

pH-Sensitive Bipolar Ion-Permselective Ultrathin Films

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Abstract: pH-Sensitive bipolar ion-permselective films of polyelectrolyte multilayers were prepared by layer-by-layer (LbL) assembly and photo-cross-linking of benzophenone-modified poly(acrylic acid) (PAA-BP) and poly(allylamine hydrochloride) (PAH-BP). The multilayer structure and ionizable group composition was finely tuned by changing the pH of the dipping solution. This structure and composition was in turn "preserved" by photo-cross-linking, forming highly stable membrane films. Since PAA-BP and PAH-BP are weak polyelectrolytes, it is possible to control the number of unbound, un-ionized -COOH or -NH₂ groups in the multilayer by changing the pH. Moreover, the pH of the deposited film also plays an important role in determining selective latter permselectivity. For example, PAA-BP/PAH-BP multilayers deposited from two pH conditions, pH = 3 (PAA-BP) and pH = 6 (PAH-BP), showed pH-switchable permselectivity for both cationic (pH = 10) and anionic (pH = 3) probe molecules in a single film. The system offers advantages in film stability and introducing reversible selective ion permeability over previous multilayer film and cross-linking methods.

Introduction

We describe the preparation of (1) anion-permselective, (2) cation-permselective, and (3) pH-switchable ultrathin polyelectrolyte multilayers with high stability and bipolar behavior through a photo-cross-linked structure. The parameters used for the preparation of the membranes have allowed tunability of permselectivity, permeability, and film thickness (swelling) both during and after film preparation by changing the pH of the solution and the films (ex situ), respectively. High stability and reversible cyclical cation and anion permselectivity were achieved in a single film.

The development of pH-responsive or pH-switchable membranes is important for technological applications such as filtration systems, membrane-based separations, bio-separations, and sensors. The permeation rates of amino acids¹ and ionic drugs² through membranes with pH-sensitive chemical groups (e.g., weak acids^{3,4} and amphoteric groups⁵⁻⁷) are greatly

influenced by the local pH and electrolyte concentration. The ionization state of such chemical groups is regulated by the pH of the solution, which generates either excess positive charge or excess negative charge on membranes. Consequently, the membranes can have either anion-permselective or cation-permselective states. In case the membrane is modified with amphoteric groups, these membranes can be reversibly switched between cation-permitting and anion-permitting states depending on the pH of the solution. Several research groups have reported theoretical^{2,8} and experimental studies of ion-permselective membranes. Martin and co-workers⁶ have reported a pH-switchable ion-transport membrane system consisting of gold nanotubules. They used electroless deposition of gold onto the pore walls of polycarbonate track-etched (PCTE) filtration membranes followed by chemisorption of an amino acid to the inside tubule walls. They showed that these membranes can be switched between cation-transporting, non-ion-permselective, and anion-transporting states. Recently, Liu et al.⁷ developed pH-switchable, permselective membranes composed of covalently linked polyamidoamine (PAMAM) dendrimer and poly-(maleic anhydride)-co-(methyl vinyl ether) containing pH-responsive amine and carboxyl groups.

Polyelectrolyte multilayer films are promising candidates for preparing a thin membrane skin due to their simplicity and versatility. Ultrathin polymer films with defined composition and uniform thickness in the nanometer range can be easily prepared by the alternate deposition of cationic and anionic

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polyelectrolytes on solid substrates.^{9,10} Several research groups have reported the applications of polyelectrolyte membranes including gas separations,¹¹ pervaporation from water/organic solvent mixtures,¹² ion separations for nanofiltration,¹³ and reverse osmosis membranes.¹⁴

Polyelectrolyte multilayer membranes are especially suitable for ion separations because of their multibipolar architecture. Krasemann and Tieke¹⁵ recently showed that polyelectrolyte multilayer membranes composed of 10–60 bilayers of PAH/PSS exhibit $\text{Cl}^-/\text{SO}_4^{2-}$ selectivity factors as high as 45 in diffusion dialysis experiments. They suggested that Donnan exclusion resulting from fixed charges in the membrane is responsible for this selectivity. The strength of the interactions is proportional to the charge density of the permeating ions and the polyelectrolytes constituting the membrane. Bruening and co-workers¹⁶ have investigated the control of permeability and ion-transport selectivity of multilayered polyelectrolyte films containing PAH and PAA through cross-linking via heat-induced amidation followed by hydrolysis. Furthermore, they used the partially esterified PAA (d-PAA) to control both hydrophobicity and charge density in PAH/d-PAA films.¹⁷ Variation of the ester functionalities in PAH/d-PAA films along with subsequent cross-linking and hydrolysis yielded stable and highly dense -COO- groups in the films that resulted in higher permeability for positively charged $\text{Ru}(\text{NH}_3)_6^{3+}$ than for $\text{Fe}(\text{CN})_6^{3-}$. They also studied controlled ion transport through multilayer polyelectrolyte membranes by increasing the net fixed-charge density in the films.¹⁸ However, in spite the number of investigations on polyelectrolyte membranes, pH-switchable bipolar membranes have not been widely reported.

In this study, we report the assembly of bipolar highly stable photo-cross-linked multilayer films of the polyelectrolytes PAA and PAH modified with benzophenone groups to demonstrate unique pH-switchable ion permselectivity. It has been known that it is possible to control the charge density of weak

polyelectrolyte films by varying the pH environment during multilayer assembly. PAA ($\text{p}K_a \approx 5$) and PAH ($\text{p}K_a \approx 9$) contain ionizable carboxylic acids and amines, respectively. Thus, depending on the deposition pH conditions, the degree of ionization of these weak polyelectrolytes (i.e., the relative number of COO^- vs COOH groups for PAA and the relative number of NH_3^+ vs NH_2 groups for PAH), as well as the number of ionic bonds ($\text{COO}^- \cdots \text{NH}_3^+$), used to assemble the multilayers may be tuned as desired.¹⁹ Shiratori and Rubner²⁰ have reported that one can systematically vary the thickness of an adsorbed weak polyelectrolyte layer over the range of 5–80 Å and control the bulk and surface composition of the multilayer film by controlling the pH of the dipping solution. However, the multilayer film of weak polyelectrolytes easily swells in solution (up to ~400% in pH = 7.4 buffer solution!) and even the ionic bonds can be broken, resulting in cleavage of the film from the substrate in highly acidic and basic solution. Therefore, the weak polyelectrolyte multilayer membranes without cross-linking are not suitable for practical use. In this study, poly(acrylic acid) (PAA) and poly(allyamine hydrochloride) (PAH) were first modified with photoreactive benzophenone groups in order to obtain stable cross-linked structures of polyelectrolyte multilayer films. The advantages of this over previous studies by other groups are the following: (1) no heating is required for cross-linking, minimizing film restructuring and destabilization; (2) the pH-switchable groups are maintained (do not participate in the cross-linking), giving both negatively and positively ionizable groups; and last (3) swelling can be minimized during pH changes or the swelled state “preserved” by photo-cross-linking. The cross-linking reactions initiated by UV irradiation of polymers containing a benzophenone unit have been extensively studied.²¹ Hydrogen abstraction via an excited benzophenone unit is a classic reaction in organic photochemistry. UV radiation causes an $n-\pi^*$ transition in the carbonyl group. The resulting biradical reacts with C–H groups of the nearby polymer chain and can cause cross-linking within polyelectrolytes.

Since PAA-BP and PAH-BP are weak polyelectrolytes, it is possible to control the number of unbound, un-ionized -COOH or -NH₂ groups in the multilayer by changing the pH. Moreover, the pH of the film plays an important role in determining selective latter permselectivity. For example, a PAA-BP/PAH-BP multilayer film deposited from two pH conditions, pH = 3 (PAA-BP) and pH = 6 (PAH-BP), showed pH-switchable permselectivity for both cationic and anionic probe molecules. The film is permeable (on) to the cationic probe but impermeable (off) to the anionic probe at pH = 10. On the other hand, the film was permeable to an anionic probe at pH = 3.2 due to the protonation of free amine ($-\text{NH}_3^+$) at low pH. Together with photo-cross-linking, these properties can be tuned and preserved in a highly stable film.

Thus, to the best of our knowledge, these results are an important demonstration of a highly stable “smart” bipolar pH-switchable, permselective polyelectrolyte multilayer membrane through photochemical cross-linking. In principle, together with

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control of the pH, the thickness of the films, the degree of cross-linking, and the substrate host used, permselectivity and permeability performance can be achieved through combinatorial methods. It is important to point out that this bipolar or reversible ion selectivity in a single film is a very interesting property for the development of ion-separation membranes.

Experimental Section

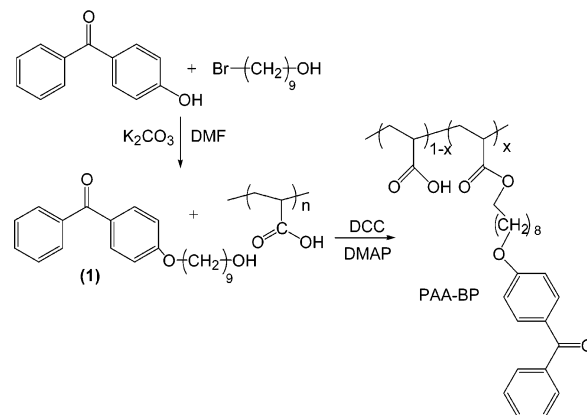
Materials. Poly(allylamine) (Aldrich, MW = 65 000), PAA (Aldrich, MW = 2000), (3-aminopropyl)triethoxysilane (APS, Aldrich), sodium 3-mercapto-1-propanesulfonate (Aldrich), Ru(NH₃)₆Cl₃ (Aldrich), and K₃Fe(CN)₆ (Acros) were used as received. Buffer solutions were made with the following salts: 0.2 M CH₃COOH + 0.0036 M CH₃COONa (pH = 3.2) and 0.025 M Na₂CO₃ + 0.025 M NaHCO₃ (pH = 10). Solutions for cyclic voltammetry contained 0.5 M Na₂SO₄ with 0.005 M K₃Fe(CN)₆ or 0.005 M Ru(NH₃)₆Cl₃.

Synthesis of 4-(9-Hydroxynonyloxy)benzophenone (1). A solution of 3.69 g of 4-hydroxybenzophenone (20 mmol) and 2.0 g of K₂CO₃ in 50 mL of *N,N'*-dimethylformamide (DMF) was stirred at 100 °C for 30 min. A solution of 4.46 g of 9-bromononan-1-ol (20 mmol) in 50 mL of DMF was then added dropwise. After addition, the reaction mixture was stirred at 100 °C for 4 h. Then it was cooled, poured into water, and extracted with CH₂Cl₂. The extract was dried over MgSO₄ and evaporated. The resulting solid was recrystallized with ethanol to give 5.44 g of pure product as blue crystals (yield = 80%). ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 7.81 (m, 2H), 7.75 (m, 2H), 7.58 (m, 1H), 7.46 (m, 2H), 6.94 (m, 2H), 4.03 (t, 2H), 3.64 (t, 2H), 1.81 (p, 2H), 1.44 (m, 12H). ¹³C NMR (CDCl₃, 300 MHz): δ (ppm) 195.54, 162.73, 138.20, 132.48, 131.73, 129.73, 129.61, 128.06, 113.88, 68.12, 62.92, 32.63, 29.37, 29.22, 29.15, 28.96, 25.85, 25.60.

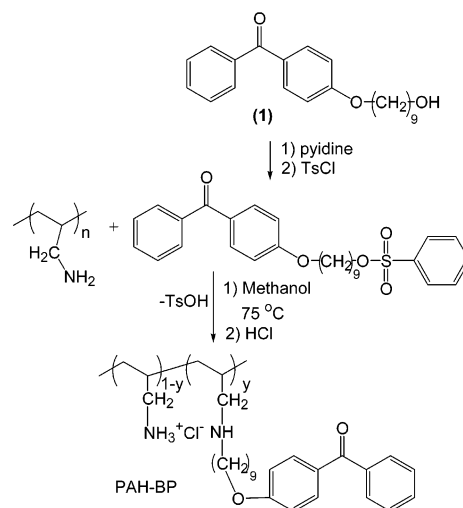
Synthesis of Benzophenone-Substituted Poly(acrylic acid) (PAA-BP).²² PAA (MW 2000; 3.42 g, 47.5 mmol), 244 mg of 4-(dimethylamino)pyridine (DMAP), and 1.7 g of 4-(9-hydroxynonyloxy)benzophenone (5.0 mmol) were dissolved in 90 mL of DMF at 0 °C. To this mixture was added 1.10 g of *N,N'*-dicyclohexyl carbodiimide (DCC) in two portions. The reaction mixture was warmed to room temperature overnight. The urea was filtered and the filtrate was concentrated under vacuum. To this residue was added 5 mL of DMF, and the white solid (trace of the urea) was filtered off. The filtrate was added dropwise to 150 mL of acetone with good stirring to precipitate. The acetone was decanted off. The solid was washed twice more with acetone (2 × 150 mL). Most of the acetone was decanted off and the rest was removed under vacuum. The flask containing the dried solid (3.17 g) was filled with nitrogen gas. The degree of substitution (DS) of the benzophenone group was found to be 39% ($x = 0.39$), calculated from elemental analysis. [C_{11.6}H_{14.1}O_{2.8}·2.2H₂O]_n Anal. Calcd: C, 58.75; H, 7.86; O, 33.39. Found: C, 55.57; H, 7.44; O, 31.64 (Scheme 1).

Tosylation of 4-(9-Hydroxynonyloxy)benzophenone. The solution of 4-(9-hydroxynonyloxy)benzophenone (1.02 g, 3 mmol) in 15 mL of dry pyridine was stirred at -20 °C for 10 min. *p*-Toluenesulfonyl chloride (TsCl; 1.72 g, 9 mmol) was added in small portions over an hour period. The mixture was stirred for an additional hour; the temperature gradually rose to 0 °C. The reaction flask was placed in a refrigerator (0–5 °C) overnight. The mixture was then added into 150 mL of ice–water, and a solid precipitated. The solid was washed with deionized water several times. Then the washed solid was purified by column chromatography with methylene chloride and hexane as eluent. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 7.78 (m, 6H), 7.56 (m, 1H), 7.46 (m, 2H), 6.94 (m, 2H), 4.01 (t, 4H), 2.43 (s, 3H), 1.79 (p, 2H), 1.63 (p, 2H), 1.47 (m, 10H). ¹³C NMR (CDCl₃, 300 MHz): δ (ppm) 195.46, 162.71, 144.53, 138.18, 133.04, 132.44, 131.71, 129.76, 129.69, 129.57, 128.05, 113.86, 70.53, 68.08, 29.16, 29.05, 28.95, 28.72, 28.67, 25.80, 25.19, 21.51.

Scheme 1. Synthetic Scheme for Benzophenone-Substituted Polyacrylic Acid (PAA-BP)



Scheme 2. Synthetic Scheme for Benzophenone-Substituted Poly(allylamine Hydrochloride) (PAH-BP)



Synthesis of Benzophenone-Substituted Poly(allylamine Hydrochloride) (PAH-BP). The polymer reaction of tosylated benzophenone with poly(allylamine) follows the partially modified procedure (Scheme 2) by Seo et al.²³ Poly(allylamine) (0.571 g, 10 mmol repeat unit) was dissolved in 20 mL of methanol and small portions of tosylated benzophenone (1 mmol, 0.4956 g) were added while stirring at 75 °C. When the solution turned clear again, the next portion was added. After the addition of the last portion, the solution was stirred for 12 h at 75 °C. The solution was acidified with 1 N hydrochloride (HCl) aqueous solution and concentrated in vacuo. The residue was dissolved in 20 mL of water. The solution was added dropwise into acetone and the polymer precipitated slowly. The polymer was then filtered off. This procedure was repeated one additional time. The degree of substitution (DS) of the benzophenone group was found to be 9.8% ($x = 0.098$), calculated from elemental analysis. [C_{5.2}H_{10.5}N₁O_{0.2}Cl_{0.9}·0.8H₂O]_n Anal. Calcd: C, 45.36; H, 8.94; N, 10.23; O, 33.39; Cl, 23.42. Found: C, 43.92; H, 8.73; N, 9.95; O, 11.65.

Film Preparation. Silicon wafers or quartz slides were immersed in a fresh piranha solution (v/v = 1:3 30% H₂O₂/98% H₂SO₄) for 2 h and carefully washed with deionized water and dried. The substrates were treated with APS (0.001 M in toluene) for 45 min and then, sonicated in toluene two times and dried for initial surface functionalization. The substrates were stored in 0.1 M HCl solution to render a positive surface charge. Freshly made gold-coated glass slides were

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washed with deionized water and dried. Then, a self-assembled monolayer (SAM) of sodium 3-mercaptopropylsulfonate was formed on the gold by immersing the slides in 2 mM ethanol solution for 45 min, rinsing with ethanol, and drying with dry air. PAH-BP dipping solution was prepared in Millipore water with a concentration of 1 mg/mL. Due to poor solubility of PAA-BP in water, PAA-BP was dissolved in DMF at a concentration of 10 mg/mL and then the dipping solution was prepared by adding one part (by volume) of PAA-BP solution to nine parts of water. The solutions were filtered with 0.75 μm syringe filter. The pH of the solutions was adjusted with NaOH or HCl.

Layer-by-layer deposition was carried out manually. The substrates were alternately immersed in aqueous solutions of PAA-BP and PAH-BP for 5 min each, with water rinsing between each deposition. Positively charged substrates (silicon wafers and quartz slides) were started with dipping in a PAA-BP solution whereas negatively charged gold substrates were started with a PAH-BP solution. The substrate was not dried between the adsorption steps except for the silicon wafer substrate for monitoring thickness growth by ellipsometry.

Photo-Cross-Linking. Polyelectrolyte films were irradiated in air with a 150 W Xe lamp (Oriel) without filter at a distance of 15 cm from the source. The irradiation intensity based on the distance, area, and intensity of the lamp was calculated to be 190 mW/cm².

Film Characterization. UV-visible absorption spectra were obtained on an Agilent 8453 UV-vis spectrophotometer. Fourier transform infrared (FT-IR) absorption spectra of polyelectrolyte films on gold substrate were measured with a Digilab FTS7000 series spectrometer with a Pike Technologies wire grid infrared polarizer (p-polarized) and a VeeMax variable-angle specular reflectance accessory (reflectance angle 75°). Spectra (4000–700 cm⁻¹) were collected from 1000 scans at 4 cm⁻¹ resolution with a mercury-cadmium-telluride (MCT) detector. A clean gold substrate was used as the background.

Null ellipsometry was applied to determine the thickness of polyelectrolyte multilayers.²⁴ All the measurements were carried out on a null-ellipsometer in a polarizer-compensator-sample-analyzer (Multiscope, Optrel Berlin) mode. As a light source, a He-Ne laser with $\lambda = 632.8$ nm was applied, and the angle of incidence was set to 70°. A multilayer model for a flat film has been used for the calculation of thickness of polyelectrolyte multilayers from the experimentally measured ellipsometric angles Δ and Ψ with the assumption of a refractive index value of 1.50 for the polyelectrolyte multilayers. The refractive indices used for the calculations were $N = 3.873 - i0.016$ and 1.46 for the silicon substrate and native silica layer, respectively.

The thickness of the film was calculated by use of a fitting program (Elli, Optrel). In situ ellipsometry measurements were performed on multilayer films on a silicon wafer in aqueous solutions of pH 3, 7, and 10 in a home-built glass cell. The tilt angle of the entrance and exit windows for the incident beam was designed at 70° with the base window of the cell. The sample was first placed in the cell and aligned to ensure that the windows were perpendicular to the beam. The buffered solutions were then poured into the cell and measurements were recorded as a function of time until stable ellipsometric angles Δ and Ψ were observed. For calculation of the thickness, a refractive index of 1.33 was used for the buffered solution.

Cyclic voltammetry measurements were performed with an Amel 2049 potentiostat and Power Lab system with a three-electrode cell at a scan rate of 100 mV/s. A platinum wire was used as the counter-electrode, and Ag/AgCl (3 M KCl) was used as the reference electrode. Aqueous solutions of 0.5 M Na₂SO₄ containing 5 mM either Fe(CN)₆³⁻ or Ru(NH₃)₆³⁺ buffered at pH 3.2 and 10 and nonbuffered at pH 7 were prepared as electrolyte solutions. The PAH-BP/PAA-BP multilayer coated gold (working) electrodes were immersed in the solution for 20 min prior to measurement. The solution containing Ru(NH₃)₆³⁺ was

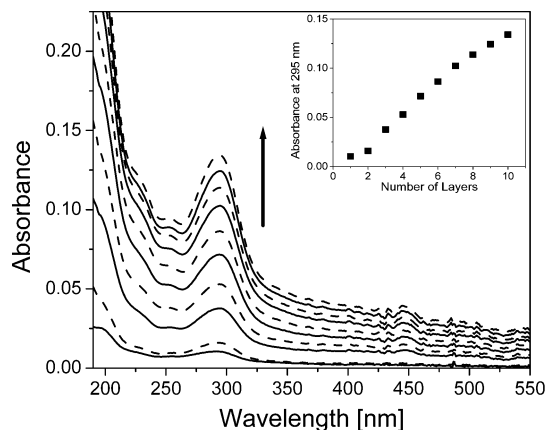


Figure 1. UV-Visible absorption spectra of 1–10 layers of PAA-BP/PAH-BP pH 3/6. (Inset) Increase in absorbance at 295 nm with the number of bilayers.

purged with nitrogen for 5 min before each measurement. The measured current was divided by the area of the sample that was immersed in solution in order to obtain current density.

Results and Discussion

Architecture of Polyelectrolyte Multilayers. Three different conditions of dipping solution pH were chosen to produce the assemblies: PAA-BP/PAH-BP at pH 3/pH 3, pH 3/pH 6, and pH 8.5/pH 8.5. For unsubstituted PAA and PAH, the linear charge density of weak polyelectrolytes is the same as the degree of ionization. When both PAA and PAH are deposited from solutions at pH 3, PAA-BP is only partially ionized (less than 10%, pK_a of PAA ~ 5), whereas PAH-BP, with a $pK_a \approx 8-9$ in solution, is fully ionized. In contrast, PAA is fully ionized at pH = 8.5, and PAH is partially ionized. Shiratori and Rubner²⁰ have reported that when PAA and PAH are adsorbed in the pH range of $\sim 7.5-9.5$, where PAA is fully ionized and PAH is close to fully ionized, a thick adsorbed bilayer (up to 160 Å) can be formed. An interesting finding was that not only PAH but also fully charged PAA can form thick layers. In this pH range, the conformational state of a previously adsorbed polyelectrolyte layer can strongly influence the thickness/conformation of an adsorbing polyelectrolyte layer. However, in our case, 38% of PAA and 10% of PAH are substituted with benzophenone groups; the linear charge density is lower than the degree of ionization. Thus, the structure and composition of multilayers is different with the combination of unsubstituted PAA/PAH.

UV-Visible spectroscopy was used to monitor the growth of the polyelectrolyte multilayer. Figure 1 shows the UV-vis absorption spectra of 1–10 layers of PAA-BP/PAH-BP assembled on a quartz slide at pH 3/pH 6 (hereafter denoted as PAA-BP/PAH-BP pH 3/6). The absorbance at 295 nm is attributed to the $\pi-\pi^*$ transition of the benzophenone groups in the film. The linear increase in absorbance at 295 nm with the number of layers (inset) indicates a regular growth of polyelectrolyte multilayers. The initial nonlinear growth (1 and 2 layers) was seen for PAA-BP/PAH-BP films due to the effect of substrate. Such behavior has often been observed, with a few polyelectrolyte layers required prior to regular multilayer growth for films assembled by the LbL technique. The pH value of a solution can produce a dramatic effect on the assembly behavior of weak polyelectrolytes. Figure 2 displays the thickness of

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Table 1. Average Thickness of Bilayers and Relative Composition for PAA-BP/PAH-BP Multilayers

	PAA-BP/PAH-BP		
	pH 3/3	pH 3/6	pH 8.5/8.5
avg layer thickness of PAA-BP (Å)	50 ± 10	58 ± 6	16 ± 2
avg layer thickness of PAH-BP (Å)	10 ± 2	45 ± 8	41 ± 3
relative composition ^a (PAA-BP/PAH-BP segments)	80:20	55:45	30:70

^a Calculated from the average thickness of each layer, with the assumption that both layers have the same density.

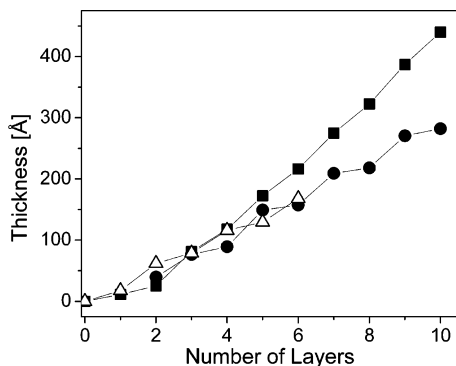


Figure 2. Ellipsometric thickness as a function of the number of PAA-BP/PAH-BP multilayer film layers deposited from pH 3/3 (●), pH 3/6 (■), and pH 8.5/8.5 (△).

PAA-BP/PAH-BP films versus the number of deposited layers for three pH conditions. The thickness of multilayer films deposited on silicon wafers was measured by ellipsometry. In general, the layer-by-layer multilayer film shows linear growth. It is important to note that the thickness of the PAA-BP/PAH-BP bilayer is highly sensitive to solution pH. The average thickness of PAA-BP and PAH-BP for each pH condition is summarized in Table 1. When both PAA-BP and PAH-BP were deposited from solutions at pH 3 (hereafter denoted as PAA-BP/PAH-BP pH 3/3), the PAA-BP layer thickness was 50 ± 10 Å, whereas the PAH-BP layer thickness was only 10 ± 2 Å. At pH 3/3, the degree of ionization of PAA-BP is less than 5%, therefore the adsorbed PAA-BP forms loops and tails that contain free carboxyl acid groups. However, PAH-BP has ~90% of charge density (fully ionized) at pH 3; therefore, they form rather flat and thin layers. These results are similar with the bilayer thickness of PAA/PAH layers reported by Yoo et al.¹⁹ They found that when PAA and PAH are prepared at pH range 2.5–4.5, the thickness of an adsorbed layer of PAH and PAA depends primarily on the charge density of the adsorbing polymer and the surface and not on the thickness, conformation, or free ionic binding sites of the previously adsorbed polymer layer.

In the case of PAA-BP/PAH-BP pH 8.5/8.5, the PAA-BP layer thickness was 16 ± 2 Å, whereas the PAH-BP layer thickness was 41 ± 3 Å, showing an opposite trend in thickness with the previous case. The relative composition of PAA-BP to PAH-BP at pH 8.5/8.5 was 30:70, whereas that of PAA-BP to PAH-BP at pH 3/3 was 80:20. At pH 8.5, PAA-BP is fully ionized; therefore its charge density is ~60%. On the other hand, the degree of ionization of PAH-BP chains starts to decrease (~75%). Both PAA-BP and PAH-BP have moderate charge density (~60–70%) and form a somewhat coiled structure in the solution. The higher composition of PAH-BP over PAA-BP can be explained by the difference in the degree of ionization of the polymers at pH 8.5. This is because an adsorbed PAA-BP layer has a higher surface charge than that of PAH-BP. More

PAH-BPs are adsorbing onto the highly ionized PAA-BP surface chains to neutralize the surface than PAA-BP adsorbs onto the surface of PAH-BP at pH 8.5.

In the case of PAA-BP/PAH-BP pH 3/6, the picture is not as simple as it is for the other cases since pH of the dipping solution affects not only the ionization of polyelectrolytes in solution but also the ionization of polyelectrolytes already adsorbed. When PAA-BP and PAH-BP were adsorbed at pH 3/6, thick bilayers were formed with 103 ± 3 Å bilayer thickness. PAA-BP is only partially ionized at pH 3, while PAH-BP is fully ionized at pH 6 with a rather coiled structure in the solution due to its lower charge density. At pH 3, an adsorbed PAA layer is composed of charged segments that penetrate into the PAH-BP surface layer. A population of loop and tail segments that are for the most part extending away from the surface are essentially not charged. When a PAH-BP chain is adsorbed onto a PAA-BP surface at pH 6, the loop segments of PAA become ionized. Thus many PAHs are needed to neutralize this charge, leading to the formation of thick bilayers. Both PAA-BP and PAH-BP molecules adsorb in loop-rich conformations, forming thick layers with a high degree of internal charge pairing at pH 3/6.

Reflectance FT-IR spectroscopy was used to investigate the structure of PAA-BP/PAH-BP at three different pH conditions. Figure 3a shows the FT-IR spectra (carbonyl region) of multilayer films of PAA-BP/PAH-BP deposited on gold-coated glass slides. The multilayer films prepared at different pH conditions clearly show different compositions from each other. The top spectrum was obtained from a film fabricated with PAA-BP and PAH-BP at pH 3/3, whereas the middle spectrum was obtained at pH 3/6, and the bottom spectrum was obtained at pH 8.5/8.5. First, the characteristic benzophenone peaks at 1642 cm^{-1} (C=O stretch) and 1601 cm^{-1} (ring C=C stretch) were shown in all the spectra.^{21b} Two carbonyl peaks of interest in these spectra are the carboxylic acid (-COOH) and carboxylate peaks (-COO⁻) at 1721 and 1566 cm^{-1} , respectively.^{19a}

For pH 3/3, about 50% of the acid groups of PAA-BP are in carboxylic acid form, whereas most of the acid groups of PAA-BP are in carboxylate form for pH 8.5/8.5. In case of pH 3/6, about 30% of the functional groups exist in the carboxylic acid group. As expected, the degree of ionization of the acid groups of PAA-BP increases with increasing solution pH. Formation of free amine groups in the multilayer can be determined by FT-IR spectra in the C–H stretching region as shown in Figure 3b. The symmetric and asymmetric N–H stretching bands of free amine group were shown at ~ 3290 and $\sim 3350 \text{ cm}^{-1}$ in the pH 8.5/8.5 spectrum.²⁵ However, the ammonium salt showed broad absorption between 2997 and 3308 cm^{-1} arising from asymmetrical and symmetrical stretching in the -NH₃⁺ group in the pH 3/3 spectrum.²⁵ For the pH 3/6 FT-IR spectrum, the

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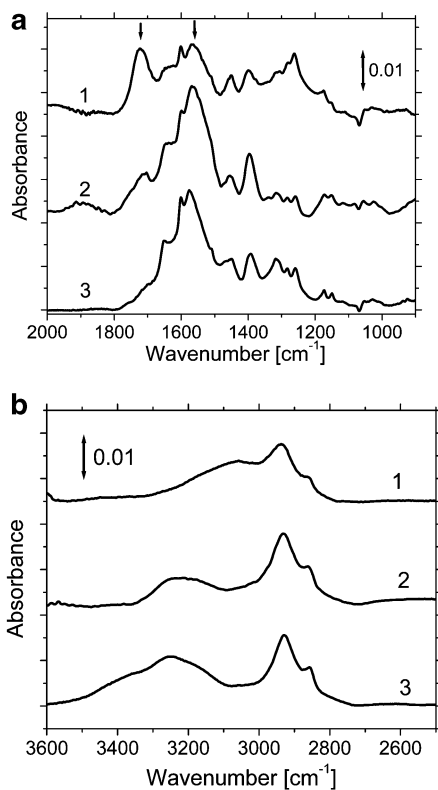


Figure 3. Reflectance FT-IR spectra of PAA-BP/PAH-BP: (1) pH 3/3, (2) pH 3/6, and (3) pH 8.5/8.5 multilayer films on gold substrates: (a) carbonyl region (2000–900 cm^{-1}) and (b) C–H stretching region (3600–2500 cm^{-1}).

N–H stretching peaks of free amine group as well as those of $-\text{NH}_3^+$ group were shown with smaller intensities, which may indicate the existence of free amine and ammonium salt in the multilayer film.

Considering the results from ellipsometry and FT-IR, it is clear that the internal structure of weak polyelectrolyte multilayers can be manipulated by varying the pH of the dipping solution. As depicted in Figure 4, the properties of the films can be summarized as follows: (a) PAA-BP/PAH-BP pH 3/3 multilayer contains a loopy PAA-BP layer that exhibits few ionic bonds because most of the PAA groups exist in their uncharged, protonated COOH state, (b) PAA-BP/PAH-BP pH 3/6 multilayer has both a loop-rich layer with some protonated COOH and free NH_2 and a high degree of internal ion pairing, and (c) PAA-BP/PAH-BP pH 8.5/8.5 contains a loopy PAH-BP layer with unpaired NH_2 and exhibits few ionic bonds.

Photo-Cross-Linking of Polyelectrolyte Multilayers. After the deposition of PAA-BP/PAH-BP multilayers on substrates, the films were photo-cross-linked by UV light. This process allows the preservation of the “swelled” and ionized states of films prepared under different pH conditions since the reaction is photochemical. However, the very nature of cross-linking should result in a small degree of contraction due to network formation of covalent bond structures. The cross-linking process was monitored by UV–vis spectroscopy. Figure 5 shows the UV–vis spectra of 5 bilayers of PAA-BP/PAH-BP pH 3/6 on a quartz slide as a function of UV irradiation time. Under UV irradiation, the absorbance at 295 nm decreased and almost disappeared after 10 min. Benzophenone is excited indirectly to the lowest triplet state ($\pi\pi^*$) by direct absorption into the

singlet state ($\pi\pi^*$) upon UV irradiation.²⁶ The hydrogen atom present in the multilayer film is easily abstracted by benzophenone triplet (3BP*). The benzophenone ketyl radical and a polymer on-chain radical readily recombine to generate a new C–C bond, causing cross-linking within polyelectrolyte films.²⁷

The ellipsometric thickness of the multilayer film typically decreased by about 15–20% after 3 min of irradiation. Further irradiation did not affect the thickness of the films. The refractive index increased by about 0.02 (from 1.5 to 1.52) due to the cross-linking. It should be noted that this photochemical cross-linking process has several advantages over thermally cross-linked systems, for example, amidation reaction of $-\text{COOH}$ and $-\text{NH}_2$ groups, which causes not only thermal destabilization of the films but also a loss of ionizable groups.

Swelling Properties of Multilayer Films. The swelling of cross-linked PAA-BP/PAH-BP films in buffered solutions of pH 3.2 and pH 10 and unbuffered Millipore water (pH 6) was investigated by in situ ellipsometry. Figure 6 shows in situ thickness as a function of time for 5 bilayers of PAA-BP/PAH-BP pH 3/3. Upon immersion in pH 3.2 and 6 solutions, the thickness of the film increased to $\sim 18\%$ and 35% , respectively, because of the adsorption of water. Swelling remains constant during the 20 min of immersion. When the film was immersed into pH 10 solution, the thickness immediately increased to 2.24 times its original dry film thickness (from 25 to 57.5 nm) and then continued to swell up to 20 min to $2.47\times$ (from 25 to 62 nm). It is important to note that the degree of swelling increased as the pH of the solution increased. When PAA-BP/PAH-BP pH 3/3 film were immersed into a solution of pH > 3 , free carboxylic acid groups in the film started to ionize and caused swelling of the film. However, since the pH of solution is larger than ~ 10 , the breakage of interchain ionic bonds occurs, followed by a conformational change of the film to a microporous structure. This type of pH-induced swelling of weak polyelectrolyte films has been investigated previously. Mendelsohn et al.²⁸ reported the fabrication of microporous thin films composed of PAA/PAH deposited from pH 3.5/7.5 by a brief exposure (60 s) to acidic aqueous solutions. The pore size was increased from 100 to 500 nm. The immersion of weak polyelectrolyte multilayer films in highly acidic ($\leq \text{pH } 1.75$) or highly basic ($> \text{pH } 10$) solutions for long periods of time ($> \sim 10$ min) can cause delamination of film, and sometimes the entire film can be dissolved/removed entirely from the substrate to reveal bare substrates.²⁹ In our case, the multilayer films were stable in the solutions of pH 1.75 and pH 10 due to the cross-linking. The cross-linked PAA-BP/PAH-BP pH 3/3 films lost less than 10% of their layers even after immersion in pH 10 solution for 1 day. It is noteworthy that the entire film was removed after 10 min of immersion in pH 10 solution before the photo-cross-linking of the film. The percentage swelling of PAA-BP/PAH-BP pH 3/3, pH 3/6, and pH 8.5/8.5 films after 40 min of immersion in the solutions is shown in Figure 7. In the case of PAA-BP/PAH-BP pH 3/6, the film swelled to about 17–32% in a pH range of 3–10 and started to show increased thickness below pH 3. The low swelling of PAA-BP/PAH-BP pH 3/6 film may be due to the coexistence of free carboxyl

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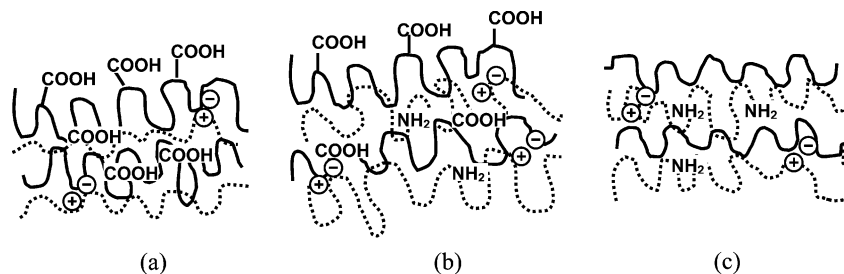


Figure 4. Schematics of the PAA-BP/PAH-BP multilayers at (a) pH 3/3, (b) pH 3/6, and (c) pH 8.5/8.5.

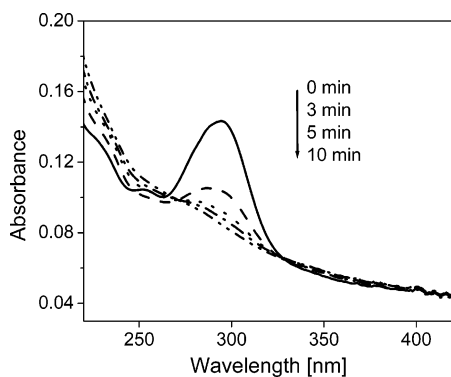


Figure 5. UV-Visible spectra of 5 bilayers of PAA-BP/PAH-BP pH 3/6 on a quartz slide as a function of UV irradiation time.

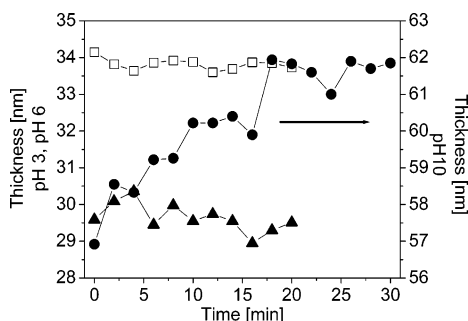


Figure 6. In situ ellipsometric thickness of 5 bilayers of PAA-BP/PAH-BP pH 3/3 as a function of immersion time at pH 3.2 (\blacktriangle), pH 6 (\square), and pH 8.5/8.5 (\bullet).

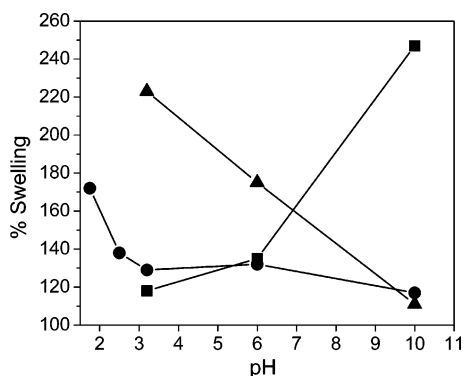


Figure 7. Swelling of PAA-BP/PAH-BP, pH 3/3 (\blacksquare), pH 3/6 (\bullet), and pH 8.5/8.5 (\blacktriangle), in the aqueous solution of pH 1.75-10.

acid groups and free amine groups in the film in moderate amounts as well as the cross-linked units in the films. In the case of PAA-BP/PAH-BP pH 8.5/8.5, it showed an opposite trend compared to PAA-BP/PAH-BP pH 3/3. In a neutral or acidic solution, PAH-BP had increased ionization of polymer chains relative to the high-pH environment in which they were constructed. The film swelled to 1.75 and 2.23 times its original

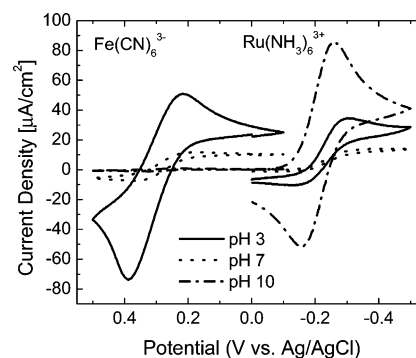


Figure 8. Cyclic voltammograms of electrodes deposited with cross-linked PAA-BP/PAH-BP pH 3/6 (3.5 bilayers, PAH-BP outmost layer) in an aqueous 0.5 M Na_2SO_4 electrolyte solution containing 5 mM either $\text{Fe}(\text{CN})_6^{3-}$ or $\text{Ru}(\text{NH}_3)_6^{3+}$ buffered at pH 3.2 and 10 and nonbuffered at pH 7.

dry film thickness in pH 6 and 3 solutions, respectively, due to the ionization of free amines.

Permselectivity Control of Multilayer Films. From the reflectance FT-IR results, it is clear that the relative amount of free carboxylic acid and amine in the PAA-BP/PAH-BP multilayer films can be controlled by changing the pH of the solution. When these films are subsequently immersed in an acidic or basic solution, amine or acid groups are selectively ionized, resulting in a positive or negative net charge in the film. The membranes then will reject ions of the same sign and transport ions of the opposite sign with a net charge in the film. In other words, these membranes can be either cation-selective or anion-selective (bipolar), depending on the pH of the solution.

Ionic permeability of the PAA-BP/PAH-BP films was investigated under different pH conditions by use of anionic $\text{Fe}(\text{CN})_6^{3-}$ and cationic $\text{Ru}(\text{NH}_3)_6^{3+}$ as redox probe molecules. Since the diameter of the two probe molecules is similar to each other [6.0 Å for $\text{Fe}(\text{CN})_6^{3-}$, 6.2 Å for $\text{Ru}(\text{NH}_3)_6^{3+}$], the differences in transport properties for the two probe molecules to electrode will be affected only by the net charge in the film but not the size of the pore.

Figure 8 shows cyclic voltammograms of electrodes deposited with cross-linked PAA-BP/PAH-BP pH 3/6 (3.5 bilayers, PAH-BP outmost layer) in an aqueous 0.5 M Na_2SO_4 electrolyte solution containing 5 mM either $\text{Fe}(\text{CN})_6^{3-}$ or $\text{Ru}(\text{NH}_3)_6^{3+}$ buffered at pH 3.2 and 10 and nonbuffered at pH 7. All measurements were conducted after 3 min of UV irradiation, followed by immersion of the polyelectrolyte multilayer-coated electrode in the electrolyte solution for 20 min to stabilize the films. The shape and magnitude of voltammograms were significantly affected by the pH of electrolyte solutions. The peak current density resulting from $\text{Fe}(\text{CN})_6^{3-}$ reduction was about 51 $\mu\text{A}/\text{cm}^2$ at pH 3.2, while it decreased ~ 50 -fold with

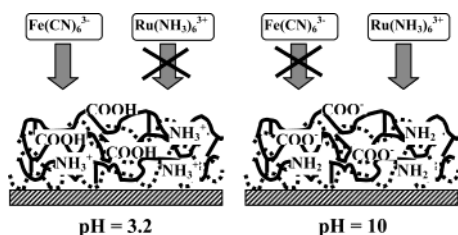


Figure 9. Schematic illustration of the pH-switchable on/off function of the multilayer film. At low pH the film has a net negative charge that excludes anions but passes cations; at high pH it is positively charged and excludes cations but passes anions.

respect to values at pH 10. In contrast, the peak current density from $\text{Ru}(\text{NH}_3)_6^{3+}$ reduction was about $85 \mu\text{A}/\text{cm}^2$ at pH 10, while it decreased to $34 \mu\text{A}/\text{cm}^2$ at pH 3.2. These results clearly demonstrate that PAA-BP/PAH-BP at pH 3/6 multilayer films show *bipolar* pH-switchable permselectivity for both cationic and anionic probe molecules. The film is permeable (on) to the cationic probe but impermeable (off) to the anionic probe at pH 10, that is, due to the deprotonation of free carboxylic acid ($-\text{COO}^-$) at high pH (Figure 9). On the other hand, the film is permeable to an anionic probe but less permeable to a cationic probe at pH 3.2 due to the protonation of free amine ($-\text{NH}_3^+$) at low pH. At pH 7, the film was only slightly permeable to both anionic and cationic probe molecules; peak current density of $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Ru}(\text{NH}_3)_6^{3+}$ was about 12 and $14 \mu\text{A}/\text{cm}^2$, respectively. At pH 7, amine and carboxylic acid groups are fully ionized; therefore, the film excludes both positively charged and negatively charged probes. This behavior was fully reversible to repetitive switching of the pH for up to at least five cycles. It is important to point out that this bipolar or reversible ion selectivity in a single film is a very interesting property for the development of ion-separation membranes.

Furthermore, it was possible to produce multilayer films that are only permeable to one type of probe molecule. Figure 10 shows cyclic voltammograms of electrodes deposited with (a) cross-linked PAA-BP/PAH-BP pH 3/3 (5.5 bilayers, PAH-BP outermost layer), and (b) cross-linked PAA-BP/PAH-BP pH 8.5/8.5 (3.5 bilayers, PAH-BP outermost layer). In the case of PAA-BP/PAH-BP pH 3/3, the permeability of the film to $\text{Ru}(\text{NH}_3)_6^{3+}$ significantly increased (about 2-fold) at pH 7 and 10 due to the ionization of carboxylic acids at high pH range. On the other hand, the membrane showed low permeability of $\text{Fe}(\text{CN})_6^{3-}$ in the pH range of 3.2–10. Increased permeability of $\text{Fe}(\text{CN})_6^{3-}$ at pH 7 and 10 occurs because of swelling of films (240% at pH 10). For PAA-BP/PAH-BP at pH 8.5/8.5 film, it is permeable to $\text{Fe}(\text{CN})_6^{3-}$ at pH 3 and 7 but not permeable to $\text{Ru}(\text{NH}_3)_6^{3+}$ in the pH range of 3.2–10 due to the ionizable amine groups in the multilayer film. It is important to note that even though the PAA-BP/PAH-BP pH 8.5/8.5 film swelled 2.23 times compared to its original thickness, the current density of $\text{Ru}(\text{NH}_3)_6^{3+}$ increased only 1.6-fold compared to that at pH 7. The swelling of the film affects the degree of permeability; however, the ion-selective permeability still can be achieved due to the net ionic charge in the films.

From these results, one important fact, for developing effective ion-selective membranes, is realized. That is, one must control the number of free ionizable groups. It should be enough to promote rejection of oppositely charged ions but not too much to induce swelling of the film. For PAA-BP/PAH-BP pH 3/6 film, the most effective ion selectivity was achieved because

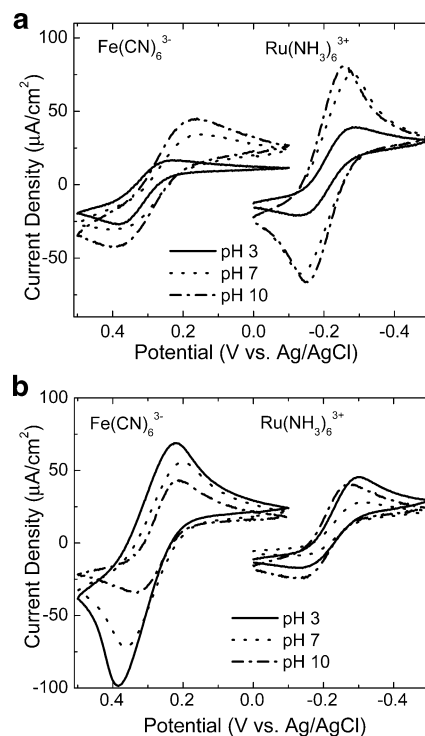


Figure 10. Cyclic voltammograms of electrodes deposited with (a) cross-linked PAA-BP/PAH-BP, pH 3/3 (5.5 bilayers, PAH-BP outermost layer), and (b) cross-linked PAA-BP/PAH-BP, pH 8.5/8.5 (3.5 bilayers, PAH-BP outermost layer), in an aqueous 0.5 M Na_2SO_4 electrolyte solution containing 5 mM either $\text{Fe}(\text{CN})_6^{3-}$ or $\text{Ru}(\text{NH}_3)_6^{3+}$ buffered at pH 3.2 and 10 and nonbuffered at pH 7.

of stable swelling throughout the pH range of 3–10. The cross-linked structure is a key factor for bipolar ion-selective membranes. Due to cross-linking, high permeability can be achieved with ultrathin films (20–45 nm) and the multilayer film maintains its stability in a wider range of pH 3–10 for the solution.

In practical applications, the ion-exchange procedure can be conducted at neutral condition. Therefore, the permeability of $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Ru}(\text{NH}_3)_6^{3+}$ in unbuffered solution (pH of the solution was found to be ~ 7) were compared. Both probe molecules are impermeable for the PAA-BP/PAH-BP pH 3/6 film. On the other hand, only negatively charged $\text{Fe}(\text{CN})_6^{3-}$ is permeable for the PAA-BP/PAH-BP pH 8.5/8.5 film, while only positively charged $\text{Ru}(\text{NH}_3)_6^{3+}$ is permeable for the PAA-BP/PAH-BP pH 3/3 film. Since both carboxylic acid and amine are fully ionized at pH 7, ionic permselectivity in neutral conditions can be achieved depending on whether both free groups exist in the film or only one type of free ionizable group exists.

Conclusion

Bipolar ion-selective multilayer membranes have been fabricated by alternating deposition of PAA and PAH modified with benzophenone groups. It was demonstrated that a pH-switchable membrane can be produced by adjusting the pH of the dipping solution and the stability maintained by cross-linking. Moreover, a highly stable film was prepared.

The multilayers were composed of weak polyelectrolytes that were modified with benzophenone and subsequently photo-cross-linked by irradiation with UV light in less than 5 min. The composition of multilayers was finely tuned by changing

the pH of the dipping solution. When PAA-BP and PAH-BP were deposited from pH 3 solution, the PAA-BP groups exist in their uncharged, protonated COOH state, while the membranes with PAH-BP layers having uncharged, unbounded NH₂ were fabricated by deposition from pH 8.5. When the PAA-BP and PAH-BP were deposited from pH 3 and 6, respectively, the film had a high degree of internal charge pairing as well as both unbounded carboxylic acid and amine groups in the layers. Depending on the ionizable group, the multilayer films showed pH-dependent permselectivity. In the case of multilayers of PAA-BP/PAH-BP pH 3/6, the membranes showed pH-switchable ion transport selectivity or reversible ion selectivity; at low pH, cations are excluded from the film but anions easily penetrate, while at high pH, the opposite behavior is obtained. It was found that the number of ionizable groups in the film as

well as the degree of cross-linking is important to produce effective permselective membranes. Thus, it was possible to vary this permselectivity performance by varying the solution pH or the film pH (*ex situ*) after cross-linking. In the future it should be possible to have a combinatorial approach in the preparation of these membranes with pH, ionic group content, degree of cross-linking, and thickness as parameters.

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