figure 6. Water contact angles for ω-functional PS as a function of its time in contact with saturated water vapor at 55 °C: (○,□,△) fluorosilane-terminated PS [molecular weight = (○) 5000, (□) 10,000, or (△) 25,000], (+) PS control, and (●,■) carboxylic acid terminated PS [molecular weight = (●) 6500 or (■) 10,000].

To complete the arsenal of tools required to properly design functional polymer surfaces, we must fully understand the reorganization process. One aspect of reorganization is already clear: reorganization is a facile

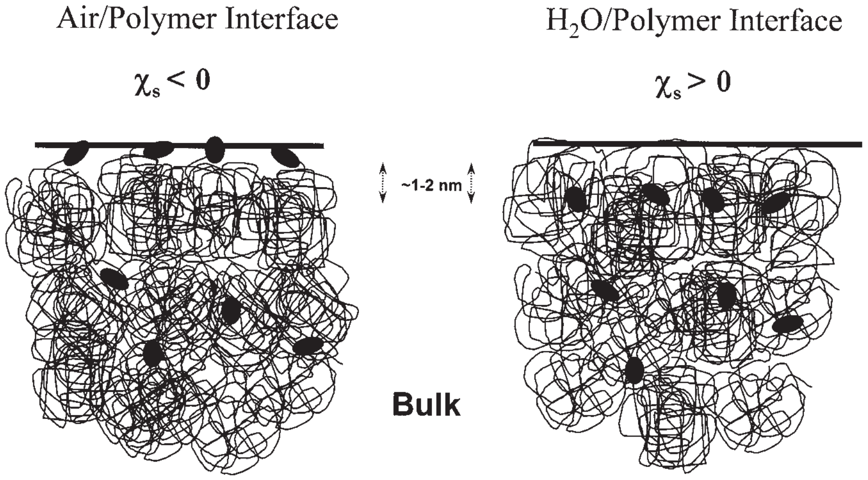

Figure 7. Schematic representation of the surface structural changes that accompany the surface reorganization process when the sample environment is switched from air to water vapor.

process because of the nature of the surface composition gradient. In the previous section, it was shown that, for end-functional polymers, the highest and lowest functional group concentrations are in the first and second lattice layers. The surface properties of these functional polymers can, therefore, switch almost completely by a simple exchange of material between the first and second lattice layers over a distance of only 1–2 nm. Because motion on this length scale occurs readily in glassy polymers, the surface structure provides an explanation of why reorganization takes place even in the glassy state. Unfortunately, this result also suggests that it is nearly impossible to prevent surface reorganization because the length scales of motion required to bring it about are so small. Figure 7 illustrates that only a relatively minor change in the surface structure is sufficient to completely modify surface properties, in large part because interactions in bulk materials are effectively screened over a distance equivalent to one lattice site.

Research designed to quantify the surface reorganization process and to model it with a modification of the lattice model is nearly completed and will be reported shortly.[31] These results demonstrate that a simple model allowing exchange within the top two to three lattice layers is sufficient to provide a nearly quantitative description of the effects of surface reorganization. The completion of this work should provide the final piece of the puzzle to enable the molecular-level design of functional polymer surface properties for virtually any desired architecture and composition and for applications in any environment of interest. The following sections describe a number of applications and engineering design solutions for surface modification that have already emerged from the application of the three design principles.

APPLICATION I: OPTIMIZING THE ARCHITECTURE OF FUNCTIONAL POLYMERS

The question of which functional polymer architecture is optimal for a particular design goal should come immediately to mind after the previous three design principles have been read. The lattice model supplies a straightforward means of answering this question. First, consider the goal of creating a low-energy release surface through the incorporation of low-surface-tension functional groups into a polymer chain. A wide variety of architectures is possible: the functional groups can be placed on the chain end and along the polymer backbone, and multiple groups can be placed basically anywhere along the chain. Alternatively, high- and low-energy functional groups can both be placed on the polymer chain (the so-called push-me/pull-you structures inspired by Doctor Dolittle[32]). The possibilities would seem to be endless. The principles of optimization, however, are easily illustrated for polymer chains containing two functional groups. The possible architectures for this case are shown in Figure 8. The criterion for selecting the best architecture for creating release systems is simply the architecture that provides the highest concentration of low-energy functional groups within the first lattice layer. This criterion yields the architecture of lowest surface tension.

The results of lattice model calculations are summarized in Figure 9, in which they are compared with monofunctional polymer controls. The groups indicated by A are attractive functional groups with $\chi_S < 0$, whereas groups indicated by R are repulsive groups with $\chi_S > 0$. The results are shown as a function of the position along the chain of

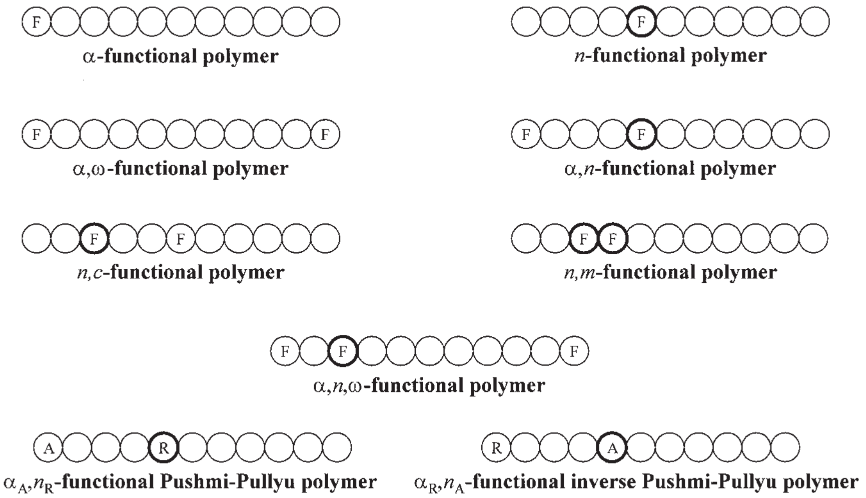

Figure 8. Possible functional polymer architectures for modifying the surface properties. The functional groups outlined in bold are moveable and are located at position n or m along the chain. Designations A and R denote functional groups that are attracted to or repelled from the surface, respectively.

the functional group highlighted in the bold circle. The volume fraction of the attractive functional groups within the first lattice layer, that is, at the surface, is represented as $\phi_{A,1}$. The optimum architecture is that which provides for the highest value of $\phi_{A,1}$. Clearly, two functional groups are better than one, regardless of the position of the groups, but the results are more complex than this. The push-me/pull-you architectures do provide for enhanced surface segregation over the monofunctional control. Because the high-energy functional groups are repelled from the surface, this force of repulsion can be used to balance entropic penalties and actually increase the number of low-energy groups at the surface. The most effective architectures based on this concept have a low-energy functional group as a chain end and a high-energy functional group as the adjacent segment. The optimal chain architecture for creating release surfaces, however, is one with two low-energy functional groups in adjacent positions at the chain end. This arrangement takes

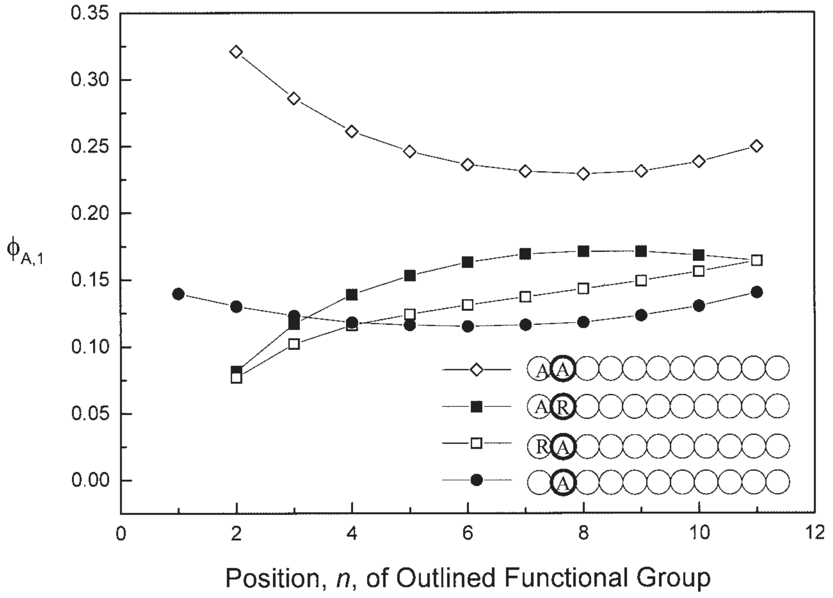

Figure 9. Fraction of low-energy functional groups in the first lattice layer for difunctional polymers as a function of the position of the second functional group (highlighted in bold) for the polymer architectures illustrated in Figure 8.

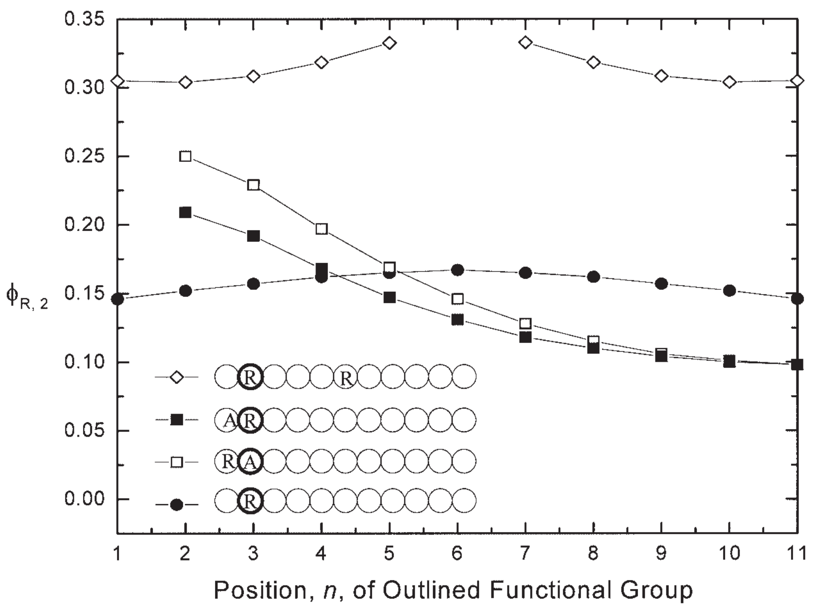

Figure 10. Fraction of high-energy functional groups in the second lattice layer for difunctional polymers as a function of the position of the second functional group (highlighted in bold) for the polymer architectures illustrated in Figure 8.

advantage of both the entropic driving force of about 0.2 kT for end-group surface segregation[24] and the adjacency effect due to chain continuity to achieve the highest surface concentration of functional groups. Principles I and II, therefore, provide a straightforward optimal molecular design for functional polymers in applications for which a release surface is required. Considerations of the effects of higher numbers of functional groups at the chain end show that these basic trends are found to be true regardless of the number of functional groups. Of course, these optimal structures are valid for the hydrophobic air–polymer interface and are not necessarily stable if the environment is changed from air to some hydrophilic medium. If the latter situation were the case, one would also have to factor in the effects of principle III, surface reorganization.

The optimization of chain architectures for creating high-energy adhesive surfaces is challenging because high-energy functional groups are intrinsically repelled from the surface according to design principle I and as shown quantitatively in principle II. The key to understanding molecular design in this case is to invoke principle III at the onset. In other words, the applications of high-energy functional polymer surfaces almost always require that they be placed in contact with another medium that will cause surface reorganization to occur. Because surface reorganization requires at a minimum only an exchange of functional groups between the first and second lattice layers, a pragmatic criterion for optimizing chain architecture becomes obvious: maximize the number of high-energy functional groups in the second lattice layer under the assumption that they will move to the new interface upon reorganization. The architectures considered for optimizing high-energy adhesive interfaces are shown in Figure 8, and the results of the lattice model calculations are presented in Figure 10 for architectures with two functional groups. In this case, the optimum architecture is that which provides the highest fraction of repulsive groups located in the second lattice layer ($\phi_{R,2}$). The push-me/pull-you architectures again provide improvements and yield optimal architectures when the repulsive and attractive functional groups are in adjacent positions at the chain end. Overall, the optimal architecture for creating a high-energy adhesive interface is one with two high-energy functional groups at the chain center. This architecture provides the highest high-energy functional group concentration in the second lattice layer. Upon contact with a polar medium, these functional groups are expected to relocate to the interface according to principle III, surface reorganization.

APPLICATION II: FUNCTIONAL ADDITIVES TO PROMOTE WETTING

The entire discussion up to this point has been focused on the design of the functional polymer as a bulk material. Considerations of cost and kinetic factors often favor the use of functional polymers as additives incorporated into a nonfunctional matrix polymer. The use of functional polymers as additives is similar to the use of

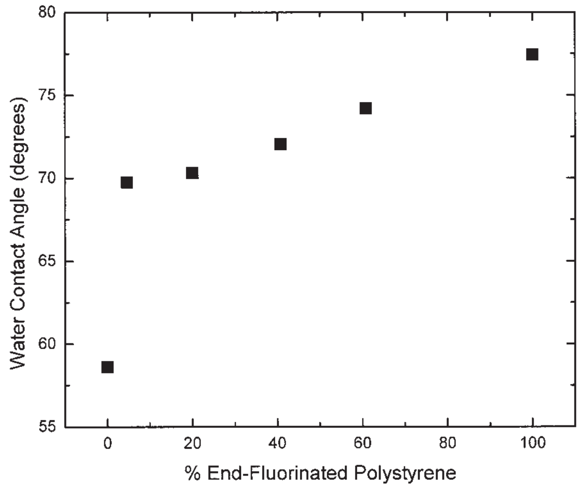

Figure 11. Increase in the water contact angle (i.e., a reduction in the surface tension) of a PS substrate due to the addition of PSF.

surfactants to modify small-molecule surfaces and interfaces, but the applications require macromolecular surfactants. Surface-active block copolymers[4(a),33,34] are perhaps the best known examples of this class of additives, and their mechanism of action is basically principle I.

To illustrate the molecular design strategy for the functional polymer additive approach, consider the wetting of a polymer film on a substrate. It is well known that wetting will occur when the spreading coefficient is positive,[4(a)] that is, when γ_S is greater than the sum of γ_P and γ_{PS}. The interfacial tension for the polymer substrate is γ_{PS}, γ_P is the surface tension of the polymer, and γ_S is the surface tension of the substrate. Wetting can be promoted, therefore, by a reduction of the surface tension of the polymer. The consideration of principle I and the optimization results from application I suggests a straightforward solution: incorporate a low-energy functional group at the polymer chain end. In this case, however, the functional polymer will be used as an additive. Figure 11 shows that fluorosilane-terminated polystyrene (PSF) is an effective additive for lowering the surface tension of a PS matrix as it increases the water contact angle. The surface structures of blends of PS with fluorosilane-terminated PS have been studied by ADXPS, and the lattice theory has been extended to treat blends containing a functional polymer. Figure 12 shows that the lattice model also provides satisfactory predictions of the surface structure of a polymer blend containing a functional polymer. Again, all necessary parameters can be estimated by group-contribution methods. Fluorosilane-terminated PSs were subsequently found to be successful as additives for promoting wetting,[35] as shown in Figure 13. The additives slow the rate of dewetting and, if incorporated at sufficient levels, will inhibit dewetting because of their ability to reduce the surface tension of the air–polymer interface. End-functional polymers that interact specifically with the substrate have also been found to be effective additives for inhibiting dewetting,[36] and in principle, their behavior can also be treated by the lattice model.

APPLICATION III: SURFACE DELIVERY VEHICLES FOR CREATING SMART SURFACES DECORATED WITH HIGH-ENERGY FUNCTIONAL GROUPS

The final question to be addressed in this review is how the molecular design principles can be applied to produce an additive that can actually increase the surface energy or reactivity of a polymer surface. This goal would at first appear to be oxymoronic according to principle I. That is, a small amount of a polymer containing high-energy functional groups used as an additive would not segregate to the surface. In fact, principle III (surface reorganization) would also be of no utility because higher energy functional groups on additive molecules would not be located in the second lattice layer but would be dispersed throughout the polymer matrix. The solution to this apparent dilemma is to design what can be termed a *surface delivery vehicle* based on the application of all three molecular design principles.

The role of a surface delivery vehicle is to deliver something, in this case a high-energy functional group, to the surface. In reality, the payload to be delivered

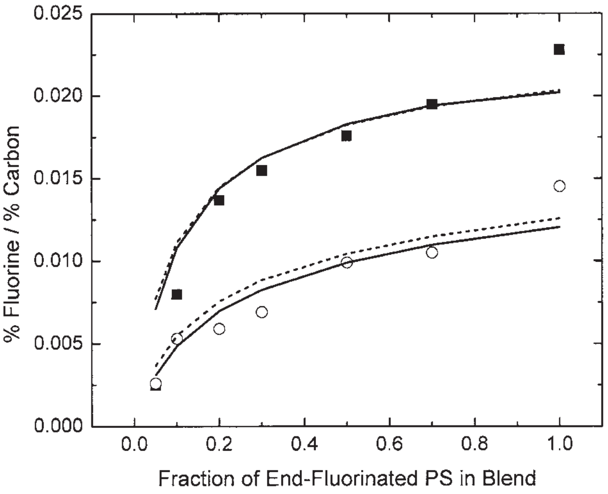

Figure 12. Comparison of (○,■) experimental and (—,- - -) calculated ADXPS composition depth profiles for blends of PS (molecular weight = 34,500) with PSF [molecular weight = (■) 17,300 or (○) 35,500].

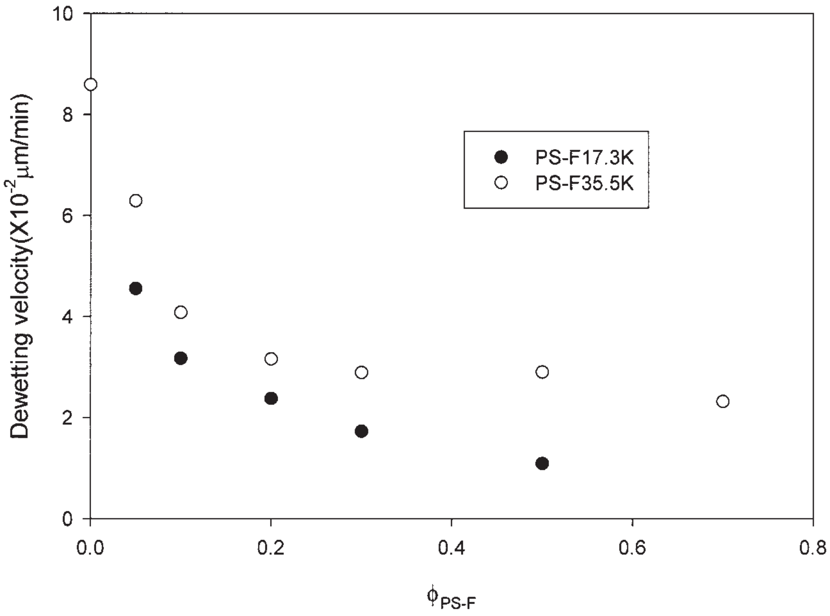

Figure 13. Effect of PSF addition [molecular weight = (●) 17,300 or (○) 35,500] on the dewetting velocity of PS (molecular weight = 34,500) on a poly(methyl methacrylate) substrate.

could be an initiator, a photoactive functional group, a UV stabilizer, a reactive functional group, or virtually anything that has a useful function when delivered to a surface. The first two requirements of a surface delivery vehicle are that the molecule must be surface-active and must contain the functional group. The third requirement is that the surface delivery vehicle must have some mechanical integrity when located at the surface. In other words, the formation of a surface layer that can be easily removed from the surface is not acceptable. Surface delivery vehicles are also designed, therefore, to have an anchor unit that provides some mechanical connection to the matrix or substrate.

The simplest molecular design for a surface delivery vehicle is an end-functional block copolymer. The first block copolymer sequence comprises the same polymer as the substrate or a polymer that is miscible with the polymer substrate and serves to anchor the surface delivery vehicle at the surface. The second block copolymer sequence is a surface-active, low-surface-tension polymer that causes the entire molecule to segregate preferentially to the surface. The second copolymer sequence is terminated by the functional group of interest. The manner in which a block copolymer surface delivery vehicle self-assembles at the surface is depicted in Figure 14. The surface-active sequence first causes the molecule to segregate to the surface of the matrix polymer to minimize the surface free energy. Once a properly designed copolymer reaches the surface, it spontaneously forms a bilayer structure with the low-energy sequence located at the air–polymer interface.[37] On the basis of our understanding of functional polymer surfaces, the highest concentration of high-energy functional groups is expected in the second lattice layer just below the sur-

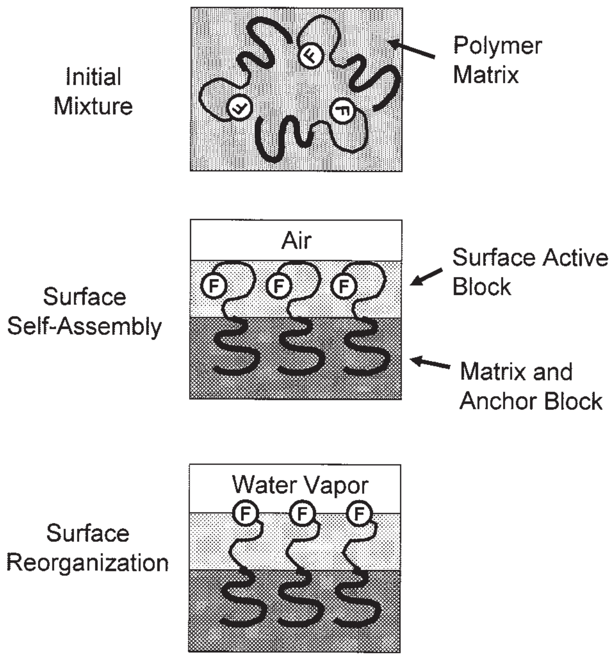

Figure 14. Schematic diagram of the self-assembly of a surface-active end-functional block copolymer at the surface of a polymeric substrate at an air–polymer interface and subsequent reorganization when it is exposed to water vapor.

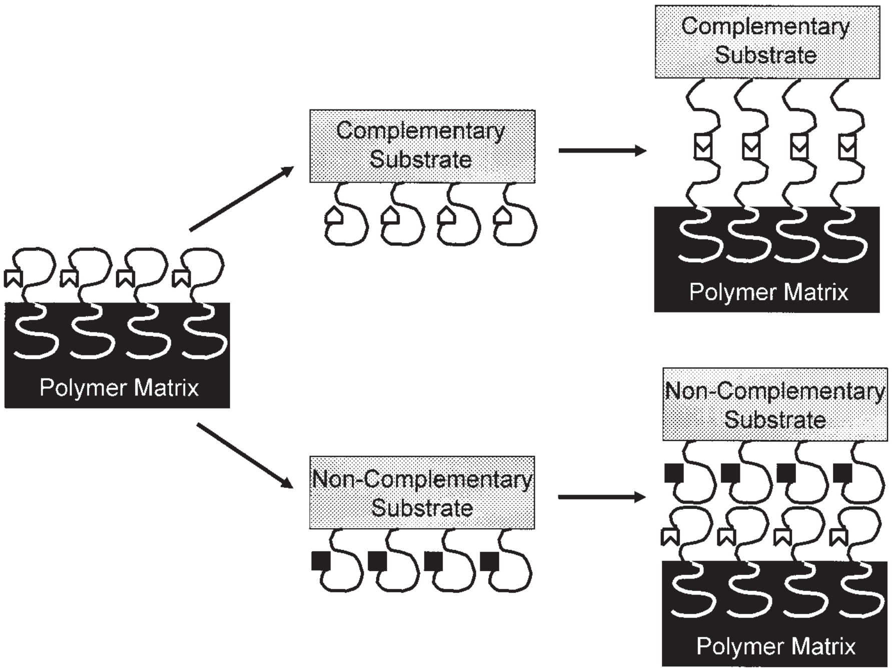

Figure 15. Schematic illustration of the mechanism by which end-functional block copolymers (i.e., surface delivery vehicles) create polymer surfaces with selective adhesion properties.

face. The functional groups can readily reorganize then to be effective reactants and so forth when they come into contact with a new medium. The reorganization step is effectively instantaneous in most cases of interest because low-surface-tension polymers that are useful for this application, such as PDMS and poly(*t*-butyl acrylate), have low glass-transition temperatures and are highly mobile at room temperature.

Figure 15 demonstrates how this strategy was used to create smart polymer surfaces that exhibited selective adhesion properties.[38] When a functionalized polymer matrix comes into contact with a complementary substrate decorated with a second functional group, adhesion can only occur when the two functional groups associate to form an aggregate or chemical bond, as pictured at the top right of Figure 15. If the two functional groups do not associate as pictured at the bottom right of Figure 15, the interface develops release properties as a result of unfavorable interactions between the polymer brushes on each side of the interface. As an illustration of this concept, end-functional poly(styrene-*b*-dimethylsiloxane) copolymers were used to modify the surface of PS substrates. When the end group was a silane, the surface showed release properties toward a poly(methyl methacrylate) substrate but provided adhesion enhancement toward a crosslinked PDMS substrate by virtue of a chemical reaction between silane groups and residual vinyl groups in the silicone elastomer. When the end-functional group was a carboxylic acid, the surface delivery vehicle enhanced the adhesion toward the poly(methyl methacrylate) substrate but provided for release behavior with the PDMS substrate elastomer. The reduction in the surface tension produced by block copolymer adsorption at the surface is effectively independent of the functional group type, as shown in Figure 16, so that it is also possible to prepare surfaces with several distinct functional groups at precise areal densities with this approach. The mechanism of these block copolymers as adhesion promoters between a PS matrix and PDMS elastomers has recently been studied in detail.[39,40] The general concept of surface delivery vehicles has subsequently been extended in our laboratories to deliver precise doses of functional groups to surfaces for the purpose of decorating surfaces with adhesion peptides and growth factors and to deliver photoactive functional groups to polymer surfaces for the purpose of patterning polymer surfaces with functional groups.[41]

Block copolymer surface deliver vehicles offer a very precise means of creating functional polymer surfaces because each molecule carries a single functional group, and the areal density of functional groups can be accurately controlled in the fabrication step. Surface delivery vehicles can be transported to a surface by self assembly from the bulk (although this process is quite slow),[42] by direct spin coating, by adsorption from solution, or most recently by adsorption from supercritical solvents.[43] The

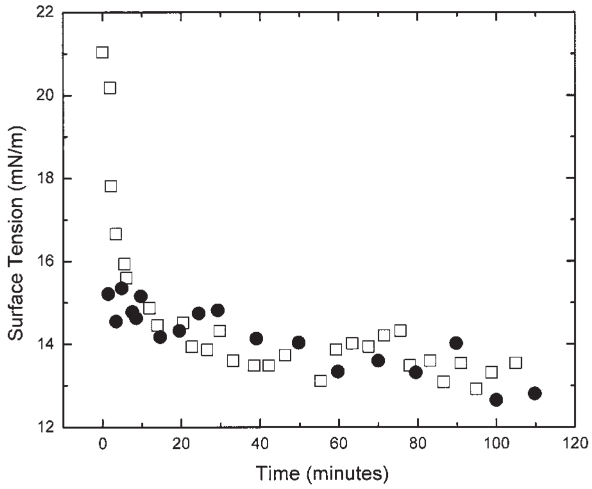

Figure 16. Dynamic surface tensions of ω-functional poly(styrene-*b*-dimethylsiloxane) block copolymers added to a PS matrix at 140 °C: (□) silane-terminated and (●) carboxylic acid terminated. The total molecular weight of the copolymers was 5500 Da, and they contained 50 wt % PS.

last development offers an exciting and environmentally friendly means of modifying the surfaces of objects of arbitrary shapes and the internal surfaces of porous materials for which capillary effects limit ordinary solvent-based delivery methods.

CONCLUSIONS

This review discusses the fundamental factors that are important to the molecular design of functional polymer surfaces. All functional polymers must be considered heterogeneous materials containing at least two constituents: the functional group and the polymer backbone. It therefore follows that the most important factor influencing the surface is surface segregation of the lower surface-tension constituent. Surface segregation is illustrated by the behavior of two end-functional polymer systems, one that shows a surface excess of a low-energy end group and one with a high-energy end group that is depleted from the surface. The structure of the surface of functional polymers is probed with the aid of self-consistent mean-field lattice model calculations. The depth profiles predicted by this approach are consistent with experimental concentration depth profiles obtained by ADXPS, with only group-contribution methods used to estimate bulk and surface interaction parameters. Therefore, the lattice model provides a useful design tool for functional polymer surfaces requiring a minimum of experimental input.

Experimental evidence shows that functional surfaces are subject to reorganization when the environment is changed, for example, when a surface is moved from an air environment to an aqueous one. The structure predicted by the lattice model provides an excellent understanding of why this occurs, even in the glassy state, because the maximum and minimum functional group concentrations are always found in the first and second lattice layers; a motion of only 1–2 nm is required to completely switch the surface composition.

The fundamental principles illustrated by the behavior of end-functional polymers have been applied to develop optimum architectures for functional polymers. For release surfaces, the optimum is to locate low-energy functional groups at one chain end; for adhesive surfaces, the optimum is to locate high-energy functional groups at the center of the chain. The lattice model is then extended to study the case of surface modification with functional polymers as additives. Polymers with low-surface-tension end groups are an effective means of lowering the surface tension and suppressing the dewetting of polymers on a substrate. An extension of this idea has been developed to deliver high-energy functional groups to surfaces with surface-active block copolymers. The smart surfaces created in this fashion present selective adhesion only to substrates that have a specific interaction with the high-energy functional group.

This material is based on work supported by, or in part by, the U.S. Army Research Office (DAAD19-00-1-0104) and the National Science Foundation through its polymers program (DMR-02-14363) and Integrated Graduate Education and Research Training (IGERT) program (IGERT-02-21589).

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