XPS Study of Surface Composition of a Segmented Polyurethane Block Copolymer Modified by PDMS End Groups and Its Blends with Phenoxy

Jianming Wen and Gabor Somorjai*

Department of Chemistry, and Materials Science Division, Lawrence Berkeley National Laboratory, University of California at Berkeley, Berkeley, California 94720

Florencia Lim and Robert Ward

The Polymer Technology Group, Inc., Emeryville, California 94608

Received September 26, 1996; Revised Manuscript Received May 12, 1997[⊗]

ABSTRACT: Quantitative angle-resolved X-ray photoelectron spectroscopy (XPS) was used to investigate surface modification of a newly developed biomaterial, segmented polyurethane capped with poly(dimethylsiloxane) (PDMS) end groups, and its blends with phenoxy. The composition of the freshly prepared films are not in equilibrium but they can be equilibrated both in air and in water. The surface segregation of PDMS is found both in nonequilibrium and in equilibrium states. XPS data also indicate that the PDMS is enriched in the film surfaces of both air/polymer and glass substrate/polymer interfaces for the pure segmented polyurethane and its blends. The surface composition is affected by annealing temperature and water. Below the polymer glass transition temperature, there is a small increase in PDMS surface concentration during annealing. Above *T*g, PDMS surface concentration can increase by a factor of 2. The presence of water will decrease the PDMS surface segregation at temperatures both below and above *T*g.

Introduction

Polyurethane block copolymers are two-phase materials have been used to fabricate biomedical devices for the last 2 decades due to their favorable tensile and fatigue properties as well as their thromboresistance.[1,2] The applications include vascular prostheses, catheters, heart valves, cardiac assist devices, and the total artificial heart. The widely spread biomedical applications of this class of polymers have resulted in extensive research activities in this field.[3] *In vivo* applications demand polymers with better chemical and mechanical properties. These properties in the surface region of the polymers are even more important since the surface chemistry between blood/body tissues and the implanted medical devices plays a significant role in the usefulness of the devices. The use of surface modification methods can greatly improve the blood/tissue compatibility and resistance to the degradation of the implanted devices and therefore can extend the lifetime of the devices and reduce the cost of implantation. One way to modify the polymer surface is to couple the surface-active end groups to the backbone polymer during synthesis.[4,5] The use of this method, therefore, leaves the original polymer backbone intact so the polymer retains strength and processability. Polymer chain ends have more degrees of freedom of motion than chemically identical chains bonded at two or more points within the backbone of the polymer. The surface modification, then, can be accomplished through the formation of the molecular overlayers produced by chain folding and alignment/packing of adjacent chains.

In this study, the surface modification effects of a newly developed segmented polyurethane (SPU) block copolymer was studied by angle-resolved photoelectron spectroscopy (XPS). The polymer is poly(dimethysiloxane) (PDMS) terminated segmented polyurethane (PDMS/SPU/PDMS, named BioSpanS SPU). The mixture of PDMS/SPU/PDMS and phenoxy has been studied by contact angle measurement, which shows a strong correlation between surface tension reduction and the amount of PDMS/SPU/PDMS blended with phenoxy.[4] The *in vivo* studies have indeed shown that the implanted devices made from this polymer have a better biocompatibility in terms of better resistance to corrosion.[5] Here we will present a more comprehensive investigation of the surface composition change of PDMS/SPU/PDMS and its blends with phenoxy in different chemical environments.

PDMS containing block copolymers have been studied by many researchers, mainly in the form of diblock copolymers.[6−8] It has been shown that when a block copolymer formed with PDMS and another copolymer, PDMS surface segregation will occur, if the other copolymer has a higher surface tension than PDMS. The extent of segregation can be influenced by many factors, such as different polymer chain lengths. The study of block copolymers with PDMS blocks bonded only at the two ends of the polymer chain is absent in the literature, and this unique structure makes it a good system to study the correlation between the surface composition and polymer structure. The study of mixture of a homopolymer phenoxy (99% by weight) and PDMS/SPU/PDMS (1% by weight) were also carried out to examine the surface modification effect of PDMS/SPU/PDMS on the phenoxy surface.

Experimental Section

PDMS/SPU/PDMS(BioSpanS SPU) is a block copolymer with poly(dimethylsiloxane) (PDMS) as end groups. It was synthesized by The Polymer Technology Group, Inc., of Emeryville, CA. The structure is shown in Figure 1a. It is a segmented polyurethane based on methylene diisocyanate (MDI), with mixed diamine chain extenders of ethylene diamine and 1,3-cyclohexanediamine, and poly(tetramethylene oxide) (PTMO). The monofunctional poly(dimethylsiloxane) was added to the polymer as end groups. The molecular weight of PDMS is about 2000. The molecular weight data of

---

* To whom correspondence should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1997.

S0024-9297(96)01442-8 CCC: $14.00

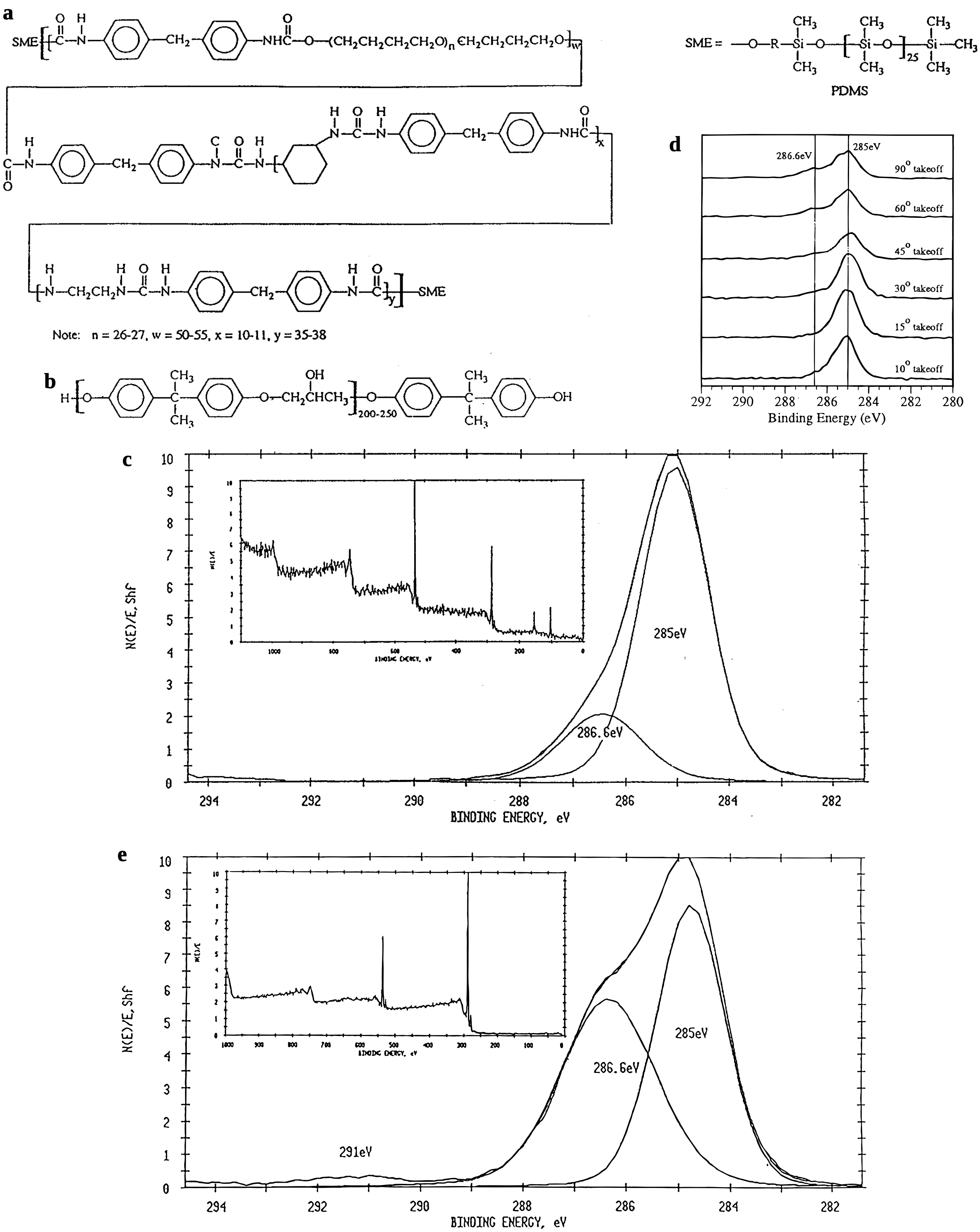

Figure 1. (a) Molecular structure of BioSpanS SPU (PDMS/SPU/PDMS copolymer). The end groups are PDMS. (b) Molecular structure of phenoxy. (c) BioSpanS XPS survey spectrum at a 45° takeoff angle. Si peaks (Si1s at 150 eV, Si2p at 103 eV) are solely due to PDMS. The C1s high-resolution spectrum of BioSpanS SPU shows two peaks. The ratio of the two peaks are angle-dependent. (d) AR-XPS spectra of C1s for PDMS/SPU/PDMS. (e) Phenoxy XPS survey spectrum at a 45° takeoff angle. The C1s high-resolution spectrum of phenoxy shows two peaks as well. A carbon shake-up peak is found at 291 eV due to the $\pi-\pi^*$ transition originating from aromatic rings in the structure.

PDMS/SPU/PDMS is listed in Figure 1a as well. For our blend studies, the homopolymer of phenoxy was purchased from Union Carbide. The structure of phenoxy is shown in Figure 1b. Both the PDMS/SPU/PDMS film and films of blends of PDMS/SPU/PDMS and phenoxy were prepared in a similar manner. First, the polymer solution was made by dissolving polymers in dimethylacetamide (DMAc). The concentration was adjusted in the range of 1−2 % by weight of polymers.

Then the films were solvent-cast onto clean glass substrates. The films were then dried in air at 65 °C for 24 h. The film thickness was measured by an Alpha-Step 50V Surface Profiler after it was cooled to room temperature. The thickness of cast films was controlled in the range 40−150 mm depending on the solution concentration and volume used. The surface composition of both air and substrate facing side of films were analyzed.

XPS experiments were performed on a Perkin-Elmer PHI 5300 XPS spectrometer with a position-sensitive detector and a hemispherical energy analyzer. The Mg Kα X-ray source of the XPS spectrometer was operated at 400 W with 15 kV acceleration voltage. A pass energy of 178 eV was used for survey spectra with a 45° takeoff angle. For angle-resolved XPS measurements, a pass energy of 17.9 eV was used for high-resolution spectra. Silicon 2p (102 eV), carbon 1s (285 eV), nitrogen 1s (400 eV), and oxygen 1s (533 eV) regions were acquired with variable takeoff angles (normally 15°, 30°, 45°, and 90°). The takeoff angle is defined as the angle between the detector and the sample surface. At a small takeoff angle, the detector will only collect electrons emitted from the shallow region near the surface. At a high takeoff angle, the detector will collect electrons emitted from deeper layers as well. Therefore, by changing the takeoff angle, a concentration depth profile can be obtained.

The elemental composition was calculated from integrated peak areas which result from the silicon 2p, carbon 1s, nitrogen 1s, and oxygen 1s core levels. The PHI sensitivity factors for the PHI Omni-Focus lens were used to calculate atomic concentrations from peak areas. The binding energy scale was referenced by setting the C−H peak maximum in the C 1s spectrum to 285.0 eV.

Poly(dimethylsiloxane) (PDMS) groups, which were bonded to the segmented polyurethane at the two ends, are the only groups in PDMS/SPU/PDMS containing Si. The −Si−O−Si− backbone of the PDMS can be used to identify the end groups. The XPS survey spectrum (with 45° takeoff angle) of pure PDMS/SPU/PDMS with 24 h annealing at 65 °C is shown in Figure 1c (inset). The silicon 1s (150 eV) and 2p (102 eV) electrons are only from the backbone of the PDMS. The carbon 1s (285 eV) and oxygen (533 eV) 1s electrons were contributed from every segment of the polymer. C1s was fit with two peaks as shown in Figure 1c. The main peak (285 eV) in the C1s spectra is due to CH$_{x,x=2-3}$. The carbons in C−O groups within the soft segment of PDMS/SPU/PDMS contribute C1s at higher binding energy (286.6 eV) with a lower intensity. At a small takeoff angle, the C−O groups give rise to the shoulder of the main peak, while at a larger angle, the shoulder becomes an individual small peak (Figure 1d). The ratio of the two C1s components are used to characterize the presence of different segments at the surface. The binding energy of carbons from both carbamate (NCOO) and urea (N$_2$CO) groups in hard segments is expected at ∼289 eV.[9] However, Figure 1c shows no peak around 289 eV. The nitrogen 1s (400 eV) electrons are only from the hard segment. This peak can be used as an indicator for the presence of the hard segment (connected with both carbamate and urea groups) of PDMS/SPU/PDMS. From Figure 1c, no N1s peak is observed. Therefore, based on C1s and N1s peak analyses, no hard segment is found from the 45° takeoff angle XPS spectra.

Figure 1e shows the XPS spectra of pure phenoxy. Only carbon and oxygen are observed in the spectra. A carbon shake up peak with a weak intensity is found at around 291 eV, which is due to a $\pi-\pi^*$ transition from the aromatic rings in phenoxy. This peak was not observed in the PDMS/SPU/PDMS spectrum. The high-resolution C1s spectra show two peaks as well. One is assigned to methyl group carbons with a lower binding energy (285 eV), and the other one with a higher binding energy (286.6 eV) is assigned to carbons connecting to an O atom (ether carbon). The C1s spectra of phenoxy, like that of PDMS/SPU/PDMS, may result from more than two types of carbon in the polymer. The small difference in binding energy among these carbons make them difficult to separate, and in this study it is not necessary to separate them. Their presence may be identified by the shake-up peak at 291 eV. The Si2p/C1s ratio is used to monitor the Si concentration change in the surface region. The depth profile of the Si-containing groups was investigated in the surface regime with a depth varying from 25 to 100 Å.[10] The maximum sampling depth of XPS for the polymer samples is estimated to be ∼100 Å.[10,11]

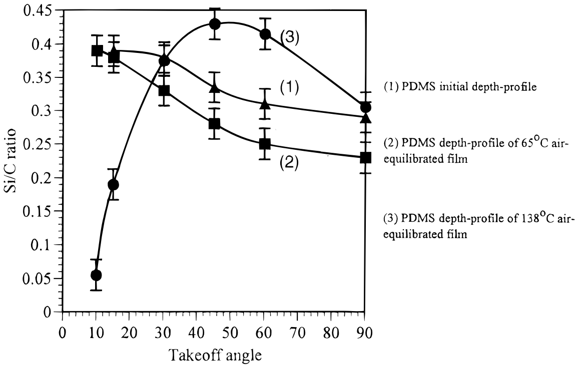

Figure 2. Air-equilibrated PDMS/SPU/PDMS film surface composition (Si/C) at 65 °C and 138 °C. The Si/C ratios are angle-dependent. The film equilibrated at 138 °C has a low Si/C ratio in the near surface region.

Results and Discussion

Functionalizing the block copolymer with groups which can modify the polymer surface composition during the implant device fabrication is of importance in polymer surface modification.[4] In this study, XPS data have shown that the silicon-containing groups (PDMS) in PDMS/SPU/PDMS are found to be enriched on both the polymer/air interface and the polymer/glass substrate interface compared to the case where a random distribution of PDMS was assumed. In the following section, the films at equilibrium state will be discussed first, and then the evolution of film surface composition from as-cast nonequilibrium to equilibrium will be addressed.

1. Surface Composition of Air-Equilibrated Polymer Films. (a) Surface Composition of a Pure PDMS/SPU/PDMS Film at Equilibrium State. We show, first, the XPS data of the pure PDMS/SPU/PDMS film which has reached its equilibrium. Figure 2 shows the angle-resolved XPS data for PDMS/SPU/PDMS at the equilibrated air/polymer interface. When the film was annealed at 65 °C over a period of 96 h, then the film is in its equilibrium state. Its surface composition did not change anymore after further annealing at this temperature. At the air/polymer interface, the Si2p/C1s intensity ratio decreases as the XPS sampling depth increases. This suggests that the concentration of the Si-containing groups is enriched at the surface, and the Si enrichment gradually becomes less pronounced away from the interface toward the polymer bulk.

For all collected data, the Si/C ratio is smaller than the stoichiometric values, assuming a complete PDMS end group overlayer on the polymer surface. The calculated values of this ratio from PDMS should be around 0.5 since two methyl groups are associated with one Si atom in the backbone. However, the measured number is around 0.39. The smaller Si/C ratios at the surface suggests that the other components of the polymer are present at the surface as well.

The results of curve fitting of the C1s peak are summarized in Table 1. As mentioned previously, two peaks are used to characterize the carbon atoms in different polymer segments, peaks for carbons in CH$_{x(x=2,3)}$ groups and C−O groups, respectively. We assign CH$_x$ to the peak at 285 eV and C−O to the peak at 286.6 eV. At the smallest takeoff angle, the C1s contains both C$_{285eV}$ and C$_{286.6eV}$ components. At high

Table 1. 65 °C Data for the Air-Equilibrated BioSpanS on the Air Facing Side

takeoff angle (deg)	Si/C	Si/C_{285eV}	$C_{285eV}/C_{286.6eV}$
10	0.39	0.42	14.9
15	0.38	0.41	14.9
30	0.33	0.4	4.7
45	0.28	0.38	2.7
60	0.25	0.34	2.7
90	0.23	0.32	2.4

takeoff angle, the ratio of the two components ($C_{285eV}/C_{286.6eV}$) decreases. The angle dependence of the ratio of $C_{285eV}/C_{286.6eV}$ suggests that segments containing the C−O groups are away from the surface while the PDMS end groups segregate at the near-surface regime. The lack of a C peak at ~289 eV (carbons in NCOO and N_2-CO) suggests that the hard segments of PDMS/SPU/PDMS are not present in the surface.

If we take the $C_{286.6eV}$ contribution to the Si/C ratio into consideration, the ratios Si/C_{285eV} are still smaller than the stoichiometric values of Si/C for PDMS end group. The smaller Si/C_{285eV} suggests that other carbon atoms with the same binding energy may be present at the surface; therefore, a larger C_{285eV} peak intensity will result in a smaller Si/C_{285eV}. In this polymer, carbon atoms which have the same binding energy peak could be carbons in the soft segment of the PDMS/SPU/PDMS as well. The soft segment is composed of two types of carbons, CH_2-CH_2- and CH_2-O-, respectively. The large molecular weight of the CH_2-CH_2- group in the soft segment may make a significant contribution to C_{285eV} . On the basis of the analysis of Si/C and Si/C_{285eV} ratios, the surface is mostly occupied by PDMS with a small amount of soft segment $-(-O-CH_2-CH_2-CH_2-CH_2-O-)_n$. The depth profile shows that the PDMS decreases in concentration in the bulk, and the soft segment it increases in concentration.

With XPS and static secondary ion mass spectrometry (SIMS), Ratner *et al.* have shown the surface segregation of soft segment in PEU's.[12,13] The PEU's were composed of soft segments (either poly(propylene glycol) (PPG) or poly(tetramethylene glycol) (PTMG)) and hard segments based on methylenebis (phenylene isocyanate) (MDI) and butanediol. These segments are similar to the segments in PDMS/SPU/PDMS.

There are studies concerning diblock copolymers of PDMS and other blocks. In these studies the PDMS blocks were found to segregate at the topmost surface region. The degree of segregation has been found as a function of copolymer structures.[11,14] Gardella *et al.* reported that the PDMS chain length has a significant effect on the PDMS surface segregation in the diblock copolymer PDMS−Bisphenol A polycarbonate (BPAC).[11] A copolymer with a longer PDMS chain was found to have a higher percentage of PDMS in the air/polymer interface region. The molecular architecture of the PDMS/SPU/PDMS can be viewed as a multiblock polymer with two small MW (2000) end groups as PDMS. The midblocks between the PDMS groups are diblocks with PTMO soft segment and MDI/diamine chain extenders hard segments. Although the PDMS groups in PDMS/SPU/PDMS have a small molecular weight compared with other domains in the copolymer, this structure has a favorable configuration for PDMS to populate the interface region. The PDMS is at the ends of the polymer chain; this position permits more freedom of motion for the end groups since only one end of the PDMS group is bound. One PDMS end group has even a higher freedom of motion than the other due to its connection with the long soft CH_2 domain. The Si-containing groups (PDMS) segregation at the near-surface regime can be understood in terms of surface tension arguments. The driving force for surface segregation to occur is the surface energy difference in the different domains of a copolymer system. Domains with low surface energy will move to the surface to minimize the overall surface energy of the system. The thermodynamically stable state is determined by the balance of decrease in surface energy and the increase in chemical potential occurring during the demixing process. In our case, the lower surface tension component PDMS will move to the surface to reduce the interfacial energies.

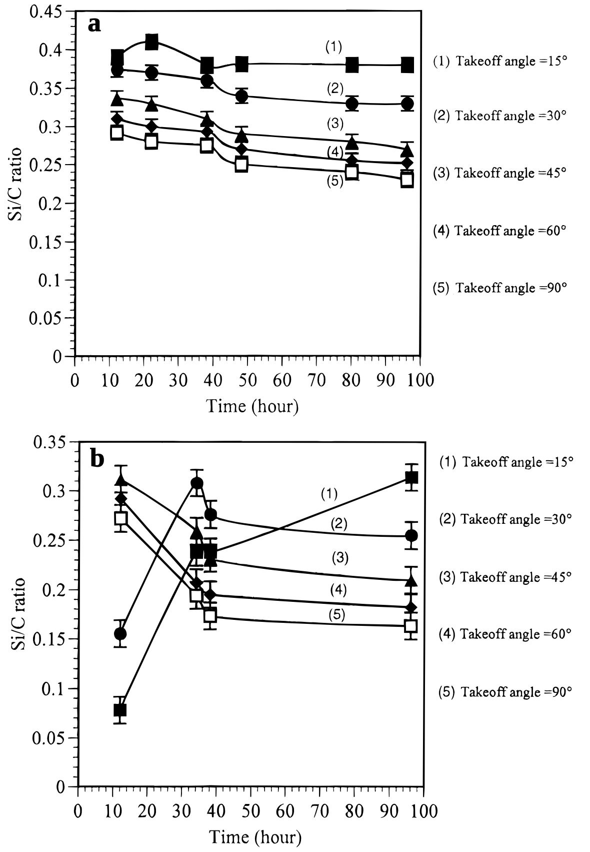

Figure 3. Pure PDMS/SPU/PDMS copolymer surface compositions change as a function of annealing time at 65 °C: (a) for air facing side surface, the change is slightly declining; (b) for substrate facing side, the change in Si/C ratio is dramatic. The Si/C ratio for a small takeoff angle increases while the Si/C ratio for a large takeoff angle decreases.

(b) Evolution of the Surface Composition of the PDMS/SPU/PDMS Film. Changes in surface composition during the course of the reaction from the non-equilibrium state to the final equilibrium state were monitored.

Figure 3 illustrates the changes in both sides in terms of the Si/C ratio for PDMS/SPU/PDMS annealed at 65 °C in air. For the substrate facing side surface, after 12 h of annealing, the Si/C is low at the small takeoff angle (15°); only 0.08 was observed. As annealing times increased to 34 h, the ratio has a substantial increase to 0.23 for the same takeoff measurement. For longer annealing time (96 h) at this temperature, the Si/C ratio reaches 0.3. For high takeoff angle (90°) measurement, the change in Si/C ratio is just the opposite. The ratio is high (0.26) for 12 h of annealing and decreases to 0.19 for 34 h of annealing. After 96 h of annealing, the Si/C ratio drops to 0.15. This clearly shows the process of PDMS segregation at the surface of the polymer. The Si/C ratio of the surface region increases at the same time the Si/C ratio of the deeper layers decreases. The PDMS is diffusing from deeper layers in the polymer film to the surface region. The movement of PDMS from bulk to surface (on the order of 10^2 Å in distance) occurs in a time scale of tens of hours at this temperature.

For the air facing side of the polymer surface, a change in the Si/C ratio is also observed, but the rate of change for the same period of time is slower. For all takeoff angles, the Si/C ratios decline slightly. After 96 h annealing at 65 °C, the Si/C ratio reaches a minimum. The decreased equilibrium Si/C ratio can also be observed for the air facing side surface of the pure PDMS/SPU/PDMS film which was air-equilibrated at a higher temperature. Figure 2 (curve 3) shows the angle-resolved XPS data of the air facing side of the film air-equilibrated at 138 °C. The film was first annealed at 65 °C for 24 h and then annealed at 138 °C for another 36 h. The film was in its equilibrium state and no further change in the surface composition was observed with additional annealing for 12 h at 138 °C. This indicates that at higher temperature the equilibrium state can be reached after a shorter period of annealing. The data show a decline in the Si/C ratio of surface region, about six times smaller than when it was annealed at 65 °C the same sampling depth.

The decline in equilibrium PDMS surface concentration at high annealing temperature can be understood by the phase separation theory. PDMS/SPU/PDMS can be qualitatively viewed as a binary system with PDMS as one component and the rest of the polymer blocks as other component. The decline in equilibrium PDMS surface concentration can be explained by the Wagner equation,[15] which described the equilibrium surface and bulk concentrations at different temperatures for a monolayer ideal-solution binary system. For an ideal binary system, $X_{2(s)}/X_{1(s)} = X_{2(b)}/X_{1(b)}\ \exp(a(\gamma_1 - \gamma_2)/RT)$, where γ_1 and γ_2 are surface tension for components 1 and 2 and a is a constant. The molar fraction ratio of the two components at the surface is proportional to the molar fraction ratio in the bulk. Both the surface and bulk compositions should approach the same value at high temperature when $\exp(a(\gamma_1 - \gamma_2)/RT)$ approaches 1. Therefore, at higher temperatures (larger T), the surface segregation effect is reduced. The experiments have shown that for a symmetric diblock copolymer the high-temperature annealing will result in a random orientation of the polymer chain, which means a decline in surface segregation. For annealing at low temperature, microphase separation between different blocks will occur, and the structure of the copolymer shows a lamellar configuration.[16] This supports our observation of the temperature dependence of the PDMS enrichment.

(c) Surface Composition of Blend at the Equilibrium State. PDMS surface segregation not only occurs in pure copolymer PDMS/SPU/PDMS but also in solution blends of PDMS/SPU/PDMS and phenoxy.

Blending a small amount of a low surface energy block copolymer into a homopolymer has been used as an effective way to modify the surface composition and reduce the surface tension of the polymeric systems.[17] In this study phenoxy was chosen for its thermodynamic compatibility with the segmented polyurethane and its high solid surface tension as a pure polymer. The blend was composed of 99% by weight of phenoxy and 1% by weight of PDMS/SPU/PDMS.

The film with 1% by weight PDMS/SPU/PDMS in phenoxy was air-equilibrated at 65 °C until the Si/C ratio no longer changes. Figure 4 shows AR-XPS data of the 1% by weight blend at the air facing side. The data indicate that the Si/C ratio has a surface gradient. Close to the surface region, the Si concentration is higher than in deeper layers. A comparison made between 1%wt PDMS/SPU/PDMS blend and pure PDMS/SPU/PDMS indicates a small difference in the Si/C ratio. At a 15° takeoff angle, the Si/C is close to each other (at ~0.38). It suggests that most of the blended PDMS/SPU/PDMS is present in the near-surface region of the blend film with PDMS oriented near the surface. The overlayer of PDMS on the blend surface shows a strong modifying effect on the surface composition. At a 90° takeoff angle, the Si/C ratio for 1% by weight blend is lower than that of pure PDMS/SPU/PDMS. For the blend film, the Si/C is ~0.17 while the Si/C ratio for the pure PDMS/SPU/PDMS is ~0.23. This indicates that in deeper layers the composition departs from the PDMS/SPU/PDMS composition.

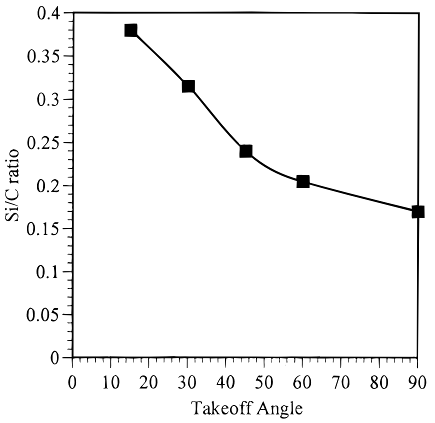

Figure 4. Air-equilibrated film surface composition (Si/C) of 1% by weight PDMS/SPU/PDMS with phenoxy blend at 65 °C. Si/C ratios are close to that of pure BioSpanS.

The surface composition of the glass substrate facing side of the polymer (during the annealing, this side was not exposed to air) is also examined when the composition of the air facing side reaches its equilibrium. The result is also presented in Figure 4. The data show that the Si/C ratios for the glass substrate facing side are segregated as well. The equilibrium Si/C ratios, however, are smaller than those for the air facing side of the polymer surface, which may be due to the contact of the polymer with the glass substrate.

(d) Polymer Blend Surface Composition Changes as a Function of Temperature. As-cast films of polymer mixture with 1% by weight bulk concentration of PDMS/SPU/PDMS in phenoxy were treated in air at different temperatures.

Figure 5 illustrates the Si/C ratio of the substrate facing side surface as a function of time when annealed at room temperature and 42, 64, and 115 °C. From DSC measurements, the 1 % by weight blend has a glass transition temperature (Tg) of 60 °C. Below the polymer Tg, annealing has a limited effect on the surface composition. Above Tg, annealing will increase the PDMS surface concentration. The surface composition of the blend was characterized by XPS at a 45° takeoff angle. At room temperature, the Si/C ratio is constant over a period of 96 h after casting. This can be explained by the fact that below the glass transition temperature the PDMS/SPU/PDMS inside of a matrix of phenoxy has little, if any, freedom of diffusion to segregate at the near-surface regime. At a slightly higher temperature, 42 °C, but still below the Tg, the Si/C ratio starts to show some change over a time period of 28 h. Increasing the Si/C ratio suggests that polymer chains have a limited freedom of motion, especially the

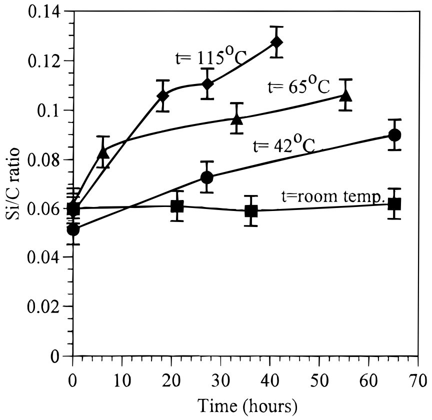

Figure 5. Change in Si/C for substrate facing side of 1% by weight PDMS/SPU/PDMS with phenoxy blend as annealing temperature increases. The polymer has a *T*g at ~60 °C. At room temperature annealing below *T*g, the surface composition is constant. At an annealing temperature above *T*g, the PDMS increases in surface concentration.

low *T*g components in the polymer. PDMS/SPU/PDMS is moving from deep in the bulk to the surface. At 115 °C, a temperature higher than the glass transition temperature, the data show that the rate of Si/C ratio increase is much faster than that at lower temperatures. In 38 h, the film has a Si/C ratio of ~0.12.

The as-cast film blends are in nonequilibrium configurations and change their compositions upon annealing at different temperatures. This can be explained in terms of kinetics. Thermodynamically, due to its low surface tension, PDMS will move to the surface to minimize the surface free energy of the polymer mixture. However, at annealing temperature below *T*g, the polymer exhibits a rigid matrix where all the polymer chains are fixed at their positions. Therefore, low surface tension components of the polymer essentially have no chance to reach their thermodynamically preferred surface compositions. The compositions of the polymer films are held at the as-cast states which are far from the equilibrium configurations over a long period of time. When the polymer is annealed at temperature above *T*g, the framework of the polymer becomes flexible and the low surface tension PDMS has a better chance to diffuse through the matrix to reach its equilibrium states. Therefore, the surface composition change of as-cast films during annealing is kinetic-limited.

2. Surface Composition of a Water-Equilibrated Polymer Film. (a) Surface Composition of 1% by Weight Blend at Equilibrium State. The interaction between H_2O and the polymer film can be very important if the presence of water changes the surface composition. The polymer composition in the hydrated enviroment may reflect the true composition as the polymer device is implanted. The 1% by weight blend film was in contact with water for over 320 h at room temperature until its Si/C did not change anymore.

Figure 6 shows the angle-resolved XPS data for the polymer blend surface compositions. For three different depths of air facing side surface (takeoff angles are 15, 45, and 90°, respectively), the Si/C ratios are close to each other and are 0.178, 0.174, and 0.155, respectively. This indicates that PDMS surface segregation is still detectable but compared to the film equilibrated in air the surface segregation is reduced as a result of interaction with water. Due to the presence of water, the near-surface regime has a much smaller Si/C ratio compared to what was measured from the air-equilibrated film.

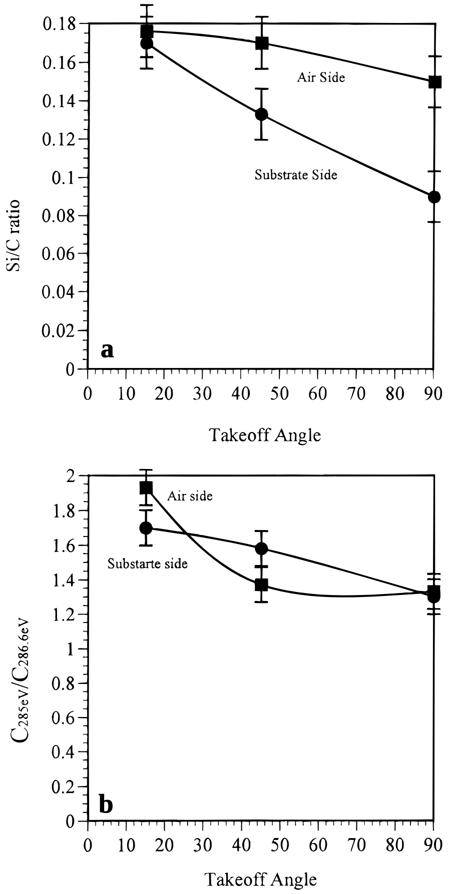

Figure 6. (a) Water-equilibrated film surface composition (Si/C) of 1% by weight PDMS/SPU/PDMS with phenoxy blend at room temperature. Si/C ratios are low compared to that of the air-equilibrated film. (b) $C_{285eV}/C_{286.6eV}$ ratio from the C1s peak of the film, showing an angle-dependent trend.

At a 15° takeoff angle, the Si/C ratio drops by 60%. On the other hand, PDMS in the deeper layers are less sensitive to water than those near the surface. At a 90° takeoff angle, the Si/C ratio drops 35%. The change in Si/C ratios of the polymer film under the influence of water suggests that the PDMS groups of PDMS/SPU/PDMS are moving from the surface into the polymer bulk.

The curve fitting of C1s peak shows similar results. The $C_{285eV}/C_{286.6eV}$ ratios for three takeoff angles are similar to each other. Compared to the strong surface segregation of PDMS in the air-equilibrated film, the presence of water changes the depth profile significantly. In water, the PDMS surface enrichment has a great decrease. The increase in $C_{286.6eV}$ intensity and decrease in C_{285eV} intensity in the surface region suggest that the $-O-CH_2-CH_2-CH_2-CH_2-O-$ groups move to the surface region and the CH_3 groups in PDMS move into the polymer film bulk. The C1s XPS spectra show no peak at 289 eV for all three depths. This suggests that the carbons from both carbamate (NCOO) and urea (N_2CO) groups in hard segments are present in the polymer bulk beyond the detection of XPS.

(b) The Effect of Water on Evolution of the Polymer Blend Surface Composition. As discussed before, in air the methyl groups on the $-Si-O-Si-$ backbone of PDMS are at the air/polymer interface. The interaction between H_2O and the blend film decreases the PDMS surface concentration. Here we examine how the PDMS surface concentration decreases in water as a function of time and temperature.

The initial surface compositions were obtained before water was introduced. Then the film was placed in

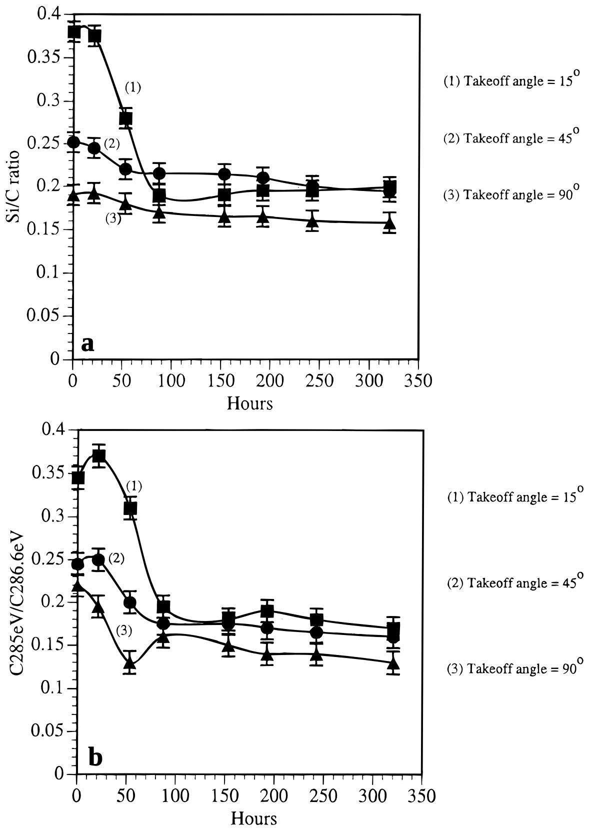

Figure 7. (a) Air facing side Si/C ratio of 1% by weight blend treated in room temperature water as a function of in-water time. (b) Air facing side ratio of C1s low bonding energy peak intensity to C1s high bonding energy peak intensity as a function of in-water time (the same blend).

water. After a few hours the film was taken out from water, dried in the air and then in a vacuum at room temperature, and introduced into the XPS chamber. After XPS acquisition, the film was placed back in water. This cycle was repeated to obtain the Si/C ratio change which reflects the water influence on the surface composition. The out-of-water time for each acquisition was estimated within 1−3 h. Two temperatures were chosen to investigate the polymer/H_2O interaction: one was below the *T*g, and the other was above *T*g.

The hydrated polymer surface structure may change when the film is transferred from water to the XPS chamber for measurements. For our polymer system, the time scale to have a significant change is much longer than the time needed to finish the XPS measurements. It was evident from sum frequency generation (SFG) measurements on the same polymer.[18] The CH_3 groups of PDMS move back to the surface layer in over several hours. Therefore, we estimate that within the XPS sampling depth, the surface restructuring during analysis is negligible.

Figure 7a shows the Si/C ratios for the air facing side of the 1% by weight blend as a function of in-water time at room temperature for 15, 45, and 90° takeoff angles. Data for all angles have similar behaviors. The Si/C ratio drops fast for the first few hours. but for times up to 80 h, the decline of the Si/C ratios become slower. It is true for all three angles. Figure 7b is a result of curve fitting of the XPS C1s peak. The ratio has pattern similar to the Si/C ratio. As mentioned previously, this is a plot of the ratio of the C1s low binding energy peak (285 eV) to the C1s high binding energy peak (286.6 eV) as a function of in-water time. The latter, corresponding to the C from the $-O-CH_2-$ group, increases in intensity as the film-in-water time increases, while the C1s low binding energy peak (285 eV) decreases in intensity. Among all three takeoff angle measurements, the rates of Si/C and $C_{285eV}/C_{286.6eV}$ ratio decrease are different. The 15° takeoff angle measurement has the fastest decrease.

At room temperature, as the XPS data suggest, in air the 1% blend film has a constant composition in terms of the Si/C ratio. The PDMS end groups of PDMS/SPU/PDMS enriched in this surface region remain unchanged due to the higher than room temperature glass transition temperature. In the H_2O environment, however, the methyl groups are in touch with H_2O, and it is an unfavorable condition for the hydrophobic groups. Therefore, the Si/C drop might be interpreted as the CH_3 groups trying to relax themselves from H_2O by folding away from the interface, and the flexible $-Si-O-Si-$ backbone permits the motion of CH_3 groups and even moves with the methyl groups. The $-Si-O-Si-$ backbone moving away from the interface into a deeper surface makes the Si/C ratio near the surface decrease. At the same time, the $-O-CH_2-$ section in the $-O-CH_2-CH_2-CH_2-CH_2-O-$ groups may move toward the interface due to its hydrophilic property. Therefore the $-Si-O-Si-$ backbone (with CH_3 groups) and the $-O-CH_2-CH_2-CH_2-CH_2-O-$ groups switching positions is most likely taking place in the same time scale. Although it is not completely understood that the $-O-CH_2-CH_2-CH_2-CH_2-O-$ groups of the PDMS/SPU/PDMS can have some degree of freedom to diffuse toward the interface under the influence of water at temperature below *T*g, the affiliation with water can be a strong driving force to move the hydrophilic group. Both carbamate (NCOO) and urea (N_2CO) groups in hard segments are hydrophilic, but under the experimental conditions, they are absent in the surface, which is suggested by the fact that no C1s 289 eV peak and no N1s 400 eV peak are detected from XPS.

It is possible that the H_2O penetrates the interface to interact with the deeper layers of the film. In fact the Si/C ratio, for 45 and 90° takeoff angles are decreased as well, although the rates are smaller (Figure 7a). This might be understood by the fact that PDMS/SPU/PDMS can absorb a small amount of water. It was reported that 3% by weight of water was found in the water-treated films at 37 °C.[19] This small amount of water can drive PDMS groups into an even deeper layer in the same fashion. The fact that the rate is slow can be explained by the following model: (1) surface PDMS are driven from the outmost region; (2) the driving force for PDMS to go deeper is small due to a smaller amount of water present inside the film. The PDMS concentration in this region is a result of a balance between those two types of PDMS motion.

It is worthwhile to note that after the Si/C ratio decrease reaches a minimum when the film has been in water for over 300 h, Si/C ratio is still considerably larger compared to the case where the PDMS were randomly distributed throughout the blend. The surface modifying effect from PDMS is still significant. This may be important since the implanted devices made from PDMS/SPU/PDMS will be in contact with water during their application life.

We also examined the effect of water on the 1% by weight blend at higher temperature. Table 2 illustrates that the fast drop in Si concentration occurs for a film that is water-treated at 65 °C. The Wagner equation can be used to explain the sharp decrease of the surface Si/C ratio as well. For a small takeoff angle, within 36

Table 2. Comparison of the Temperature Effect on 1% BioSpanS Blend in Water

takeoff angle (deg)	Si/C ratio *t* = 0 h	Si/C ratio *t* = 36 h
Air Side Surface at Room Temperature		
15	0.379	0.275
45	0.252	0.219
90	0.19	0.18
Air Side Surface at 65 °C		
15	0.379	0.021
45	0.252	0.21
90	0.19	0.19

h, the Si/C ratio decreases from 0.38 to 0.02. For other two angles, however, Si/C ratios drop more than that at room temperature. At a temperature above the *T*g of the polymer, the flexibility of the polymer chains reaches a degree so that not only the low *T*g $-Si-O-Si-$ backbone has freedom to move but also the $-O-CH_2-CH_2-$ CH_2-CH_2-O- soft segment is able to move. The increased mobility of the polymer chains at higher temperature may provide open channels for water molecules to penetrate the polymer surface easier and therefore drive PDMS into the bulk further. However, due to a large amount of $-Si-O-Si-$ backbone moving into deeper layers, the high takeoff angle measurements show only a small decline in the Si concentration.

On the basis of this study, the surface PDMS concentration of PDMS/SPU/PDMS is affected by both the annealing temperature and water. Annealing at temperature below the polymer *T*g will have a limited effect on the PDMS surface concentration. Water will reduce the PDMS surface concentration both below and above *T*g.

Conclusions

In this study, quantitative angle-resolved XPS was used to investigate surface modification of PDMS/SPU/PDMS biomaterial and its blends with phenoxy. The freshly prepared films are not in their equilibrium configuration and they can be equilibrated both in air and in water. The surface segregation of PDMS of the PDMS/SPU/PDMS copolymer is found both in nonequilibrium and in equilibrium states. XPS data also indicate that the PDMS is enriched in the film surfaces of both air/polymer and glass substrate/polymer interfaces for pure PDMS/SPU/PDMS and its blends. An enrichment gradient is also observed from these surfaces which shows that the deeper layer has less segregation than shallower surface layers. The surface composition is affected by annealing temperature and water. Below the polymer glass transition temperature, the PDMS surface concentration has a limited increase during annealing. Above *T*g, the PDMS surface concentration can increase by a factor of 2. The presence of water will decrease the PDMS surface segregation at temperatures both below and above *T*g.

Acknowledgment. We thank Drs. Enrico Magni and Frank Ogletree of Lawrence Berkeley National Laboratory for their help in XPS measurements. J.W. acknowledges financial support from The Polymer Technology Group, Inc. This work was supported in part by Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, U.S. Department of Energy, under Contract No. DE-AC03-76SF00098.

References and Notes

(1) Lelah, M. D. and Cooper, S. L. *Polyurethanes in Medicine*; CRC: Boca Raton, FL, 1986.
(2) *Surface and Interfacial Aspects of Biomedical Polymers*; Andrade, J. D., Ed.; Plenum: New York, 1988.
(3) Wirpsza, Z. *Polyurethanes, Chemistry, Technology, and Applications*; Chichester: New York, 1993.
(4) White, K. A.; Ward, R. S.; Wolcott, C. A.; Wong, K. Presented at the ACS Polymer Division Symposium, Polymer Surface Modification for Biomedical Applications, Anaheim, CA, April 2−5, 1995.
(5) Ward, R. S.; Coviello, S; Gill, R. S.; White, K. A; Bertolet, R. D. Presented at the Fifth World Biomaterials Congress, Toronto, Canada, May 29−June 2, 1996.
(6) Jalbert, C. J.; Koberstein, J. T.; Balaji, R.; Bhatia, Q.; Salvati, L., Jr.; Yilgor, I. *Macromolecules* **1994**, *27*, 2409.
(7) Chen, X.; Gardella, J., Jr.; Cohen, R. *Macromolecules* **1994**, *27*, 2206.
(8) Fleischer, C. A.; Koberstein, J. T.; Krukonis,V.; Wetmore, P. A. *Macromolecules* **1993**, *26*, 4172.
(9) Castner, D. G.; Ratner, B. D. *J. Vac. Sci. Technol.* **1988**, *A6*, 964.
(10) Jalbert, C. J.; Koberatein, J. T.; Balaji, R.; Bhatia, Q. *Macromolecules* **1994**, *27*, 2409.
(11) Seah, M. P.; Dench, W. A. *Surf. Interface Anal.* **1979**, *1*, 2.
(12) Hearn, M. J.; Ratner, B. D.; Briggs, D. *Macromolecules* **1988**, *21*, 2951.
(13) Hearn, M. J.; Briggs, D.; Yoon, S. S.; Ratner, B. D. *Surf. Interface Anal.* **1987**, *10*, 384.
(14) Vavasour, J. D.; Whitemore, M. D. *Macromolecules* **1992**, *25*, 5477.
(15) Somorjai, G. A. *Introduction to Surface Chemistry and Catalysis*; John Wiley & Sons: New York, 1994; p 286.
(16) Coulon, G.; Russell, T. R.; Deline,V. R.; Green, P. F. *Macromolecules* **1989**, *22*, 2581.
(17) Hu, W.; Koberstein, J.; Lingelser, J.; Gallot, Y. *Macromolecules* **1995**, *28*, 5209.
(18) Zhang, D.; Somorjai, G. A. To be published.
(19) Ward, R. S.; White, K. A.; Wolcott, C. A. *Transactions of the 20th Annual Meeting of the Society for Biomaterials*; Society for Biomaterials: Boston, MA, 1994.

MA961442R