Controlling Polymer-Surface Interactions with Random Copolymer Brushes

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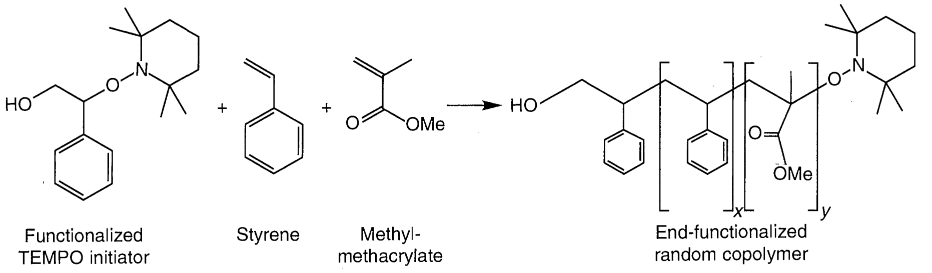
A simple technique for precisely controlling the interfacial energies and wetting behavior of polymers in contact with solid surfaces is described. End-functionalized statistical random copolymers of styrene and methylmethacrylate were synthesized, with the styrene fraction *f* varying from 0 to 1, and were end-grafted onto silicon substrates to create random copolymer brushes about 5 nanometers thick. For $f < 0.7$, polystyrene (PS) films (20 nanometers thick) rapidly dewet from the brushes when heated well above the glass transition temperature. The contact angle of the resulting polymer droplets increased monotonically with decreasing *f*. Similar behavior was observed for poly(methylmethacrylate) (PMMA) films but with an opposite dependence on *f*. The interfacial energies of the random copolymer brushes with PS and PMMA were equal when *f* was about 0.6. Thus, precise control of the relative surface affinities of PS and PMMA was possible, demonstrating a way to manipulate polymer-surface interactions.

The behavior of multicomponent systems at surfaces or interfaces can differ significantly from that in the bulk because of preferential affinities of one or more components to the interface. This occurs in simple fluid mixtures (*1*, *2*), complex fluids such as polymer blends and copolymers (*3*–*9*), and biological systems (*10*) and gives rise to a wide range of important phenomena such as surface enrichment, surface-directed spinodal decomposition, surface-induced ordering and orientation, critical point wetting, and adhesion. Although these phenomena have been studied extensively at interfaces where strong segregation occurs (such as at vacuum or solid interfaces), controlling or even neutralizing the differential surface affinities may be highly desirable in order to elicit a specific response of a material at an interface. However, little work has been done on controlling the relative affinities of the components of an interface. Here we report that interfacial energies of polymers at a solid surface can be manipulated by end-grafting statistical random copolymers onto the surface, where the chemical composition of the copolymer can be controlled by synthesis. This strategy for surface modification is both simple and versatile and can be extended to a wide range of polymers. Dewetting and contact angles were measured for thin polystyrene (PS) and poly(methylmethacrylate) (PMMA) films on silicon substrates coated with end-grafted layers of the corresponding styrene and methylmethacrylate random copolymer, denoted P(S-r-MMA).

Surfaces with a controlled polar character have been prepared previously with self-assembled monolayers (SAMs) made from mixtures of n-alkane thiols with polar and nonpolar end groups (*11*). SAMs are well suited to controlling the wetting properties of small-molecule fluids because the crystalline packing of the alkane chains makes the surface atomically flat and impenetrable. Although this approach may be used to control the surface behavior of polymer blends and block copolymers, the use of random copolymer brushes has several distinct advantages. The ability to create a surface that consists of the same monomers as found in a particular blend or copolymer is a great simplification and guarantees tunability over a wide range of surface affinities, including neutrality. Polymer chains undergo a large conformational entropy loss at a solid interface, whereas a penetrable polymer brush reduces the entropic driving force for dewetting, improves adhesion, and ensures that the brush-polymer interactions are averaged over a large volume. Because the polymer brushes are amorphous, surface coverage will be uniform, and the detailed structure and morphology of the brush are not important.

The use of random copolymers to modify and control the interactions between polymers and a surface has been examined previously (*12*, *13*). These studies showed that a random copolymer can modify surface interactions, but the method used—casting a random copolymer film on a surface—was far from ideal. Because the random copolymer chains were not chemically attached to the surface, they could diffuse away from it. In addition, random copolymers prepared by a free-radical polymerization have a broad molecular weight distribution (MWD).

Control of the interfacial energy with anchored random copolymer chains having low polydispersities is demonstrated here. P(S-r-MMA) random copolymers were prepared with narrow MWDs by a "living" free-radical polymerization technique using a unimolecular initiator based on 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) (*14*–*17*). Polymers synthesized with this initiator are terminated on one end with a moiety containing a hydroxyl (OH) group and on the other end with the TEMPO group (Scheme 1). The OH group is used to end-graft the chains to the native silicon oxide layer.



Scheme 1.

The characteristics of the copolymers used in this study are shown in Table 1.

Solutions of the random copolymers in toluene (1% w/v) were spin coated at 1000 rpm onto silicon wafers, yielding films ~60 nm thick. The silicon wafers were first cleaned by a procedure described elsewhere

Table 1. Copolymer characteristics. M_w and M_n are the weight- and number-average MWDs.

f	M_w	M_w/M_n
1.00	9,800	1.11
0.90	11,000	1.39
0.80	10,600	1.39
0.72	10,350	1.50
0.67	10,800	1.49
0.58	9,600	1.80
0.52	10,700	1.79
0.34	8,900	1.57
0.00*	8,000	1.10

*Polymer was synthesized by a group-transfer polymerization and not a TEMPO polymerization.

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and contained a thin ($\sim$1.5 nm) native oxide layer at the surface (*18*). The polymer-coated substrates were then heated under vacuum at 140°C, well above the glass transition temperature (T_g) of both PS and PMMA, to allow the terminal OH groups to diffuse to and react with the native oxide layer. The substrates were removed from the oven after 2 days and quenched to room temperature. Unattached polymer chains were removed by repeated rinsing with toluene. The thickness of the grafted layers as measured by ellipsometry was $\sim$5 nm. This thickness is approximately twice the radius of gyration of the grafted chains and corresponds to a grafting density of $\sim$3 nm^2 per chain.

The grafted P(S-r-MMA) layer thickness (Fig. 1) showed an initial rapid increase with annealing time that slowed markedly after $\sim$24 hours. This result is similar to that observed by Reiter *et al.* (*19*) and suggests that over long periods, the attachment of additional chains is hindered by the large entropic barrier associated with the stretching of the existing grafted chains. The brush thickness was highly uniform over the entire area of each substrate ($\pm$2%) and was independent of the thickness of the initial P(S-r-MMA) film cast onto the surface as long as this thickness was at least several times the ultimate thickness of the grafted layer.

Control experiments were performed to ensure that the copolymers were actually grafted onto the surface by the termnal OH group (*20*). PS and PMMA homopolymer films were spin-coated onto brushes of PS and PMMA, respectively, and annealed for 24 hours at 170°C. After thorough rinsing with toluene, a film having a thickness approximately equal to that of the original PS or PMMA brush was found. This shows that the polymer remains attached to the substrate under the conditions used in subsequent experiments.

Films of perdeuterated PS (M_w = 27,000) and perdeuterated PMMA (M_w = 18,000) with thicknesses of $\sim$20 nm were spin-coated directly onto the surface of substrates to which the P(S-r-MMA) had been anchored, where the styrene fraction f was varied from 0 to 1 on different substrates. The samples were then annealed in vacuum at 170°C. After 24 hours, samples coated with PS remained shiny and reflective on brushes with $f > 0.7$ but became progressively hazier with decreasing f for $f < 0.7$. The haziness arises from dewetting and droplet formation of the PS on the surface. The opposite behavior was found in the case of PMMA homopolymer films; these samples became hazier with increasing f for $f > 0.5$ and remained reflective for $f < 0.5$. These simple observations provide compelling evidence that the interactions between the homopolymers and the brush can be finely tuned by varying f. Autophobic dewetting (*19*, *21*) was not seen with the homopolymers of lower M_w but was observed with increasing homopolymer M_w.

Contact angles were measured on the droplets in dewetted films by atomic force microscopy (*22*) at room temperature (below the T_g's of both homopolymers) and were repeated after further annealing at 170°C to ensure that the samples were equilibrated (Fig. 2). The error bars represent the standard deviation for all droplets measured on a given sample. The contact angle increases with increasing degree of chemical mismatch between the homopolymer layer and the grafted random copolymer. The interfacial tension γ_{jf} between homopolymer j (j = S or M for PS and PMMA, respectively) and the random copolymer brush with styrene content f can be obtained from the measured contact angle by using Young's equation (*23*)

$$\gamma_{jf} = \gamma_f - \gamma_j \cos\theta_{jf} \qquad (1)$$

where γ_j and γ_f are the surface tensions of the homopolymer and the random copolymer, and θ_{jf} is the contact angle for homopolymer j on the brush with styrene content f. γ_M and γ_S differ by 1% at most, according to the literature (*24*). From experiments on block copolymers, $\gamma_M > \gamma_S$ (*8*, *9*, *18*). Because the surface tensions depend on the M_w, temperature, and isotopic substitution and the analysis is sensitive to the ratio γ_M/γ_S, literature values cannot be used to interpret the contact angle data. From the measured contact angles of PS on a PMMA brush and PMMA on a PS brush, γ_M/γ_S is estimated as 1.004 $\pm$ 0.002 at 170°C. Using γ_S = 29.9 erg/cm^2 (*24*), then γ_M = 30.02 $\pm$ 0.06 erg/cm^2. The surface tension of P(S-r-MMA), γ_f, was taken to be

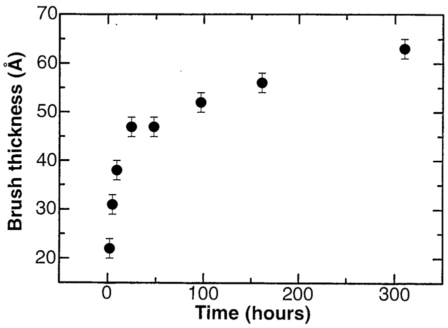

Fig. 1. Grafted layer thickness as a function of the annealing time for hydroxyl-terminated polystyrene (M_w = 1 × 10^4) at 140°C.

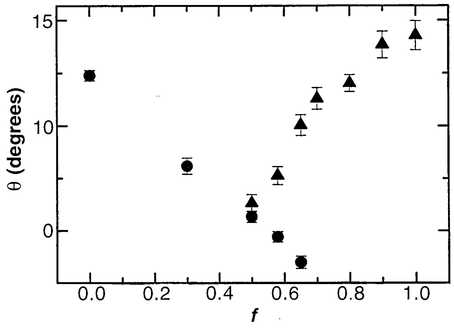

Fig. 2. Contact angles (θ) for PS (circles) and PMMA (triangles) on P(S-r-MMA) brushes as a function of f in the random copolymer. The droplet height h and diameter $d = 2r$ were measured for 10 different droplets on each sample, and the contact angle was calculated by assuming a spherical cap shape and using the formula $\cos\theta = 1 - 2(h/r)^2$. For a typical droplet, h was $\sim$150 nm, r was $\sim$10 μm, and $h \ll r$.

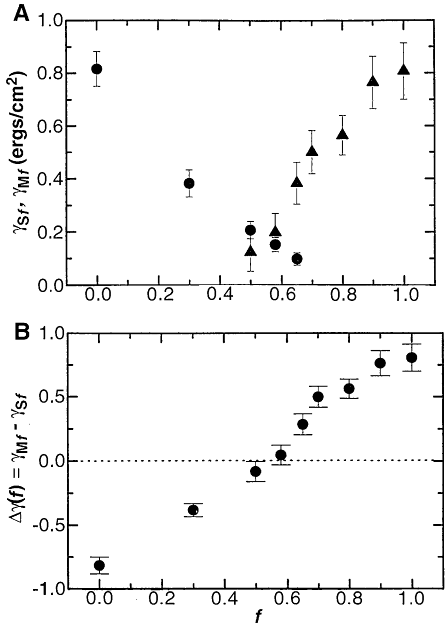

Fig. 3. (**A**) Interfacial energies γ_{Sf} and γ_{Mf} and (**B**) $\Delta\gamma(f) = \gamma_{Mf} - \gamma_{Sf}$ for PS (circles) and PMMA (triangles) on a P(S-r-MMA) brush as a function of f. The near-linear variation of $\Delta\gamma$ with f is in keeping with theoretical arguments (*26*).

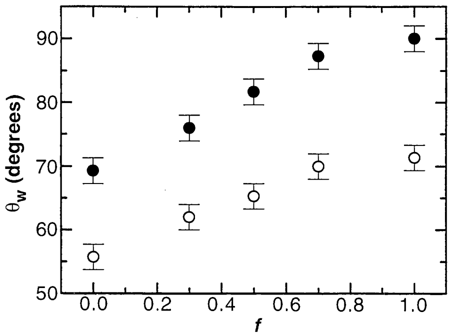

Fig. 4. Advancing (solid circles) and receding (open circles) contact angles for water (θ_w) on the random copolymer brush surfaces as a function of f.

the weighted average of γ_M and γ_S (*25*). Therefore,

$$\gamma_f = f\gamma_S + (1 - f)\gamma_M \qquad (2)$$

The resulting interfacial energies γ_{Sf} and γ_{Mf} and the interfacial energy difference $\Delta\gamma(f) = \gamma_{Mf} - \gamma_{Sf}$ are shown in Fig. 3, A and B. $\gamma_{Mf} = \gamma_{Sf}$ at $f = 0.57 \pm 0.05$. The uncertainty in f results from uncertainties in the contact angles. When $\gamma_{Sf} = \gamma_{Mf}$, the interactions between the polymers and the surface are balanced and the surface is neutral. Thus, grafting a random copolymer brush with this composition onto a surface will produce a surface with no preferential affinity for either component.

Because the homopolymer penetrates several nanometers into the random copolymer brush, these experiments do not provide information on the composition of the random copolymer immediately at the surface. X-ray photoelectron spectroscopy cannot provide quantitative information, because MMA portions of the random copolymer can decompose in the x-ray beam. To address this, the contact angle of water (θ_w) on the random copolymer brush surfaces was measured as a function of f (Fig. 4). θ_w increased monotonically with the styrene content of the copolymer, possibly saturating at higher values of f. These results show that the surface energy can be tuned precisely between that of PS and PMMA, and that the composition of the brush at the surface is quite similar to that in the interior of the brush.

By simply varying the composition of a random copolymer grafted onto a surface, the wetting behavior of a homopolymer on that surface can be changed in a highly controllable fashion. This technique should prove especially useful for controlling the surface behavior of polymer blends and block copolymers, because the relative surface affinity of the two components can be precisely controlled. Thus, it is a simple matter to produce a surface having nonpreferential interactions for a given pair of polymers. This method is applicable to any pair of polymers for which an end-functionalized random copolymer can be prepared in a well-controlled fashion. Other architectures besides linear copolymerization may also be used, such as graft copolymers with controllable graft length and density. The method discussed here should also be useful in controlling the interfacial behavior of simple fluids and in modifying surfaces to achieve biocompatibility.

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Dinitrogen Bridged Gold Clusters

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A family of dinitrogen complexes, $[(LAu)_6(N_2)]^{2+}$ (L = a phosphine), with the dinitrogen unit bridging two clusters of three gold atoms have been prepared from hydrazine and $[(LAu)_3(O)]^+$. Structural characterization of the $PPh_2{}^iPr$ (Ph, phenyl; ^{i}Pr, isopropyl) derivative shows a nitrogen-nitrogen single-bond distance indicative of hydrazido ($N_2{}^{4-}$) character for the dinitrogen unit. The complexes can be reduced and protonated to give low [13% when L = PPh_2Me (Me, methyl)] to quantitative [100% when L = $P(p\text{-}MeOC_6H_5)_3$] yields of ammonia, establishing that bonding of dinitrogen to six metal atoms can lead to facile cleavage of the nitrogen-nitrogen bond.

Many metal-N_2 complexes are known, the vast majority of which involve only one or two metal atoms, with just a few involving three metal atoms (Fig. 1) (*1*). Here, we report the preparation and characterization of a family of N_2 complexes with six metal atoms, in clusters of three, bonding simultaneously to the N_2 unit. In addition, these N_2 complexes can be reduced and protonated to give NH_3, establishing that N_2 in such an environment can be activated, leading to reduction to NH_3.

The synthesis of the N_2 complexes—$[(LAu)_6(N_2)]^{2+}$ (**1**) with L = PPh_2Me, PPh_2Et (Et, ethyl), PPh_3 (*2*), $P(p\text{-}MeC_6H_5)_3$, $P(p\text{-}MeOC_6H_5)_3$, $P(p\text{-}CF_3C_6H_5)_3$, $PPh_2{}^iPr$, or $P(o\text{-}MeC_6H_5)_3$—involves the addition of excess (2 to 3 equivalents) anhydrous hydrazine to dichloromethane solutions of $[(LAu)_3(\mu\text{-}O)]^+$ (*3*) as $BF_4{}^-$, $PF_6{}^-$, or $CF_3SO_3{}^-$ salts

$$2[(LAu)_3(\mu\text{-}O)]^+ + NH_2NH_2 \rightarrow \underset{\mathbf{1}}{[(LAu)_6(N_2)]^{2+}} + 2H_2O \qquad (1)$$

The addition of diethylether or pentane to the reaction mixtures gives the products as thermally stable yellow to orange-yellow solids in 80 to 98% yield based on Au. The complexes were characterized by elemental analyses and nuclear magnetic resonance spectroscopy (*4*). We determined the structure of three derivatives by single-crystal x-ray diffraction analyses. Two of these are salts of **1** with L = PPh_3 and showed apparent multiple phenyl ring and anion orientations. The orientational disorder could not be adequately modeled, and the structure of a third derivative was determined. The structure of **1** with L = $PPh_2{}^iPr$, as the $BF_4{}^-$ salt, is well ordered (*5*) (Fig. 2). The dication **1** in this structure is situated on an inversion center, and the overall core structure is that of a trigonally elongated octahedron (a trigonal antiprism) of Au atoms with the N_2 lying at the center along the trigonal axis. The same core structure is observed in the disordered structures of **1** with L = PPh_3.

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