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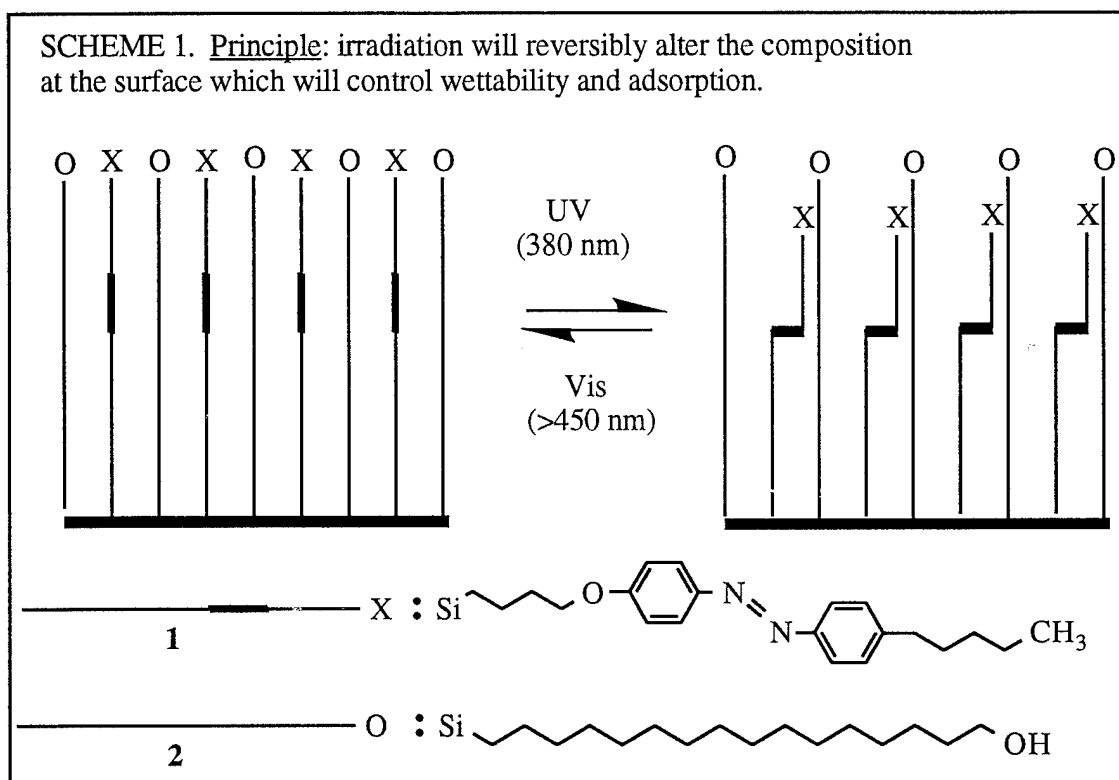
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# STATIC AND MOBILE POLYMER SURFACES OF WELL-DEFINED STRUCTURE FINAL REPORT

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DAAL03-92-G-0402  
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## PROBLEM STUDIED

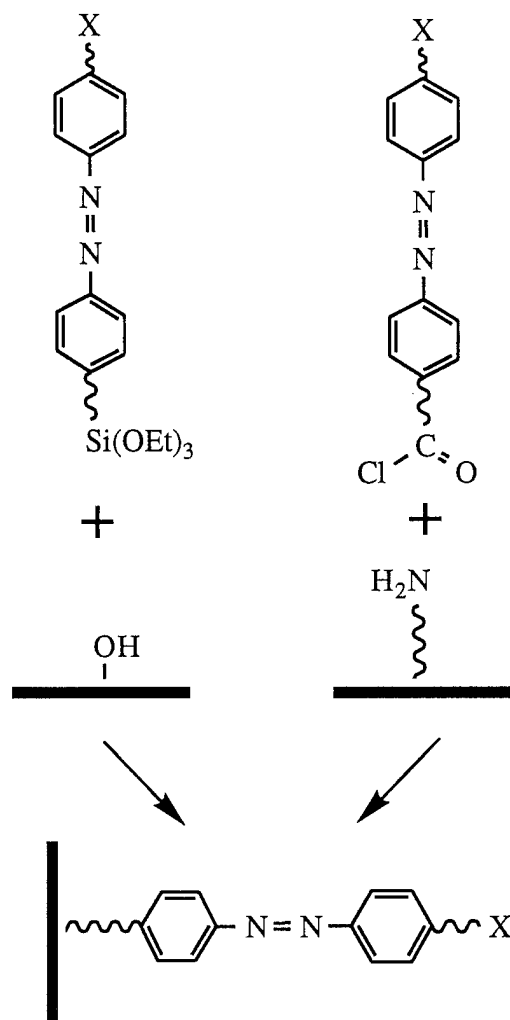
Photoactive self-assembled monolayers (SAMs) containing azobenzene chromophores were prepared and studied (see Scheme 1). The photoresponsive group induced reversible changes in the wettability of the surface depending on whether the surface is exposed to visible or ultraviolet light. Because protein adsorption is tied to wettability, protein adsorption studies utilizing self-assembled monolayers were performed. Molecular modeling of azobenzene SAMs revealed important structural considerations for the optimization of the photoresponsive effect.



## SUMMARY OF MOST IMPORTANT RESULTS

### Synthesis of Photoactive Monolayers

Scheme 2 depicts the two synthetic approaches to azobenzene monolayers that produced the best photoresponsive effect. One involved the direct deposition of triethoxysilanes and the second was the in situ functionalization of amine-terminated SAMs with azobenzene derivatives containing an acid chloride group.



Scheme 2. Synthetic Approaches to Photoactive SAMs

Highlights of this synthetic work include:

- SAMs containing azobenzene were fully characterized using a combination of ATR-IR spectroscopy, water contact angles, ellipsometry, X-ray reflectometry, and ESCA.
- Characterization was consistent with the attachment of azobenzene to the surface. However, X-ray reflectometry indicated a film thickness that was approximately 40-50% of the calculated film thickness for fully extended chains. The X-ray results suggest that film coverage was less than 100%.
- SAMs were prepared where the terminal functional group was either a hydrogen or a pentyl group ( $X = \text{H}, \text{C}_5\text{H}_{12}$  in Scheme 2). The length of the spacer between the azo linkage and the surface was also varied. The photoresponsive effect was measured by the change in the water contact angle upon exposure to 365 nm light. Under ambient conditions (normal interior lighting), the contact angle of an azobenzene SAM ranged from 75-85 degrees. Exposure effected a 5-10 degree decrease in the water contact angle. This decrease was reversible for many cycles.

- Attempts to prepared mixed monolayers according to Scheme 1 were unsuccessful.

### In-situ Study of Protein Adsorption to Functionalized SAMs

Novel in situ neutron reflectivity investigation of the absorption of HSA from solution onto functionalized SAM surfaces confirmed that the absorption of a proteins to a tailored surface could be varied using the synthetic techniques developed in this project. An important contribution was also made to the general field of adsorption characterization, as the spatial resolution offered by the in situ reflectivity measurements is improves upon that previously available by several orders of magnitude. In a collaborative effort involving scientists at the National Institute of Standards and Technology's Reactor Radiation Division and Becton Dickinson we have quantified differences in the near interface composition profiles for HSA in solutions next to  $-CH_3$ ,  $-NH_3^+$ , and silicon oxide surfaces. This approach collects information on the solution-surface interaction while the surface is in a biologically relevant state. Complementary NR measurements made using variable scattering contrast as well as X-ray reflectometry measurements of the functionalized monolayers themselves before exposure to solution were key to refining concentration profiles from the data.

While no adsorption is detected at the native oxide of silicon, adsorption does occur for both the  $-CH_3$ , and  $-NH_3^+$  terminated surfaces. Both overall amount adsorbed in the protein rich layer next to the surface and the concentration immediately adjacent to the surface increased with bulk solution concentrations in the range from 0.005% to 0.1% HSA. Concentration profiles next to the  $-NH_3^+$  terminated surfaces consist of at least two distinct regions connected by a diffuse interface, as shown in Figure 1. The first region, immediately adjacent to the surface, presents a plateau in concentration at a level more than two orders of magnitude higher than the bulk concentration. This region has a nominal thickness close to 4 nm, which is comparable to the smallest dimension of the protein's molecular envelope. A second region contains a very slowly decaying concentration at levels less than one tenth that of the very concentrated layer. No such second region is found for the concentration profiles next to the  $-CH_3$  terminated surfaces.

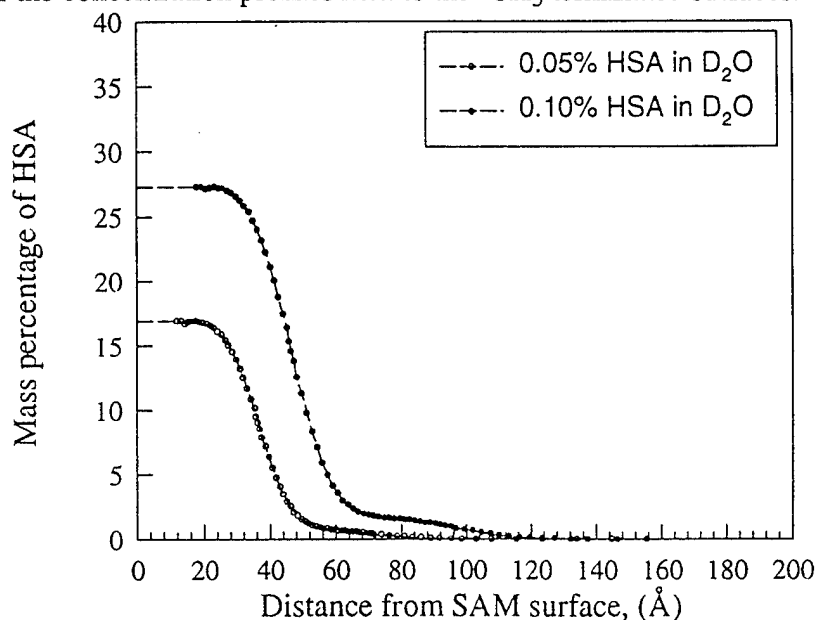


Figure 1. Composition profile of the interphase separating the bulk HSA solution and SAM surface derived from NR data for 0.05% and 0.1% HSA solutions.

## Molecular Dynamics Simulations of Azobenzene Monolayers

- Dense-packed SAMs (one chain for every 21 Å<sup>2</sup>) prepared with azobenzene in the *trans* conformation do not provide sufficient free volume for relaxation of the end-to-end distance of the chain when the azobenzene unit undergoes the photoinduced *trans-to-cis* isomerization.
- However, if the surface area accessible to the azobenzene is tripled, to 63 Å<sup>2</sup>, there is sufficient free volume for significant relaxation of the end-to-end distance of the chain when the azobenzene unit undergoes the photoinduced *trans-to-cis* isomerization. Merely doubling the accessible free volume (42 Å<sup>2</sup> per azobenzene-containing chain) is insignificant.
- The easiest way to insure that there is sufficient free volume for relaxation of the end-to-end distance in the chain with *cis* azobenzene is to prepare the SAM with the azobenzene-containing chain in the *cis* conformation, which implies preparing the SAM under uv irradiation.
- Therefore reversible photocontrol of the surface of the SAM will be marginal, at best, if the SAM is prepared under ordinary bench conditions (with the azobenzene in the *trans* conformation), but will be more impressive if the SAM is prepared under uv irradiation, with the azobenzene in the *cis* conformation.
- Slightly better performance might be expected for SAMs in which the azobenzene is placed near the head group, or near the tail, rather than in middle of the chain. However, this effect is not as important as the ones described above.

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