

Synthesis and Characterization of Surface-Grafted, Hyperbranched Polymer Films Containing Fluorescent, Hydrophobic, Ion-Binding, Biocompatible, and Electroactive Groups

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Received November 13, 1996[Ⓢ]

We report the derivatization of hyperbranched poly(acrylic acid) (PAA) films with a wide range of amino- or alcohol-terminated molecules. These molecules can include moieties such as pyrene, ferrocene, poly(ethylene glycol), 15-crown-5, and a dye. To derivatize PAA films, we activate their carboxylic acid groups with isobutyl chloroformate and allow them to react with amine- or alcohol-containing molecules. Infrared spectroscopy demonstrates the formation of amide and ester bonds upon coupling as well as the presence of the derivative functional groups. Excimer fluorescence from pyrene-containing films implies a high density of pyrene groups. However, we can control the amount of pyrene in the film (and obtain monomer fluorescence) by varying the concentration of $\text{Py}(\text{CH}_2)_3\text{CONH}(\text{CH}_2)_2\text{NH}_2$ in the derivatization solution. Cyclic voltammetry of ferrocene-containing films shows an electrochemically addressable ferrocenyl surface coverage of $(6 \pm 3) \times 10^{-9}$ mol/cm² in three-layer PAA films. PAA films and their derivatives are stable under sonication, Soxhlet extraction, and acidic and basic conditions. PAA films also respond to external stimuli. The ellipsometric thickness of PAA films increases by $\approx 45\%$ upon deprotonation of the film's carboxylic acid groups and returns to its original thickness after acidification. Using surface acoustic wave mass sensors, we observed that pure PAA films adsorb or absorb volatile organic compounds (VOCs), although the amount is in the monolayer range. Fluorination of PAA films increases the amount of polar VOCs absorbed by an order of magnitude.

Introduction

We recently reported the synthesis of hyperbranched poly(acrylic acid) (PAA) films.¹ To prepare these films, we first graft poly(*tert*-butyl acrylate) onto a mercapto-undecanoic acid monolayer on gold. Hydrolysis of the *tert*-butyl esters then yields a PAA graft. Additional grafting at multiple CO₂H sites on each prior graft leads to hyperbranched PAA films. Here we demonstrate the versatility of hyperbranched PAA films by derivatizing them with molecules containing a wide range of moieties such as a fluorescent group, an ion-binding macrocycle, a dye, a biocompatible polymer chain, and an electroactive group. Scheme 1 illustrates the synthesis and derivatization of hyperbranched PAA films. The wide range of derivatized polymer films should be relevant to applications involving chemical sensing, corrosion, adhesion, wetting, and friction. A variety of spectroscopic, electrochemical, and physical characterization methods show that these films can be highly functionalized. Additionally, we show that these films respond to changes in pH and are stable to treatment with acid, base, ultrasound, and mild heating.

Several methods exist for attaching polymer films to surfaces including physisorption, chemisorption, covalent attachment to monolayers, and electrostatic adsorption. Spin coating is a well-known method of depositing polymer films by physisorption.^{2,3} To chemisorb monolayers of polymer films to gold surfaces, several research groups

introduced thiol-containing side chains on polymer backbones.⁴⁻¹⁴ Such monolayer films are generally <30 Å thick. Similarly, PAA chains adsorb on aluminum oxide as carboxylates to yield films that are 5-10 Å thick.¹⁵ Allara and co-workers modified these films through reaction of the carboxylic acid groups that are not bound to the surface.¹⁵ Polymer chains have also been covalently linked to surface-confined, reactive monolayers.¹⁶⁻²²

Polymer multilayers have been previously prepared using a layer-by-layer growth strategy. For example, Ringsdorf and co-workers attached polymer chains containing many reactive sites to amino-silanized glass.²²

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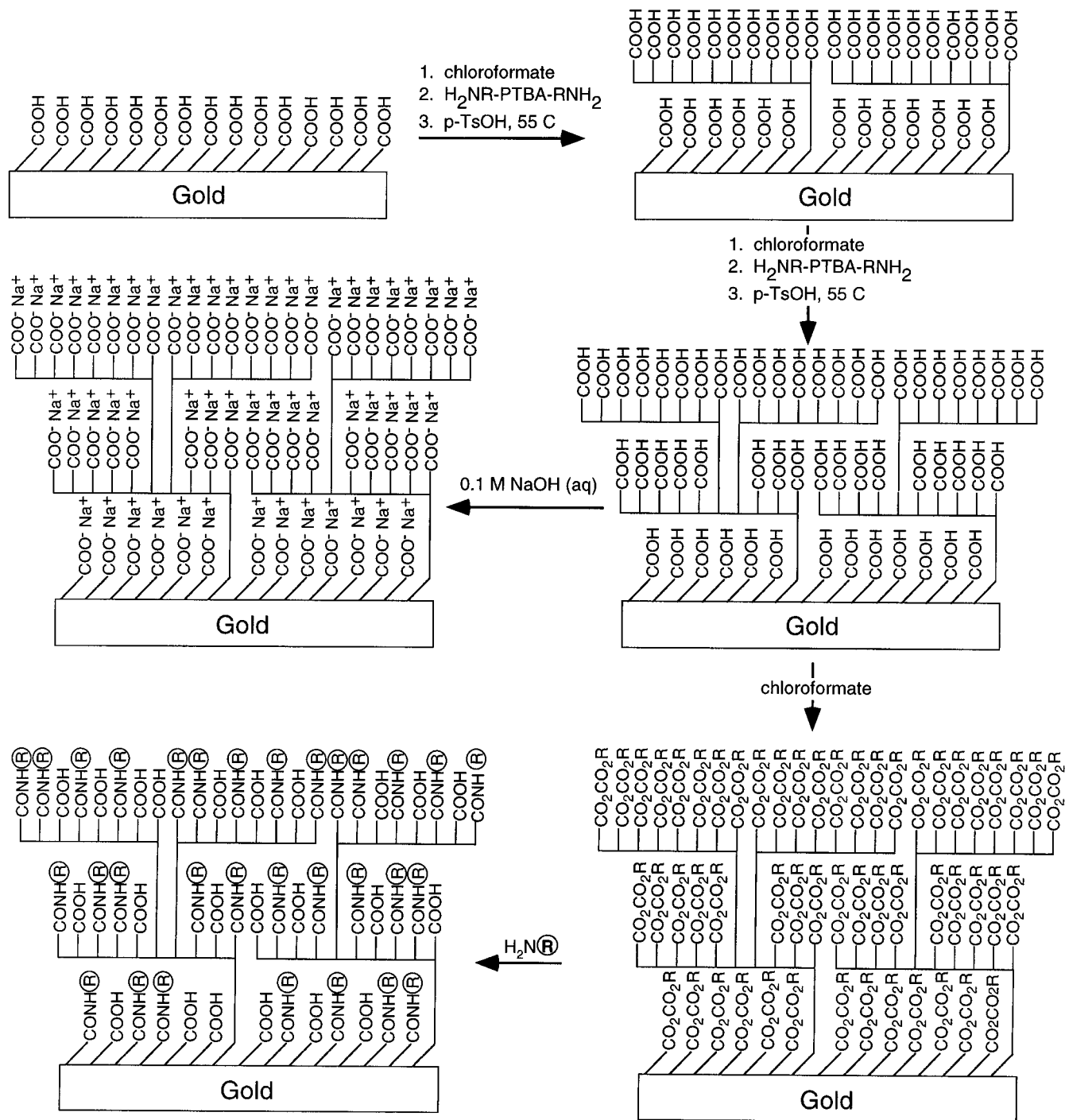
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Scheme 1



They then prepared covalently linked polymer multilayers using the unreacted functional groups in the grafted polymer layers. Decher and co-workers utilized electrostatic adsorption of oppositely charged polymer chains to form polymer multilayers.^{23–28} Ferguson prepared mixed polymer/inorganic films using the electrostatic method

and showed that this method is very forgiving in that it can cover defects in the previously adsorbed layers.²⁹ In all of these layer-by-layer approaches, film thickness increases linearly with the number of layers.

Our work follows and extends this layer-by-layer growth strategy.¹ In contrast to previous work, however, the thickness of hyperbranched films increases rapidly and nonlinearly with the number of layers because we use a protection/deprotection strategy which results in highly branched grafting. For example, thicknesses range from 30 to > 1000 Å in films containing from one to more than five PAA layers. We recently reported derivatizing these PAA films with perfluorinated alkanes,³⁰ and here we greatly expand the scope of this PAA derivatization

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chemistry to prepare fluorescent, electroactive, and bio-compatible surfaces. These derivatives demonstrate the wide range of properties that can be incorporated into hyperbranched PAA films.

Experimental Section

Film Preparation. Au-coated Si wafers (1000–2000 Å of Au on an adhesion layer of 50–100 Å of Cr or Ti) were cleaned in a Harrick plasma cleaner (medium power) for 1.5 min. The slides were immersed in 0.001 M mercaptoundecanoic acid (MUA) in ethanol (EtOH) for 0.5 h and rinsed with EtOH and H₂O to form a self-assembled monolayer (SAM). The MUA SAM was then immersed in 10 mL of dried DMF to which 80 μL of *N*-methylmorpholine and 100 μL of isobutyl chloroformate were added while stirring. After 10 min, the slide was removed, rinsed with ethyl acetate, and dried with N₂. The slide was then immersed in a solution of α,ω-diaminopoly(*tert*-butylacrylate) (H₂NR(PTBA)RNH₂, R = (CH₂)₂NHCO(CH₂)₂C(CN)(CH₃)) in DMF (200 mg of H₂NR(PTBA)RNH₂ in 4 mL of DMF) for 1 h with stirring. The slide was then removed, rinsed with EtOH, and dried with N₂. The *tert*-butyl ester groups of the grafted PTBA were then hydrolyzed by immersing the sample for 1 h in benzene saturated with *p*-toluenesulfonic acid monohydrate at 55 °C to yield grafted PAA. The slide was then removed, rinsed with EtOH, and dried with N₂.

To prepare additional PAA layers, the newly formed acid groups of the grafted PAA film were activated using the same procedure as for the MUA SAM, and the grafting procedure was repeated. A large excess (>50-fold in the first three layers) of H₂NR(PTBA)RNH₂ was used to minimize cross-linking, but some H₂NR(PTBA)RNH₂ could have reacted with CO₂H groups on two different grafted chains. We have prepared films using up to seven grafting stages and have used batches of H₂NR(PTBA)RNH₂ with *M_n* values (determined by acid/base titration) ranging from 1.5 × 10⁴ to 2.5 × 10⁴. In most of the experiments described here, we used batches of H₂NR(PTBA)RNH₂ with *M_n* values between 1.9 × 10⁴ and 2.0 × 10⁴.

To derivatize PAA films with amine-containing molecules, the acid groups of PAA were also activated using isobutyl chloroformate and the film was exposed to a solution of the appropriate amine. The following amine solutions were used: ethylenediamine (2.0 N in DMF), allylamine (1.0 N in DMF), Py(CH₂)₃-CONH(CH₂)₂NH₂ (I, Chart 1) (1.6 × 10⁻⁵ to 0.05 N in DMF), NH₂CH₂(CF₂)₆CF₃ (0.1 N in DMF), isopropyl amine (1.0 N in DMF), 2-(aminomethyl)-15-crown-5 (III) (0.1 N in CH₂Cl₂), H₂N(PEG₄₆₀₀)NH₂ (0.02 N in CH₂Cl₂), *N,N'*-bis(3-aminophenyl)-3,4,9,10-perylenetetracarboxylic diimide (APPCDI) (V) (0.02 N in DMF), and NHEt₂ (1.0 N in DMF). After a 1-h immersion in the amine-containing solutions, most films were immediately rinsed in EtOH. Pyrene-derivatized films were first rinsed in DMF and then rinsed in EtOH. PEG-derivatized films were rinsed first in CH₂Cl₂ and then in EtOH.

To couple PyCH₂OH (II) to PAA, the film was activated as described above and immersed for 1 h in 10 mL of CH₂Cl₂ containing PyCH₂OH (100 mg, 0.43 mmol), NEt₃ (70 μL, 0.5 mmol), and 4-(dimethylamino)pyridine (DMAP) (28 mg, 0.25 mmol). The film was then rinsed in CH₂Cl₂ and EtOH. Coupling of ferrocenemethanol (FcCH₂OH, IV) (0.1 N in CH₂Cl₂) to hyperbranched PAA proceeded similarly. Some of these films were sonicated in CHCl₃ to remove material that was visibly physisorbed.

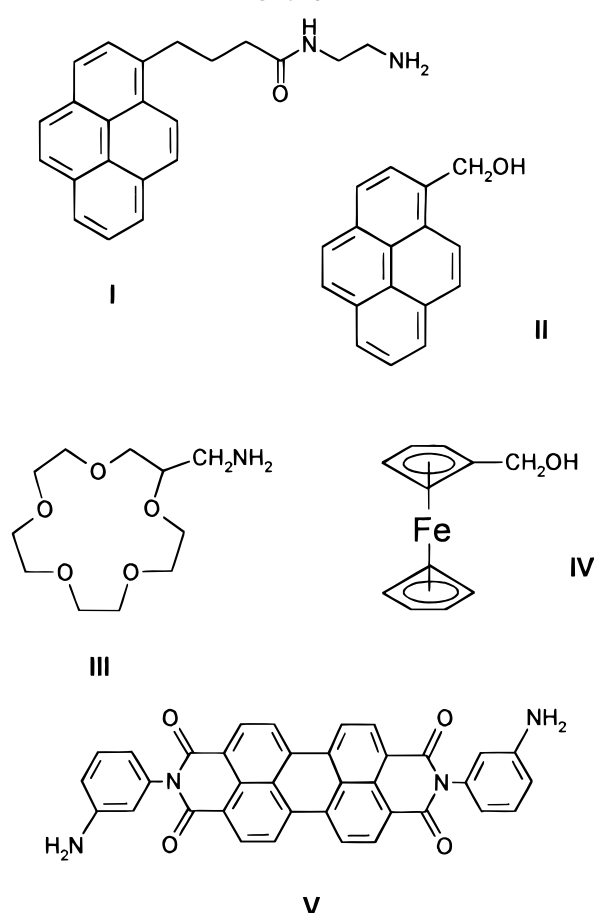
In some cases, we used diacetylene-containing SAMs prepared from HS(CH₂)₁₀C≡C≡C(CH₂)₁₀COOH (DA)^{31,32} rather than MUA to link hyperbranched films to the gold substrate. These DA SAMs were prepared by immersing plasma-cleaned gold substrates (as described above) in a 0.001 M solution of DA in CHCl₃ for 4–5 h. The substrate was then sequentially rinsed in chloroform, acetone, EtOH, and H₂O. These films were polymerized by a 45-min exposure to ultraviolet light to yield a polydiacetylene (PDA) film. The procedure for grafting polymers to PDA monolayers is identical to that used for MUA.

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Chart 1



Characterization. Fourier Transform Infrared External Reflection Spectroscopy (FTIR-ERS). FTIR-ERS spectra were measured using a Bio-Rad FTS 40 infrared spectrophotometer with a mercury/cadmium telluride detector. Spectra were obtained at a grazing angle of 85° using a Harrick Seagull attachment and were obtained at 4-cm⁻¹ resolution using between 100 and 256 scans.³³ A N₂-purged home-built glovebox over the sample compartment eliminates the need for long purging times to remove water vapor.

Ellipsometry. Ellipsometric measurements were performed on dry films in air using a Gaertner L2W26D ellipsometer with a 70° angle of incidence. Thicknesses and refractive indices were calculated using Gaertner software. Most measurements were made with a He/Ne (633.8-nm) laser, but measurements using an Ar⁺ laser (488.0 nm) confirmed these thickness values. Most of the thicknesses were calculated assuming a film refractive index (*n_f*) of 1.46. For thicker films, (three to four layers), *n_f* values could be obtained using the Ar⁺ laser. The measured *n_f* value is 1.49 ± 0.01 for PTBA films and 1.54 ± 0.02 for PAA films. The He/Ne laser does not give consistent values for *n_f* likely due to lower ellipticities at the longer wavelength. It was not possible to accurately measure the *n_f* of thinner (one to two layers) PAA films. We find experimentally that using our estimated *n_f* value of 1.46 for the refractive index rather than a measured value overestimates the PTBA thickness by ≈9% and PAA thicknesses by ≈15%.

Fluorescence Spectroscopy. The fluorescence spectra of pyrene-containing films were recorded with a SLM SPF-500C steady-state spectrofluorometer using a 343-nm excitation wavelength and slit widths of 5 and 2 nm for excitation and emission, respectively. The film-coated wafer (≈1 × 3 cm) was placed in a metal holder containing an opening (≈0.8 × 3 cm) to expose the center of the film. The holder was then placed diagonally into a cuvette which was inserted in the instrument sample holder. This sample holder was adjusted from its normal setting so that the incident angle of the excitation light was 59°.

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With this incident angle, a peak due to luminescence of the gold substrate was minimized. Spectra were taken within 3 min after the samples were placed in the cuvette, which was open to air and filled with distilled H₂O.

Surface Acoustic Wave (SAW) Device Measurements. SAW device measurements were made at 25.0 ± 0.2 °C using 98-MHz ST-cut quartz oscillators housed in a home-built flow system.³⁴ The SAW devices were designed at Sandia National Laboratories and fabricated by Lance Goddard Associates (Foster City, CA). The active surface region of the SAW device was coated with 2000 Å of Au on a Ti adhesion layer. The relationship between the change in frequency (Δf) of the SAW device and the change in mass per unit area (m_A) is given in eq 1, where f_0 is the operating frequency of the device, κ is the fraction of the center-to-center distance between the transducers that is covered by the Au film (0.65 in this case), and c_m is the mass sensitivity of ST-cut quartz (1.33 cm²/g).^{35,36}

$$\Delta f/f_0 = -\kappa c_m f_0 m_A \quad (1)$$

Electrochemistry. Cyclic voltammograms were recorded using a BAS100B electrochemical analyzer (Bioanalytical Systems, West Lafayette, IN). Measurements were made vs a Ag/AgCl (3 M NaCl) reference electrode (BAS). The working electrode was a Au film contained within a Teflon holder that exposes 0.1 cm² of the film. The 0.1 M LiClO₄ electrolyte solution was degassed with N₂ for ≈15 min, and experiments were performed while gently bubbling the solution with N₂. The film-modified electrode was immersed in the electrolyte solution for 5 min prior to the measurement.

Contact Angle Measurements, NMR, and Sonication. Contact angles were measured with a Ramé Hart Model 100 goniometer using doubly distilled water. The contact angle values reported are the average of at least four measurements obtained at different spots on the same film. The estimated error is usually ±2°, but it increases for low angles. ¹H and ¹³C NMR spectra were recorded using a Varian XL-200 spectrometer. Chemical shifts are reported in ppm using hexamethyldisiloxane as the internal standard. Sonication was performed using a Bransonic 52 ultrasonic cleaner (47 kHz, 200-W maximum output).

Materials. General. Unless otherwise specified, all commercial reagents were used without additional purification. Poly(ethylene glycol), *tert*-butyl acrylate, 2-(aminomethyl)-15-crown-5, 1-pyrenecarboxaldehyde, 1-pyrenebutyric acid, ferrocene-methanol, *N,N*-bis(3-aminophenyl)-3,4,9,10-perylene-tetracarboxylic diimide, *N*-methylmorpholine, 4-(dimethylamino)pyridine, and hydrochloric acid volumetric standard solution in water (1.019 N) (for molecular weight titrations) were obtained from Aldrich (Milwaukee, WI). 1*H*,1*H*-Pentadecafluorooctylamine was purchased from PCR (Gainesville, FL). DMF was dried over molecular sieves for at least 1 day before use. MUA was prepared according to a literature procedure.³⁷ 1-Pyrenemethanol was synthesized by hydrogenation of 1-pyrenecarboxaldehyde using sodium borohydride.

H₂NR(PTBA)RNH₂. 4',4'-Azobis(4-cyanovaleric acid) (380 mg, 1.36 mmol), 1,4-dioxane (60 mL), and 20 mL (136 mmol) of *tert*-butyl acrylate were added to a flame-dried, three-necked flask under argon. The solution was allowed to reflux for 20 h. The polymer product was then precipitated from a mixture of EtOH and distilled water and dried overnight under vacuum to give 16.0 g of polymer. The product, HOOCR(PTBA)RCOOH (R = C(CN)(CH₃)(CH₂)₂), was then analyzed by ¹H and ¹³C NMR spectroscopy and was titrated with 0.01 M KOH in EtOH. Termination of polymerization through processes other than combination of chains will yield a few chains with only one COOH terminus. A solution containing 5.0 g of the above polymer in 30 mL of CH₂Cl₂ was added to a flame-dried flask under Ar, then 324 mg of 1,1'-carbonyldiimidazole was added under argon with vigorous stirring, and the mixture was stirred for 5 h. Ethylenediamine (0.2 mL) was introduced, and the stirring continued

overnight. After reaction, 100 mL of CH₂Cl₂ was added. The organic layer was washed with H₂O (3 × 30 mL) and dried over anhydrous MgSO₄. The solvent was evaporated, and the product was dried overnight *in vacuo* to give a white solid, H₂NR(PTBA)-RNH₂ (R = C(CN)(CH₃)(CH₂)₂CONH(CH₂)₂) in 80% yield. Although we used a large excess of ethylenediamine, it is still possible that a few polymer chains combined through reaction of both amine groups of ethylenediamine. The product was titrated with 0.01 M HCl in EtOH. *M_n* values, which ranged from 1.5 × 10⁴ to 2.5 × 10⁴, were calculated assuming two amine termini per chain. A small number of chains probably contain only one amine terminus. FTIR (KBr, cm⁻¹): 3438, 1734, 1633, 1262, 1155. ¹H NMR (200 MHz, CDCl₃): δ 1.20–2.00 (m), 2.25 (br, s). ¹³C NMR (50 MHz, CDCl₃): δ 28.06, 35.70, 35.84, 35.97, 36.11, 37.39, 41.94, 42.31, 80.35, 174.20.

N-2-(Aminoethyl)-1-pyrenebutanamide (Py(CH₂)₃CONH-(CH₂)₂NH₂) (I). 1-Pyrenebutyric acid (1.0 g, 3.47 mmol) was placed in a 250-mL round-bottomed flask. To this flask was then added 125 mL of benzene, 3.0 mL of thionyl chloride, and a catalytic amount of dimethylformamide. This mixture was stirred at room temperature until it became homogeneous and then stirred an additional 1.5 h. The solvent was evaporated, leaving a dark brown oily residue. FTIR analysis of the residue showed no evidence of the carboxylic acid carbonyl peak (1710 cm⁻¹) and the appearance of a strong carbonyl peak at 1800 cm⁻¹ arising from the acid chloride. The residue was dissolved in 100 mL of methylene chloride and added dropwise (over a 1-h period) to a solution of ethylenediamine (50 mmol in 50 mL of methylene chloride) at 0 °C. The resulting reaction mixture was stirred an additional 10 h and washed with saturated NaCl (aqueous) (2 × 250 mL) and pure H₂O (150 mL). The organic layer was dried over anhydrous MgSO₄ and evaporated to give a brownish yellow solid. This solid was recrystallized from a toluene-hexane mixture to give a light yellow solid in 65% yield. Mp 110–113 °C (dec). FTIR (KBr, cm⁻¹): 3425, 3312, 3042, 1646, 1545, 841, 759, 715, 683, 621. ¹H NMR (200 MHz, CDCl₃): δ 1.45 (br s, NH₂), 2.18–2.35 (m, 4 H), 2.78 (t, 2H), 3.25 (q, 2 H), 3.38 (t, 2 H), 5.85 (br, s, 1 H), 7.82–8.31 (m, 9 H). ¹³C NMR (50 MHz, CDCl₃): δ 27.42, 32.76, 36.06, 41.35, 41.88, 123.39, 124.76, 124.89, 124.97, 125.07, 125.83, 126.69, 127.35, 127.46, 128.77, 129.93, 130.89, 131.40, 135.86, 172.86. HRMS (*m/e*) calcd for C₂₂H₂₂N₂O⁺: 331.1810. Found: 331.1795. In addition to characterization by spectroscopy and HRMS, I was also characterized by elemental analysis. In this case, it analyzed correctly as a hydrate, C₂₂H₂₂N₂O⁺·1/2H₂O. MS Calcd for C₂₂H₂₂N₂O⁺·1/2H₂O: C, 77.85; H, 6.83; N, 8.25. Found: C, 78.12; H, 6.63; N, 8.11.

NH₂(PEG₄₆₀₀)NH₂. Conversion of poly(ethylene glycol) (HO-(PEG₄₆₀₀)OH) to an α,ω -diamine in 78% yield was accomplished using a literature procedure that proceeds via an intermediate dichloride.³⁸ Mp 57–59 °C. ¹H NMR (200 MHz, CDCl₃): δ 2.02 (s, br), 2.87 (t), 3.65 (s). ¹³C NMR (50 MHz, CDCl₃): δ 41.50, 70.27, 73.14.

Results and Discussion

Derivatization of Hyperbranched PAA Films through Amide and Ester Linkages. Derivatization of grafted, hyperbranched PAA is a simple route to an array of films. As examples of the wide variety of amino-terminated molecules that can couple to PAA films, we derivatized films with Py(CH₂)₃CONH(CH₂)₂NH₂ (I, Chart 1) (a fluorescent group), H₂NCH₂-15-crown-5 (III) (a macrocycle known for alkali metal-ion binding), APPCDI (V) (a rigid aromatic dye), α,ω -NH₂-poly(ethylene glycol) (PEG, a biocompatible polymer), 1*H*,1*H*-pentadecafluorooctylamine (H₂N(CH₂)(CF₂)₆CF₃), allylamine, and alkylamines. The fact that all of these amines couple to hyperbranched PAA films shows that derivatization of PAA via amide bonds is a general procedure.

We couple amine-containing molecules to hyperbranched films by activating the pendant carboxylic acid groups of PAA with isobutyl chloroformate and allowing the newly formed anhydrides to react with the amino

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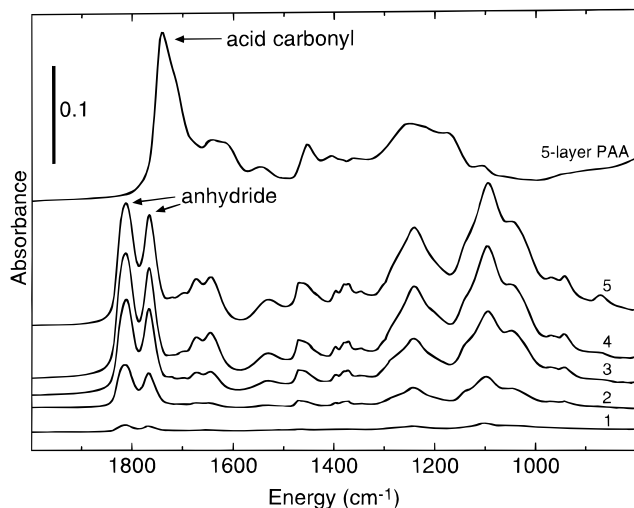


Figure 1. FTIR-ERS spectra of one- to five-layer PAA films after activation with isobutyl chloroformate. The spectrum of the five-layer PAA film before activation (top) is given for comparison.

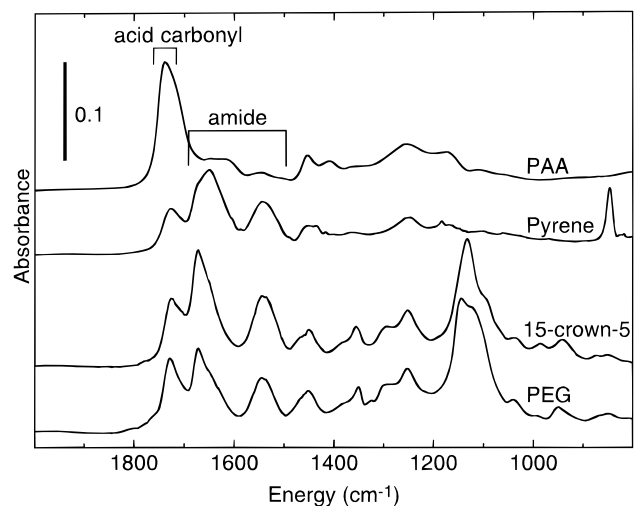


Figure 2. FTIR-ERS spectra of three-layer PAA films derivatized with $\text{H}_2\text{N}(\text{PEG}_{4600})\text{NH}_2$, H_2NCH_2 -15-crown-5, and $\text{Py}(\text{CH}_2)_3\text{CONH}(\text{CH}_2)_2\text{NH}_2$. The spectrum of a three-layer PAA film before derivatization (top) is given for comparison. The spectra of the derivatized films were taken after immersion in 0.1 M HCl in EtOH (EtOH rinse) to convert unreacted carboxylate groups to the acids.

groups. FTIR-ERS shows that upon activation with isobutyl chloroformate, the peak due to the acid carbonyl (1730 cm^{-1}) of PAA disappears and new anhydride peaks appear at 1816 and 1767 cm^{-1} . The disappearance of the peak due to the acid carbonyl shows that the activation process is nearly quantitative. We observed this high level of activation in PAA films containing one to five PAA layers (Figure 1). Thus, PAA films are very permeable and reactive to isobutyl chloroformate in DMF.

After reaction with an amine, the anhydride absorptions of the activated PAA film disappear, and amide peaks at ≈ 1660 and $\approx 1545\text{ cm}^{-1}$ appear as shown in Figure 2 for three-layer PAA films derivatized with $\text{H}_2\text{N}(\text{PEG}_{4600})\text{NH}_2$, H_2NCH_2 -15-crown-5, and $\text{Py}(\text{CH}_2)_3\text{CONH}(\text{CH}_2)_2\text{NH}_2$. An acid carbonyl peak is also seen, showing that a fraction of the mixed anhydride reforms the acid, probably by reaction of the amine with the carbonic acid carbonyl of the mixed anhydride or moisture. Upon derivatization, peaks characteristic of specific functional groups also appear. For example, Figure 2 contains peaks due to a H wagging mode of pyrene at 847 cm^{-1} and the C–O–C

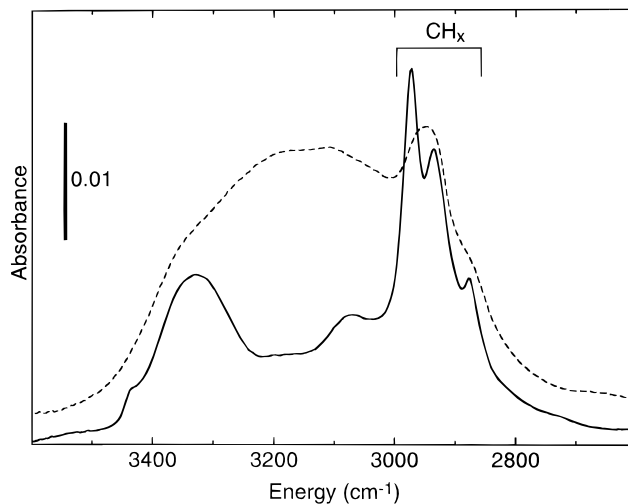


Figure 3. FTIR-ERS spectra of a three-layer PAA film (hydrocarbon region) before (dashed line) and after (solid line) derivatization with isopropylamine.

stretching modes of the ether peaks of PEG and 15-crown-5 at 1144 and 1133 cm^{-1} , respectively.

The hydrocarbon region of the FTIR-ERS spectrum provides additional support for derivatization. Figure 3 shows the hydrocarbon region for a three-layer PAA film before and after derivatization with isopropylamine. After derivatization, sharp peaks due to the CH_3 and CH stretches of the isopropyl group appear at 2972 (CH_3), 2877 (CH_3), and 2936 (CH) cm^{-1} . The N–H stretch at 3330 cm^{-1} and the decrease in the broad OH stretch of the carboxylic acid around 3100 cm^{-1} confirm conversion of the acid to the amide. Spectral changes similar to those shown in Figures 2 and 3 occurred in all of the amide-derivatized films as a result of the conversion of many of the carboxylic acid groups to amides.

We estimate coupling yields using the ratio of the acid carbonyl peak height ($\approx 1730\text{ cm}^{-1}$) after coupling to that before coupling. The yields for the coupling of primary amines are allylamine, 36%; isopropylamine, 41%; $\text{H}_2\text{N}(\text{PEG}_{4600})\text{NH}_2$, 39%; H_2NCH_2 -15-crown-5, 51%; $\text{H}_2\text{NCH}_2(\text{CF}_2)_6\text{CF}_3$, 47%; $\text{Py}(\text{CH}_2)_3\text{CONH}(\text{CH}_2)_2\text{NH}_2$, 64%; and APPCDI, 41%.³⁹ The yield for the coupling of diethylamine to PAA is the lowest of any of the amines (28%) and presumably reflects the lower reactivity of secondary amines toward amidation. In preliminary experiments, we also derivatized PAA films using thionyl chloride and carbonyldiimidazole as activating agents. These activation methods appear to be less effective for amidation than isobutyl chloroformate activation.

Estimates of yields are probably conservative because the new amide peaks overlap somewhat with the acid carbonyl peaks. Additionally, the residual acid carbonyl peaks generally have half-widths that are smaller than those of unmodified PAA. To take into account the possible formation of carboxylate salts during coupling, we measured the FTIR-ERS spectra of derivatized films after acidification (5 min of immersion in 0.1 M HCl in EtOH followed by an EtOH rinse). We used these spectra to calculate the yields given above.

(39) The reported yields are the average of two different samples. Yields for $\text{H}_2\text{NCH}_2(\text{CF}_2)_6\text{CF}_3$, $\text{Py}(\text{CH}_2)_3\text{CONH}(\text{CH}_2)_2\text{NH}_2$, and APPCDI were measured on PAA films synthesized using a batch of $\text{H}_2\text{NR}(\text{PTBA})\text{RNH}_2$ with a M_n value of 2.02×10^4 . In the case of diethylamine, allylamine, and $\text{H}_2\text{N-PEG}_{4600}\text{-NH}_2$, we used $\text{H}_2\text{NR}(\text{PTBA})\text{RNH}_2$ with a M_n value of 1.87×10^4 . Yields from duplicate experiments differed by at most 6%, except in the case of isopropylamine (18% difference) and H_2NCH_2 -15-crown-5 (8% difference) where one experiment was performed on each of the above-mentioned $\text{H}_2\text{NR}(\text{PTBA})\text{RNH}_2$ batches. The value of M_n may slightly influence the yields.

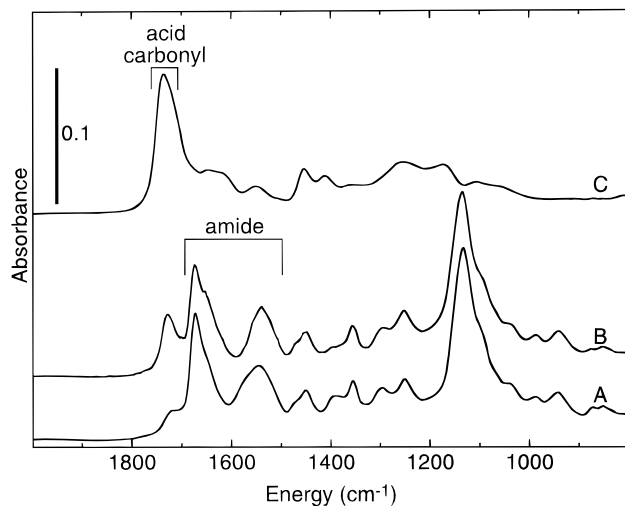


Figure 4. FTIR-ERS spectra of a three-layer PAA film derivatized with $\text{H}_2\text{NCH}_2\text{-15-crown-5}$ before (A) and after (B) immersion in 0.1 M HCl in EtOH (EtOH rinse). The spectrum of a three-layer PAA film (C) is shown for comparison.

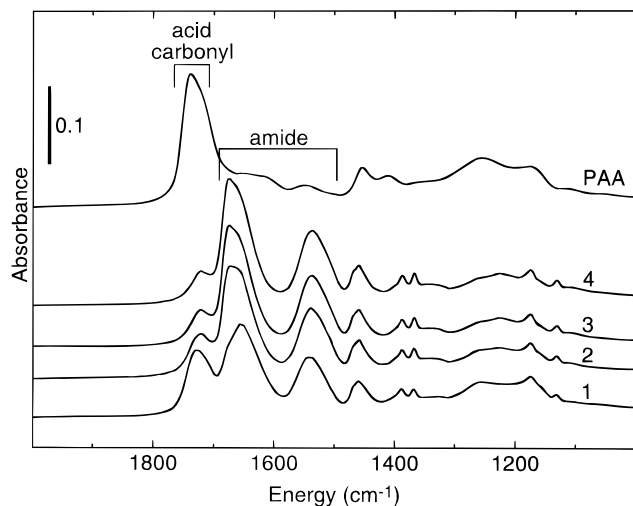


Figure 5. FTIR-ERS spectra of a three-layer PAA film after one to four cycles of activation with isobutyl chloroformate and reaction with isopropylamine. The spectrum of the three-layer PAA film before activation (top) is shown for comparison.

In most cases, the increase in the acid carbonyl peak after acidification is substantial as shown in Figure 4 for a film derivatized with $\text{H}_2\text{NCH}_2\text{-15-crown-5}$. In control experiments, we exposed unactivated PAA films to $\text{H}_2\text{N(PEG}_{4600}\text{)NH}_2$, $\text{H}_2\text{NCH}_2\text{-15-crown-5}$, and $\text{Py(CH}_2\text{)}_3\text{-CONH(CH}_2\text{)}_2\text{NH}_2$. FTIR-ERS spectra and ellipsometric thicknesses show that in some cases ammonium salts formed, but they are completely removed from the film by acidification.

We can increase the coupling yield for isopropylamine and other amines by reactivating the residual carboxylic acid groups and again exposing them to a solution of the amine. Figure 5 shows the FTIR-ERS spectra of a three-layer PAA film after one, two, three, and four cycles of activation with isobutyl chloroformate and reaction with isopropylamine. Although the reaction yield increases with each cycle, isopropylamine coupling yields greater than 80% are impractical using this method.

Thickness changes upon derivatization can be dramatic. We previously reported that derivatization with $\text{H}_2\text{-NCH}_2(\text{CF}_2)_6\text{CF}_3$ approximately doubles the thickness of three-layer PAA films.³⁰ Derivatization with $\text{Py(CH}_2\text{)}_3\text{-CONH(CH}_2\text{)}_2\text{NH}_2$ increases the ellipsometric thickness by a factor of 2–3, while derivatization with the oligomer,

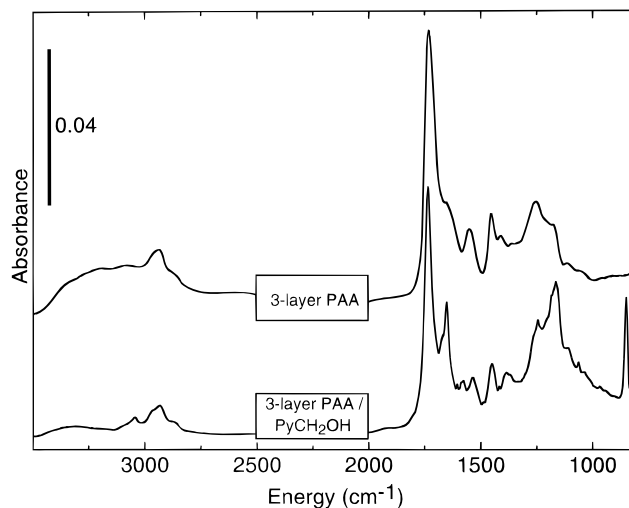


Figure 6. FTIR-ERS spectra of a three-layer PAA film before and after derivatization with PyCH_2OH .

$\text{NH}_2(\text{PEG}_{4600})\text{NH}_2$, more than doubles the film thickness (from ≈ 330 to 700 \AA). Coupling of smaller amines like isopropylamine and allylamine produced smaller thickness increases (1.2- to 1.5-fold). The large magnitude of thickness changes upon derivatization (measured after acidification of the film to remove salts) shows that the amino-terminated molecules are reacting throughout most of the film because reactions occurring only near the surface would yield much smaller changes. The fact that larger molecules can double or triple thickness shows that size does not restrict access to anhydride groups in the activated PAA film.

Coupling of alcohols to PAA via ester formation is also possible. To couple alcohol-terminated molecules to PAA films, we activate the carboxylic acid groups in the film with isobutyl chloroformate and then allow an alcohol to react with the anhydride groups in the presence of triethylamine and 4-(dimethylamino)pyridine. Figure 6 shows the FTIR-ERS spectra of a three-layer PAA film before and after derivatization with PyCH_2OH . Because the newly formed ester carbonyl peak appears at nearly the same frequency as that of the acid groups ($\approx 1730 \text{ cm}^{-1}$), we cannot estimate the yield in these reactions using the intensity of the acid carbonyl absorption. However, the strong pyrene peak at 847 cm^{-1} in the FTIR-ERS spectrum shows that the film contains a large number of pyrene groups and the peak at 1166 cm^{-1} is likely due to the newly formed ester groups. The decrease of the broad OH stretch ($\approx 3100 \text{ cm}^{-1}$) upon derivatization also suggests that the acid groups reacted to form esters. The fluorescence measurements discussed below confirm a high density of pyrene groups in these films. We discuss derivatization of PAA films with FcCH_2OH in the section on cyclic voltammetry.

Fluorescence of Pyrene-Containing Films. Fluorescence is a useful tool for investigating the distribution of pyrene groups in derivatized films because pyrene strongly emits as both a monomer and an excimer depending on the nearest-neighbor distance.⁴⁰ PAA films (three-layer) derivatized using a high concentration of either PyCH_2OH (0.04 M) or $\text{Py(CH}_2\text{)}_3\text{-CONH(CH}_2\text{)}_2\text{NH}_2$ (0.05 M) show almost exclusively excimer fluorescence. This demonstrates that pyrene groups are in close proximity and, therefore, the film must contain a high density of pyrene groups. Excimer fluorescence due to

(40) Taniguchi, Y.; Mitsuya, M.; Tamai, N.; Yamazaki, I.; Masuhara, H. *Chem. Phys. Lett.* **1986**, *132*, 516.

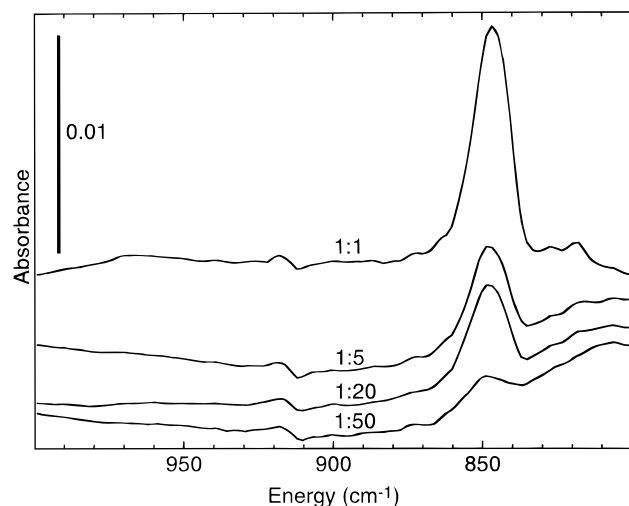


Figure 7. FTIR-ERS spectra of two-layer PAA films after simultaneous grafting of $\text{Py}(\text{CH}_2)_3\text{CONH}(\text{CH}_2)_2\text{NH}_2$ and $\text{H}_2\text{NR}(\text{PTBA})\text{RNH}_2$ using mole ratios of 1:50, 1:20, 1:5, and 1:1 ($\text{Py}(\text{CH}_2)_3\text{CONH}(\text{CH}_2)_2\text{NH}_2$ to $\text{H}_2\text{NR}(\text{PTBA})\text{RNH}_2$) in the grafting solution.

phase segregation of pyrene molecules on the surface is ruled out by the large increase in thickness (2–3-fold) upon derivatization with PyCH_2OH or $\text{Py}(\text{CH}_2)_3\text{CONH}(\text{CH}_2)_2\text{NH}_2$.

In some applications, control over the amount and distribution of a moiety in the film is crucial. To control the amount of $\text{Py}(\text{CH}_2)_3\text{CONH}(\text{CH}_2)_2\text{NH}_2$ coupled to PAA films, we simultaneously grafted $\text{H}_2\text{NR}(\text{PTBA})\text{RNH}_2$ and $\text{Py}(\text{CH}_2)_3\text{CONH}(\text{CH}_2)_2\text{NH}_2$ to the films and varied the ratio of $\text{Py}(\text{CH}_2)_3\text{CONH}(\text{CH}_2)_2\text{NH}_2$ to $\text{H}_2\text{NR}(\text{PTBA})\text{RNH}_2$ in the grafting solution ($\text{H}_2\text{NR}(\text{PTBA})\text{RNH}_2$ concentration was held constant, while $\text{Py}(\text{CH}_2)_3\text{CONH}(\text{CH}_2)_2\text{NH}_2$ concentration was varied). Figure 7 shows the FTIR-ERS spectra of several two-layer PAA films after activation and exposure to solutions containing different ratios of $\text{Py}(\text{CH}_2)_3\text{CONH}(\text{CH}_2)_2\text{NH}_2$ to $\text{H}_2\text{NR}(\text{PTBA})\text{RNH}_2$. Grafted PTBA was hydrolyzed before measuring the spectra. The intensity of the pyrene absorption at 847 cm^{-1} decreases with a decreasing ratio of $\text{Py}(\text{CH}_2)_3\text{CONH}(\text{CH}_2)_2\text{NH}_2$ to $\text{H}_2\text{NR}(\text{PTBA})\text{RNH}_2$ in the coupling solution. The fluorescence spectra of these samples showed that excimer fluorescence (broad peak at 478 nm) decreases with a decreasing ratio of $\text{Py}(\text{CH}_2)_3\text{CONH}(\text{CH}_2)_2\text{NH}_2$ to $\text{H}_2\text{NR}(\text{PTBA})\text{RNH}_2$, while monomer fluorescence (peaks at 379 and 399 nm) increases as shown in Figure 8. Thus, we can prepare polymer films with dilute concentrations of fluorescent labels. While the lower concentrations of pyrene in the above-described films could be due to competition between $\text{Py}(\text{CH}_2)_3\text{CONH}(\text{CH}_2)_2\text{NH}_2$ and $\text{H}_2\text{NR}(\text{PTBA})\text{RNH}_2$, other experiments show that the low concentration of $\text{Py}(\text{CH}_2)_3\text{CONH}(\text{CH}_2)_2\text{NH}_2$ in the coupling solution ($1.6 \times 10^{-5}\text{ N}$ in the case of the 1:50 ratio) is the major factor. For example, monomer fluorescence also resulted when we used $1.6 \times 10^{-5}\text{ N}$ $\text{Py}(\text{CH}_2)_3\text{CONH}(\text{CH}_2)_2\text{NH}_2$ in coupling experiments performed in the absence of $\text{H}_2\text{NR}(\text{PTBA})\text{RNH}_2$.

Cyclic Voltammetry of Ferrocene-Containing Films. Cyclic voltammetry of FcCH_2OH -derivatized PAA films in the absence of other electroactive species in solution shows the oxidation and reduction of the ferrocene groups in the film (Figure 9). Ferrocene groups are therefore present in sufficiently high concentration to be within electron-hopping distance. Murray and co-workers previously observed similar voltammetry using poly(vinylferrocene) films.^{41,42} Integration of the oxidation or

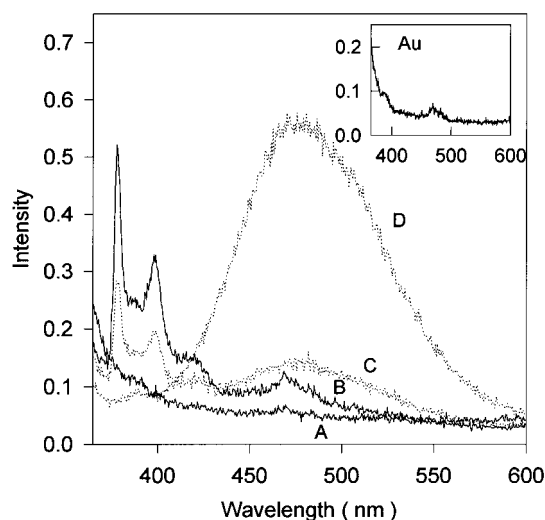


Figure 8. Fluorescence spectra of two-layer PAA films before (A) and after simultaneous grafting of $\text{Py}(\text{CH}_2)_3\text{CONH}(\text{CH}_2)_2\text{NH}_2$ and $\text{H}_2\text{NR}(\text{PTBA})\text{RNH}_2$ using 1:50 (B), 1:20 (C), and 1:1 (D) ratios of $\text{Py}(\text{CH}_2)_3\text{CONH}(\text{CH}_2)_2\text{NH}_2$ to $\text{H}_2\text{NR}(\text{PTBA})\text{RNH}_2$ in the grafting solution. The fluorescence spectrum of bare Au (inset) is shown for comparison.

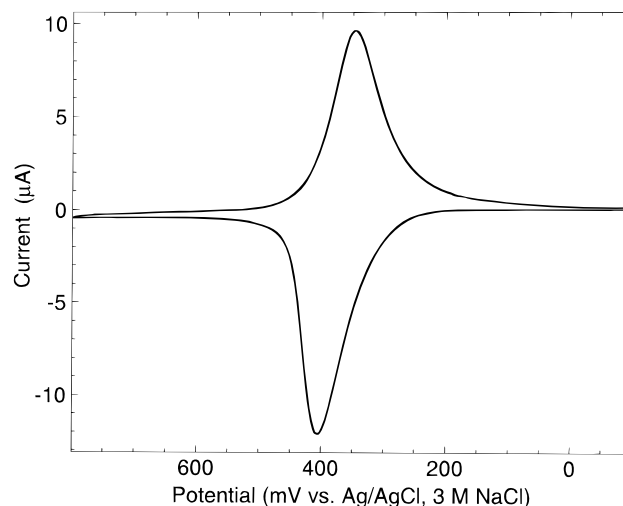


Figure 9. Cyclic voltammetry of a three-layer PAA film derivatized with FcCH_2OH (aqueous 0.1 M LiClO_4 , scan rate = 20 mV/s).

reduction peak shows that the film contains at least $(6 \pm 3) \times 10^{-9}\text{ mol/cm}^2$ of ferrocene. A fraction of the ferrocene in the film may be electrically isolated and thus not electroactive, so this value of ferrocenyl surface coverage represents a lower limit. From this surface coverage and the ellipsometric thickness of N_2 -dried films ($\approx 500\text{ \AA}$), there are approximately $1.2 \times 10^{-3}\text{ mol/cm}^3$ of ferrocene in the film. The density of the ferrocene groups in a homopolymer of $[\text{CH}_2\text{CH}(\text{CO}_2\text{CH}_2\text{-ferrocene})]_n$ would be about $3.6 \times 10^{-3}\text{ mol/cm}^3$ (assuming a mass density of 1 g/cm^3). The level of derivatization in the hyperbranched polymers is, therefore, quite high.

Stability of PAA Films and Their Derivatives. We intend to incorporate hyperbranched PAA films and their derivatives into sensor and anticorrosion applications. Thus, the stability of these films is an important issue. We examined the stability of films under various conditions including mild heating, sonication, solvent extraction in a Soxhlet apparatus, and immersion in aqueous acid

and base. Except in one limited case (*vide infra*), the films proved to be quite stable.

We sonicated a three-layer PAA film for 15 min in both 0.1 M HCl and acetone and observed no change in its FTIR-ERS spectrum. We have also sonicated films derivatized with FcCH₂OH, PyCH₂OH, and H₂NCH₂(CF₂)₆-CF₃ in CHCl₃ and find that all of these films are stable. Soxhlet extraction using methylene chloride did not change the ellipsometric thickness or FTIR-ERS spectra of PAA films even when the extraction was performed overnight. The fact that the hydrolysis step used for preparing PAA films occurs at 55 °C shows that these films are stable under mild heating in benzene.

Exposure to aqueous acid does not damage PAA films. However, treatment with base can remove the PAA film from the Au substrate in the case of very thick films. Thinner films are more stable. Ellipsometric thicknesses and FTIR-ERS spectra of two-layer PAA films (200 Å thick) are unchanged by an overnight immersion in 0.1 M NaOH (aq) followed by a 5-min immersion in 0.1 M HCl (aq) and an EtOH rinse. Three-layer PAA films thinner than 350 Å are stable to treatment with 0.1 M NaOH and subsequent acidification (0.1 M HCl). Four- and five-layer PAA films made from polymer batches that yield thin three-layer PAA films are also stable under these conditions. However, we have observed that some thick (>500-Å) three-layer PAA films are completely removed (film thickness decreases to ≈30 Å) from the substrate upon a 5-min exposure to 0.1 M NaOH (aq) followed by an EtOH rinse. (Film thicknesses depend on the batch of H₂NR-(PTBA)RNH₂ used. At present, we do not know which distinctions among different H₂NR-(PTBA)RNH₂ batches contribute to differing film thicknesses.) Some thick three-layer PAA films are even partially removed by a 5-min immersion in a pH 7 buffer. The FTIR-ERS spectrum of a thinner three-layer PAA film (350 Å) shows that most acid groups in PAA films are deprotonated after exposure to a pH 7 buffer. We hypothesize that upon salt formation, PAA becomes so soluble that it is in effect plucked up by its single Au-thiolate root. In one case, we divided a thick three-layer PAA sample (550 Å) in two and derivatized one piece with H₂NCH₂(CF₂)₆CF₃.³⁰ The fluorinated film was stable to an overnight immersion in 0.1 M NaOH (aq), while the underivatized film was removed by a 5-min immersion in 0.1 M NaOH (aq). We think that the presence of the perfluorinated alkane chains rendered the film hydrophobic and insoluble in water, thus stabilizing the film in basic solution.

To make thick, underivatized PAA films stable under basic conditions, we used a monolayer of HS(CH₂)₁₀-C≡CC≡C(CH₂)₁₀COOH (rather than MUA) as an adhesion layer for grafting PAA. The diacetylenic monolayer has the advantage that it polymerizes under UV light to yield a poly(diacetylene) (PDA) monolayer that is stable under aggressive conditions.⁴³ If our hypothesis concerning film removal is correct, then polymerization of the monolayer would stabilize grafted PAA films as removal of grafted PAA from the Au substrate requires breaking multiple Au-thiolate bonds. Indeed, when we prepared ≈460-Å-thick three-layer PAA films on PDA monolayers, these films were stable towards a 5-min immersion in 0.1 M NaOH. Four- and five-layer PAA films on PDA monolayers (1000 and 1700 Å thick, respectively) are also stable in 0.1 M NaOH.⁴⁴

(43) Kim, T.; Chan, K. C.; Crooks, R. M. *J. Am. Chem. Soc.*, in press.

(44) The stability of PAA films on PDA monolayers supports our hypothesis, but we note that thick three-layer PAA films on PDA were about 50 Å thinner than MUA-grafted films that were removed from the substrate. A slightly different PAA film structure could also contribute to the stability of films grafted on PAA.

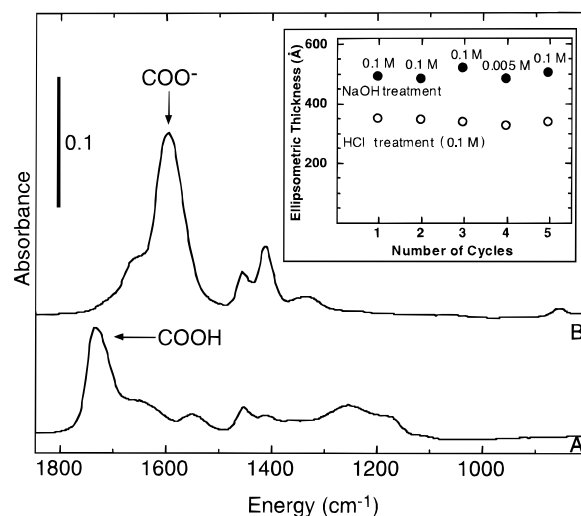


Figure 10. FTIR-ERS spectra of a three-layer PAA film before (A) and after (B) immersion in 0.1 M NaOH (aq) (EtOH rinse). The inset shows the ellipsometric thickness of a three-layer PAA film after several acid and base treatments. The thicknesses were measured after rinsing the sample with EtOH.

The stability of the PAA films under a variety of conditions likely results from the covalent bonds between grafted layers. In a previous paper, we pointed out that amide peaks in the FTIR-ERS spectrum showed that the PAA chains are covalently grafted. However, because the grafting chains contain amide groups, new amide peaks can result from the polymer chains, as well as from amide linkages formed upon grafting. Thus, amide peaks in the FTIR-ERS spectrum of these films do not definitively demonstrate covalent linkages. Derivatization with NH₂-(PEG₄₆₀₀)NH₂, however, shows the unambiguous formation of amide linkages to an amino-terminated PEG chain that does not contain amide groups. A similar linkage should occur with H₂NR-(PTBA)RNH₂. Covalent bonding in PAA layers is also strongly implied by the stability of the films and by the fact that when we attempted to graft a layer of PTBA onto the MUA monolayer or a layer of PAA without using isobutyl chloroformate activation, the film thickness increased by only a few angstroms.¹

Changes in Ellipsometric Thickness and Contact Angles with pH. The ellipsometric thicknesses and water contact angles of PAA films depend upon the state of CO₂H ionization in the film. Figure 10 shows the FTIR spectra of a three-layer PAA film after a 5-min immersion in 0.1 M NaOH (aq) (EtOH rinse) and after a subsequent 5 min immersion in 0.1 M HCl (aq) (EtOH rinse). After treatment with NaOH, salt peaks appear and the acid carbonyl peak vanishes. The disappearance of the acid carbonyl peak shows that virtually all of the acid groups in the film are accessible to OH⁻. The ellipsometric thickness of the film is greater in the deprotonated form, as shown in the inset of Figure 10. For the three-layer films we tested, the ellipsometric thickness cycled between 340 and 500 Å after treatment with 0.1 M HCl and 0.1 M NaOH, respectively. We rinsed the sample with EtOH to prevent residual NaOH from increasing the film thickness. To further check that residual, precipitated NaOH was not increasing the film thickness, we decreased the OH⁻ concentration to 0.005 M. In this case, we see the same result as with 0.1 M NaOH. Two- and four-layer PAA films showed similar trends. The film thickness changed from 170 to 250 Å for a two-layer film and from 620 to 950 Å for a four-layer film. These thickness increases likely arise from the incorporation of Na⁺ ions along with solvent into the film and the breaking of H-bonds.

One other possible reason for the changes in ellipsometric thickness upon deprotonation is that the refractive index of the film changes upon ionization while the thickness is relatively constant. In our measurements, we assumed a refractive index of 1.46 for both forms of the film. To test this assumption, we measured both the refractive index and the thickness of the three-layer PAA films before and after deprotonation. We find that the refractive index actually decreases slightly from 1.54 to 1.51 at 488 nm upon deprotonation. Using the measured refractive indices to determine the thickness instead of assuming an index of 1.46 (633.8 nm) gives no significant difference in thickness changes upon deprotonation.

We measured thickness changes due to deprotonation on samples containing from two to five layers of PAA and observed changes ranging from 40% to 55% in all samples, regardless of the number of layers. Therefore, thicker films undergo much larger absolute thickness changes.

The water contact angles of PAA films also change after deprotonation. Advancing water contact angles decreased from 21° to <5° after treating a three-layer PAA film with 0.1 M NaOH (aq) and rinsing with EtOH. Treatment with 0.1 M HCl (aq) (EtOH rinse) returns the contact angle to ≈21°. We have repeated the cycling of PAA films between acid and carboxylate forms (with the subsequent cycling of thickness and contact angle) 8 times without degradation of the film. In a four-layer PAA film, the contact angle changes from 24° to <5° upon deprotonation.

Dosing PAA Films with Vapors of Volatile Organic Compounds (VOCs). We intend to use derivatized hyperbranched films as chemically sensitive interfaces in sensor applications, and therefore, we present here preliminary results regarding the absorption of VOCs into PAA films. We synthesized hyperbranched PAA films on Au-coated SAW devices and used them to measure mass changes in PAA films upon exposure to vapors of VOCs. Figure 11 shows the mass changes of MUA, three-layer PAA, and $\text{H}_2\text{NCH}_2(\text{CF}_2)_6\text{CF}_3$ -derivatized three-layer PAA films upon exposure to vapors of VOCs (25% of saturation). The responses of one-, two-, and three-layer PAA films are similar to that of a MUA monolayer. This suggests that the VOCs are not able to penetrate the PAA films. This might occur because the film is very tightly packed due to hydrogen bonding or because potential VOC binding sites are occupied with the solvents used in synthesis and rinsing. Derivatization of a three-layer PAA film with $\text{H}_2\text{NCH}_2(\text{CF}_2)_6\text{CF}_3$, however, increases the amount of polar VOCs absorbed in the film by an order of magnitude. The large hydrophobic side chains in the polymer probably open the film. They may also reduce the amount of solvent in the film.

Conclusions

Derivatization of hyperbranched PAA films through amide or ester linkages is a general procedure for inserting a wide variety of functionalities into PAA films. The size of the derivative molecules does not restrict coupling to PAA films. Derivatized films can contain a high density of many different types of functional groups as shown by FTIR-ERS, large increases in ellipsometric thicknesses upon derivatization, the dominance of excimer peaks in fluorescence spectra, and cyclic voltammetry of films

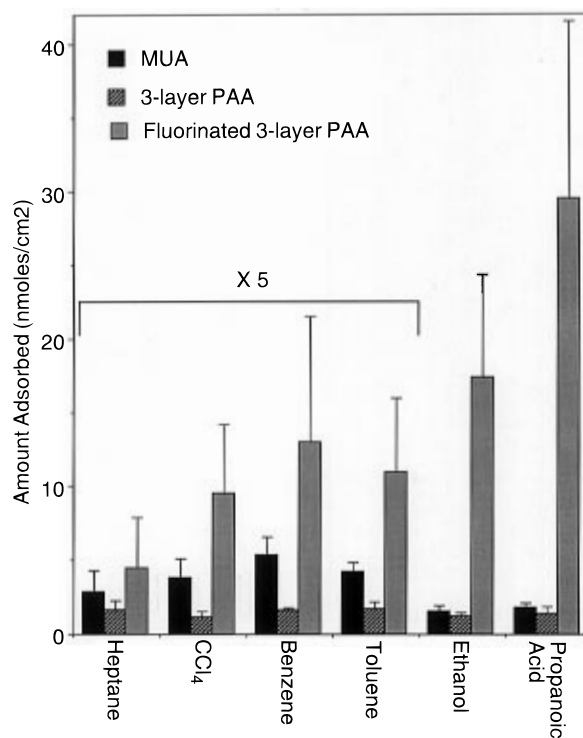


Figure 11. Mass changes of MUA monolayers, three-layer PAA films, and $\text{H}_2\text{NCH}_2(\text{CF}_2)_6\text{CF}_3$ -derivatized three-layer PAA films upon dosing with several volatile organic compounds (25% saturation vapor pressure). The mass changes were measured using SAW devices.

containing ferrocene groups. High densities of derivatives suggest that the PAA films are relatively open in solution and accessible to a wide variety of reactants. Although unmodified PAA films do not absorb vapors of VOCs to an appreciable extent, derivatization of PAA films with $\text{H}_2\text{NCH}_2(\text{CF}_2)_6\text{CF}_3$ expands the film and increases the amount of polar VOCs absorbed by up to an order of magnitude.

Hyperbranched PAA films are stable under acidic, sonication, and Soxhlet extraction conditions. Polymerization of the monolayer (PDA) to which the PAA is grafted stabilizes thick PAA films toward basic conditions. Stability in basic and acidic solutions occurs in spite of large changes in film thickness upon deprotonation. Due to their stability and the wide range of derivatives that can be prepared, we are investigating PAA films for applications in areas such as corrosion-resistant coatings and chemical sensing.

Acknowledgment. We are grateful for financial support of this research from the National Science Foundation (DEB, DMR-9634196, and RMC, CHE-9313441) and the state of Texas (Texas Higher Education Coordinating Board) through the Advanced Technologies Program. M. B. acknowledges a NIH postdoctoral fellowship. We thank Prof. Taisun Kim (Hallym University) for providing the $\text{HS}(\text{CH}_2)_{10}\text{C}\equiv\text{CC}\equiv\text{C}(\text{CH}_2)_{10}\text{COOH}$ and Dan Dermody for help with the SAW experiments.

LA961098R