

Formulation, Characterization, and Sensing Applications of Transparent Poly(vinyl alcohol)–Polyelectrolyte Blends

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Several new optically clear polymer blends have been formulated for selectively incorporating solution-phase anions and cations. In all of the blends poly(vinyl alcohol) was the host matrix and it was cross-linked with glutaraldehyde to entrap polyelectrolytes including poly(acrylic acid), Nafion, poly(diallyldimethylammonium chloride), poly(vinylbenzyltrimethylammonium chloride), and poly(styrenesulfonic acid). $[\text{Ru}(\text{BiPy})_3]^{2+}$ and $\text{Fe}(\text{CN})_6^{3-}$ were used as prototypical analytes to study the ion-exchange properties of the new blends. The thicknesses of spin-coated thin films of the blends were variable over a wide range (0.70 μm being typical), as determined by an optical interference method. Thin film coatings of three of the blends were optimized for single-step covalent coating on activated oxide surfaces. Two silane coupling agents, 3-glycidoxypropyltrimethoxysilane and 3-aminopropyltriethoxysilane, were used to covalently attach these three blends to glass and ITO-coated glass surfaces. The potential use of these materials for chemical sensing has been demonstrated by applying them to multiple internal reflection and spectroelectrochemical devices as thin films.

Introduction

Optically clear polymers have played an important role in chemical sensing as surface-modifying materials.^{1,2} A variety of formulations have been used including pure polymers,^{3–10} dye-doped polymers,^{11–16} and polymer blends.^{17,18} For example, Grate et al.⁷ reported the synthesis of hybrid organic/inorganic copolymers for acoustic wave and optical sensors. The copolymers were prepared by incorporating fluoroalkyl-substituted bisphe-

nol groups linked with oligosiloxane spacers. It was demonstrated that these materials had a suitable viscosity and refractive index to be used as claddings on silica optical fibers. Song et al.¹⁴ described a method to entrap the fluorescent dye 5-(and 6)-carboxynaphthofluorescein (CNF) in a polyacrylamide gel matrix by photopolymerization at the silanized end of an optical fiber to make a fiber optic pH sensors for physiological measurements. In work closely related to the chemistry discussed in this paper, Somasundrum and Bannister¹⁷ described depositing mixtures of Nafion and poly(vinyl alcohol) (PVA) on electrodes followed by in situ cross-linking of the blend with glutaraldehyde to form an ion-exchange/hydrogel composite film. These authors describe in detail the electrochemistry of selected analytes in these membranes but did not report on any of the optical properties or on any optimization of the Nafion–PVA mixtures.

There are three common ways to modify sensor surfaces with polymers:¹⁹ (1) strong chemisorption, (2) covalent attachment, and (3) polymer layering. Although chemisorption certainly involves bondlike interactions, in only a few instances are such interactions sufficiently stable for usage in sensor applications.²⁰ Covalent attachment is an attractive way of surface modification because of the strong link between the modifier and the sensor surface. However, not all appropriate polymers have a chemical group which can be used to covalently bond with the sensor surface. A

(1) Harsanyi, G. *Polymer Films in Sensor Applications*; Technomic Publishing Co., Inc.: Lancaster, PA, 1995.

(2) Wolfbeis, O. S. *Fiber Optic Chemical Sensors and Biosensors*; CRC Press: Boca Raton, FL, 1991; Vols. I & II.

(3) Burck, J.; Conzen, J. P.; Beckhaus, B.; Ache, H. J. *Sensors Actuators* **1994**, B 18–19, 21.

(4) Degrandpre, M. D.; Burgess, L. W. *Appl. Spectrosc.* **1990**, 44, 273.

(5) Klunder, G. L.; Russo, R. E. *Appl. Spectrosc.* **1995**, 49, 379.

(6) Blair, D. S.; Burgess, L. W.; Brodsky, A. M. *Anal. Chem.* **1997**, 69, 2238.

(7) Grate, J. W.; Kaganove, S. N.; Patrash, S. J.; Craig, R.; Bliss, M. *Chem. Mater.* **1997**, 9, 1201.

(8) Zhujun, Z.; Zhang, Y.; Russel, R.; Shkhsher, Z. M.; Grant, C. L.; Seitz, W. R.; Sundberg, D. C. *Anal. Chem.* **1989**, 61, 202.

(9) Mohr, G. J.; Wolfbeis, O. S. *Anal. Chim. Acta* **1994**, 292, 41.

(10) Aquino-Binag, C. N.; Kumar, N.; Lamb, R. N.; Pigram, P. J. *Chem. Mater.* **1996**, 8, 2579.

(11) Madden, J. E.; Cardwell, T. J.; Catrall, R. W.; Deady, L. W. *Anal. Chim. Acta* **1996**, 319, 129.

(12) Tan, W.; Shi, Z.; Kopelman, R. *Sensors Actuators B*, **1995**, 28, 157.

(13) Ambrose, T. M.; Meyerhoff, M. E. *Anal. Chem.* **1997**, 69, 4092.

(14) Song, A.; Parus, S.; Kopelman, R. *Anal. Chem.* **1997**, 69, 863.

(15) Pohlert, G.; Scaiano, J. C.; Sinta, R. *Chem. Mater.* **1997**, 9, 3222.

(16) Pohlert, G.; Virdee, S.; J. C. Scaiano, J. C.; Sinta, R. *Chem. Mater.* **1996**, 8, 2654.

(17) Somasundrum, M.; Bannister, J. *Electroanalysis* **1997**, 9, 56.

(18) Gao, L.; Seliskar, C. J.; Milstein, L. *Appl. Spectrosc.* **1997**, 51, 1745.

(19) Bard, A. J. *J. Chem. Ed.* **1983**, 60, 302.

(20) Murry, R. W. Chemically Modified Electrodes. In *Electroanalytical Chemistry*; Bard, A. J., Ed., Marcel Dekker: New York, 1984; pp 191–368.

commonly used method for "covalent" coating of sensor surfaces functionalizes the surface with a silane coupling agent which provides sites for the covalent attachment of the polymer. Silane coupling agents are bifunctional silicon-containing organic molecules that are able to form covalent bonds with glass or other oxide surfaces bearing free hydroxyl groups,^{21–31} and this includes indium tin oxide surfaces.^{32–36}

Polymer layering may be the easiest way to modify sensor surfaces, but the polyelectrolytes suitable for this kind of modification are limited, because those commonly available are either too soluble or undergo rapid ion exchange, resulting in a rapid loss of species absorbed within such coatings.³⁷ In addition, poor adhesion of the polymer coating to the sensor surface is another problem for most of the available polyelectrolytes. The commonly used polyelectrolytes for layering include Nafion³⁸ and poly(4-vinylpyridine) (PVP).³⁹

In an interesting alternative approach, Bergbreiter and co-workers^{40,41} have modified the surfaces of more reactive polymer films and were able to introduce functional groups onto these surfaces. It therefore appears possible to use their technique to directly modify certain polymer-coated sensor surfaces and to achieve sensor surface characteristics which would be of direct use. In the first part of this research we demonstrated¹⁸ an evanescent wave sensing application of a polymer blend which consisted of poly(acrylic acid) (PAA) entrapped in cross-linked PVA deposited on the core of a fiber optic. Recently, we very briefly summarized our work on chemically selective optical materials.⁴² In this work, the detailed formulations of cross-linked PVA-based polymer blends containing several polyelectrolytes, i.e., Nafion, poly(diallyldimethyl-

ammonium chloride) (PDMDAAC), poly(vinylbenzyltrimethylammonium chloride) (PVTAC), and poly(styrenesulfonic acid) (PSSA), are described. Compared with the sol-gel matrix which is not compatible with such polyelectrolytes as PAA and NaPSS,⁴³ the PVA matrix offers two advantages: it is compatible with all of the polyelectrolytes we have studied, thus providing more optically clear polymer blends, and the films are crack-free, even as thick films.

Experimental Section

Chemicals and Materials. Nafion perfluorinated ion-exchange material (5 wt % in a mixture of lower aliphatic alcohol and 10% water; hydrogen ion form; equiv wt 1100), PVA (MW 85 000–146 000, 98–99% hydrolyzed), PDMDAAC (20 wt % in water, MW 250 000–350 000), tris(2,2'-bipyridyl)-ruthenium(II) chloride hexahydrate, 3-aminopropyltriethoxysilane (APTS), and 3-glycidioxypropyltrimethoxysilane (GPTS) were purchased from Aldrich. Glutaraldehyde (reagent grade, 50% w/w), hydrochloric acid (ACS Reagent), buffers (pH 4, 7, and 10), sodium hydroxide, and sodium acetate were supplied by Fisher Scientific. PAA (25% solids in water, MW 150 000) and PSSA (30% in water, MW 500 000) were purchased from Polyscience, Inc. PVTAC (30 wt % in water, MW 400 000) was purchased from Scientific Polymer Products. Stock solutions for polymer blending were prepared by either dilution of commercial solutions or by dissolution of solid polymer in deionized water. All chemical reagents were used as received without further purification.

Microscope glass slides were obtained from Fisher Scientific. Indium tin oxide (ITO)-coated glass (11–50 Ω /sq, 150 nm thick ITO layer over tin float or 7059 glass) was purchased from Thin Film Devices and cut into 1 in. \times 3 in. slides.

Formulation of Blends. All blends with polyelectrolytes discussed in this paper are based on additions to a 10% PVA stock solution. A typical preparation of the blended polymer film is as follows: all of the components (PVA, polyelectrolyte, glutaraldehyde, HCl) were put into a beaker and stirred until homogeneous. The mixture was then immediately poured into a cylindrical Teflon form (thick films) or spin-coated onto substrates (thin films). After casting or spinning, the blend was cured in the air at ambient temperature for at least 1 day before use. All cured blends were hydrated by soaking in water or supporting electrolyte solution for at least 1 day before use.

Covalent Attachment of Blends onto Planar Glass and ITO-Glass Substrates. Two methods of functionalization of glass and ITO-glass surfaces were used: epoxysilanization and aminosilanization. Glass or ITO-glass slides were soaked in 2 M NaOH overnight and then rinsed with deionized water. Freshly cleaned slides were then heated in 5% (v/v) APTS or 1% (v/v) GPTS in a buffer solution at 90 $^{\circ}$ C for 5 h. Silane coupling reagent solutions were made in 0.1 M sodium acetate buffer whose pH was adjusted to 5.5 with 1 M HCl. The functionalized slides were rinsed with deionized water to get rid of unreacted silane coupling reagent. In some cases, both ends of the slides were masked with tape prior to spin-coating, leaving small sections of the surface uncoated for prism coupling. Slides were first spun at 2000 rpm for a few seconds to ensure a clean and dry surface for polymer bonding. Then about 0.30 mL of freshly formulated polymer blend was pipetted onto the surface of the slide, which was then spun at 2000 rpm (except as noted) for 1 min to coat the slide surface. The curing of the coating simultaneously resulted in covalent attachment to the functionalized oxide surface through reaction of the bifunctional cross-linking reagent (glutaraldehyde) with the OH groups of PVA and the exposed groups (OH or NH₂) on the surface.

Film Characterization Measurements. Refractive indices were obtained for both dry and hydrated films using the

(21) Lesho, M. J.; Sheppard, N. F., Jr. *Sensors Actuators* **1996**, *B* **37**, 61–66.

(22) Jiang, J.; Halsall, H. B.; Heineman, W. R. *J. Agric. Food Chem.* **1995**, *43*, 1098.

(23) Yoshioka, M.; Mukai, Y. *J. Chromatogr.* **1991**, *566*, 361.

(24) Wood, L. L.; Cheng, S. S.; Edmiston, P. L.; Saavedra, S. S. *J. Am. Chem. Soc.* **1997**, *119*, 571.

(25) Hale, Z. M.; Payne, F. P.; Marks, R. S.; Lowe, C. R.; Levine, M. M. *Biosensors Bioelectronics* **1996**, *11*, 137.

(26) Lu, B.; Xie, J.; Lu, C.; Wu, C.; Wei, Y. *Anal. Chem.* **1995**, *67*, 83.

(27) Haller, I. *J. Am. Chem. Soc.* **1978**, *100*, 8050.

(28) Baldini, F.; Bracci, S. *Sensor Actuators* **1993**, *B11*, 353.

(29) Emoto, K.; Harris, J. M.; Alstine, J. M. V. *Anal. Chem.* **1996**, *68*, 3751.

(30) Elender, G.; Kuhner, M.; Sackmann, E. *Biosensors Bioelectronics* **1996**, *11*, 565.

(31) Piehler, J.; Brecht, A.; Geckeler, K. E.; Gauglitz, G. *Biosensors Bioelectronics* **1996**, *11*, 579.

(32) Moses, P. R.; Wler, L.; Murray, R. W. *Anal. Chem.* **1975**, *47*, 1882.

(33) Chen, K.; Caldwell, W. B.; Mirkin, C. A. *J. Am. Chem. Soc.* **1993**, *115*, 1193.

(34) Polzius, R.; Schneider, T.; Biert, F. F.; Bilitewski, U. *Biosensors Bioelectronics* **1996**, *11*, 503.

(35) Wilson, R.; Kremeskotter, J.; Schiffrin, D. J.; Wilkinson, J. S. *Biosensors Bioelectronics* **1996**, *11*, 805.

(36) Wilson, R.; Schiffrin, D. J. *Analyst* **1995**, *120*, 175.

(37) Montgomery, D. D.; Shigehara, E. T.; Anson, F. C. *J. Am. Chem. Soc.* **1984**, *106*, 7991.

(38) Rubinstein, I.; Bard, A. J. *J. Am. Chem. Soc.* **1980**, *102*, 6641.

(39) Oyama, N.; Anson, F. C. *J. Electrochem. Soc.* **1980**, *127*, 247.

(40) Xu, G. F.; Bergbreiter, D. E.; Letton, A. *Chem. Mater.* **1992**, *4*, 1240.

(41) Bergbreiter, D. E.; Kabza, K.; Small, B. L. *Chem. Mater.* **1993**, *5*, 257.

(42) Shi, Y.; Slaterbeck, A. F.; Aryal, S.; Seliskar, C. J.; Heineman, W. R.; Ridgway, T. R.; Nevin, J. H. *Proc. SPIE* **1998**, *3258*, 56. Gao, L.; Shi, Y.; Slaterbeck, A. F.; Seliskar, C. J.; Heineman, W. R. *Proc. SPIE* **1998**, *3258*, 66.

(43) Shi, Y.; Seliskar, C. J. *Chem. Mater.* **1997**, *9*, 821.

Table 1. Formulations for Blends

base film mixture	remaining additives	monomer ratio ^a
	Thick Films	
3.00 mL of 10% PVA,	1.20 mL of 25% PAA (for PVA–PAA)	0.63
0.30 mL of 5% glutaraldehyde,	0.80 mL of 5% Nafion (for PVA–Nafion)	0.0047
0.30 mL of 0.5 M HCl, and	1.00 mL of 30% PSSA (for PVA–PSSA)	0.26
1.2 mL of H ₂ O	0.50 mL of 15% PVTAC (for PVA–PVTAC)	0.051
	0.20 mL of 20% PDMDAAC (for PVA–PDMDAAC)	0.037
	Thin Films	
2.50 mL of 10% PVA and	0.50 mL of 25% PAA, 0.50 mL of 5% glutaraldehyde,	0.31
0.20 mL of 0.50 M HCl	and 1.0 mL of H ₂ O (for PVA–PAA)	
	1.0 mL of 5% Nafion, 0.50 mL of 5% glutaraldehyde,	0.0070
	and 0.50 mL of H ₂ O (for PVA–Nafion)	
	0.50 mL of 15% PVTAC and 1.50 mL of 5% glutaraldehyde	0.061
	(for PVA–PVTAC)	

^a The ratio of polyelectrolyte to PVA.

double-image method of Schulz.⁴⁴ Values reported are averages of three measurements made at different film positions. For thick films, the swelling index was defined as the ratio of the volume of the hydrated film to the volume of the dry film. Film volume was calculated from the diameter and thickness measured with a caliper. For spin-coated thin films that were covalently bonded to a substrate surface, no expansion on hydration of the film in the plane of the glass or ITO–glass was found by optical microscopy. Thus, all of the film swelling on hydration appeared to occur normal to the plane of the coating surface. In this case the swelling index was calculated as the ratio of the hydrated film thickness to the thickness of the dry film, as measured by an interference fringe method (see below).

UV–visible absorbance spectra were determined with a Hewlett-Packard 8425A or 8453 diode array spectrophotometer. For such measurements the glass substrate or free-standing film was positioned at normal incidence to the light path of the instrument. Thicknesses of films on glass substrates were determined using the optical interference fringe method described by Goodman.⁴⁵

Scanning electron microscopy (SEM) of polymer blend films spin-coated on glass substrates was performed on a Stereoscan 90 microscope (Cambridge Instruments) operated at 25 kV and a 25° degree tilt angle. Both dry and wet specimens were prepared for each polymer blend. The wet specimen was prepared by soaking a dry film in water for 1 day before the measurement. To obtain the information about the microstructure of the inner bulk film and the thickness of the film, a portion of each film specimen was removed with a razor blade, leaving a step for cross-section examination. Film specimens were sputter-coated with ~300 Å of gold prior to examination.

Spectroelectrochemical Measurements. Spectroelectrochemical measurements were performed on the instrument previously described.⁴² Very briefly, light from a source (blue LED, Panasonic) was launched into a 600 μm silica step-index optical fiber (Fiberguide Superguide G, NA = 0.22) which was coupled to the glass or ITO–glass slide with a Schott SF6 coupling prism (Karl Lambrecht, Chicago, IL) using a microscope objective. A high viscosity refractive index standard fluid (Cargille, $n = 1.517$) was used to span the prism/glass gap. Light propagating through the glass slide was decoupled by using another SF6 coupling prism, detected by a phototube, digitized, and stored on a personal computer. Computer data acquisition was done at a rate of one point per second. Data records were manipulated and analyzed using standard personal computer spreadsheet programs. The angle of the light into the prism and the alignment of the cell were adjusted to maximize the attenuated total internal reflection throughput, as determined by measuring the intensity of the decoupled light. All electrochemistry was performed with the sample cell that has been described previously.⁴² Sensor absorbance

values were obtained by recording the light intensity through the prism-coupled slide when exposed to pure deionized water or supporting electrolyte (I_0) and the intensity after being exposed to an analyte solution (I). Absorbance in the multiple reflection arrangement was defined as $A = \log(I_0/I)$.

Results and Discussion

Blend Formulations. The polymer blends, as we prepare them, are all formed from aqueous stock solutions of polyelectrolytes and 10% PVA. The PVA–polyelectrolyte blend is then cross-linked with glutaraldehyde in the presence of HCl to form an optically clear matrix. The cross-linking reaction of glutaraldehyde with PVA entraps the polyelectrolyte in the PVA network. The ratio of PVA to polyelectrolyte can be varied over a considerably wide range while the transparency of the material is maintained. Through use, however, we have fine-tuned these compositions for sensing purposes by selecting PVA–polyelectrolyte ratios and curing conditions that produce thin and thick films of these materials that are robust and have acceptable ion-exchange rates. Several different polyelectrolytes, the structures of which have been given previously,⁴³ have been entrapped in PVA: Nafion, PVTAC, PDMDAAC, PSSA, and PAA. We have developed two specific formulations for use in sensing. One formulation is designed for making free-standing, thick films, the second for thin-film coatings on glass and ITO–glass surfaces with covalent attachment.

A typical preparation for the casting of thick, free-standing films of the blends consisted of mixing PVA, glutaraldehyde, HCl, and the polyelectrolyte in appropriate proportions (see Table 1 and ref 18 for details). The mixture was then quickly poured into a mold and cured at room temperature. Comparison of this formulation with those for thin films (see below) shows that this formulation is leaner in glutaraldehyde. As a result, free-standing films were less highly cross-linked and cured into transparent elastic materials.

To make coatings on planar substrates, the blends need to be covalently bonded to glass or ITO–glass substrates; without such bonding the films immediately detached from the substrates on hydration of the films. As a result, all coatings described in this paper have been covalently attached to glass or ITO substrates. By optimizing the amounts of the components in the blends we have obtained three covalently attached coatings (PVA–Nafion, PVA–PVTAC, and PVA–PAA) that are well-adhered, optically clear, and rapidly ion-exchange-

(44) Schulz, L. G. *J. Chem. Phys.* **1949**, *17*, 1153.

(45) Goodman, A. M. *Appl. Opt.* **1978**, *17*, 2779.

able, as shown in the following sections of this paper. The formulations for these three coatings are given in Table 1. Optimization of the content of glutaraldehyde was crucial for these coatings, because it works both for the formation of the blend network and for the covalent linking of the blend to the substrate. Qualitatively, a higher content of glutaraldehyde produced a lower swelling index and a better linked coating (see below). However, if the glutaraldehyde content was too high, a slower ion-exchange rate resulted, presumably because of a reduction in the network's pore size. The type and the amount of the polyelectrolyte in the blends were also important factors affecting the quality and the ion-exchange capacity of the film coatings. The optical clarity of the blends can also be influenced by the amount of the polyelectrolyte. The lower the content of the polyelectrolyte, the clearer and tougher the blend films were, but this is achieved with a reduction in the ion-exchanging capacity of the material. Thus, the formulations given in Table 1 for thin films on glass or ITO-glass represent compromises between adequate film (covalent) attachment to the substrate and acceptable rate of and capacity for ion-exchange.

The formulations for the coatings of PVA-Nafion, PVA-PAA, and PVA-PVTAC blends were optimized to give acceptable simultaneous linking to functionalized (surface activated) glass or ITO-glass surfaces. However, we have not been able to find suitable formulations for a one-step surface linking and cross-linking of the PVA-PDMDAAC and PVA-PSSA blends. The PVA-PDMDAAC and PVA-PSSA films have comparatively higher swelling indices and in thick film form are more fragile. Increasing the glutaraldehyde contents in these curing blends did not result in simultaneous linking to activated oxide surfaces. Leaching of PSSA from the PVA-PSSA blend was found by UV-visible absorbance spectroscopy of the solutions exposed to the blend for a period of time (24–48 h). No leaching of polyelectrolyte was found for any of the other blends. The reasons for the increased leaching of PSSA from the cross-linked PVA host are not totally clear but may be related to the following factors. First, to make up for the fact that the sulfonate group in PSSA has a low binding constant for the cations of interest to us, we have made the PVA-PSSA blend relatively rich in PSSA. In turn this may have reduced the efficiency of the cross-linking of the host PVA by glutaraldehyde and increased the leaching of PSSA. Second, PSSA is quite hydrophilic as, for example, compared to Nafion, and this might directly result in more leaching of PSSA in comparison with the other polyelectrolytes used in the blends.

A series of thick films was made with the same formulations as those of the thin films for the purpose of measuring the swelling index, refractive index, and spectroscopic properties of these particular formulations. All of these freshly prepared wet films are optically clear, except PVA-PAA, which only became clear after the first drying and rehydration of the cross-linked blend.

Coating of Thin Film Formulation on Planar Oxide Surfaces. The bifunctional reagents GPTS and APTS can be used to modify the surface of glass or ITO-glass by making use of the reaction between the silanol group of the reagent and the OH groups of the clean

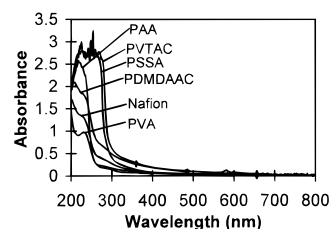


Figure 1. The absorbance spectra of hydrated thick films of five polymer blends and pure cross-linked PVA measured at normal incidence over the range 200–800 nm are shown. The film thickness in each case was about 0.65 mm. The blends are indicated by listing the entrapped polyelectrolyte.

oxide surface. We have modified Jiang's²² method of using an acetate buffer as the medium for surface modification. In turn, APTS and GPTS, possessing an amine and an epoxide functional group, respectively, react with glutaraldehyde in the acid-catalyzed curing polymer blend. In the case of APTS, glutaraldehyde reacts to form a Schiff base linkage; in the case of GPTS, upon acid-catalyzed ring opening of the epoxide, glutaraldehyde forms a hemiacetal or an acetal linkage. HCl is a catalyst for all three of these reactions, and thus, the curing of the polymer blend and its covalent attachment to APTS- or GPTS-activated glass or ITO-glass can be achieved in one step. The coated glass or ITO-glass slides can be stored in air for months without any observable deterioration; the optical and electrochemical performance of rehydrated stored slides is identical to those of newly coated slides.

A greater the degree of surface modification with GPTS or APTS gave better adhesion. But there was a maximum content for APTS or GPTS in the reaction buffer (2% v/v for GPTS and 6% v/v for APTS). Self-gelation begins at higher concentrations than these at this temperature. To avoid self-gelation, we have routinely used 1% v/v GPTS and 5% v/v APTS. The adhesion of the blend film to the substrate is better for the APTS-derived surfaces because of the higher concentration of silane coupler.

Generally speaking, the coatings are very stable in neutral or acid aqueous solutions, usually going for weeks without peeling from the substrate. In strongly basic solutions (for example, pH 10), only PVA-Nafion and PVA-PAA coatings stand up for weeks at a time. It is probable that the silyl ether linkage between the oxide surface of glass or ITO-glass and GPTS or APTS is more easily cleaved by base than by acid. Perhaps this is the reason the covalently bonded coatings resisted much higher concentrations of acid than of base.

Optical Properties of Blends: UV-Vis Transmission and Refractive Index. Typical absorbance spectra of thick hydrated films are shown in Figure 1. As the spectra show, the PAA, Nafion, and PDMDAAC blends can be used directly for spectroscopic measurement down to about 250 nm. Both PVTAC and PSSA blend films have strong absorbances in the near-UV region which stem from the π -conjugated structures of the polyelectrolytes themselves.

We have measured the refractive indices of both dry and wet films and these values are listed in Table 2. Although all of the hydrated forms gave clear second images under Abbe refractometry, dry PVA-Nafion blend did not because of its mottled surface. The

Table 2. Refractive Indices for Blends

material	refractive index	
	dry	hydrated
PVA	1.512	1.442
PVA–PAA	1.515	1.440
PVA–Nafion	<i>a</i>	1.445
PVA–PVTAC	1.507	1.447
mean value	1.511	1.443

^a Refractive index of dry PVA–Nafion immeasured by Abbe refractometry.

refractive indices of the dry films are about 1.51 (except possibly for the PVA–Nafion blend), which may be attributed to the dominance of the host PVA. The refractive index of all the wet films is about 1.44, which is essentially that of wetted cross-linked PVA. From the above results we conclude that all of the wetted blends are suitable as optical claddings for both crown glass waveguide (base glass RI = 1.51) and silica-core fiber optic (core RI = 1.46) sensors.

Thin Film Thickness and Swelling Index. To make films of differing thickness, the spin speed of the spin-coating was varied for a given polymer formulation. The thickness can also be varied by changing the total concentration of the coating solution. For example, by diluting the coating mixture with water, the coating thickness was made as thin as 0.25 μm . Examination of thin films over a wide area of coated slides typically gave similar fringe patterns, suggesting that the coating was quite uniform in thickness. The edges of coated slides typically show thicker regions, as expected for the spin-coating method.

For the calculation of the film thickness by the interference fringe method, the effect of any small difference in the refractive index value was not very significant. For example, the spectrum of the dry PVA–Nafion coating spun at 1500 rpm shows three fringes within the range 325–600 nm. Since no refractive index is available for this particular material in the dry state (vide supra), we were forced to approximate the index. The thickness of this film calculated from the fringes was 0.70 μm when calculated with the highest refractive index value measured for any film (1.52, PVA–PAA). The thickness was calculated to be 0.71 μm when the lowest refractive index value measured for any film (1.51, PVA–PVTAC) was used. As a result, we have chosen the value based on an assumed index of the dry film of 1.51; we then calculated the thickness and swelling indices of a series of PVA–Nafion films prepared by spin-coating. Table 3 shows the results for PVA–Nafion thin films bonded to glass and prepared at different spin speeds. The wet thin films are thicker than the corresponding dry films because of swelling on hydration of the film. Even after days of hydration in water, no lateral expansion of the coating from the edges of the slide was found. In turn, this suggested that the width and length of the film was held approximately fixed by the covalent attachment to the surface. On the other hand, thickness measurements clearly showed that the film expanded normal to the surface. Assuming no expansion of the film in a plane parallel to the surface, the swelling index of the film was calculated as the ratio of the film thicknesses, and these results are also shown in Table 3. The mean value of the swelling index was found to be 1.18.

Table 3. Thicknesses and Swelling Indices for Blend Films

Thin Films Spun at 2000 rpm			
polymer blend	film thickness, μm		swelling index
	dry	hydrated	
PVA	0.39	0.53	1.36
PVA–PAA	0.68	0.72	1.06
PVA–Nafion	0.53	0.68	1.28
PVA–PVTAC	0.62	0.78	1.26
		mean value:	1.20 ^b
PVA–Nafion			
spin-speed (rpm)	film thickness, μm		swelling index
	dry	hydrated	
800	1.22	1.43	1.17
1000	0.99	1.19	1.20
1300	0.85	0.89	1.04
1500	0.59	0.74	1.25
1800	0.57	0.68	1.19
2000	0.53	0.68	1.28
3000	0.53	0.61	1.15
		mean value:	1.18

^a Swelling index calculated as ratio of thicknesses of swollen film and dry film. ^b Mean value does not include pure PVA value

Table 4. Swelling Indices of Thin Film Formulation in Free-Standing Thick Films

material	swelling index ^a		
	pure H ₂ O	1 M KNO ₃	3 M KNO ₃
PVA	2.14	1.94	1.56
PVA–PAA	1.71	1.83	1.63
PVA–Nafion	1.76	1.89	1.51
PVA–PVTAC	1.58	1.40	1.22

^a Swelling index calculated as ratio of volumes of swollen film and dry film.

In an effort to evaluate the effect of covalent attachment on the thin film swelling index, we made thick films with the thin film formulation and measured swelling indices in water and salt solutions (Table 4). Overall, the results show that the free-standing blend films have swelling indices which are about 40% higher in pure water than the corresponding covalently anchored films (compare Tables 3 and 4). Thus, it is clear that covalent attachment of the blend to an oxide surface reduces the ability of the blend to expand on hydration. The free-standing PVA film has an index which is about 60% larger, suggesting that the added polyelectrolyte tends to reduce the ability of the network to swell on hydration. The effect of increasing salt concentration on the swelling index is more complicated. For the cation exchangers (PVA–PAA and PVA–Nafion), addition of salt first expands the network and then at higher concentration shrinks the network. For the anion exchanger (PVA–PVTAC), the addition of salt reduces the swelling index, and this behavior is also found for the pure PVA network. The overall trend for both cation and anion exchangers to shrink with increasing salt concentration may be attributed to a decrease in blend hydration or the “salting out” of water. However, the reasons for the more complicated behavior of the cation exchangers at low salt concentrations are not clear and remain to be determined.

Thin Film Surface Morphology. Scanning electron microscopy (SEM) was used to examine the morphology of the blends covalently bonded to the surface

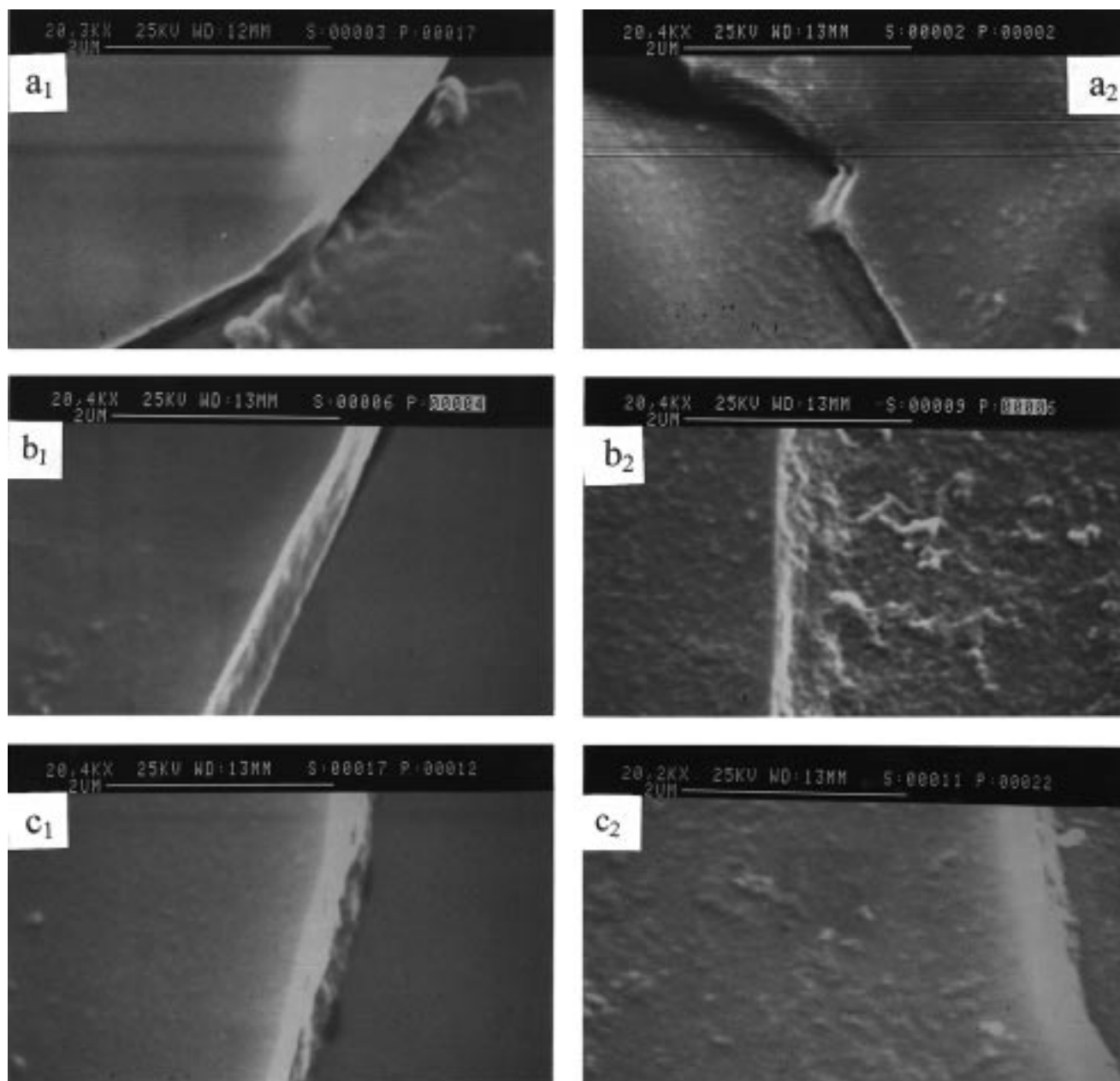


Figure 2. SEM photographs of (a) cross-linked pure PVA, (b) PVA–Nafion, and (c) PVA–PVTAC are shown. The dry film surfaces (a_1 , b_1 , c_1) are compared with the partially hydrated film surfaces (a_2 , b_2 , c_2). Photographs are of a step (cut down to the glass substrate) through each material made with a razor blade. The designations a_1 , a_2 , etc., are positioned on the film surface in each photograph. The large fragments which are seen on the glass substrate (see especially a_1 and b_2) are remnants of the blend left after making the gash and scraping a portion of the film off of the glass substrate.

of glass. SEM photographs of air-dried samples were compared to those of samples which had been equilibrated in water before surface coating with gold under vacuum. In this way it was found that the partially hydrated samples could be compared to those which had been thoroughly air-dried. This comparison is shown in Figure 2 for pure PVA, PVA–Nafion, and PVA–PVTAC bonded to glass. Two inferences can be made from comparisons of these images. First, there does not appear to be any evidence at SEM resolution ($\sim 0.1 \mu\text{m}$) for phase-separation in the bulk phase (see exposed edges) of the blends. Second, the surfaces of both the dry and the hydrated films show some mottling. This mottling is exaggerated by hydration and film swelling. The degree of surface mottling is greater for the blends than for the parent PVA material. Whether or not this

mottled surface corresponds to irregular cross-linking in the surface of the film or a partial segregation of the polyelectrolyte into clusters in the surface is not known at this time. In the formation of silica–polyelectrolyte composites we found⁴³ SEM evidence for the exclusion of polyelectrolyte during the curing and shrinking of the glassy matrix. It may be that the curing (cross-linking) of the PVA is also accompanied by partial segregation of the polyelectrolyte in the film surface, leaving a somewhat irregular surface. Further detailed examinations of these surfaces need to be done to resolve this point.

Optical and Electrochemical Sensing Applications of the Blends. All of the blends described can be made into free-standing thick films for direct sensing of charged analytes. We have previously described¹⁸ the

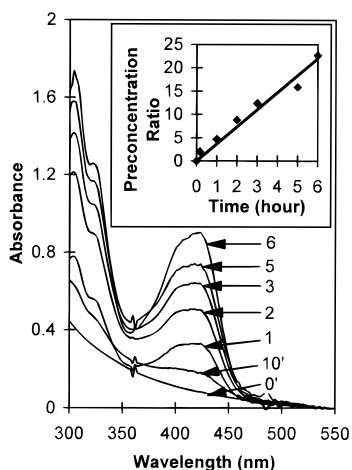


Figure 3. The absorbance spectra of a thick free-standing film of PVA–PDMDAAC exposed to 5×10^{-4} M $\text{Fe}(\text{CN})_6^{3-}$ measured at normal incidence. The spectra are labeled with times after first exposure (0 and 10 min, 1, 2, 3, 5, 6 h) to a solution containing $\text{Fe}(\text{CN})_6^{3-}$. The inset shows the preconcentration ratio as a function of time for the same film. The solid line drawn through the data points represents a least-squares fit (fixed zero intercept, $R^2 = 0.96$).

use of a thick film of the PVA–PAA blend for sensing of cations. A similar approach can be used with PVA–PDMDAAC for the sensing of anions. For studies of thick film uptake of selected analytes, a “preconcentration ratio” was defined as the ratio of the concentration of the analyte in the film divided by that in the ambient solution. Figure 3 shows the uptake of the $\text{Fe}(\text{CN})_6^{3-}$ anion and the preconcentration ratio achieved with a free-standing film (thick film formulation).

One goal of this work was to develop new polymer blends for applications that include use as chemically selective optical materials in fiber optic, planar waveguide, and spectroelectrochemical sensors. The application of a PVA–PAA blend directly to a fiber optic sensor (without covalent surface attachment) has been demonstrated previously.¹⁸ In that work one of the disadvantages encountered was the lack of a method to produce a uniform, ruggedly attached fiber optic cladding with the PVA–PAA blend. In this paper we demonstrate the feasibility of using thin highly uniform films of these blends for both planar optical sensors and spectroelectrochemical sensors. Representative results for cation and anion exchange films are presented below.

Performance of Cation-Exchange Thin Films on Glass. PVA–PAA blend coated planar glass substrates were evaluated using prism coupling to determine their ion-exchange performance with $\text{Ru}(\text{BiPy})_3^{2+}$. The refractive index of the base glass (soda lime glass) is 1.512 and 1.440 for the hydrated PVA–PAA film. Thus, the combination of this base glass and the PVA–PAA film forms an appropriate optical configuration for evanescent wave sensing under multiple internal reflection of light in the glass substrate. Because $\text{Ru}(\text{BiPy})_3^{2+}$ has an optical absorbance peak at 450 nm in the PVA–PAA matrix, light at 450 nm was used to monitor the dynamics of exchange of this cation by evanescent wave spectroscopy. For comparison, eight separate, equivalently made PVA–PAA-coated glass slides were exposed to aqueous solutions of varying concentrations of $\text{Ru}(\text{BiPy})_3^{2+}$ and the changes in absorbance with time of exposure were measured (Figure 4). For each curve, Ru-

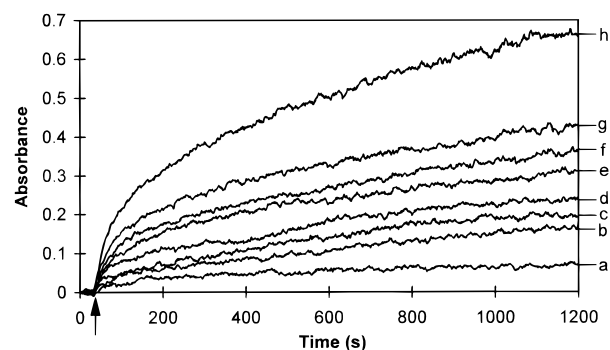


Figure 4. The absorbance of $\text{Ru}(\text{BiPy})_3^{2+}$ at 450 nm versus time recorded using attenuated total internal reflection optics and a soda lime glass microscope slide covalently coated with a thin film (thickness, $0.70 \mu\text{m}$) of the PVA–PAA blend. The figure shows curves for eight different concentrations of $\text{Ru}(\text{BiPy})_3^{2+}$ in aqueous solution measured with eight different, but similarly coated, slides. The time of injection of $\text{Ru}(\text{BiPy})_3^{2+}$ was at 30 s, which is marked by a vertical arrow. The concentrations are: a, 1×10^{-6} ; b, 2×10^{-6} ; c, 3×10^{-6} ; d, 4×10^{-6} ; e, 5×10^{-6} ; f, 6×10^{-6} ; g, 8×10^{-6} ; and, h, 1×10^{-5} M.

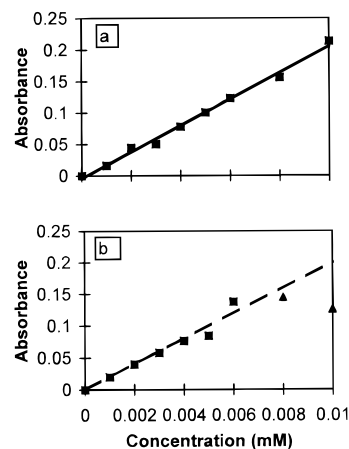


Figure 5. The calibration curves (absorbance vs concentration) for the detection of $\text{Ru}(\text{BiPy})_3^{2+}$ using PVA–PAA (a) and PVA–Nafion (b) covalently coated glass slides as described for PVA–PAA in Figure 4. Calibration points (solid squares) were determined at 70 s of exposure of the coatings to $\text{Ru}(\text{BiPy})_3^{2+}$ standards. The solid line in Figure 5a represents a linear regression fit to the experimental data points with $R^2 = 0.99$. The dashed line in Figure 5b represents a least-squares fit to the first six data points with $R^2 = 0.95$.

$(\text{BiPy})_3^{2+}$ was injected into the system after 30 s of recording the background signal (defining the zero of absorbance). $\text{Ru}(\text{BiPy})_3^{2+}$ partitioned into the thin film by ion-exchange and interacted with the evanescent field at each position of total internal reflection. In turn, this interaction produced an attenuation of the light propagating by multiple reflection within the base glass. Thus, the curves in Figure 4 represent the time-dependent uptake of the cation by the thin film.

The curves for different concentrations in Figure 4 have similar shapes but different amplitudes. At any specific time, the absorbance values are directly proportional to the concentration of $\text{Ru}(\text{BiPy})_3^{2+}$ in the initial solution. For example, at 100 s (70 s after sample injection), a working curve for the sensing can be constructed, and this is shown in Figure 5a. The working curve is a linear relationship within the range from 0.001 to 0.01 mM with $R^2 = 0.992$. At lower

concentrations the film does not accumulate enough cation to give an adequate absorbance at 100 s of exposure.

PVA-Nafion thin films were evaluated in the same way as those with the PVA-PAA blend. The time responses of eight separate, equivalently made slides that were exposed to aqueous $\text{Ru}(\text{BiPy})_3^{2+}$ were measured, and a working curve was constructed. This curve is also shown Figure 5b. Although not linear overall, the curve has an acceptably linear range ($R^2 = 0.95$) at low concentrations down to 0.001 mM and deviates negatively at higher concentrations. The overall profile fits the character of ion-exchange partitioning, where the ion-exchanger approaches saturation at the higher concentrations.

It is interesting to compare the behavior of the PVA-PAA and PVA-Nafion materials. The PVA-PAA thin film has a larger linear calibration range than the PVA-Nafion thin film. Evaluation of the initial rate of uptake by these two blends shows that the PVA-PAA blend incorporates $\text{Ru}(\text{BiPy})_3^{2+}$ at a rate which is up to three times faster than PVA-Nafion. The concentrations of ion-exchange groups inside these hydrated films have been estimated to be 5.0 M for PVA-PAA blend and 0.15 M for PVA-Nafion blend. Thus, the concentration of the ion-exchange group COO^- in the PVA-PAA film is about 34 times that of the SO_3^- in the PVA-Nafion film. (Similarly, from Table 1, the monomer ratios are 0.31 and 0.0070, respectively, leading to a ratio of 44, which does not account for the volume of the film.) On this basis it is not surprising that the PVA-PAA film shows a larger linear range and a faster uptake rate than the PVA-Nafion film.

Spectroelectrochemical Modulation with PVA-PVTAC-Coated ITO-Glass. The incorporation of the anion ferricyanide, $\text{Fe}(\text{CN})_6^{3-}$, into PVA-PVTAC occurs by ion exchange at the quaternary ammonium functions of the polyelectrolyte. Since ferricyanide absorbs at 430 nm, the use of the prism-coupling technique allows sensitive detection of this anion by multiple internal reflection evanescent wave spectroscopy.⁴⁶ In addition, the ferri/ferrocyanide redox couple allows measurement of the incorporation of ferricyanide into the thin film using the ITO layer on the glass surface as an electrode. Figure 6a shows the cyclic voltammograms for the incorporation of ferricyanide into the PVA-PVTAC thin film as monitored by cyclic voltammetry. It is important to note that the voltammograms are obtained using the ITO layer as the electrode and thus any signal must⁴⁶ originate from ferricyanide which has permeated the film and has diffused to the electrode (ITO) surface. The voltammograms displayed well-defined oxidation and reduction waves corresponding to the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple located at about 0.170 V. The increasing peak currents with each scan clearly show the time-dependent incorporation of ferricyanide into the thin film. After about 23 cycles (about 30 min after initial exposure of the film to the ferricyanide solution) the peak current became relatively constant ($i_a = 1.10$ mA, $i_c = 0.80$ mA), suggesting equilibration of the ferricyanide in the film with the ferricyanide which remained in the bulk solution.

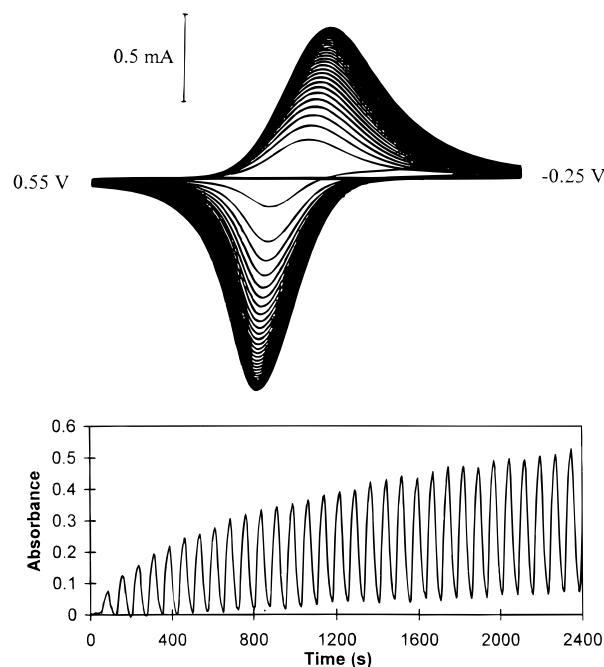


Figure 6. Cyclic voltammograms recorded for a PVA-PVTAC thin film covalently coated onto ITO-glass exposed to aqueous 1×10^{-4} M $\text{Fe}(\text{CN})_6^{3-}$ as a function of time following initial exposure are shown in the top portion of the figure. The potential (E/V vs Ag/AgCl) was scanned between + 0.55 and -0.25 V at a scan rate of 20 mV/s (80 s/cycle) and 0.1 M KNO_3 was used as the supporting electrolyte. The associated modulation of the absorbance at 430 nm with multiple internal reflection optics recorded at the same time as the cyclic voltammograms is shown in the bottom portion of the figure.

At the same time the ferri/ferrocyanide couple cycled in response to changing the potential, the absorbance at 430 nm modulated in-phase, and this is also shown in Figure 6b. Since ferrocyanide does not absorb at 430 nm, the points in the waveform of minimum absorbance correspond to ferrocyanide, $\text{Fe}(\text{CN})_6^{4-}$; each maximum corresponds to ferricyanide, $\text{Fe}(\text{CN})_6^{3-}$. After about five cycles, a trough begins to develop at the bottom of the modulation that becomes more prominent with increasing time (incorporation). Examination of this effect showed that within the first five or six cycles, all of the ferricyanide/ferrocyanide at the ITO surface was reduced/oxidized as the potential was cycled. However, after six cycles, not all of the ferricyanide/ferrocyanide was reduced/oxidized during each cycle, leaving the minimum absorbance value greater than zero (all ferrocyanide). This incomplete electrochemical cycling became more prevalent as the uptake of ferricyanide continued at a scan rate of 20 mV/s. It is interesting to note by comparing the cyclic voltammograms and the electro-modulation of the absorbance (top and bottom portions of Figure 6, respectively) that the absorbance modulation does not indicate that the film is approaching steady state at the same time the voltammograms do. It, therefore, appears that the evanescent field penetration depth and the depth to which electrochemical modulation occurs are different. We are currently examining this interesting behavior in such film-coated devices.

Electrochemical modulation of the optical properties of the ferricyanide-loaded film was conditioned by the potential scan rate used. This is illustrated in Figure

(46) Shi, Y.; Slaterbeck, A. F.; Seliskar, C. J.; Heineman, W. R. *Anal. Chem.* **1997**, *69*, 3679-3686.

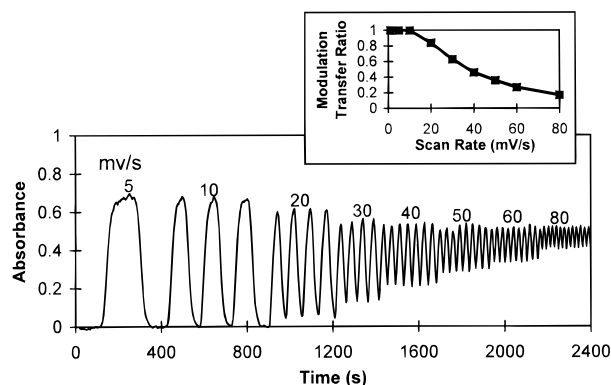


Figure 7. The modulation of the absorbance at 430 nm for a PVA–PVTAC thin film covalently coated on ITO–glass at steady-state film loading in 1×10^{-4} M $\text{Fe}(\text{CN})_6^{3-}$ (0.1 M KNO_3 supporting electrolyte) while cycling the potential between +0.55 and –0.25 V at varying scan rates. The potential scan (triangular wave) rate in mV/s is marked over each portion of the time trace. The inset shows the modulation transfer ratio (see text) vs scan rate for this same system.

7, where the modulation of the absorbance for a series of different scan rates is shown. At low scan rate (<20 mV/s) the modulation faithfully traces out the absorbance changes for the complete reduction/oxidation of the incorporated ferricyanide. At higher scan rates (≥ 20 mV/s) the modulation of the absorbance was attenuated as the chemical redox cycle for ferri/ferrocyanide lagged behind the potential modulation. Thus, at these scan rates not all of the ions in the film in the proximity of the ITO surface were cycled through the redox process. The inability of the electrochemistry to keep pace with higher scan rates limits these materials to relatively slow electromodulation. Analogous to the modulation transfer function in imaging optics,⁴⁷ we define a simple ratio of the absorbance modulation amplitude (ΔA_{mod}) to that at zero scan rate (ΔA_0), $\text{mtr} = \Delta A_{\text{mod}}/\Delta A_0$, which serves to characterize the polymer blend–analyte system's ability to respond optically to electrochemical

(47) Smith, W. J. *Modern Optical Engineering*; McGraw-Hill: New York, 1990; p 345 ff.

modulation. The modulation transfer ratio for the PVA–PVTAC thin film covalently bonded to ITO–glass is also shown in Figure 7 (inset).

Conclusions

We have formulated a series of optically transparent and ion-exchangeable polymer blends based on a glutaraldehyde cross-linked PVA host material. The compositions of the new blends were optimized for clarity, ion exchangeability, and the coating of oxide surfaces with covalent attachment. These materials readily concentrate cations and anions from aqueous solutions into a medium which has a suitable refractive index for an optical cladding on glass or silica surfaces. Evaluation of the physical properties of these blends showed that three of them were directly suitable for both planar waveguide and fiber optic sensors. These three, PVA–Nafion, PVA–PAA, and PVA–PVTAC, could be covalently attached to planar glass and ITO–glass surfaces using silane coupling reagents, i.e., APTS or GPTS. Such covalently attached thin films remained well-adhered to oxide surfaces, even in solutions of low pH. The overall strategy of anchoring the blends to oxide surfaces employs a simple one-step process. This technique should be applicable to a wide variety of planar oxide surfaces, including tantalum oxide. A suitable change of the coupling agent to a bifunctional thiol should permit the covalent attachment of these blends to semitransparent gold surfaces. Our continuing work in this area includes developing more new blends and their applications to new spectroelectrochemical and planar waveguide sensors.

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