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This report provides titles, abstracts and references to publications associated with and acknowledging this grant.

### **Buried Interface Modification Using Supercritical Carbon Dioxide**

Xinqiao Jia and Thomas J. McCarthy

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Chemical modification of the buried interfaces between silicon wafers and either polystyrene or poly(methyl methacrylate) (PMMA) with the reagent (tridecafluoro-1,1,2,2-tetrahydrooctyl)dimethylchlorosilane (FDSC) was studied using liquid and supercritical carbon dioxide as the solvent and infusing agent. Above the critical point of CO<sub>2</sub>, FDSC reacts with surface silanols at the SiO<sub>2</sub>/polystyrene interface to form a monolayer, which was analyzed after removal of the polystyrene film. This is not the case below the critical point, and likely the lower diffusivity and solvent properties of the CO<sub>2</sub>-swollen film are the causes. The reaction was much less successful at the SiO<sub>2</sub>/PMMA interface. We suspect that because of strong hydrogen bonding between PMMA and the silicon substrate, modification of the SiO<sub>2</sub>/PMMA interface is achieved to only a limited extent.

Published in *Langmuir* **2002**, *18*, 683-687.

Available on line at <http://pubs.acs.org/about.html>

### **Controlled Growth of Silicon Dioxide from “Nanoholes” in Silicon-Supported Tris(trimethylsiloxy)silyl Monolayers: Rational Control of Surface Roughness at the Nanometer Length Scale**

Xinqiao Jia and Thomas J. McCarthy

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Controlled growth of silicon dioxide (SiO<sub>2</sub>) using tetrachlorosilane (SiCl<sub>4</sub>) and water as precursors on tris(trimethylsiloxy)chlorosilane (trisTMSiCl)-modified silicon wafer templates was studied. By manipulating the kinetics of the vapor-phase reaction of trisTMSiCl with silicon wafers, surfaces with varying densities and distributions of unreacted silanols (in nanoholes) were obtained. Subsequent treatment with SiCl<sub>4</sub>/H<sub>2</sub>O led to site-specific growth of silica from the nanoholes that was monitored by atomic force microscopy (AFM). Different nanoscale structures with varying surface roughness and wettability were fabricated by controlling the growth kinetics. Modification of the

newly grown silica with tridecafluoro-1,1,2,2-tetrahydrooctyldimethylchlorosilane (FDSCS) allowed the growth kinetics to be followed by X-ray photoelectron spectroscopy. Chemical etching effectively removed the organic residues, resulting in hydrophilic silica surfaces with nanoscale roughness. Further modification with FDSCS rendered the surfaces hydrophobic. Water contact angle analysis and AFM clearly indicate that nanometer scale topography has a profound effect on surface wettability.

Published in *Langmuir* **2003**, *19*, 2449-2457.

Available on line at <http://pubs.acs.org/about.html>

### **Adsorption of Poly(vinyl alcohol) onto Hydrophobic Substrates. A General Approach for Hydrophilizing and Chemically Activating Surfaces**

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The adsorption of poly(vinyl alcohol) onto hydrophobic surfaces is described. Three different commercial polymer film samples, poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP), poly(ethylene terephthalate) (PET), and poly(4-methyl-1-pentene) (PMP), four different silicon-supported covalently attached monolayers prepared from tridecafluoro-1,1,2,2-tetrahydrooctyl-dimethylchlorosilane, n-decyldimethylchlorosilane, 10-(carbomethoxy)decyldimethylchlorosilane, and 3-[methoxy(polyethyleneoxy)]propyltrimethoxysilane, and a gold-supported self-assembled monolayer of 1-dodecanethiol were used as adsorption substrates. The kinetics of the irreversible adsorptions and the concentration dependence of adsorbed layer thickness are reported for FEP and the fluoroalkyl monolayer. The adsorbed films render the surfaces of the substrates hydrophilic with advancing water contact angles ranging from 40 to 68°. PVOH films on hydrophobic alkyl and fluoroalkyl monolayers are 1-5 nm thick, depending on solution concentration, and less thick on the less hydrophobic carbomethoxy-containing monolayers. Crystallization is implicated as a major driving force for adsorption as evidenced by infrared spectroscopy and electron diffraction. The supported PVOH thin films are stable in water at room temperature but dissolve in hot water. Cross-linking of the PVOH with glutaraldehyde causes the films to be stable to hot water.

Published in *Macromolecules* **2003**, *36*, 6054-6059.

Available on line at <http://pubs.acs.org/about.html>

## **Adsorption of Poly(Vinyl Alcohol) from Water to a Hydrophobic Surface: Effects of Molecular Weight, Degree of Hydrolysis, Salt, and Temperature**

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The adsorption of poly(vinyl alcohol) (PVOH) from aqueous solutions to a silicon-supported fluoroalkyl monolayer is described. Thickness, wettability, and roughness of adsorbed films are studied as a function of polymer molecular weight, degree of hydrolysis (from the precursor, poly(vinyl acetate)), polymer concentration, salt type and concentration, and temperature. The data suggest a two-stage process for adsorption of the polymer: physisorption due to a hydrophobic effect (decrease in interfacial free energy) and subsequent stabilization of the adsorbed layer due to crystallization of the polymer. Adsorption of lower-molecular-weight polymers results in thicker films than those prepared with a higher molecular weight; this is ascribed to better crystallization of more mobile short chains. Higher contents of unhydrolyzed acetate groups on the poly(vinyl alcohol) chain lead to thicker adsorbed films. Residual acetate groups partition to the outermost surface of the films and determine wettability. Salts, including sodium chloride and sodium sulfate, promote adsorption, which results in thicker films; at the same time, their presence over a wide concentration range leads to formation of rough coatings. Sodium thiocyanate has little effect on PVOH adsorption, only slightly reducing the thickness in a 2M salt solution. Increased temperature promotes adsorption in the presence of salt, but has little effect on salt-free solutions. Evidently, higher temperatures favor adsorption but cause crystallization to be less thermodynamically favorable. These competing effects result in the smoothest coatings being formed in an intermediate temperature range.

Published in *Langmuir* **2004**, *20*, 9170-9176.

Available on line at <http://pubs.acs.org/about.html>

## **Chemical Surface Modification of Poly(p-xylylene) Thin Films**

Margarita Herrera-Alonso and Thomas J. McCarthy

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Electrophilic aromatic substitution reactions were studied at poly(p-xylylene) (PPX) film surface - reaction medium interfaces. The extent of the reactions (depth of penetration and degree of substitution) was determined by the interaction of the polymer with the reaction solution. Reaction with chlorosulfonic acid to produce sulfonyl chloride and sulfone functionalities occurred readily in the bulk of PPX, and yields were sensitive to time and temperature. Confinement of this reaction to the PPX surface was achieved by controlling the concentration of the acid. Functionalization of PPX with N-methylol-2-chloroacetamide in sulfuric acid to produce the chloroamidomethylated derivative occurred in high yield and was confined to the surface region of PPX. Hydrolysis of the amide to generate aminomethylated PPX was assessed by XPS and a derivatization reaction. Friedel-Crafts type chemistry (acylation and alkylation reactions) also produced functionalized surfaces, but with lower degrees of substitution than the other two reactions and was strictly surface-confined.

Published in *Langmuir* **2004**, *20*, 9184-9189.

Available on line at <http://pubs.acs.org/about.html>

### **Nylon surface modification. Part 1. Targeting the amide groups for selective introduction of reactive functionalities**

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Nylon is a widely used synthetic polymer because it has a combination of strength, flexibility, toughness, and abrasion resistance. For a variety of applications, however, it is necessary to impart desired surface properties by introducing specific functional groups in specific locations and densities. Several chemical modification methods were developed for the introduction of functional groups to nylon surfaces using amide-selective reactions without cleaving the polymer chains. Activation of amides by reaction with potassium tert-butoxide (t-BuOK) facilitates the N-alkylation of surface amides. When 2-bromoethylamine hydrobromide (BEA-HBr) was employed as an alkylating agent, surfaces with a mixture of primary/secondary/tertiary amine groups were obtained. Alkylation with (3-glycidoxypropyl)triethoxysilane (GPTES) was utilized to prepare surfaces with silica-like reactivity. Chemical reduction with borane-THF complex (BH<sub>3</sub>-THF) results in a 69% conversion of surface amide groups to the corresponding secondary amines. A kinetic study of this reaction for different types of nylon films revealed that the yield was dependent on the segmental mobility of the polymer. These surfaces are useful substrates for the fabrication of nylon-supported composite films.

Published in *Polymer* 2006, 47, 4916-4924.

Available on line at [www.sciencedirect.com](http://www.sciencedirect.com)

## **Nylon Surface Modification: 2. Nylon-Supported Composite Films**

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We have developed techniques for the introduction of reactive functional groups to nylon surfaces via site-specific reactions targeting at the naturally abundant amide repeating units on the surface. In this report, we describe the fabrication of nylon-supported composite surfaces using the most efficient modification methods we have developed. N-Alkylation with (3-glycidoxypropyl)triethoxysilane (GPTES) in the presence of potassium tert-butoxide (t-BuOK) leads to surfaces with silica-like reactivity. Subsequent chemical vapor deposition using tetrachlorosilane ( $\text{SiCl}_4$ ) and water results in composite films with a thin layer of silica, which was made hydrophobic by reaction with a fluorinated silane reagent. Reduction of the amide groups with borane-THF ( $\text{BH}_3$ -THF) complex leads to a 69% conversion of surface amides to the corresponding secondary amine groups. Alginate was chosen as the model polyelectrolyte for the introduction of a hydrated surface layer. Because of the strong electrostatic interaction between alginate and the amine-enriched nylon surfaces, the adsorption is fast and concentration-independent (within the concentration range studied). The polysaccharide coats the surface homogeneously, without the formation of large aggregates. The amine surfaces obtained by reduction with  $\text{BH}_3$ -THF ( $\text{BH}_3$ -THFnylon-NH) and by alkylation with 2-bromoethylamine hydrobromide (BEA-HBr, EBA-HBrnylon-NH<sub>2</sub>) were also used to study gold deposition through electroless plating. Immobilization of a negatively charged metal complex ( $\text{AuCl}_4^-$ ) was achieved through electrostatic interaction. Gold particles disperse preferentially in the bulk of EBA-HBrnylon-NH<sub>2</sub> films, while they remain confined to the outer surface layer of  $\text{BH}_3$ -THFnylon-NH films.

Published in *Langmuir* 2006, 22, 1646-1651.

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