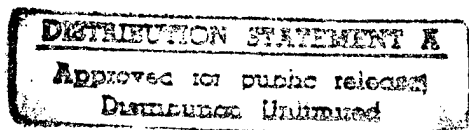


**Final Report**  
**for**  
**ONR N00014-93-C-0105**

**“STRUCTURAL DETERMINATION OF THE FACTORS  
WHICH INFLUENCE MOLECULAR ADHESION TO  
POLYMER SURFACES”**

**J. F. Rabolt**

**Materials Science Program  
University of Delaware**



**August 18, 1997**

**DTIC QUALITY INSPECTED 2**

**19970916 146**

## I. Introduction

The local structural characteristics of a surface is believed to have profound effects on the adhesion and other tribological properties of the surface. The quest for surfaces better suited for functions that require tight control of these properties, has been the main thrust for this investigation. Our approach is to establish better understanding of the molecular structure-surface properties relations. In the current funding period, molecules with different chemical functionalities and architectural arrangement have been studied to identify the relative importance of different factors.

## II. Results

### A. Self-Assembled Small Molecule Thiols

We have established a robust database for the film structures of  $\text{CF}_3(\text{CF}_2)_7\text{N}(\text{H})\text{C}(\text{O})(\text{CH}_2)_2\text{SH}$  in the previous period. A related system with short and long alkyl segments between the fluorinated blocks and thiol groups, namely,  $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{SH}$  and  $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_{11}\text{SH}$ , plus their mixtures with the previously characterized amide thiol, are studied. The fluorinated part of these molecules are rigid and the alkyl part are, on the other hand, quite flexible. Spectroscopy techniques were used to characterize the structure and orientation of these films. The morphology built by mixing thiols of different lengths was tested for its correlation with surface adhesion properties. Our results show that the inclusion of a long hydrocarbon sequence into the backbone of a semifluorinated n-alkyl thiol molecule has a marked effect on its orientation on gold surface. Furthermore, the orientation of the fluorocarbon helix is also affected and appears to be more tilted in marked contrast to other semifluorinated n-alkyl thiols with short hydrocarbon sequences. Monolayer formed from two-component mixtures of  $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_{11}\text{SH}$  (long) and  $\text{CF}_3(\text{CF}_2)_7\text{N}(\text{H})\text{C}(\text{O})(\text{CH}_2)_2\text{SH}$  (short) and a consistent depletion of the shorter  $\text{CF}_3(\text{CF}_2)_7\text{N}(\text{H})\text{C}(\text{O})(\text{CH}_2)_2\text{SH}$  on the surface was observed relative to the initial solution concentration. On the other hand, the surface concentration of  $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{SH}$  (short) and  $\text{CF}_3(\text{CF}_2)_7\text{N}(\text{H})\text{C}(\text{O})(\text{CH}_2)_2\text{SH}$  (short) closely reflected the solution concentration in marked contrast to the  $\text{CF}_3(\text{CF}_2)_7\text{N}(\text{H})\text{C}(\text{O})(\text{CH}_2)_2\text{SH} / \text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_{11}\text{SH}$  case.

## **B. Self-Assembled Crystalline Polymers**

By codeposition of a self-assembling polymer (S-PMMA) and a compatible partner (PEO), we formed an ultra thin blended film with a unique morphology. The blended amorphous regions serve to anchor the two polymers to the substrate surface; the crystalline regions are anisotropic with the helical axes preferentially assuming an orientation perpendicular to the substrate. The association of the two polymers in solution appears to be partially responsible for this final film architecture since crystallites in cast films of the semicrystalline polymer (PEO) by itself are randomly oriented. The change in orientation of a thin cast film of PEO upon annealing indicates that the presence of a surface or interface is also important in determining the morphology of this polymer. Hence the small film dimensions and the interaction of the two polymers in the blended film are apparently both necessary conditions for achieving the special orientation of PEO crystallites.

## **C. Self-Assembled Rubbery Polymers**

As a contrast to surfaces composed of crystalline polymers, thiol-modified PDMS were self-assembled onto gold surfaces and their surface properties have been investigated by different spectroscopy techniques. Three samples with 1-3%, 5-10% and 100% propyl thiol modification respectively, have been studied. The results indicate that only a part of the thiol stickers are bonded to the surface, with the remaining thiol groups dispersed quite uniformly throughout the film thickness. By controlling the sticker population, we can control the thickness of the self-assembled films; the higher the sticker concentration, the thinner the film thus formed. Polarized IR results also showed that the Si-O backbone of the self-assembled films are preferentially lying parallel to the surface. This is likely to be due to the anchoring of the polymer chains. On a different test, dynamic contact angle data were used to determine the surface composition and mobility. In the 100%SH-PDMS case, the excess thiol groups "seen" simultaneously with PDMS chains by water are believed to be responsible for the large hysteresis. In the 1-3%SH PDMS sample, the surface heterogeneity is minimized by the reduction of thiol

stickers. However, the anchoring of the polymer chains still reduces the reorganization of chains which is also responsible for the hysteresis phenomenon. By reducing both contributing factors for hysteresis, self-assembled silicone thin films may be used as water repellent surface coating. The observed 1-2 degree hysteresis in water contact angle for 1-3%SH PDMS is as low as that of a highly crosslinked bulk PDMS surface, but with a thickness of only a few nanometers.

#### **D. Side Chain Effects in Polymer Films**

A specifically designed amphiphilic copolymer with long hydrocarbon side groups, hydrophilic spacers, and disulfide sticky side groups was synthesized and its thin films were produced by self-assembly and Langmuir-Blodgett techniques on gold surfaces. The films were studied by ellipsometry, x-ray photoelectron spectroscopy, contact angle measurements, and infrared spectroscopy. No structural order was found in the self-assembled film. The formed film has poor structural integrity and is largely porous. Annealing and swelling with other materials could not improve the ordering of the long side chains of the copolymer. As an alternative way, Langmuir-Blodgett films of this copolymer were produced at 50 mN/m surface pressure. The film structure was studied by reflection-absorption FT-IR spectroscopy on water surface in-situ. The crystallization of the long hydrocarbon was observed as increasing the surface pressure of the surface film on water. The film was then transferred onto gold surface and its microstructure was studied. It has been found this side chain order has lost during or after the transferring process. It is believed that the strong interaction between the disulfide groups and the Au atoms are responsible to this structural rearrangement. This hypothesis has been confirmed by examining the S<sub>2p</sub> high resolution XPS scans. Bonded and free sulfur are both exist in the film. This strong interaction will disrupt the ordering of the side chains. Side chain order is confirmed to be preserved when film was transferred onto a non-interaction substrate ZnSe. This study provides the importance of the molecular architecture as well as the film-substrate interaction to the film microstructure and integrity.

## E. Organic/Inorganic Hybrid Polymers

Among the linear polymers which contain silicon atoms in their backbones, the polycarbosilanes have been the least studied, despite their unique position in relation to the all-carbon (polyolefin) and all-silicon (polysilane) backbone polymers. The simplest example of the linear polycarbosilanes is poly(silylenemethylene) or polysilaethylene ( $[\text{SiH}_2\text{CH}_2]_n$ ) (PSE), which can be viewed as a hybrid of the prototypical all-organic polymer, polyethylene  $[\text{CH}_2\text{CH}_2]_n$ , and the all-inorganic polysilane,  $[\text{SiH}_2\text{SiH}_2]_n$ . In addition to the interest in PSE as an analog of PE and the parent member of an emerging family of poly(silylenemethylenes), this polymer is also of interest as a precursor to silicon carbide, an important ceramic material. The recent synthesis of PSE (Prof. Len Interrante at RPI ) in a pure, high molecular weight form via the ring-opening polymerization of tetrachlorodisilacyclobutane has now made it available for detailed study and preliminary results have provided ample justification for such a study, both as a SiC precursor and as a novel hybrid inorganic/organic polymer. Our interest in this organic/inorganic hybrid polymer lies in the fact that the function/structure dilemma often encountered in material applications may be resolved by the incorporation of organic sections with desired functions such as electrochemical activity, and inorganic section with desired structural properties such as grain size or strength. Vibrational spectroscopy and wide angle x-ray diffraction methods, in conjunction with ab initio calculations have been employed to characterize the solid state conformation of polysilaethylene (PSE), a mono-silicon analog of polyethylene and the parent member of a growing family of poly(silylenemethylenes). The existence of a phase transition at about  $-20^\circ\text{C}$  was also observed, below which the PSE backbone takes on a planar zig-zag conformation. Thermal studies (DSC) reveal a single exothermic melting peak in the same temperature range. Many of the vibrational bands of PSE were identified by the combination of Raman and IR spectroscopy, and assigned with the aid of symmetry analysis and ab initio quantum chemistry calculations. The sharp Raman band observed at  $706\text{ cm}^{-1}$  upon cooling PSE below about  $-20^\circ\text{C}$  was found to be associated with the all-trans conformation of the polymer in its crystalline form. Wide angle x-ray diffraction

provided further verification for the all-trans, planar zig-zag conformation. The understanding we gained from this simplest organic/inorganic hybrid polymer can lead us to further exploration of hydriis polymers with desired structure and functionalities.

#### **F. Protein Adsorption Tests**

Protein adsorption tests were carried in collaboration with Prof. Ratner at U of Washington. The tests were first done on SAMs made with the semifluorinated thiol system discussed in "A". 10%  $^{125}\text{I}$ -labeled bovine serum solution was used for the adsorption tests. Testing period was set at 2 hours and the termination was done by dilution displacement with buffer solution. A gamma counting system was used to detect the amount of adsorbed protein on the SAMs. The results from this test showed that the surfaces made with  $\text{CF}_3(\text{CF}_2)_7\text{N}(\text{H})\text{C}(\text{O})(\text{CH}_2)_2\text{SH}$ ,  $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{SH}$  and their mixtures at different compositional percentages all showed unusually high protein adsorption. SAMs made with the longer  $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_{11}\text{SH}$ , on the other hand, show lower adsorption than the shorter systems. However, both the short and long semifluorinated SAMs give adsorption levels higher than the PTFE surface. Based on our previously established database on the structure of these systems, this observation seems to indicate that either the chain orientation at the surface or the thickness, or perhaps both, are playing a role in determining the sticking of the protein molecules in this case since the shorter semifluorinated thiols tend to stay normal the surface, while the longer ones are tilted away from the surface normal. PTFE, nevertheless, keep its chains parallel to the surface. Semifluorinated thiols potentially capable of forming SAMs with even higher tilt angles are in the process of being synthesized (Prof. Ringsdorf, U of Mainz). We will put this hypothesis to test in the future.

#### **G. Liquid Crystals as Surface Probes**

Besides surface spectroscopy techniques, we started using liquid crystal molecules as probes for surface structure of different SAMs. When a liquid crystal in its isotropic phase is loaded between two parallel surfaces with SAM on each side, the orientation of the liquid crystal after it is cooled into nematic or smetic phases will

depends heavily on the interaction between the liquid crystal and the two template surfaces. By making the substrate of the SAMs transparent, we used transmission polarized microscopy to study the effects of different SAMs on the liquid crystal. Dramatic difference in optical textures was observed in different SAM systems. These textures manifest the optical birefringence caused by different orientation of the liquid crystal molecules. In general, degree of surface order and mobility can be detected by this technique. For example, the crystalline S-PMMA described in "B" gives schlieren texture which is characteristic of planar-oriented liquid crystal. For the different PDMS SAMs described in "C", the 1-3% and 5-10%SH PDMS SAMs, i. e., the two loosely bound surfaces, give homeotropic alignment of the liquid crystal (normal to the surface); on the other hand, the tightly bound 100%SH PDMS gives schlieren texture just like the crystalline PMMA. The optical textures shown by this probing technique clearly illustrate the difference in mobility for these polymeric surfaces. The semifluorinated thiol system has also been tested in collaboration with Prof. Nick Abbott at UC Davis.

## **H. Ab Initio Calculations**

During the investigation in the PDMS and PSE systems, we started a series of ab initio calculations using Mulliken, a software package developed by researchers at IBM Almaden Research Laboratory, San Jose, California. We focused on the vibrational spectroscopic information from these calculations and compared the results with our experimental data. These ab initio calculations involve oligomers (of polymers) with 40 to 60 atoms and different basis sets (3-21G\*, 6-31G\* and DZP) as well as oligomer sizes are used to establish the robustness of the calculations. Dynamic viewing feature of the Mulliken software further enable us to "see" the vibrational motion of each calculated band. This feature can be used to assist band assignment, especially for new material systems that have never been studied before. The calculated spectra show excellent agreement with experimental data and indeed help the band assignment effectively. Furthermore, two strong features around  $1100\text{cm}^{-1}$  in the PDMS infrared spectrum previously assigned as Si-O stretching without distinction were identified as symmetric (higher frequency) and asymmetric (lower frequency) Si-O stretching modes,

respectively. This identification is further confirmed by our polarized IR experimental data and can be used for an indicator for PDMS chain orientation in the future. Our calculations have shown that ab initio calculation of polymeric systems is possible when enough care is used.

### **III. Summary**

The extent of interaction between a protein layer and a surface is influenced by three major factors: the chemical architecture of the surface, its mobility, and its complexity. This project has provided the chance to prepare well characterized surfaces with controlled architecture which could be used to test various hypotheses of protein adhesion. The results of this comprehensive study will provide clear guidelines for the molecular design and the processing protocols required to produce minimally adhesive surfaces and those which provide optimum release under hydrodynamic shear.

### **IV. Publications Resulting from this Funding Period**

1. "Structural Investigation of Molecular Organization in Self-Assembled Monolayers of a Semifluorinated Amidethiol", T. J. Lenk, V. M. Hallmark, C. L. Hoffmann, J. F. Rabolt, D. G. Castner, C. Erdelen and H. Ringsdorf, *Langmuir* **10**, 4610 (1994)
2. "Surface Chemical Activation of Quartz Crystal Microbalance Gold Electrodes: Analysis of Frequency Changes, Contact Angle Measurements and Grazing Angle FTIR", E. M. Pachinger, D. N. Furlong, F. Caruso, C. L. Hoffmann and J. F. Rabolt, *Thin Solid Films* **260**, 192 (1994)
3. "Self-Assembled Thin Film Blends by Polymer Codeposition: Poly(ethylene oxide) and Poly(methyl methacrylate)", C. L. Hoffmann and J. F. Rabolt, *Macromolecules* **29**, 2543 (1996)



4. "Anchoring of Nematic Liquid Crystals on Self Assembled Monolayers Formed from Semifluorinated Alkanethiols", W. Miller, V. K. Gupta, N. L. Abbott, M.-W. Tsao and J. F. Rabolt, *Liquid Crystal* **23**, 175 (1997)
5. "Studies of Molecular Orientation and Order in Self Assembled Semifluorinated n-Alkylthiols: Single and Dual Component Mixtures", M.-W. Tsao, C. L. Hoffmann, J. F. Rabolt, H. Johnson and D. G. Castner, *Langmuir* **13**, 4317 (1997)
6. "Formation and Characterization of Self Assembled Films of Thiol-Derivatized Poly(dimethyl siloxane) on Gold", M.-W. Tsao, K.-H. Pfeifer, J. F. Rabolt, D. G. Castner, L. Haeussling and H. Ringsdorf, *Macromolecules* (accepted)
7. "Thin Film Structure and Properties of Sulfur-Derivatized Amphiphilic Brush Copolymers", Y. Ren, C. L. Hoffmann, M.-W. Tsao, J. F. Rabolt, D. G. Castner, S. L. Hsu, L. Haeussling and H. Ringsdorf, *Langmuir* (submitted)
8. "Studies of the Solid State Conformation of Poly(silaethylene): An Organic/Inorganic Hybrid Polymer with an Alternating C/Si Backbone", M.-W. Tsao, K.-H. Pfeiffer, J. F. Rabolt, D. B. Holt, B. L. Farmer, L. V. Interrante and Q. Shen, *Macromolecules* **29**, 7130 (1996)
9. "FTIR Study of the Changes in Orientation and Chemistry of Langmuir-Blodgett Films of Cadmium Arachidate During the Formation of O-State CdS Nanoparticles", R. S. Urquhart, C. L. Hoffmann, J. F. Rabolt, D. N. Armstrong, N. J. Geddes and F. Grieser, *J. Phys. Chem.* **99**, 15987 (1995)
10. "Reactions of Complex Ions of Platinum and Palladium in Langmuir-Blodgett Films of Metal Arachidates", D. Elliot, D. N. Furlong, T. R. Gengenbach, F. Grieser, R. S. Urquhart, C. L. Hoffmann and J. F. Rabolt *Langmuir* **11**, 4773 (1995)

11. "Structure in Thin and Ultrathin Spin-Cast Polymer Films", C. W. Frank, V. Rao, M. M. Despotopoulou, R. F. W. Pease, W. D. Hinsberg, R. D. Miller and J. F. Rabolt  
*Science* **273**, 912 (1996)