Synthesis of Hyperbranched, Hydrophilic Fluorinated **Surface Grafts**

Yuefen Zhou, Merlin L. Bruening, Yuelong Liu, Richard M. Crooks,* and David E. Bergbreiter*

Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255

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The synthesis of 60–1000 Å thick films of fluorinated polymers on gold and silica substrates via amidation of layered, hyperbranched poly(acrylic acid) surface-graft films with a fluorinated octylamine is described. These syntheses proceed either by formation and fluoramidation of layers of poly(acrylic acid) or by stepwise formation of layers of a mixture of poly(acrylic acid) and a fluorinated poly(acrylamide) on a carboxylic acid-containing self-assembled monolayer on gold or on aminopropylated silica. Depending on the chemistry used, these grafts can be prepared so that they have fluorinated interiors and either hydrophobic or hydrophilic exteriors. Ellipsometric studies of these grafts on gold show that the thickness of the layers can be controlled on the basis of the number of PAA layers present and that fluorination using a fluorinated octylamine roughly doubled layer thickness. Infrared and X-ray photoelectron spectroscopy studies were used to characterize these surfaces.

Here we describe a new approach to the synthesis of 60-1000 Å thick films of fluorinated polymers on gold and silica substrates. These films derive from layered, hyperbranched poly(acrylic acid) (PAA) surface-graft films and can be prepared so that they have fluorinated interiors and either hydrophobic or hydrophilic surfaces. The specific examples shown illustrate this procedure for surface grafts on a self-assembled monolayer (SAM) on gold. Preliminary work shows that similar procedures produce highly fluorinated surface grafts on modified glass surfaces.

The synthesis and modification of fluorinated polymers and films is of interest in many applications in polymer and materials science.¹ Consequently, there are a number of synthetic routes to such surfaces including plasma grafting,² plasma polymerization,³ radiation-induced grafting,⁴ and spin coating.⁵ Recently ultrathin, fluorinated films were prepared by chemisorption of fluorinated polymers on surfaces.⁶ While fluorinated surfaces are considered unreactive and hydrophobic, it is possible to alter their physical and chemical properties using radiation and/or chemical etching.7 However, these procedures are harsh and often offer only modest control over film thickness and composition. We have developed a synthetically versatile route to such films and surfaces that is generally applicable and offers control over film thickness and both interior and exterior chemical composition.

The synthesis of surface-grafted, fluorinated films is an extension of our recently reported synthesis of layered,



Scheme 1

 $= Au \Big|_{-}^{S \operatorname{ww}} [CONHCH_2(CF_2)_6 CF_3]_m \Big|_{-}^{S \operatorname{ww}} [CONHCH_2(CF_2)_6 CF_4]_m \Big|_{-}^{S \operatorname{ww}}$

S ~~{CONHR-PTBA-RNH₂]_n

i, CICO₂-i-Bu

Au|S MCOOH

MUA

N-methyl morpholine

ii, H₂NR-PTBA-RNH₂ +

	S vvv[CONHR-PAA-RNH ₂] _n		
i, CICO ₂ - <i>i</i> -Bu N-methyl morpholine	ii, H ₂ NR-PTBA-RNH ₂ or H_2 NR-PTBA-RNH ₂ + NH ₂ CH ₂ (CF ₂) ₆ CF ₃	iii, p-TsOH⁺H ₂ O	Layered, Fluorinated Hyperbranched Surface Grafts

hyperbranched PAA films.⁸ To synthesize the PAA films, α, ω -amino-terminated poly(*tert*-butyl acrylate) (H₂NR-PTBA-RNH₂, $R = CH_2CH_2NHCOCH_2CH_2C(CN)(CH_3)$ is grafted onto a mercaptoundecanoic acid (MUA) SAM via an amide linkage. Hydrolysis of the tert-butyl esters then yields a PAA graft. Additional grafting at multiple carboxylic acid sites on each prior PAA graft leads to hyperbranched, combburst-like PAA films containing a dense array of CO₂H groups. Film thickness increases rapidly and nonlinearly with the number of layers (grafting steps). Here we show that it is possible to derivatize the CO₂H groups of these PAA films with amino fluorocarbons. Moreover such synthetic modifications can be accomplished without precluding further grafting of PAA.

We couple amino-terminated perfluoroalkanes to hyperbranched PAA films using two approaches. In the first method, we prepare a homogeneous film containing the desired number of layers of PAA, activate the carboxylic acid groups throughout the film, and then allow them to react with $NH_2CH_2(CF_2)_6CF_3$ (0.1 M in DMF). This yields films with fluorinated interiors and hydrophobic surfaces whose thicknesses depend upon the number of PAA layers used. The second approach involves preparation of structurally heterogeneous films by grafting a mixture of $H_2NR-PTBA-RNH_2$ (200 mg in 10 mL of DMF, $M_n = 2.0$ \times 10⁴)⁹ and NH₂CH₂(CF₂)₆CF₃ in some or all of the layers

^{*} Authors to whom correspondence should be addressed. Fax: (409) 845-1399. E-mail: bergbreiter@chemvx.tamu.edu and crooks@c hemvx.tamu.edu.

[®] Abstract published in *Advance ACS Abstracts*, October 15, 1996. (1) (a) Maruo, Y. Y.; Andoh, Y.; Sasaki, S. *J. Vac. Sci. Technol., A* **1993**, *11*, 2590. (b) Chan, C.-J.; Chang, C.-A.; Farrel, C. E. *Mater. Res.* Soc. Symp. Proc. 1991, 227, 363 and references therein.
(2) Momose, Y.; Takada, T.; Okazaki, S. J. Appl. Polym. Sci.: Appl.

Polym. Symp. 1988, 42, 49.

⁽³⁾ Durrant, S. F.; Mota, R. P.; de Moraes, M. A. B. Thin Solid Films 1992, 220, 295.

⁽⁴⁾ Hegazy, E.-S. A.; Dessouki, A. M.; El-Assy, N. B.; El-Sawy, N. M.; El-Ghaffar, M. A. J. Polym. Sci., Part A: Polym. Chem. 1992, 30, 1969.

 ⁽⁵⁾ Chapman, T. M.; Marra, K. G. Macromolecules 1995, 30, 1969.
 (5) Chapman, T. M.; Marra, K. G. Macromolecules 1995, 28, 2081.
 (6) (a) Sun, F.; Castner, D. G.; Mao, G.; Wang, W.; Mckeown, P.; Grainger, D. W. J. Am. Chem. Soc. 1996, 118, 1856. (b) Rühe, J.; Blackman, G.; Novotny, V. J.; Clarke, T.; Street, G. B.; Kuan, S. J. Appl. Polym. Sci. 1994, 53, 825.
 (7) (a) Page T. C.; McCenthy, T. L. Macromology, 1092, 25, 2002 and

^{(7) (}a) Bee, T. G.; McCarthy, T. J. *Macromolecules* **1992**, *25*, 2093 and references therein. (b) Rye, R. R.; Knapp, J. A.; Chi, K.-M.; Hampden-Smith, M. J.; Kodas, T. T. *J. Appl. Phys.* **1992**, *72*, 5941 and references therein.

⁽⁸⁾ Zhou, Y.; Bruening, M. L.; Bergbreiter, D. E.; Crooks, R. M.; Wells, M. J. Am. Chem. Soc. 1996, 118, 3773.
(9) M_n values were determined by acid/base titration. Most of the

⁽⁹⁾ M_n values were determined by actionate thratton, must of the experiments reported here were performed with a batch of H₂NR– PTBA–RNH₂ with a M_n of 2.0 × 10⁴, but we also successfully used batches of H₂NR–PTBA–RNH₂ with M_n values ranging from 1.8 × 10⁴ to 2.0 × 10⁴. Films made from the different batches of polymer have similar FTIR-ERS spectra and ellipsometric thickness trends, but absolute thicknesses and absorbances can vary, as discussed in note 12.



Figure 1. FTIR spectra of a three-layer hyperbranched PAA film (A) before and (B) after coupling to $H_2NCH_2(CF_2)_6CF_3$. Spectrum B was measured after immersing the sample in 0.1 M HCl in EtOH and rinsing with EtOH in order to remove any salts adsorbed in the film. The $H_2NR-PTBA-RNH_2$ used in preparing these films had a M_n value of 1.9×10^4 .



Figure 2. XPS survey spectrum of a three-layer PAA film after coupling to $NH_2CH_2(CF_2)_6CF_3$. The inset is the high-resolution C_{1s} spectrum of this film.

(Scheme 1). In this approach, the amine groups of H_2 -NR–PTBA–RNH₂ and NH₂CH₂(CF₂)₆CF₃ react with the activated CO₂H groups of MUA to form a mixed layer. Hydrolysis of the grafted PTBA yields a layer that contains a mixture of PAA and NH₂CH₂(CF₂)₆CF₃. Subsequent layers can contain pure PAA or NH₂CH₂(CF₂)₆CF₃ or a mixture of NH₂CH₂(CF₂)₆CF₃ and PAA. Capping a mixed, fluorinated film with pure PAA layers can yield films with fluorinated interiors and hydrophilic surfaces.

Fluorination throughout PAA films produces thick, fluorinated films with low surface energies, as shown by Fourier-transform infrared external reflection spectroscopy (FTIR-ERS), X-ray photoelectron spectroscopy (XPS), contact angle analysis, and ellipsometry. Figure 1 shows the FTIR-ERS spectra of three layers of hyperbranched PAA before and after fluorination with NH₂CH₂(CF₂)₆-CF₃. Upon fluorination, amide peaks appear (1680 and 1550 cm⁻¹) and the acid carbonyl peak (1733 cm⁻¹) decreases, which indicates that a large fraction of the carboxylic acid groups react to yield fluorinated amides. Figure 1 also shows the appearance of CF₂ and CF₃ stretching modes at 1250, 1220, and 1150 cm⁻¹.¹⁰ The XPS survey spectrum of this film (Figure 2) along with the high-resolution C_{1s} spectrum (inset) also indicates a high level of fluorination. The film surface contained 46 atom % F, which represents 86% of the atomic concentration expected in a homopolymer of $(CH_2CHCONH-CH_2(CF_2)_6CF_3)_n$. A large C_{1s} peak at 291.0 eV that arises from the CF_2 carbon and a smaller C_{1s} peak at 284.6 eV due to the CH_x carbon are consistent with extensive fluorination.¹¹ No peak due to the underlying gold was observed, suggesting complete coverage of the substrate. Grafting an additional pure PAA layer onto a fluorinated three-layer PAA film changed the thickness by <15%. (Grafting a fourth PAA layer on a pure three-layer PAA film approximately doubles film thickness.) This suggests that most of the accessible carboxylic acid groups in the film react with $NH_2CH_2(CF_2)_6CF_3$ and are unavailable for further grafting.

Fluorination of hyperbranched PAA films also changes film thickness. Coupling of $NH_2CH_2(CF_2)_6CF_3$ to a film composed of three layers of PAA doubled the ellipsometric thickness to about 1000 Å.¹² Such a large increase in thickness shows that grafting takes place throughout most of the film because addition of a single monolayer of NH_2 - $CH_2(CF_2)_6CF_3$ would increase film thickness by only 10 Å. The total film thickness can be easily varied by changing the number of PAA layers. For example one- and threelayer PAA films derivatized with $NH_2CH_2(CF_2)_6CF_3$ are about 60 and 1000 Å thick, respectively.¹²

Contact-angle measurements show that addition of NH₂-CH₂(CF₂)₆CF₃ lowers the surface energy of the film, as expected. The advancing water contact angle (Θ_a) for a film composed of three layers of PAA changed from 30° to 107° upon fluorination. By comparison, coupling of pure NH₂CH₂(CF₂)₆CF₃ to a MUA monolayer increased Θ_a from <10° to 113°.

While the first fluorination method provides fully fluorinated films of varying thickness, the second approach yields more complex nanocomposite-like materials with fluorinated interiors and hydrophilic surface layers. Because complete fluorination with pure $NH_2CH_2(CF_2)_6$ -CF₃ hinders subsequent grafting of PAA, we employed mixed grafting of NH₂CH₂(CF₂)₆CF₃ and NH₂R-PTBA-RNH₂ (Scheme 1) to generate a mixed film containing a small but sufficient number of CO₂H groups (from hydrolyzed PTBA) that are accessible for subsequent grafting. Figure 3A shows the FTIR-ERS spectrum of a two-layer PAA film after grafting of a mixture of NH2-CH₂(CF₂)₆CF₃ and NH₂R-PTBA-RNH₂ (30:1 molar ratio in the grafting solution) and subsequent hydrolysis. Peaks due to CF_x stretching modes at 1250, 1220, and 1150 cm⁻¹ confirm fluorination. Figure 3B shows the spectrum of this film after grafting an additional layer of pure PAA. This spectrum confirms the addition of PAA (the carbonyl peak at 1740 cm⁻¹ increases) and the retention of the fluorinated layer (the CF_x stretching peaks are still present). The top layer of pure PAA fully attenuated the F XPS signal, indicating that the fluorinated film was covered with PAA. The FTIR-ERS and XPS data demonstrate the formation of a nanocomposite-like film with a fluorinated interior.

⁽¹¹⁾ Peak positions are referenced to the CH_x carbon, which was assumed to be at 284.6 eV.

⁽¹²⁾ The increase in ellipsometric thickness is not due to changes in film refractive index (n_c). We usually measured ellipsometric thicknesses assuming a n_t value of 1.46, but we occasionally measured n_t and thickness simultaneously. The n_t value of the fluorinated film is about 1.44, and the n_t value of a three-layer PAA film is about 1.54. We measured n_t values or an assumed value of 1.46. The thickness of fluorinated three-layer PAA films made from several different batches of H₂NR-PTBA-RNH₂ ranged from 600 to 1400 Å depending on the initial thickness of the three-layer PAA film. Film thickness of the three-layer PAA film. Thickness of the three-layer from the FTIR-ERS spectra. Fluorinated one-layer PAA films were prepared from a batch of H₂NR-PTBA-RNH₂ with a M_n value of 1.9 × 10⁴.



Figure 3. FTIR spectra of (A) a film containing two layers of PAA capped with a mixed layer of $NH_2CH_2(CF_2)_6CF_3$ and PAA (30:1 molar ratio in the grafting solution), (B) the film in part A after grafting an additional pure PAA layer, and (C) a film containing three layers of pure PAA (shown for comparison). The bands in the CF_x region in spectrum C arise from COOH (not CF_x) and disappear upon deprotonation.

On the above-described mixed layer of NHCH₂(CF₂)₆-CF₃ and PAA (30:1 ratio in the grafting solution), Θ_a was only 41°. Increasing the molar ratio of NH₂CH₂(CF₂)₆-CF₃ to NH₂R–PTBA–RNH₂ in the grafting solution to 500:1 increased Θ_a to 56°.¹³ The surfaces of the mixed layers are somewhat hydrophilic because long PAA chains cover the shorter, neighboring perfluoroalkanes. Attenuation of the F XPS signal in these layers confirms that PAA chains cover the NHCH₂(CF₂)₆CF₃ even though both are grafted in the same layer.

We observe larger effects of perfluoroalkanes on Θ_a values when we graft mixed layers directly onto the MUA SAM. The surface of a layer made from $NH_2CH_2(CF_2)_6$ -CF₃ and PAA (500:1 ratio in the grafting solution) grafted directly onto MUA was hydrophobic ($\Theta_a = 100^\circ$). After grafting two additional layers of pure PAA onto this mixed layer, the surface became hydrophilic ($\Theta_a = 14^\circ$). Moreover, this surface was completely wet after exposure to 0.1 M NaOH (aq) due to deprotonation of the CO₂H groups of PAA.¹³ Thus we can make a very hydrophobic F-

containing film very hydrophilic simply by covalently capping this layer with pure PAA layers.¹⁴

Preliminary work suggests that the synthesis of fluorinated graft films can be extended to other substrates. Silica gel or glass can be activated and treated successively with (EtO)₃Si(CH₂)₃NH₂ and succinic anhydride to form a carboxylated silica surface.¹⁵ These carboxylic acidcontaining silica surfaces can be modified by the same hyperbranched grafting chemistry we developed for the MUA-coated gold surfaces. Three to five grafting steps are sufficient to completely cover silica with grafted PAA (on the basis of the absence of the Si_{2p} peak in the XPS spectrum of a modified glass slide). In the case of a 3-PAA graft on glass, modification with $NH_2CH_2(CF_2)_6CF_3$ led to a surface with 41 atom % F (by XPS analysis) and a Θ_a value of 105°. Coupling of $NH_2(CH_2)_3CH_3$ to silica gel coated with a three-layer PAA film yielded a hydrophobic silica gel with about 92% of the PAA-CO₂H groups converted to a butanamide (on the basis of titration of the residual CO₂H groups.)

In summary, coupling of $NH_2CH_2(CF_2)_6CF_3$ to hyperbranched PAA films yields a highly fluorinated polymer with a low surface energy. Layer-by-layer grafting can produce nanocomposite-like films containing fluorinated interiors and hydrophilic PAA surfaces. Because a wide range of primary amines can couple to hyperbranched PAA films on several CO₂H-containing surfaces, synthesis of a variety of composite films should be possible. We are presently investigating the effectiveness of these materials for corrosion inhibition applications and as components of chemically sensitive interfaces.

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⁽¹³⁾ In this case, we used $HS(CH_2)_{10}C \equiv CC \equiv C(CH_2)_{10}COOH$ as the constituent of the SAM because it can be polymerized with UV light. (See: Kim, T.; Crooks, R. M.; Tsen, M.; Sun, L. *J. Am. Chem. Soc.* **1995**, *117*, 3963.) Hyperbranched polymer films on a polymerized monolayer are more stable in basic solution than those grafted on MUA.

⁽¹⁴⁾ The intensity of the CF_x absorbances in the FTIR-ERS spectrum of this film decreases by \approx 40% upon grafting of the first pure PAA layer and by \approx 80% upon grafting of a second PAA layer. We think that this is due to a change in orientation of the C–F bonds in the initial layer that attenuates the IR absorption according to the surface selection rule. (See: Porter, M. D. Anal. Chem. **1988**, 60, 1143A.)

⁽¹⁵⁾ Weetall, H. H. In *Methods in Enzymology*, Mosbach, K., Ed.; Academic Press: New York, 1976; Vol. 44, p 135.