Chemically Grafted Polymeric Filters for Chemical Sensors: Hyperbranched Poly(acrylic acid) Films Incorporating β-Cyclodextrin Receptors and Amine-Functionalized Filter Layers

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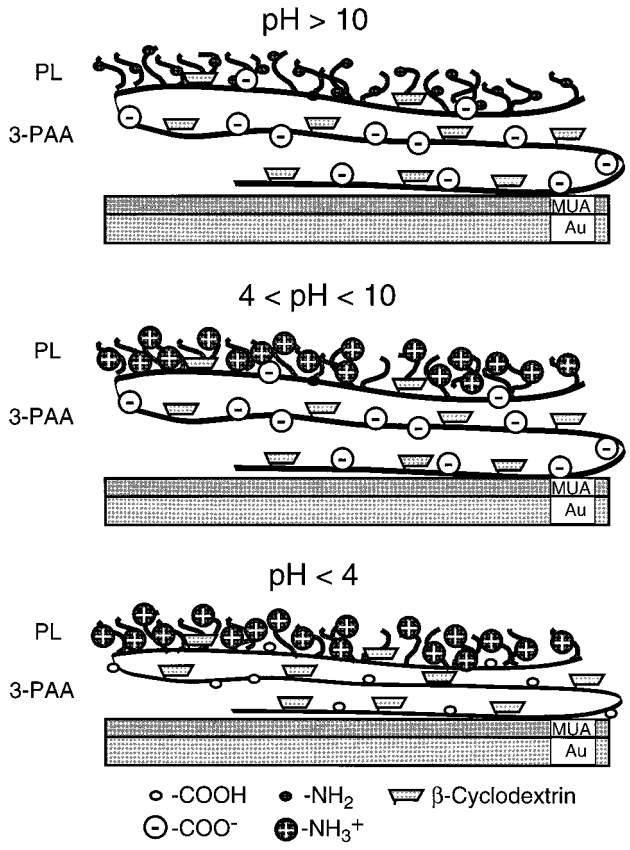
We report a new "molecular-filter" approach for enhancing the selectivity of chemical sensors. Specifically, we describe electrochemical sensors prepared from Au electrodes coated with β-cyclodextrin-functionalized, hyperbranched poly(acrylic acid) (PAA) films capped with a chemically grafted, ultrathin polyamine layer. The hyperbranched PAA film is a highly functionalized framework for covalently binding the β-cyclodextrin molecular receptors. The thin, grafted polyamine overlayer acts as a pH-sensitive "molecular filter" that selectively passes suitably charged analytes. Poly(amidoamine) dendrimers or poly-D-lysine is used as 10−15-nm-thick filter layers. The results show that at low pH, when the polyamines are fully protonated, positively charged redox probe molecules, such as benzyl viologen (BV), do not permeate the filter layer. However, at high pH, when the filter layer is uncharged, BV penetrates the filter layer and is reduced at the electrode. The opposite pH dependence is observed for negatively charged redox molecules such as anthraquinone-2-sulfonate (AQS). Both BV and AQS specifically interact with the β-cyclodextrin receptors underlying the polyamine filter layers.

Introduction

We report a new method, which is based on polymer-grafted "molecular filters", for enhancing the selectivity of chemical sensors. Specifically, we describe electrochemical sensors prepared from Au electrodes coated with β-cyclodextrin-functionalized, hyperbranched poly(acrylic acid) (PAA) films[1−6] capped with a chemically grafted, ultrathin polyamine layer. The hyperbranched PAA film is a highly functionalized framework for covalently binding the β-cyclodextrin molecular receptors. The thin, grafted polyamine overlayer acts as a pH-sensitive molecular filter that selectively passes suitably charged analytes to the underlying β-cyclodextrin molecular receptors (Chart 1) while rejecting others. The chemistry required to prepare these versatile materials is simple and easily adaptable to specific applications.

There are two key findings described in this paper. First, hyperbranched polymer (HBP) films can be selectively functionalized: in this case β-cyclodextrin receptors are homogeneously distributed throughout the HBP film whereas the polyamine filter layer is confined just to the outermost stratum. Second, the filter layer effectively blocks particular ions even though it is only on the order of 10 nm thick. This is important because thicker, free-standing filter layers that exhibit this function generally lead to high resistances to mass and/or electron transfer.

Chart 1



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In principle, the very general approach described here should minimize these limitations.

Electrodes are chemically modified to introduce specific functions to an otherwise passive electron sink/source.[7−9] Polymers are the most common materials used to modify electrodes owing to the vast diversity of chemistries they exhibit.[7] Polymers can be immobilized onto electrodes by dip-coating, spinning, electropolymerization, layer-by-layer assembly,[10−13] and plasma[14,15] and chemical[6,16] grafting. Here, we introduce a new chemical grafting method that is unique in the degree of simplicity, versatility, and structural control it affords. Proof of the concept is demonstrated by a very simple electrochemical experiment, but more important applications to chemical sensing and biosensing, catalysis, and corrosion passivation applications are easily envisaged.

The idea of using a polymeric overlayer to inhibit mass transfer of interferents between a solution and a transducer surface or chemically sensitive interface is not new. For example, Adams,[17] Adams and Martin,[18] and Wightman[19] studied polymer-modified microelectrodes for in-vitro measurement of neurotransmitters. In all of these studies, the cation-exchange polymer Nafion was used to prevent anionic interferents from reaching the electrode surface. Similarly, Walt et al. simultaneously measured H^+, CO_2, and O_2 concentrations using a multianalyte imaging fiber sensor. The sensing elements were prepared by the sequential deposition of two polymer layers: a chemically sensitive polymer layer incorporating fluorescent indicators (∼7 μm thick), and a thin, gas-permeable siloxane polymer membrane.[20,21] Finally, Heller and coworkers have reported sensors having three ∼10-μm-thick, sequentially deposited polymer layers, a sensing layer (containing glucose oxidase as the sensing agent), a mass-transport limiting layer (to increase film stability), and a biocompatible layer (to inhibit cell growth and reduce protein fouling).[22]

While these examples clearly demonstrate the advantages of using polymeric filter layers, they also hint at one of the major drawbacks: to the best of our knowledge, the coatings that have been used for this purpose are all quite thick, which slows mass and electron transfer. Additionally, these layers are only weakly bonded to the substrate and therefore likely to delaminate over time. The composite hyperbranched polymer films reported here address both of these problems: they are covalently linked to the substrate, and their thickness can be easily controlled to be on the order of 10 nm and perhaps less.

Experimental Section

Buffer Solutions. Buffer solutions were prepared in an aqueous 0.1 M NaCl solution using 18 MΩ·cm deionized water (Milli-Q, Millipore) to provide a nearly constant refractive index and ionic strength. The composition and measured pH values of the buffers were 0.018 M Na_2SO_4 + 0.004 M HCl (pH = 2.7), 0.01 M Na_2HPO_4 + 0.01 M NaH_2PO_4 (pH = 6.7), and 0.018 M Na_2CO_3 + 0.002 M $NaHCO_3$ (pH = 11.0).

Other Chemicals. Amine-terminated, fourth-generation (G4) Starburst PAMAM Dendrimers (Dendritech, Inc., Midland, MI), pentadecafluorooctylamine (PCR, 97%), ethylenediamine (Aldrich, 99%), poly-D-lysine hydrobromide (Aldrich, M_v = 4000−15000), *N*-hydroxysuccinimide (NHS) (97%, Aldrich), 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (EDC) (98+%, Aldrich), 4-(dimethylamino)pyridine (DMAP) (99+%, Aldrich), *N*,*N*-dimethylformamide (DMF) (99.8%, Aldrich), triethylamine (NEt_3) (Aldrich, 99%), benzyl viologen dichloride (Aldrich, 97%), anthraquinone-2-sulfonic acid sodium salt monohydrate (Aldrich, 97%), and triethanolamine hydrochloride (TEA) (Aldrich, 98%) were used as received. β-Cyclodextrin (Aldrich) was freeze-dried before use.

Substrate Preparation. Substrates were prepared by electron-beam deposition of 100 Å of Ti followed by 2000 Å of Au onto Si(100) wafers. Before use, all substrates were cleaned in an ozone cleaner for 10 min (Boekel Industries, Inc., model 135500, Feasterville, PA).

Preparation of Hyperbranched Poly(acrylic acid) (PAA) Films. As described previously,[3,6] hyperbranched PAA films on Au-coated Si wafers are prepared by first grafting α,ω-amino-terminated poly(*tert*-butyl acrylate) (PTBA) onto an ethyl chloroformate-activated self-assembled monolayer (SAM) of mercaptoundecanoic acid (MUA). The PTBA polymer had a M_n of 18 000 and dispersity of 2.0 (measured by GPC).[5] Hydrolysis of the *tert*-butyl ester groups followed by two additional stages of activation, grafting, and hydrolysis yields grafted three-layer hyperbranched PAA films (3-PAA) that are 230 ± 30 Å thick. Amidation of 3-PAA films with ethylenediamine and pentadecafluorooctylamine, after chloroformate activation, was performed following our previously described procedure.[4,5]

Preparation of 3-PAA/β-CD Films. β-Cyclodextrin (β-CD) was covalently linked to 3-PAA films by first activating the acid groups with ethyl chloroformate and then immersing the 3-PAA films for 18 h in 10 mL of DMF containing 200 mg of β-cyclodextrin, 50 mg of DMAP, and 0.15 mL of NEt_3. After derivatization the 3-PAA/β-CD films were sonicated in H_2O and rinsed with H_2O and EtOH to remove physisorbed β-CD.

Preparation of (3-PAA/β-CD)/PL, (3-PAA/β-CD)/G4, and (3-PAA/β-CD/F)/G4 Films. Poly-D-lysine-capped films ((3-PAA/β-CD)/PL) were prepared starting from a 3-PAA/β-CD film via a *N*-hydroxysuccinimide (NHS) ester.[23] The NHS ester was formed by exposing the 3-PAA/β-CD films to an aqueous solution of 100 mg of NHS and 200 mg of EDC for 0.5 h at 0 °C followed by 0.5 h at room temperature. The NHS ester-modified polymer film was rinsed with H_2O and then allowed to react for 18 h in a 10 mL aqueous solution containing 55 mg of PL hydrobromide. The solution also contained a TEA buffer (0.1 M, pH 8) and 150 mg of NaCl to minimize electrostatic repulsions between NH_3^+ groups on the PL. After reaction, the (3-PAA/β-CD)/PL films were rinsed with H_2O and placed in a pH 12 NaOH solution for 15 min to remove NHS byproducts.

G4 PAMAM dendrimer-capped films ((3-PAA/β-CD)/G4) were prepared by first activating 3-PAA/β-CD films with ethyl chloroformate and then immersing the modified films for 2 h in 10 mL of DMF containing 0.15 mL of NEt_3 and 10 mg of dry G4 PAMAM dendrimer (isolated by removal of methanol from 0.1 mL of a 10% solution in methanol). (3-PAA/β-CD/F)/G4 films

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were prepared by first activating 3-PAA/β-CD films with ethylchloroformate and then immersing the modified films for 0.5 h in 10 mL of DMF containing 0.4 mL of pentadecafluorooctylamine and 0.15 mL of NEt_3. After perfluorination, the 3-PAA/β-CD/F films were again activated with ethyl chloroformate and immersed for 2 h in 10 mL of DMF containing 0.15 mL of NEt_3 and 10 mg of dry G4 PAMAM dendrimer. 3-PAA/G4 and 3-PAA/PL films were prepared following the same amidation reaction described above. After preparation, all covalently modified 3-PAA films were dipped in a pH $\sim$ 2 ethanol solution for 10 min to protonate unfunctionalized acid groups, thereby eliminating salts from the films. The films were then rinsed with ethanol and dried under flowing N_2.

Fourier Transform Infrared−External Reflectance Spectroscopy (FTIR-ERS) and X-ray Photoelectron Spectroscopy (XPS) Measurements. FTIR-ERS measurements were made using a Bio-Rad FTS-40 spectrometer (Cambridge, MA) equipped with a Harrick Scientific Seagull reflection accessory (Ossining, NY) and a liquid-N_2-cooled MCT detector. Spectra were obtained using *p*-polarized light at an 85° angle of incidence with respect to the substrate normal. Spectra were measured at 4 cm^{-1} resolution using between 100 and 256 scans.[24] XPS spectra were acquired using a Perkin-Elmer (PHI) Model 5500 spectrometer (Norwalk, CT). XPS data acquisition employed a pass energy of 187.85 eV, a step increment of 0.125 eV, and a Mg anode power of 400 W. The F composition ratios were calculated using Perkin-Elmer XPS analysis software.

Ellipsometry. Ellipsometric measurements were performed using a Gaertner L2W26D ellipsometer (Chicago, IL) employing a 488.0 nm Ar^+ laser and a 70.00 $\pm$ 0.02° angle of incidence relative to the substrate normal. Film thicknesses and refractive indices (n_f) were calculated assuming a standard homogeneous film model using Gaertner software. To calculate the thickness of dry PAA films, a refractive index of 1.54 was used.[6] In-situ ellipsometry was performed using a trapezoidal-prism-shaped cell having glass windows oriented perpendicular to the incident laser beam.[5] The refractive index of the 0.1 M buffer solutions was calculated to be 1.338, and the refractive index of pure water at 488.0 nm is 1.337.[25,26] The error in the in-situ measurements of the film thickness is $\pm$30 Å.[5] The magnitude of this error is a consequence of the similar refractive indices of the buffer solutions and the swollen films. For all ellipsometric measurements, it was assumed that the refractive index was constant throughout the film.

Electrochemistry. Cyclic voltammograms were obtained using a BAS100B electrochemical analyzer (Bioanalytical Systems (BAS), West Lafayette, IN). Measurements were made versus a Ag/AgCl (3M NaCl) reference electrode (BAS) and a Pt gauze counter electrode in a 0.1 M NaCl electrolyte solution. The electrolyte solutions were buffered at pH 2.7, pH 6.7, and pH 11.0. The polymer-modified Au substrates used as working electrodes were contained within a Teflon/O-ring holder that exposed 0.09 cm^2 of the surface. The solutions were purged with N_2 before each experiment to remove O_2.

Results and Discussion

Part a of Figure 1 shows an FTIR-ERS spectrum of an unmodified 3-PAA film confined to a Au substrate. The dominant feature is an acid carbonyl band at 1740 cm^{-1}.[6] After derivatization with β-CD (part b of Figure 1), three new bands appear at 1160, 1085, and 1045 cm^{-1}, which arise from C−O bonds within β-CD.[27] Additionally, the band originally present at 1740 cm^{-1} shifts to 1735 cm^{-1} reflecting the presence of two overlapping carbonyl bands from unreacted acid groups and the new ester linkages between the PAA film and β-CD. To confirm the presence

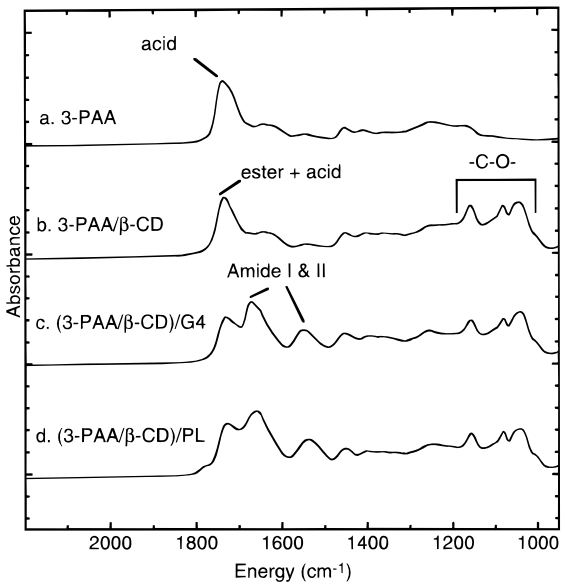

Figure 1. FTIR-ERS spectra of a (a) 3-PAA film and a (b) 3-PAA/β-cyclodextrin film modified with (c) G4 dendrimer and (d) poly-D-lysine.

of the esters, we soaked the 3-PAA/β-CD films in a pH 11.0 buffer solution for 10 min to deprotonate unesterified acid groups. This results in replacement of the original acid carbonyl band with asymmetric and symmetric carboxylate bands located at 1600 and 1415 cm^{-1}, respectfully. However, a strong ester band at 1730 cm^{-1} remains.

Amine-terminated, fourth-generation (G4) poly(amidoamine) (PAMAM) Starburst dendrimers are linked to the top of the 3-PAA/β-CD films by amidation. After this reaction, two new peaks corresponding to amide I and II modes at 1660 and 1550 cm^{-1} are observed (part c of Figure 1). These bands arise both from the amide linkages between 3-PAA and G4 and from the 124 amide groups present within each dendrimer. Poly-D-lysine can be attached to the 3-PAA/β-CD film in a manner similar to that used for linking G4. Amide I and II modes at 1665 and 1548 cm^{-1} are also observed after this reaction (part d of Figure 1). As for G4, these bands arise from the amide linkages between the film and poly-D-lysine as well as from the amide groups in the backbone of poly-D-lysine.

To confirm that the polyamines lie atop the 3-PAA/β-CD composite films, rather than fully permeating it to yield a homogeneous structure, we modified a 3-PAA/β-CD film with pentadecafluorooctylamine before reaction with the polyamines and then examined the film by XPS. Fluorine is a good XPS tag, and on the basis of previous work, we know that the fluorinated amine fully penetrates into the PAA film.[4] By measuring the F 1s atom % before and after derivatization with the polyamine, it is possible to estimate the extent to which the polyamine layer is spatially segregated from the rest of the film.

Modification of a 510-Å-thick 3-PAA/β-CD film with pentadecafluorooctylamine results in a 560-Å-thick 3-PAA/β-CD/F film. XPS measurements indicate that the modified 3-PAA/β-CD/F film contains $\sim$10 atom % F.[4] Subsequent derivatization with G4 dendrimer increases the film thickness to 710 Å. Grafting the thin G4 filter layer (150 Å) onto the 3-PAA/β-CD/F film results in the complete attenuation of the F 1s XPS signal, indicating that most of the G4 lies atop the modified 3-PAA film.

To further confirm the layered structure shown in Chart 1, we prepared a 3-PAA film cross-linked with ethylenediamine prior to grafting on the polyamine layer. Cross-

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Table 1. Thicknesses of 3-PAA and Covalently Derivatized 3-PAA Films

	thickness (Å)		
film	dry	wet (pH 2.7)[a]	wet (pH 11.0)[a]
3-PAA	230	730	1260
3-PAA/β-CD	500	790	1140
(3-PAA/β-CD)/G4	650	1050	1180
(3-PAA/β-CD)/PL	610	870	890
3-PAA/G4	410	760	990
3-PAA/PL	610	630	730

[a] Wet film thicknesses were obtained in situ from buffered, solvent-swollen films (see ref 5).

linking limits solvent-induced swelling[5] and thus minimizes access of G4 to the film interior. Derivatization of a 3-PAA film (220 Å) with ethylenediamine (ED) results in a 315-Å-thick 3-PAA/ED film. Grafting G4 dendrimer onto this composite results in a thickness increase of 80 Å. Recall that grafting of G4 to a 3-PAA/β-CD film results in a thickness increase of 150 Å. Taken together, these control experiments strongly suggest that most of the polyamine lies atop the 3-PAA/β-CD film.

To better understand why polyamines tend to bind on top of modified PAA films rather than diffusing throughout, we examined 3-PAA/polyamine and (3-PAA/β-CD)/polyamine salt films. We have previously shown that G4 and PL readily ion exchange into 3-PAA films and are held there by multiple electrostatic interactions.[5] For example, soaking a 230-Å-thick 3-PAA film in a pH 7 buffered solution of G4 or PL increases the film thickness by factors of 3.0 and 2.7 for 3-PAA/G4 and 3-PAA/PL salt films, respectively.[5,28] In contrast to this result, soaking a 500-Å-thick 3-PAA/β-CD film in a pH 7 buffered solution of G4 or PL increases the film thickness by only a factor of 1.5. FTIR-ERS confirms that this swelling is due to inclusion of G4 and PL. Moreover, semiquantitative measurements of the FTIR-ERS amide I and II band intensities for the 3-PAA and 3-PAA/β-CD salt films indicate there is approximately twice as much G4 and PL in the 3-PAA films relative to the 3-PAA/β-CD films. Thus, derivatization of the 3-PAA films with β-CD limits the accessibility of the large polyamines into the 3-PAA films. This effect is amplified in the covalently modified films because polyamine mobility is further attenuated by irreversible covalent binding of the very large polyamines to the exterior of the PAA film, which blocks further penetration of additional polyamines into the film.

Table 1 compares the measured ellipsometric thicknesses of 3-PAA, 3-PAA/β-CD, (3-PAA/β-CD)/G4, (3-PAA/β-CD)/PL, 3-PAA/G4, and 3-PAA/PL films in air (dry) and in buffered solutions (wet).[5] The 3-PAA/G4 and 3-PAA/PL films were included as control experiments. A typical 3-PAA film has a dry thickness of 230 Å. Derivatization with β-CD results in a film thickness increase of 270 Å. Further covalent derivatization of the 3-PAA/β-CD film with G4 dendrimer or poly-D-lysine results in additional thickness increases of 150 and 110 Å, respectfully. 3-PAA films modified with G4 and PL yield 3-PAA/G4 and 3-PAA/PL films that are 410 and 610 Å thick, respectfully. These control experiments indicate that the large, spherical G4 tends to react more at the 3-PAA/solution interface with both derivatized and underivatized 3-PAA films while the more linear PL tends to reptate into the unmodified 3-PAA films.

(28) 3-PAA films expand significantly upon exposure to base (typically 140%). This is a consequence of electrostatic repulsion of the many carboxylate groups within the film (see ref 5). The relative film expansion factors noted here are referenced to a fully protonated 3-PAA film.

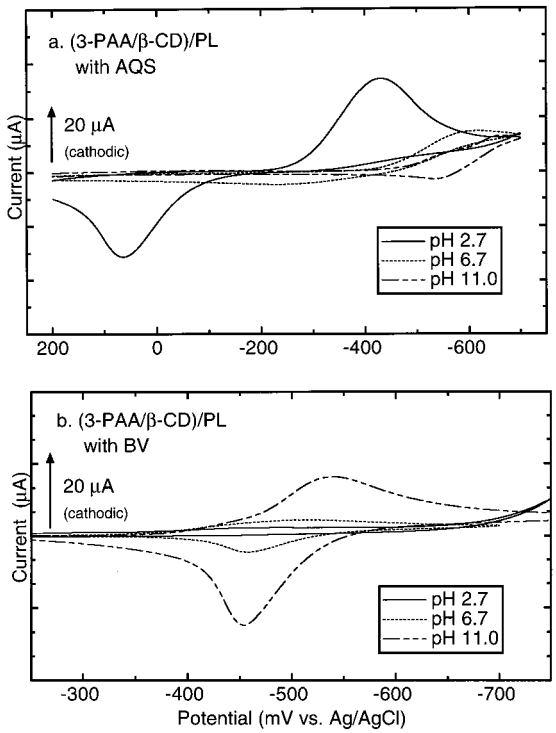

Figure 2. Cyclic voltammetry of 1 mM (a) anthraquinone-2-sulfonate (AQS) and (b) benzyl viologen (BV) in a 0.1 M NaCl electrolyte solution at a (3-PAA/β-CD)/PL-modified Au electrode at pH 2.7, 6.7, and 11.0: electrode area, 0.09 cm^2; scan rate, 50 mV/s.

Due to solvation, a 230-Å-thick 3-PAA film (dry) swells by 500 Å upon immersion for 5 min in a pH 2.7 buffer. When the pH increases from 2.7 to 11.0, the film undergoes an additional thickness increase of 530 Å, resulting from deprotonation of the acid groups.[5] The 3-PAA/β-CD film swells to 790 Å upon immersion in pH 2.7 buffer and to 1140 Å at pH 11.0. The (3-PAA/β-CD)/G4 and (3-PAA/β-CD)/PL films swell to 1050 and 870 Å at pH 2.7 and to 1180 and 890 Å at pH 11.0, respectively. We speculate that the limited pH-dependent swelling of the polyamine-capped films, relative to 3-PAA and 3-PAA/β-CD films, is a consequence of polyamine-induced cross-linking of the upper region of the 3-PAA films similar to the way ED cross-links PAA films and reduces swelling.[5] The 3-PAA/G4 and 3-PAA/PL films show pH-dependent swelling behavior similar to that of the (3-PAA/β-CD)/G4 and (3-PAA/β-CD)/PL films. The 3-PAA/PL film exhibits the least amount of film swelling of all the modified 3-PAA films, reflecting its high degree of cross-linking.

Figure 2 shows cyclic voltammetric data obtained from the (3-PAA/β-CD)/PL-coated Au film at pH 2.7, 6.7, and 11.0. As signaled by the high peak currents (part a of Figure 2), the negatively charged anthraquinone-2-sulfonic acid (AQS) probe molecule (Scheme 1) easily passes through the film at pH 2.7, because the PL filter layer is positively charged under these conditions (p$K_a \sim 10.5$).[29] At intermediate pH (6.7) the PAA film has a net negative charge (p$K_a \sim 4.3$),[5] which hinders penetration of the negatively charged AQS probe, thus limiting electrochemical reduction at the electrode surface. At pH 11.0, the PAA film is fully deprotonated and access of the probe into the film is further attenuated (Chart 1).

The opposite pH-dependent redox-probe penetration behavior is observed for the positively charged benzyl

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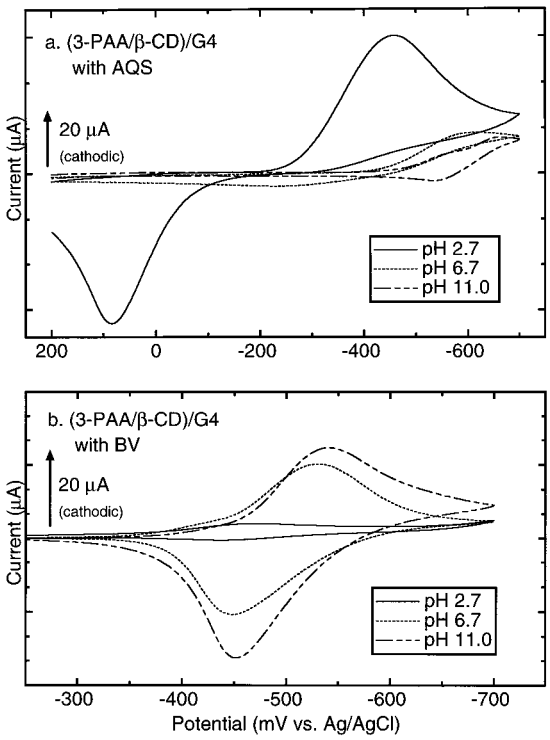
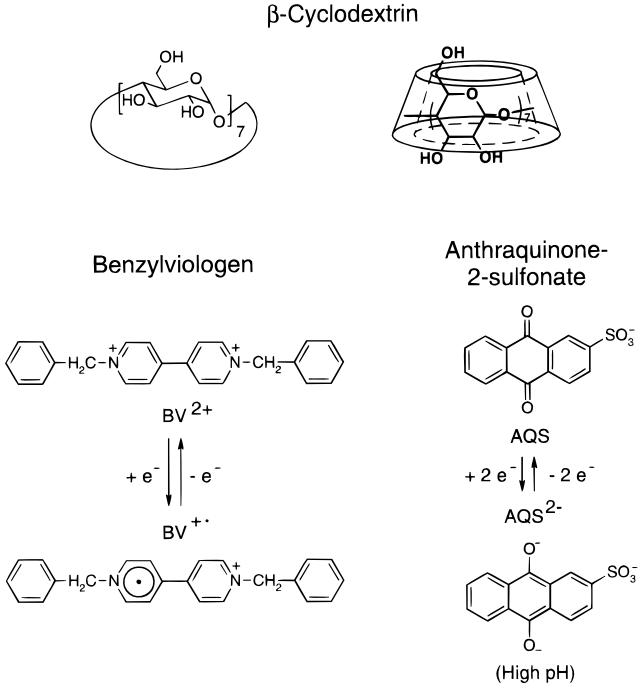


Figure 3. Cyclic voltammetry of 1 mM (a) anthraquinone-2-sulfonate (AQS) and (b) benzyl viologen (BV) in a 0.1 M NaCl electrolyte solution at a (3-PAA/β-CD)/G4-modified Au electrode at pH 2.7, 6.7, and 11.0: electrode area, 0.09 cm^2; scan rate, 50 mV/s.

Scheme 1



viologen (BV) probe molecule (part b of Figure 2). At low and intermediate pH values, the PL filter layer has a net positive charge and the BV probe molecule is blocked from the electrode surface. However, at pH 11.0, protonation of the PL filter layer is greatly reduced and BV penetrates the film.

Figure 3 shows pH-dependent cyclic voltammetric data obtained for a (3-PAA/β-CD)/G4-coated Au film. In the presence of the AQS probe, it behaves very similarly to the (3-PAA/β-CD)/PL film (part a of Figure 3). At low pH the negatively charged AQS probe molecule easily passes through the film, at intermediate pH the PAA film hinders penetration, and at high pH access into the film is strongly attenuated. At low pH the terminal amine groups (p$K_a \sim$ 9.5)[30] and the interior tertiary amine groups (p$K_a \sim 5.5$)[30] of the G4 dendrimers are protonated, so that the filter layer has a net positive charge and the BV probe molecule is blocked from the electrode surface (part b of Figure 3). However, at intermediate pH values the G4 film does not block as efficiently as the PL layer does. At pH 11.0, the G4 filter layer is less protonated and no longer presents a significant electrostatic barrier to BV penetration. Cyclic voltammetry of BV and AQS at the 3-PAA/G4 and 3-PAA/PL films shows pH-dependent blocking behavior similar to that just described for the (3-PAA/β-CD)/G4 and (3-PAA/β-CD)/PL films, respectively, but there is one important difference: the voltammetric current is much smaller than that for the CD-free films. The increase in permeability of the (PAA/β-CD)/G4 and (3-PAA/β-CD)/PL films is likely induced by the presence of the CDs.

Both the BV and AQS redox probe molecules are known to bind with β-CD in solution.[31−33] The association constant (K_{assoc}) of the BV^{2+}/β-CD complex was determined to be 1.4×10^4 L/mol by Willner et al. using fluorescence methods.[31] In a related paper Lee et al. investigated the electrochemical behavior of BV/β-CD inclusion complexes and observed a positive shift in the potential corresponding to the peak cathodic current (E_{pc}) of BV^{2+}, reflecting stronger β-CD binding of BV$^{\bullet+}$ relative to BV^{2+}.[32] In a NMR study Djedaïni and Perly reported a K_{assoc} value of 600 L/mol for the AQS/β-CD complex.[33] In a similar system, Dang et al. investigated the electrochemistry and binding of anthraquinone/β-CD complexes using Osteryoung square wave voltammetry (OSWV). The authors observed a negative shift in the potential corresponding to the peak cathodic current (E_{pc}), reflecting preferential β-CD binding of anthraquinone relative to the reduced form.[34]

We investigated the inclusion of AQS and BV guests by the β-CD hosts of the composite, hyperbranched films. Electrochemical characterization of AQS/β-CD and BV/β-CD interactions is difficult given the pH-sensitive nature of the (3-PAA/β-CD)/polyamine films and the effect of the 3-PAA films themselves on the reduction potentials of the two probe molecules. However, our results are in general agreement with previous findings.[32,34] For example, at pH 6.7 the presence of the 3-PAA film results in a 50 mV positive shift in E_{pc} for BV and a 43 mV negative shift in E_{pc} for AQS relative to the naked gold electrode. After grafting β-CD into the 3-PAA film, we observe an additional positive shift for the BV E_{pc} relative to that for the 3-PAA-only film. The (3-PAA/β-CD)/G4 and (3-PAA/β-CD)/PL systems show the same general trend. This arises from the stronger β-CD binding of BV$^{\bullet+}$ compared to BV^{2+} making reduction more energetically favorable. We observe the reverse behavior for AQS. There is a negative shift in E_{pc} for the 3-PAA/β-CD, (3-PAA/β-CD)/G4, and (3-PAA/β-CD)/PL films relative to the 3-PAA-only film. This arises from the stronger β-CD binding of AQS compared to the reduced form. For example, at pH 6.7 the 3-PAA/β-CD film results in a 20 mV positive shift in E_{pc} for BV and a 54 mV negative shift in E_{pc} for AQS

(30) Technical data supplied by Dendritech, Inc. (Midland, MI).
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relative to the 3-PAA-only system. These results suggest that the β-CDs in the 3-PAA/β-CD films act as receptor sites.

Summary and Conclusions

In summary, we have prepared and characterized electrode coatings comprised of hyperbranched poly(acrylic acid) films incorporating β-cyclodextrin receptors and amine-terminated G4 and PL molecular filter layers. FTIR-ERS, XPS, and ellipsometry indicate that the grafted polyamine filter layers reside at or near the surface of the 3-PAA/β-CD films.

Cyclic voltammetry of benzyl viologen and anthraquinone-2-sulfonate at different pH values indicates that grafting of the thin polyamine filter layers (110−150 Å) on 3-PAA/β-CD films (500 Å) greatly enhances the selectivity of the composite film toward these ionic redox-active probe molecules. This pH-dependent selectivity arises from the acid/base chemistry of the composite film.

To the best of our knowledge this is the first example of a chemical sensor, albeit quite primitive, having an integral, ultrathin polymeric filter covalently linked to the receptor surface. We feel this is a very general approach for enhancing discrimination between analytes. In principle, because the polymeric filter layer is so thin, the rate of permeation of analytes to the underlying receptors should not be unduly compromised. Finally we envision that the general concept described in this paper will also be appropriate for preparing biocompatible[35] and vapor-phase sensors.

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