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Self-Assembled Organic Monolayer Films

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SUMMARY OF ACCOMPLISHMENTS

→ This project comprised three components, all relevant to organic surface chemistry.

1) Polymer Surface Functionalization. This research has developed a comprehensive surface chemistry for surface-oxidized low-density polyethylene film, and used the resulting surface-functionalized materials to define the stability and properties of this class of materials. Although the specific results are directly applicable only to polyethylene, the principles and techniques should be widely applicable in organic polymer chemistry.

2) Self-Assembled Organic Monolayer Films. This work has tested methods for making several classes of self-assembled organic monolayer films, and has examined the structures of these films using a range of spectroscopic techniques (especially X-ray photoelectron spectroscopy, polarized reflectance infrared spectroscopy, and low-angle X-ray reflection). The best ordered monolayers (which are quasi 2-D crystals) are obtained by reaction of alkyltrichlorosilanes on silicon or chemisorption of alkanethiols on gold.

3) Physical-Organic Chemistry of Wetting. Wetting has been extensively explored as a probe of surface structure and composition. It has useful characteristics that complement the spectroscopic methods: it is very sensitive to surface structure, and responds only to the top ~5 Å of the surface; it is applicable to the solid-liquid interface; it is inexpensive to study. A reasonably sound understanding of static wetting at equilibrium is now in hand; the kinetics of wetting are still being explored. (AUD)

List of Papers Published, in Press, or Submitted

1. "Acid-Based Behavior of Carboxylic Acid Groups Covalently Attached at the Surface of Polyethylene: The Usefulness of Contact Angle in Following the Ionization of Surface Functionality" Holmes-Farley, S.R.; Reamey, R.H.; McCarthy, T.J.; Deutch, J.; Whitesides, G.M. Langmuir 1986, 1, 725-740.
2. "Fluorescence Properties of Dansyl Groups Covalently Bonded to the Surface of Oxidatively Functionalized Low-Density Polyethylene Film" Holmes-Farley, S.R.; Whitesides, G.M. Langmuir 1986, 2, 266-282.
3. "Improved Adhesion of Thin Conformal Organic Films to Metal Surfaces" Stewart, K.R.; Whitesides, G.M.; Godfried, H.P.; Silvera, I.F. Rev. Sci. Instrum. 1986, 57, 1381-1383.
4. "The Role of Chemistry in Materials Science" Whitesides, G.M.; Wrighton, M.S.; Parshall, G. in "Advancing Materials Research," National Academy of Sciences, Washington, D.C., 1986, 203-224.

5. "The Reactivity of Carboxylic Acid and Ester Groups in the Functionalized Interfacial Region of 'Polyethylene Carboxylic Acid' (PE-CO₂H) and Derivatives: Differentiation of the Functional Groups into Shallow and Deep Subsets Based on a Comparison of Contact Angle and ATR-IR Measurements" Holmes-Farley, S.R.; Whitesides, G.M. Langmuir, 1986, 3, 62-76.
6. "Reconstruction of the Interface of Oxidatively Functionalized Polyethylene (PE-CO₂H) and Derivatives on Heating" Holmes-Farley, S.R.; Reamey, R.H.; Nuzzo, R.; McCarthy, T.J.; Whitesides, G.M. Langmuir 1987, 3, 799-815.
7. "Monolayer Films Prepared by the Spontaneous Self-Assembly of Symmetrical and Unsymmetrical Dialkyl Sulfides from Solution onto Gold Substrates: Structure, Properties, and Reactivity of Constituent Functional Groups" Troughton, E. B.; Bain, C. D.; Whitesides, G. M.; Nuzzo, R. G.; Allara, D. L.; Porter, M. D. Langmuir 1988, 4, 365-385.
8. "The Structures of Self-Assembled Monolayer Films of Organosulfur Compounds Adsorbed on Gold Single Crystals: Electron Diffraction Studies" Strong, L.; Whitesides, G. M. Langmuir 1988, 4, 546-558.
9. "Wetting of Functionalized Polyethylene Film Having Ionizable Organic Acids and Bases at the Polymer-Water Interface: Relations between Functional Group Polarity, Extent of Ionization, and Contact Angle with Water" Holmes-Farley, S. R.; Bain, C.; Whitesides, G. M. Langmuir 1988, 4, 921-937.
10. "Molecular-Level Control over Surface Order in Self-Assembled Monolayer Films of Thiols on Gold" Bain, C. D.; Whitesides, G. M. Science 1988, 240, 62-63.
11. "Correlations between Wettability and Structure in Monolayers in Alkanethiols Adsorbed on Gold" Bain, C. D.; Whitesides, G. M. J. Am. Chem. Soc. 1988, 110, 3665-3666.
12. "Organic Chemistry in Two Dimensions: Surface-Functionalized Polymers and Self-Assembled Monolayer Films" Whitesides, G. M.; Ferguson, G. S. Chemtracts 1988, 1, 171-187.
13. "Depth Sensitivity of Wetting: Monolayers of ω -Mercaptoethers on Gold" Bain, C. D.; Whitesides, G. M. J. Am. Chem. Soc. 1988, 110, 5897-5898.
14. "Materials for Advanced Electronic Devices" Whitesides, G. M. In Biotechnology and Materials Science: Chemistry for the Future; Good, M. A., Ed.; American Chemical Society: Washington, 1988; Chapter 9, pp 85-99.
15. "Formation of Two-Component Surfaces by the Spontaneous Assembly of Monolayers on Gold from Solutions Containing Mixtures of Organic Thiols" Bain, C. D.; Whitesides, G. M. J. Am. Chem. Soc. 1988, 110, 6560-6561.



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16. "The Anthranilate Amide of 'Polyethylene Carboxylic Acid' Shows an Exceptionally Large Change with pH in Its Wettability by Water" Wilson, M.; Whitesides, G. M. J. Am. Chem. Soc. 1988, 110, 8718-8719.
17. "Formation of Monolayer Films by the Spontaneous Assembly of Organic Thiols from Solution onto Gold" Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M. J. Am. Chem. Soc. 1989, 111, 321-335.
18. "Attenuation Lengths of Photoelectrons in Hydrocarbon Films" Bain, C. D.; Whitesides, G. M. J. Phys. Chem. 1989, 93, 1670-1673.
19. "Comparison of Self-Assembled Monolayers on Gold: Coadsorption of Thiols and Disulfides" Bain, C. D.; Biebuyck, H. A.; Whitesides, G. M. Langmuir 1989, 5, 723-727.
20. "The Structure of Self-Assembled Monolayers of Alkylsiloxanes on Silicon: A Comparison of Results from Ellipsometry and Low-Angle X-Ray Reflectivity" Wasserman, S. R.; Whitesides, G. M.; Tidswell, I. M.; Ocko, B. M.; Pershan, P. S.; Axe, J. D. J. Am. Chem. Soc., in press.
21. "Monolayers of 11-Trichlorosilylundecyl Thioacetate: A System that Promotes Adhesion between Silicon Dioxide and Evaporated Gold" Wasserman, S. R.; Biebuyck, H.; Whitesides, G. M. J. Mat. Res. 1989, 4, 886-892.
22. "The Structure and Reactivity of Alkylsiloxane Monolayers Formed by Reaction of Alkyltrichlorosilanes on Silicon Substrates" Wasserman, S. R.; Tao, Y.-T.; Whitesides, G. M. Langmuir, in press.
23. "X-Ray Specular Reflection Studies of Silicon Coated by Organic Monolayers (Alkylsiloxanes)" Tidswell, I. M.; Ocko, B. M.; Pershan, P. S.; Wasserman, S. R.; Whitesides, G. M.; Axe, J. D. Phys. Rev. B, submitted.
24. "Formation of Monolayers by the Coadsorption of Thiols on Gold: Variation in the Length of the Alkyl Chain" Bain, C. D.; Whitesides, G. M. J. Am. Chem. Soc., in press.
25. "Formation of Monolayers by the Coadsorption of Thiols on Gold: Variation in the Head Group, Tail Group, and Solvent" Bain, C. D.; Evall, J.; Whitesides, G. M. J. Am. Chem. Soc., in press.
26. "A Study by Contact Angle of the Acid-Base Behavior of Monolayers Containing ω -Mercaptocarboxylic Acids Adsorbed on Gold: an Example of Reactive Spreading" Bain, C. D.; Whitesides, G. M. Langmuir, in press.
27. "Modelling Organic Surfaces with Self-Assembled Monolayers" Bain, C. D.; Whitesides, G. M. Angew. Chem. 1989, 101, 522-528.
28. "Combining Spontaneous Molecular Assembly with Microfabrication to Pattern Surfaces: Selective Binding of Isocyanide to Platinum Microwires and Characterization by Electrochemistry and Surface Spectroscopy" Hickman, J. J.;

Zou, C.; Ofer, D.; Harvey, P. D.; Wrighton, M. S.; Laibinis, P. E.; Bain, C. D.; Whitesides, G. M. J. Am. Chem. Soc., in press.

29. "Orthogonal Systems for Self-Assembled Monolayers: Alkanethiols on Gold and Alkane Carboxylic Acids on Alumina" Laibinis, P. E.; Hickman, J. J.; Wrighton, M. S.; Whitesides, G. M. Science, in press.

30. "Local Molecular Structure Determines Wetting at the Interface between Surface-Functionalized Polyethylene and Water" Wilson, M. D.; Whitesides, G. M. J. Am. Chem. Soc., submitted.

31. "The Physical-Organic Chemistry of Surfaces, and Its Relevance to Molecular Recognition" Whitesides, G. M.; Biebuyck, H. Proceedings, Symposium on Chemical and Biochemical Problems, Exeter, England, in press.

List of Technical Reports

TR No. 1: "The Reactivity of Carboxylic Acid and Ester Groups in the Functionalized Interfacial Region of 'Polyethylene Carboxylic Acid' (PE-CO₂H) and Derivatives: Differentiation of the Functional Groups into Shallow and Deep Subsets Based on a Comparison of Contact Angle and ATR-IR Measurements" Holmes-Farley, S.R.; Whitesides, G.

TR No. 2: "Reconstruction of the Interface of Oxidatively Functionalized Polyethylene (PE-CO₂H) and Derivatives on Heating" Holmes-Farley, S.R.; Reamey, R.H.; Nuzzo, R.; McCarthy, T.J.; Whitesides, G.M.

TR No. 3: "Monolayer Films Prepared by the Spontaneous Self-Assembly of Symmetrical and Unsymmetrical Dialkyl Sulfides from Solution onto Gold Substrates: Structure, Properties, and Reactivity of Constituent Functional Groups" Troughton, E. B.; Bain, C. D.; Whitesides, G. M.; Nuzzo, R. G.; Allara, D. L.; Porter, M. D.

TR No. 4: "The Structures of Self-Assembled Monolayer Films of Organosulfur Compounds Adsorbed on Gold Single Crystals: Electron Diffraction Studies" Strong, L.; Whitesides, G. M.

TR No. 5: "Molecular-Level Control over Surface Order in Self-Assembled Monolayer Films of Thiols on Gold" Bain, C. D.; Whitesides, G. M.

TR No. 6: "Wetting of Functionalized Polyethylene Film Having Ionizable Organic Acids and Bases at the Polymer-Water Interface: Relations between Functional Group Polarity, Extent of Ionization, and Contact Angle with Water" Holmes-Farley, S. R.; Bain, C.; Whitesides, G. M.

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- TR No. 9: "Organic Chemistry in Two Dimensions: Surface-Functionalized Polymers and Self-Assembled Monolayer Films" Whitesides, G. M.; Ferguson, G. S.
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- TR No. 11: "Formation of Monolayer Films by the Spontaneous Assembly of Organic Thiols from Solution onto Gold" Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.
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- TR No. 20: "Modelling Organic Surfaces with Self-Assembled Monolayers" Bain, C. D.; Whitesides, G. M.

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