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Charge and Mass Balance in Polyelectrolyte Multilayers

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Abstract: The ion and polymer content of polyelectrolyte multilayers constructed via layer-by-layer deposition have been directly probed using radioanalytical methods. Multilayers were fabricated using salt-containing or salt-free solutions. Charges on polyions quantitatively balance each other. As-deposited multilayers contain no salt ions within a limit of detection of a few ppm. All excess charge, which is reversed on each deposition step, resides at the surface. Surface charge controls the amount of polymer deposited and represents, on average, *one-half* of the charge within a single molecular layer. Internal charge can be regulated following deposition if one of the polyelectrolytes employed is redox-active, such as a polyviologen. Under electrochemical reduction, bulk charge compensation in a polyviologen/poly(styrene sulfonate) multilayer is preserved mainly by cation influx. Residual salt ions accumulate as conformational changes occur during repeated electrochemical cycling. When a thermally labile precursor to poly(*p*-phenylene vinylene) is incorporated as polycation, salt cation uptake is observed when positive charge is thermally eliminated from the multilayer. Evidence for disruption of this structure is observed when the charge density on one of the constituents approaches zero. For typical deposition times, usually up to 1 h, polymer deposition is kinetically irreversible, and the top layer is not stripped from the surface on exposure to its oppositely charged counterpart. These results provide further confirmation of extensive interpenetration and disorder as well as limited mobility within polyelectrolyte multilayers.

Introduction

Constructing films of defined composition has long been a priority of applied polymer science. A recent disclosure by Decher *et al.*[1] of a method to build multilayers of polyelectrolytes has added to the suite of techniques available for the synthesis of thin films: when a surface is exposed alternately to polyelectrolytes of opposite charge, a polymer composite film of uniform thickness is obtained. The potential utility of the method was quickly demonstrated by Rubner et al.[2] who showed that it was possible to obtain thin, uniform electrically conductive films on a variety of surfaces. Combinations of polyelectrolytes with other materials, including proteins,[3] clay minerals,[4] viruses,[5] dendrimers,[6] gold colloid,[7] silica,[8] and other inorganics,[9] have mushroomed... evidence for the flexibility and promise of the technique. Applications have been quick to surface. In addition to the preparation of conducting layers the following have been demonstrated: multilayers containing bound, active enzymes;[10] light-emitting thin films;[11] permselective gas membranes;[12] noncentrosymmetric films for nonlinear optics;[13] selective area patterning;[14] electrochromic films;[15] electrocatalysis;[15a] and sensors.[16]

Some important questions regarding the fundamental structure of polyelectrolyte multilayers, PEMs, have been addressed in recent structural studies.[17] It is now well established that PEMs

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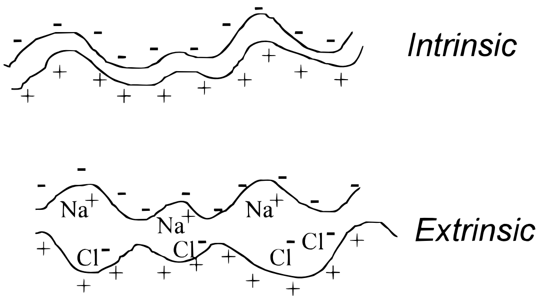
(at least those films composed of polymer molecules only) are quite disordered and interpenetrating.[1c,f] That is, the polymer in a particular layer is dispersed up to 3 or 4 layers away from its nominal location within the thin film. Other questions concern the way in which net charge neutrality is conserved within the structure. Charges on polymer repeat units can be balanced by those on oppositely charged chains or by small ("salt") ions occluded within the film. The two scenarios for charge balance are illustrated below. In one case, which we term *intrinsic* compensation, a polymer positive charge is balanced by a negative charge, also on a polymer. In the alternative mechanism, *extrinsic* compensation, much of the polymer charge is balanced by salt counterions derived from the bathing solution used to construct the multilayers. Preliminary studies of ion content using, for example, XPS, have suggested an absence of ions within multilayers.[15b,18] However, XPS has a poor detection limit and must be performed *ex situ* in ultrahigh vacuum.

Chart 1. Intrinsic vs Extrinsic Charge Compensation



Whether compensation is intrinsic or extrinsic bears directly on the properties and proposed applications of polyelectrolyte multilayers. For example, multilayers containing salt ions should be thicker, less interpenetrating, and individual chains would have more mobility, yielding less stable structures. For electronics applications requiring high electric fields, such as light-emitting diodes,[11] mobile ions would be highly undesirable. Also, entrapment and immobilization via charge is an important way of incorporating smaller "guest" species within "host" films. For applications requiring permselectivity for ions, the permeability is a product of the ionic content within a film and the ionic mobility.

A complete accounting of charge balance includes ascertaining the surface charge of a growing multilayer. Since the interaction between layers is electrostatic, charge reversal as the structure is immersed in polyelectrolyte is a crucial step in ensuring that the surface is primed for the next layer. In this work we determine directly the amount of each polymer within a multilayer, the salt-ion content, and the charge of the outermost polymer layer. Finally, we demonstrate two methods of controlling the salt content within layers, using electrochemically active multilayers, and structures made from a precursor for a popular conjugated polymer.

Experimental Section

The following reagents were used as received: KBr (Fisher, 99.9%), $CaCl_2 \cdot 2H_2O$ (99.9% Fisher), and NaCl (ACS grade, Fisher). $^{45}CaCl_{2(aq)}$ was obtained from Dupont NEN Research products. Poly(styrene sulfonate), PSS,[19] sodium salt ($M_w = 10^5$, $M_w/M_n = 3.4$, Scientific Polymer Products), and poly(diallyldimethylammonium chloride), PDADMA[19] ($M_w = 250\,000-400\,000$, $M_w/M_n = 2.9$), were dialyzed extensively against distilled water using 12 000−14 000 molecular-weight-cutoff (mwco) dialysis tubing. Poly(butanyl viologen dibromide), PBV, was synthesized from 4,4′-bipyridine and 1,4-dibromobutane as described by Factor and Heinsohn.[20] The molecular weight of the product was not determined, but it was dialyzed against distilled water using membrane tubing of 12 000−14 000 mwco. The dialyzed polymer was filtered though 0.45 mm filter membrane. All polymer concentrations are quoted with respect to the polymer repeat unit.

^{14}C-labeled narrow molecular weight distribution poly(*N*-methyl-2-vinyl pyridinium chloride), PM2VP, was prepared by the addition of 30 μL (0.5 mmol) of iodomethane spiked with 1 mCi $^{14}CH_3I$ (Dupont NEN) to 2 mL of tetramethylene sulfone containing 30 mg (0.285 mmol) of poly(2-vinyl pyridine) ($M_w = 102\,000$, $M_w/M_n = 1.07$, American Polymer Standards). The mixture was allowed to stand at room temperature for 20 h and was then warmed to 40 °C for 40 h. The product was precipitated with toluene and thoroughly washed with toluene and ethyl ether. The specific activity of the polymer was 1.5 Ci mol^{-1}. A sample of polymer methylated in an identical manner, with the exception of the radiolabel, was subjected to elemental analysis (Atlantic Microlab, Norcross, GA). Found wt %: C, 47.05; H, 4.87; N, 6.99; I, 41.00. Calc. for $([C_7H_7N]_{0.374}[C_8H_{10}NI]_{0.626})_n$ (i.e., 63% methylation); C, 47.2; H, 4.58; N, 7.22; I, 41.0. The quaternized polymer was dialyzed against dilute HCl, then against water, to convert it to the chloride form.

^{35}S-labeled poly(styrene sulfonic acid) was synthesized by mixing 10.4 mg (0.1 mmol) polystyrene ($M_w = 401\,340$, $M_w/M_n = 1.02$, Aldrich) and 0.10 mL of concentrated H_2SO_4 (98%, Fisher) spiked with 10 mCi $H_2{}^{35}SO_4$ (ICN Radiopharmaceuticals). The mixture was heated in a sealed vial at 90 °C for 72 h. The product was purified by extensive dialysis against distilled water and taken to dryness under vacuum at room temperature. Additional water was not removed under elevated temperature to avoid decomposition. Yield 93%. Specific activity at time of synthesis 7 Ci mol^{-1}. Elemental analysis of unlabeled surrogate sample: found wt %; C, 46.9; H, 4.7; S, 15.4. Calculated for $(C_8H_8SO_3.H_2O)_n$, i.e., 100% sulfonated; C, 47.5; H, 4.95; S, 15.84.

Scintillator plastic for multilayer and proximity detection experiments was 12 × 12 × 3 mm polystyrene (2% cross-linked) containing <1% blue-fluorescing ($\lambda_{max} = 420$ nm) dyes (Kuraray Inc.). The surface of the scintillator was sulfonated by exposure to concentrated H_2SO_4 for 10 min at room temperature.[21] Other substrates were quartz, treated with "piranha" (7:3 mixture of concentrated H_2SO_4 and 30% H_2O_2; *caution*, piranha reacts violently with organic compounds and should not be stored in closed containers) for 10 min, and gold foil, which was polished with a series of alumina powders (Buehler Inc.) ranging from 5 μm to 0.05 μm and then sonicated in distilled water. The gold was also treated with 1 mM aqueous 3-mercapto-1-propanesulfonic acid (sodium salt, Aldrich) for 12 h at room temperature to render a layer of negative charge on the surface.

Multilayers of $^{14}C-PM2VP$ and $^{35}S-PSS$ were prepared by alternately immersing surface-modified gold or scintillator into 10^{-4} M aqueous solutions of the polyelectrolyte for 120 min with intermediate rinses in distilled water. PDADMA/PSS multilayers on all substrates were made using 50 mM polyelectrolyte solutions and 20 min exposure times. Multilayers capped with PDADMA are defined as having 10.5 layer pairs. Redox active, viologen-containing multilayers were prepared from 1 mM solutions of polyelectrolyte (PBV and PSS) in 0.5 M $KBr_{(aq)}$ using 1 h exposure times.

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Scintillation counting[22] was performed in a dark box using a 2″ end-on Hamamatsu R331 photomultiplier (PMT) biased to 1650 V with a Bertan 313B high-voltage power supply. Counts were acquired with a Philips PM 6654C counter/timer interfaced to a computer. Measurements on nonscintillating substrates (i.e., gold foil) were made by bringing the dry sample into contact with scintillator. Standards for polymers and ^{45}Ca were prepared by dispensing a few microliters of solution uniformly over a scintillator and drying. Standard counts were acquired in the same geometry as sample counts. A standard for ^{14}C-acetate could not be prepared in the same manner, due to volatility of the acetate. For use as a reference, it was assumed that a 35 mm-thick layer of solution contributed to the ^{14}C-acetate background count rate (as determined from our prior experiments with ^{14}C-labeled polymers).[23]

Determination of internal and surface ion content was accomplished using multilayers with 10 or 10.5 PDADMA/PSS layer pairs. Modified scintillator was placed in 25 mL 10^{-4} M $CaCl_{2(aq)}$ in a beaker. The beaker was positioned on top of the PMT and the background signal recorded. Twenty microliters of $^{45}CaCl_2$ (7.1 mCi/mL) were then added to give a specific activity of 58.6 Ci mol^{-1}. After the count rate had stabilized, 50 μL of 1.0 M (unlabeled) $CaCl_2$ (a 20-fold excess) was added to self-exchange with the $^{45}Ca^{2+}$. The count rate after this procedure was due only to the $^{45}Ca^{2+}$ in the thin layer of liquid adjacent to the scintillator and was subtracted from all measurements.[24] Acetate ion, $^{14}C-CH_3COONa$ (NEN, 3.1 Ci mol^{-1}), was used to determine anion content. The multilayer-bearing scintillator was added to 8 mL of 2.0 × 10^{-4} M $^{14}C-CH_3COONa$. At the end of the exchange, 50 μL of 1.0 M unlabeled acetate was added to determine the solution background.

Redox active films,[15b] prepared on gold-coated scintillator, comprised eight layer pairs of PBV/PSS. Labeled electrolyte was prepared by spiking 10 mL of 1 mM $CaCl_{2(aq)}$ with 71 μCi $^{45}Ca^{2+}$(specific activity of the electrolyte was thus ca. 7 Ci mol^{-1}). Cyclic voltammetry and potential control of gold-coated scintillator were performed in N_2-blanketed 1 mM $CaCl_{2(aq)}$ using a Princeton Applied Research 362 potentiostat equipped with a Recorder Company 200 XY recorder. Counter and reference electrodes were platinum and silver wire, respectively.

Poly(*p*-xylene-α-tetrahydrothiophenium chloride)$_{(aq)}$, PXT, precursor to PPV was prepared as described previously.[25] Multilayers of PXT and PSS were deposited onto quartz or surface-sulfonated scintillator from solutions containing no salt (the addition of salt was found to induce gelation of PXT). To determine the number of thermally eliminated sites within the multilayer, the PXT/PSS-modified scintillator in 25 mL of 10^{-4} M $CaCl_2$ was spiked with 142 μCi $^{45}CaCl_2$ (producing 57 Ci mol^{-1}). After 1 h of counting, 50 μL unlabeled 1 M $CaCl_2$ was added to exchange cations. The scintillator was then rinsed with distilled water and heated while submerged in water in a sealed vial at 90 °C for a specified time. The scintillator was removed, and the radiometric measurement for cation content was repeated.

UV−vis absorption spectra were recorded on quartz-supported multilayers using a Cary 45 spectrometer. Film thicknesses were estimated by depositing multilayers of polyelectrolytes onto polished silicon wafers (Si 100, from Virginia Semiconductor Inc.) using the same conditions as for other substrates. The surface of the Si was modified, after cleaning with piranha, with 4-aminobutyldimethylmethoxysilane (United Chemical Technologies) to promote adhesion of the first (negative) layer.[17a] Thickness was measured using a Tencor Alpha Step 200 profilometer with a 10 μm stylus and 8 mg of measuring force. The profilometer was calibrated with a 486 Å standard (VLSI Standards Inc.). It has been shown that the substrate has little influence on multilayer buildup as long as hydrophilic surfaces are employed.[1e]

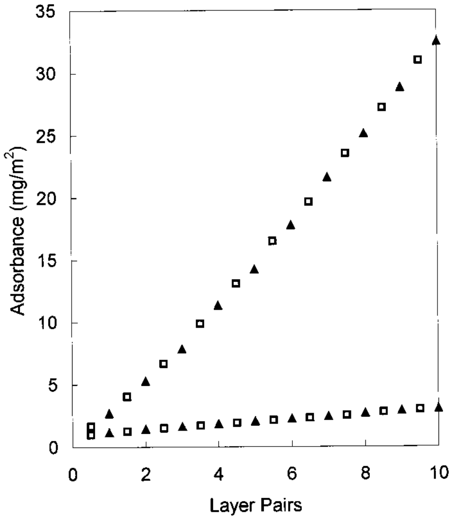

Figure 1. Buildup of a multilayer of PM2VP (squares) and PSS (triangles) on surface-sulfonated polystyrene scintillator from 0.1 M $NaCl_{(aq)}$ (upper curve) and pure water (lower curve).

Results and Discussion

Polymers in Multilayers. Multilayers of ^{14}C-poly(*N*-methyl-2-vinylpyridinium) and ^{35}S-poly(styrene sulfonate) were deposited onto surface-charged polystyrene scintillator or gold substrates from solutions containing no salt or 0.1 M NaCl. The concentration of polymer was 10^{-4} M, which is lower than generally used for PEMs, but above the 5 ppm level that Berndt *et al.*[26] found necessary for surface charge reversal in PSS deposition on positive monolayers. Figure 1 depicts the buildup of 10 layer pairs of PM2VP/PSS on polystyrene. Table 1 summarizes the total amount of *each* polymer deposited, and the average for *each* polyelectrolyte per layer pair. An additional entry in the table includes approximately 2 × 10^{-10} mol negative charges per cm^2 on the polystyrene surface, induced by the substrate sulfonation procedure. The accuracy is ±10% for multilayers deposited from aqueous salt and ±15% for polymer deposited from salt-free solutions.

A strong dependence of multilayer thickness on salt concentration is consistent with prior observations on PEMs.[1e] The coverage of a single, dense monolayer of styrene sulfonate units, ca. 4 × 10^{-10} mol cm^{-2}, may be compared with an increment of ca. 8 × 10^{-11} mol cm^{-2} per component (no salt case), and 8 × 10^{-10} mol cm^{-2} (0.1 M NaCl) for either substrate. Note that the repeat unit of the partially quarternized positive polyelectrolyte (Chart 2) carries a charge of 0.63. When the coverage is normalized for the charge per repeat unit (see Table 1), approximately the same number of polyelectrolyte positive and negative charges exist within the multilayer. Thus, polymer charges are in the appropriate ratio to balance each other without the requirement for additional salt ions. This finding is in contrast to the results of Hoogeveen *et al.*[27] who found, using the same polymers, a 3-fold ratio of positive to negative polymer charge in multilayers. Although different deposition conditions and a silicon substrate were employed, the reason for this discrepancy is not clear.[28] A 1:1 stoichiometry between positive and negative charges was found by Michaels and his group in early work on polyelectrolyte complexes,[29] and more recent

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[22] The maximum counting efficiency for the in situ proximity detection technique is 25%, since half the decay particles go away from the scintillator and half the light generated in the scintillator goes away from the PMT. Counting efficiency ranged from 8 to 20%, depending on the isotope and the geometry.

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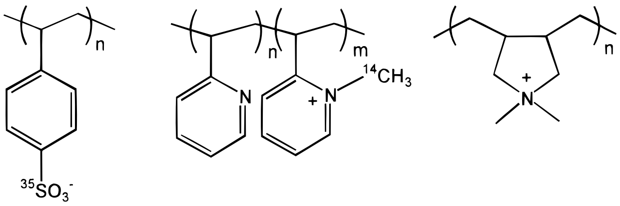
[28] Indirect evidence for 0.5−0.8 salt ion per polyelectrolyte repeat unit was obtained by Schmitt et al. in structural studies on PEMs (see ref 17a).

Table 1. Surface Coverages of Polyions on Polystyrene Scintillator

amount adsorbed[a,b]	PM2VP layers[c] from salt-free solution	PSS layers[d] from salt-free solution	PM2VP layers[c] from 0.1 M NaCl	PSS layers[d] from 0.1 M NaCl
total for 10 layer pairs, mg m^{-2}	1.64	1.04	18.4	15.1
total for 10 layer pairs, mol $cm^{-2} \times 10^{-10}$	12.5	5.7	140	82
average per layer, mol $cm^{-2} \times 10^{-10}$	1.25	0.57	14.0	8.2
total, mol charge $cm^{-2} \times 10^{-10}$	7.9	5.7	88	82
average per layer, mol charge $cm^{-2} \times 10^{-10}$	0.79	0.57	8.8	8.2
total, mol charge $cm^{-2} \times 10^{-10}$, including substrate[e]	7.9	7.7	88	84
first PM2VP layer, mg m^{-2}	0.9		1.7	

[a] Coverages are quoted to an accuracy of ±15% for deposition from no salt and ±10% for deposition from 0.1 M NaCl. [b] For coverage calculations, the mass of the counterion (Cl^- or H^+) in the polymer repeat unit has been included. [c] The repeat unit for PM2VP is $[C_8H_{10}NCl]_{0.63}[C_7H_7N]_{0.27}$. [d] The repeat unit for PSS is $[C_8H_8SO_3]$. [e] Substrate charge is ca. 2×10^{-10} mol charge cm^{-2}.

Chart 2. Structures of Polymers



PSS

PM2VP
(m=0.63, n=0.27)

PDADMA

studies have confirmed this general result for complexes formed by mixing polyelectrolyte solutions.[30]

Multilayer buildup on gold foil (data provided as Supporting Information) was similar to that on polystyrene—the final coverages are the same within experimental error. The only slight difference observed (comparing the 0.1 M NaCl case) was that the first few layers on gold were not a little thinner than the "equilibrium" or steady-state thickness of subsequent layers. Another interesting finding was that the first layer of PM2VP, in the absence of salt, was considerably thicker than subsequent layers (Table 1). This "first layer" effect results from compensation of the high negative charge density on this substrate.

Salt Content within Multilayers and Surface Charge. The finding that polyelectrolyte charges are in 1:1 stoichiometry within multilayers argues against, but does not preclude, the existence of a balanced number of salt ions also within the structure. Direct measurements on multilayers with XPS have not revealed the presence of salt ions within a detection limit of about ±5%.[15b,18] However, these UHV studies were necessarily performed on water-rinsed, dry multilayers emersed from solution. Since multilayers swell in water, ion uptake in aqueous environments is a distinct possibility. We used radiolabeled probes to measure directly the salt ion content within a multilayer. In this study, PDADMA was employed as the positive polyelectrolyte, since it carries a full positive charge per repeat unit, and has been used extensively for PEMs. The experimental approach was to add the radiolabeled probe ions to water in which the multilayer on polystyrene scintillator was immersed. The probe ions would then exchange with any salt ions in the multilayer, leading to an increase in the count rate.

Overcompensation, and therefore *reversal*, of surface charge on polymer adsorption is an essential requirement for polyion multilayer assembly.[1e] In our procedure, exchange of ions within multilayers includes those that are compensating the excess surface charge. If the multilayer is capped with a positive polyelectrolyte (i.e., the final layer is the polycation), anion exchange includes bulk *plus* surface charge. The reverse holds true for polyanion-capped multilayers. Thus, the same exchange experiment, repeated for polyanion and polycation-capped multilayers, provides explicitly the bulk and surface excess polymer charge.

The cationic and anionic small-ion probes were $^{45}Ca^{2+}$ (β-emitter, $E_{max} = 0.255$ MeV) and ^{14}C-acetate (β-emitter, $E_{max} = 0.156$ MeV), respectively. After these ions are added to the system, and ample time permitted for ion exchange equilibration, an excess (20-fold) of unlabeled ion is added to self-exchange with ions within the multilayer and on the surface. The signal (counts per second) is from radiolabel ad(b)sorbed to the multilayer and from a thin layer of liquid adjacent to the scintillator ("solution background").[24] The addition of an excess of unlabeled ion leads to removal of ad(b)sorbed label via self-exchange but does not change the solution background, permitting discrimination between the two.[31]

Four ion probe experiments were performed: two with $^{45}Ca^{2+}$ as probe (Figure 2) and two with ^{14}C-acetate (Figure 3), with either PSS or PDADMA as the outer layer. For the $^{45}Ca^{2+}$ probe and PDADMA as the outer layer, no evidence for extrinsic positive charge (i.e., from salt ions) could be found within the bulk of the multilayer. Using the measured standard deviation of 1.6×10^{-12} mol charge cm^{-2} (scatter in Figure 2), an upper limit of 3.2×10^{-12} mol charge cm^{-2} can be quoted for the 10-layer pair sample. From the measured thickness of a 10 layer-pair sample (245 ± 20 Å), the molecular weight of a PDADMA/PSS repeat unit (310 g mol^{-1}), and assuming a density of 1.2 g cm^{-3}, we estimate a total multilayer[32] charge density of 9.4×10^{-9} mol cm^{-2}.[33] Thus, the upper limit of cations within this multilayer, in terms of percent total charge, is (0.034 ± 0.01)% (25 ppm by weight $^{45}Ca^{2+}$ or Na^+). In other words, positive charge compensation is at least 99.97% intrinsic. The same approach, taken with the acetate ion, indicates no more than 9×10^{-12} negative salt ion charges cm^{-2}, which places an upper limit of 0.10% anionic salt content within the multilayer. The scatter (uncertainty) is greater with ^{14}C-acetate because its specific activity (and thus the count rate) is lower than that for $^{45}Ca^{2+}$.

Since there are no ions within the bulk of the multilayer, the total exchangeable charge resides only at the surface. This

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(29) (a) Michaels, A. S.; Miekka, *G. J. Phys. Chem.* **1961**, *65*, 1765. (b) Bixler, H. J.; Michaels, A. In *Encylcopedia of Polymer Science and Technology*; Interscience: New York, 1969; Vol. 10, p 765.

(30) (a) Dautzenberg, H.; Jaeger, W.; Kötz, J.; Philipp, B.; Seidel, Ch.; Stscherbina, D. *Polyelectrolytes: Formation, Characterization and Application*; Hanser, Munich, 1994. (b) Significant efforts have been made to identify procedures for making nonstoichiometric polyelectrolyte complexes. See, for example, work by Dautzenberg and co-workers (Dautzenberg, H.; Linow, K.-J.; Philipp, B. *Acta Polym.* **1981**, *32*, 225) and Kabanov et al. (Kabanov, V. A.; Zezin, A. B. *Pure Appl. Chem.* **1984**, *56*, 343).

(31) Concerns regarding the possibility of slow exchange kinetics within PEMs may be alleviated by considering the rapid exchange shown in Figures 4 and 8.

(32) Total positive *or* total negative charge density.

(33) This coverage for 10 layer pairs is similar to that for PM2VP/PSS multilayer (see Table 1), which is reasonable, since the same salt concentration and polyanion are used in both and the charge densities (charge per carbon) for PM2VP and PDADMA are close.

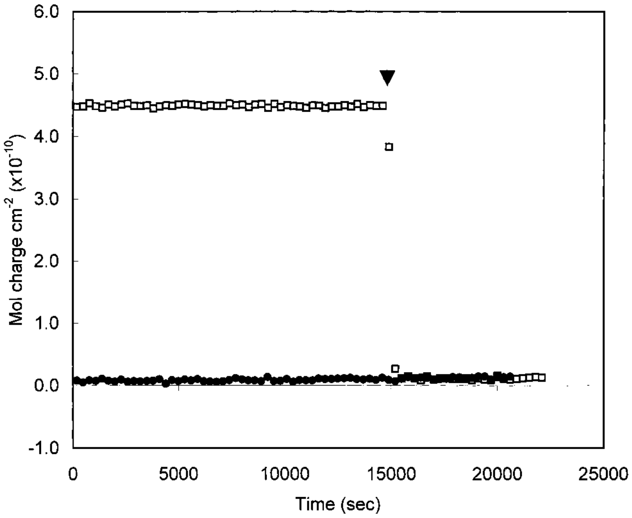

Figure 2. Salt cation content, in terms of areal charge density, of a PDADMA/PSS multilayer deposited from 0.1 M NaCl, with PDADMA as the top layer (circles, 10.5 layer pairs) or PSS as the top layer (squares, 10 layer pairs). $^{45}Ca^{2+}$ (10^{-4} M) has been used as a probe. At the point indicated an excess of unlabeled Ca^{2+} was added to self-exchange salt cations in the PEM. The multilayer contains exchangeable positive charge, at the surface only, when PSS is the top layer. A charge density of 5×10^{-10} cm^{-2} corresponds to a count rate of 68 cps cm^{-2} (raw data). ^{45}Ca specific activity was ca. 60 Ci mol^{-1} or 3.1×10^{11} cps mol^{-1}.

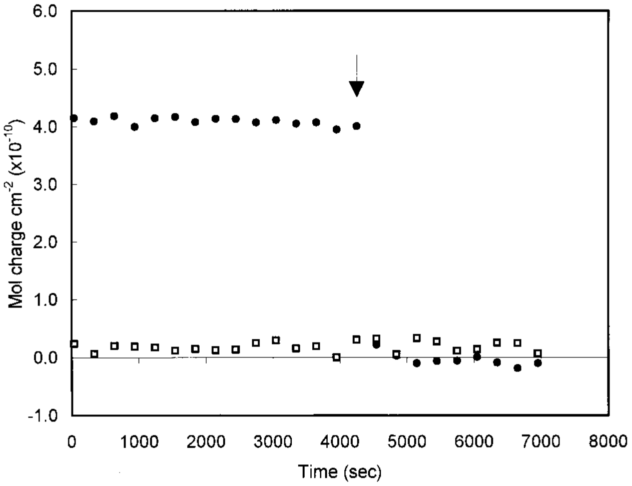

Figure 3. Salt anion content of a PDADMA/PSS multilayer deposited from 0.1 M NaCl, with PDADMA as the top layer (circles, 10.5 layer pairs) or PSS as the top layer (squares, 10 layer pairs). ^{14}C-acetate (2×10^{-4} M) has been used as a probe. At the point indicated an excess of unlabeled CH_3COO^- was added to self-exchange salt anions in the PEM. The multilayer contains exchangeable negative charge, at the surface only, when PDADMA is the top layer. A charge density of 5×10^{-10} mol cm^{-2} corresponds to a count rate of 4.0 cps cm^{-2} (raw data). ^{14}C-acetate specific activity 3.1 Ci mol^{-1} or 8×10^{10} cps mol^{-1} (counting efficiency 7%).

surface charge is revealed when probed with the complementary radiolabeled ion. For PDADMA-capped multilayers, exchange of 4.2×10^{-10} mol cm^{-2} surface counteranions is evidenced in Figure 3. Similarly, Figure 2 shows the presence of 4.3×10^{-10} mol cm^{-2} surface polymer negative charge when $^{45}Ca^{2+}$ ions are self-exchanged. Assuming each individual layer of polymer has 9.4×10^{-10} mol charges cm^{-2} ($= \sigma_{\text{layer}}$), these results correspond to 45% and 46%, respectively, of charge within the top positive or negative layer remaining *uncompensated*. (In the model below these should sum to 100%.)

Viewed from the perspective of the literature on solution polyelectrolyte complexes, certain contradictions exist in the fact that overcompensation of surface charge occurs. Extensive work on PECs holds that 1:1 stoichiometry between + and − charge is the rule.[29,30] Such a balanced economy in the use of charge is exploited in polyelectrolyte "titrations," where a polyion of unknown concentration is determined with a standard polyelectrolyte of the opposite charge.[34] While our results clearly demonstrate stoichiometry within multilayers, the surface bears considerable excess charge. This phenomenon is simply a manifestation of the same forces that control the conformation of polyelectrolytes (and polymers in general) adsorbed to liquid/solid interfaces: an adsorbed polymer can preserve some degrees of freedom by forming loops into solution.[35] According to theory, polyelectrolyte adsorption driven by electrostatics is controlled by the screening between polymer charges and surface charges.[36] The addition of salt, which enhances screening, serves to decrease polymer/surface interactions, permitting more loop formation.

A microscopic consideration of the growth mechanism of PEMs reveals the significance of charge overcompensation. The conformation of the topmost adsorbed polymer layer is a combination of trains contacting the growing multilayer and free loops into solution ("tails", in this analysis, are treated as loops). Under conditions of intrinsic compensation, to propagate a multilayer with a constant "steady state" growth increment per cycle, the following must be true:

increment per layer, $\sigma_{\text{layer}} = (-\text{ve loops}) + (-\text{ve trains}) = (+\text{ve loops}) + (+\text{ve trains})$.

It is also true that the loops of one layer compensate the trains of the next, since we have shown that only one type of salt ion is found at the surface. Thus, +ve trains = −ve loops, and −ve trains = +ve loops, and $\sigma_{\text{layer}} = (-\text{ve loops}) + (+\text{ve loops})$.

The growth is therefore controlled by the loop size or the degree of surface charge overcompensation. This is illustrated in Chart 3, which shows the overlap of polymer charges between positive and negative layers assuming the former overcompensates by 60% of σ_{layer} and the latter by 40%. In this simplified view, no interpenetration between layers of the same charge occurs. In reality, there is interpenetration beyond one layer,[1f,15b] and the excess charge profile that might result is sketched in the chart. For our system loop formation appears to be (fortuitously) similar for both polymers.

Thus, the picture that emerges is one where interface-induced nonstoichiometry enables multilayers to form and propagate. The increment per layer is controlled by the excess surface charge, and, by definition, *the increment equals the sum of the surface charge* for positive and negative layers. One may look to polymer adsorption theory to explain the trends found in multilayer formation. For example, substrate surface charge compensation in the absence of salt, a regime of low screening, is nearly stoichiometric, which leads to low excess charge and very thin subsequent layers. According to the theory of Scheutjens and Fleer,[37] for high-affinity polymer adsorption, a pseudoplateau in the adsorption isotherm exists. Thus, one

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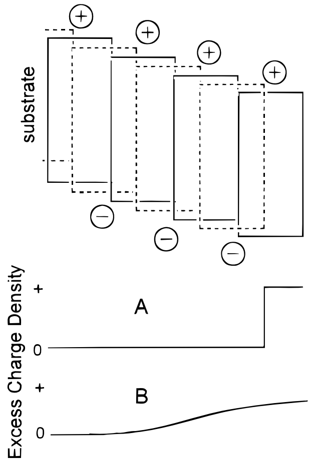
[34] Horn, D. *Prog. Coll. Polym. Sci.* **1978**, *65*, 251.

[35] Fleer, G. J.; Cohen Stuart, M. A.; Scheutjens, J. M. H. M.; Cosgrove, T. Vincent, B. *Polymers at Interfaces*; Chapman and Hall: London, 1993.

[36] (a) Papenhuijzen, J.; van der Schee, H. A.; Fleer, G. J. *J. Coll. Interfac. Sci.* **1985**, *104*, 540. (b) Muthukumar, M. *J. Chem. Phys.* **1987**, *86*, 7230. (c) van de Steeg, H. G. M.; Cohen Stuart, M. A.; de Keizer, A.; Bijsterbosch, B. H. *Langmuir* **1992**, *8*, 2538.

[37] Reference 35, Chapter 4.

Chart 3. Overlap of Charge in Consecutive Positive and Negative Polyelectrolyte Layers Assuming Positive Polymer Overcompensates Surface Charge by 60%



[a] The layers have been displaced vertically for clarity. Positive layers are represented by solid lines, and negative ones are dashed. Excess charge density is depicted in "A" assuming no interpenetration and in "B" assuming interpentration between layers of the same charge.

would not expect a strong dependence of layer pair thickness on polymer concentration, as is observed.

As seen in Figure 1, and as is generally observed, the increment per layer pair is somewhat smaller for the first few layers. The layer thickness increases as the charge per layer transitions from that at the surface of the substrate, σ_{subst}, to the "steady-state" surface (loop) charge of the positive, $\sigma_{+\mathrm{ve}}$, or negative, $\sigma_{-\mathrm{ve}}$, layer. This effect will be more pronounced for substrates with low charge density and/or when using high salt concentrations.

Two significant experiments were performed where a 10-layer pair PDADMA/PSS multilayer, made from solution containing either 0.1 M NaCl or 1.0 M NaCl, was capped with a single layer of $^{14}\mathrm{C}$−PM2VP. First, these modified multilayers were exposed to 10 mM PSS in 0.1 or 1.0 M NaCl for 1 h, as in a normal PSS deposition step. No loss of $^{14}\mathrm{C}$−PM2VP from the surface was measured (within a detection limit of 3% of a monolayer). In other words, no polymer was stripped off the surface by oppositely charged polyelectrolyte to form solution phase complexes: polymers are held tenaciously to the surface even in the presence of strongly binding solution species.

A second experiment probed the thermodynamic reversibility of adsorbed polymer. $^{14}\mathrm{C}$−PM2VP-capped multilayers were exposed to 10 mM PDADMA in 0.1 and 1.0 M NaCl. No exchange of surface (labeled) with solution (unlabeled) polymer was observed for exposure times up to 2 h. Partial exchange only (about 20%) was observed after several days. This is direct evidence that the polyelectrolytes on the multilayer are *irreversibly* absorbed, i.e., the process is under kinetic control. Slow kinetics and incomplete displacement/exchange is generally observed for adsorbed polyelectrolytes,[38] although the presence of salt tends to accelerate the process. Since the layers in a PEM are interpenetrating, one would expect exceptionally slow exchange kinetics. These findings do not rule out mobility of a polymer molecule in the *plane* of the surface once it has attached, indeed, some degree of movement is required for polymer segments to compensate all surface charges. One may envisage transport of short runs of polymer on localized, uncorrelated scale (inchworm style).

It should be noted that the ion probe results obtained here employed low solution salt concentration. These conditions approach, in the limit, those typically employed for PEM formation, since a rinse in pure water is the final step in a deposition cycle. It is possible that the PEM counterion content becomes significant at much higher salt concentration. Sukhorukov et al. were able to control the thickness of PEMs with postdeposition "annealing" in solutions of different ionic strength.[39] It would not be possible to extend radiochemical methods to highly concentrated salt solutions, since the specific activity of the label would decrease proportionately. Another caveat is that component polyelectrolytes in our study were deposited under similar conditions, whereas PEMs have also been made from various combinations of salt concentration. For synthesis under "asymmetric" conditions of salt strength, or other variables such as polymer chain flexibility (polymer/inorganic composites represent an extreme of this condition) or degree of dissociation, charge may not be intrinsically compensated. We have no data on polymer/particle multilayers but we are able to make some predictions assuming compensation remains intrinsic. For example, if a positive polyelectrolyte and a particle with a negative surface charge were employed, the coverage of particle per layer, Γ (g cm^{-2}), would be given by $\Gamma = \sigma_{\mathrm{layer}}/A_{\mathrm{sp}}\sigma_{\mathrm{surf}}$, where A_{sp} is the specific surface area (cm^2 g^{-1}) and σ_{surf} is the surface charge density of the particle (moles charge cm^{-2}). For negatively charged plates, such as clay minerals,[4]

$$\sigma_{\mathrm{layer}} = n_{-\mathrm{ve}} 2\sigma_{\mathrm{surf}}$$

where $n_{-\mathrm{ve}}$ is the number of layers of negative plate deposited *per cycle*. In other words, it is possible to have apparent multilayer deposition of particles on a single exposure. Some polymer mobility *along* the surface would be required.

Ion Transport in Redox Multilayers. We have not been able to detect any salt ion in as-made multilayers. However, if the charge on any of the constituent polyelectrolytes can be manipulated *after* multilayer construction, it is quite possible that salt ion content can be varied. For example, we recently described a multilayer incorporating an electrochemically active polyviologen polycation.[15] Two consecutive electrons reduce the viologen moiety first to the (purple) cation radical and then to the (colorless) neutral form.[40] To maintain a net zero electrical charge within the thin film, compensation of electrons injected into the structure may be accomplished by losing anions from the multilayer, viz

$$[(^1/_2\mathrm{PBV}^{2+})/(\mathrm{PSS}^-)_x(\mathrm{A}^-)_{1-x}]_y + nye^- \rightarrow [(^1/_2\mathrm{PBV}^{(2-2n)+})/(\mathrm{PSS}^-)_x(\mathrm{A}^-)_{(1-x-n)}]_y + ny\mathrm{A}^- \quad (1)$$

where PBV^{2+} and PSS^- are PBV and PSS repeat units, respectively. Here, x is between 0 and 1, y is the number of layer pairs, and n is the number of electrons transferred per layer pair. A^- is an anion that, together with the negative charge on the PSS, balances the positive charge. Alternatively, cations may be gained from the solution.

$$[(^1/_2\mathrm{PBV}^{2+})/(\mathrm{PSS}^-)]_y + nye^- + ny\mathrm{C}^+ \rightarrow [(^1/_2\mathrm{PBV}^{(2-2n)+})/(\mathrm{PSS}^-)\mathrm{C}^+_n]_y \quad (2)$$

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(38) (a) Pefferkorn, E.; Elaissari, A. J. *Coll. Interfac. Sci.* **1990**, *138*, 187. (b) Tanaka, H.; Ödberg, L.; Wågberg, L.; Lindström, T. *J. Coll. Interfac. Sci.* **1990**, *134*, 229. (c) Tanaka, H.; Swerin, A.; Ödberg, L. *Langmuir* **1994**, *10*, 3466. (d) Hoogeveen, N. G.; Cohen Stuart, M. A.; Fleer, G. J. *J. Coll. Interfac. Sci.* **1996**, *182*, 146.

(39) Sukhorukov, G. B.; Schmitt, J.; Decher, G. *Ber. Bunsen-Ges. Phys. Chem.* **1996**, *100*, 948.

(40) Bird, C. L. *Chem. Soc. Rev.* **1981**, *10*, 49.

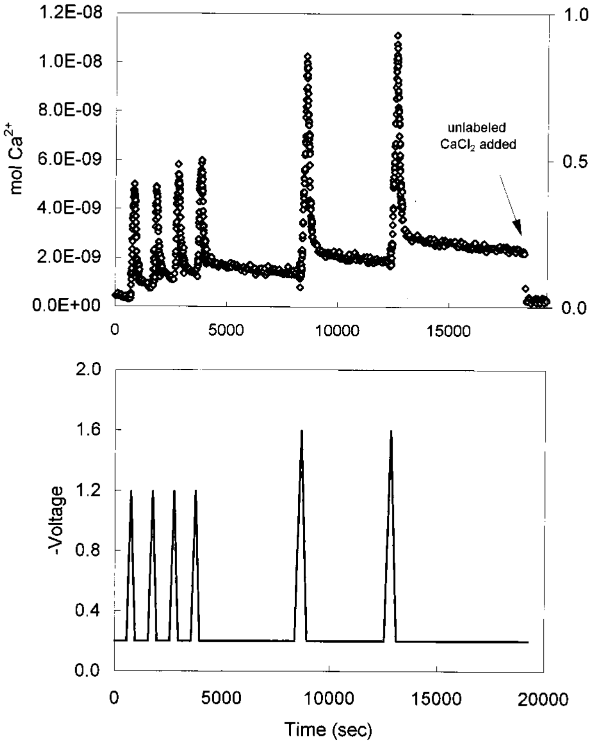

Figure 4. Ca^{2+} ion content (upper trace) of an eight layer-pair PEM of PBV/PSS, deposited from 0.5 M KBr, cycled electrochemically on gold-coated plastic scintillator under N_2 in 1 mM $^{45}CaCl_2$ using the potential:time profile depicted in the lower trace. The charge density of the PEM is ca. 1.5×10^{-9} mol layer^{-1} cm^{-2}. The first four cycles are in the one-electron reduction regime of PBV, whereas the last two are two-electron reductions. Scan rate 5 mV s^{-1}.

where C^+ is a cation. A combination both cation and anion transport is also possible. Assuming polymers remain trapped within multilayers, if no anions are occluded within the structure, the only option would be cation uptake as in eq 2.

To elucidate the ion transport mechanism within these redox multilayers we constructed a small electrochemical cell which comprised a square (1 cm × 1 cm) polystyrene tubing affixed to a plate of plastic scintillator covered with a thin (150 nm) layer of gold (see Supporting Information). The gold, bearing a multilayer of PBV/PSS, served as the working electrode and was thin enough to permit easy passage of β-particles from ^{45}-Ca^{2+} probe cations. Using this "E-Rad" cell, we were able to detect simultaneously the electrochemical response of the multilayer and its uptake/release of $^{45}Ca^{2+}$.

The cyclic voltammetry (CV) for the first reduction step from a eight-layer pair assembly of PBV/PSS immersed in 1 mM $CaCl_2$ (provided as Supporting Information) shows anodic and cathodic peaks which are broader and more separated than the electrochemical response observed in sodium or potassium salts,[15b] indicating slower charge transfer when Ca^{2+} is employed as counterion. The radiochemical signal for this multilayer and the corresponding profile of applied potential are shown in Figure 4 for a CV scan rate of 5 mV s^{-1}. In Figure 4, four scans to the one-electron reduction regime of PBV are followed by two cycles to potentials required for two-electron reduction. Each ramp is separated by a rest period. Figure 5 depicts the result of excursion over the same potential ranges, but at a slower rate (1 mV s^{-1}), providing for greater precision in the radioanalytical data. In Figures 4 and 5 it is clear that calcium ions are the main contributors to ion flux. As expected, for each one-electron reduction approximately $^1/_2Ca^{2+}$ enters the multilayer. The two-electron reduction is not as chemically reversible as the initial reduction,[40] we thus limited the number of scans more negative than −1.2 V. It is also evident that on reoxidation of the PBV radical cation, calcium egress is combined with anion (Cl^-) ingress, leaving both salt ions within the multilayer after a cycle.

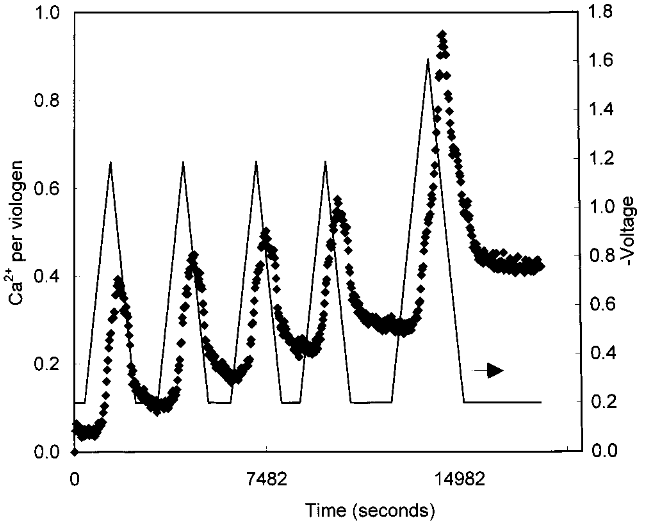

Figure 5. Ca^{2+} content of PEM under electrochemical control as in Figure 4. Scan rate 1 mV s^{-1}.

The residual salt content is at a pseudo steady-state level, since only a small loss in $^{45}Ca^{2+}$ is observed during the waiting period. An interesting feature of repeated cycling is that Ca^{2+} (and thus Cl^- also) continues to build up within the multilayer: on reduction, Ca^{2+} migration into the multilayer continues to be favored over Cl^- expulsion. The charge within this redox multilayer is thus controlled by the applied potential *and* by the number of electrochemical cycles. Clearly, there are morphological changes occurring within the multilayer. It may be inferred that the residual Ca^{2+} and Cl^- ions are contained within extrinsically compensated regions of polyelectrolyte that do not regain contact with the oppositely charged component. (If intrinsic compensation were reestablished, the salt counterions would be free to move back into bulk solution under a large concentration gradient.) This segregation of charge will allow the multilayer to act as a host for small cationic or anionic "guest" species. The residual ion content is under kinetic control since more Ca^{2+} remains with a slower scan rate (compare Figures 4 and 5). Presumably, longer contact of sulfonated segments of PSS with Ca^{2+} during reduction permits more PSS rearrangement into persistent extrinsic phases.

At the end of each experiment (as with all the in situ proximity detection experiments) a large excess of unlabeled Ca^{2+} is added to determine the background. As shown in Figure 4, $^{45}Ca^{2+}$ ions within the multilayer are rapidly self-exchanged.

Our results may be compared to mass transport studies on poly(viologen)/PSS complexes performed by Ostrom and Buttry.[41] Using the quartz microbalance, it was shown that the ion responsible for transport during redox activity of a poly(xylyl viologen), PXV, complex (but not a multilayer) with PSS could be controlled by the ratio of polyanion to polycation within the complex.

Ion Balance in Multilayers Containing Precursor to Poly(phenylene vinylene). An alternative approach to controlling polyelectrolyte charge involves constructing multilayers from the precursor to poly(*p*-phenylene vinylene), PPV, a conjugated polymer which has found extensive use in light-emitting thin

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[41] Ostrom, G. S.; Buttry, D. A. *J. Phys. Chem.* **1995**, *99*, 15236.

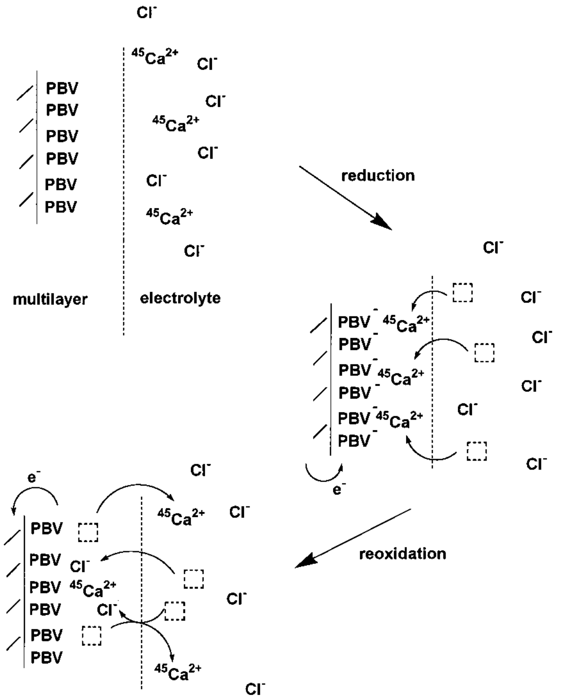

Figure 6. Proposed ion transport in PBV/PSS PEM during electrochemical cycling.

films.[11,42] The precursor, PXT, a positive polyion, is converted to the final conjugated polymer via thermal elimination of tetrahydrothiophene (THT) and acid HA.[25b,43] If PSS is used in conjunction with PXV, counterion A^- is the sulfonate group of PSS and is therefore immobile. HA, which would evolve in the standard processing of PPV thin films, is trapped within the multilayer. If the multilayer were allowed to come into contact with an aqueous solution of ions, ion exchange could occur. Here, our PXT/PSS multilayer films were eliminated by heating in 10^{-4} M aqueous $CaCl_2$, providing ample opportunity for continuous ion exchange. The overall transformation is represented by

$$[PXT^+/PSS^-]_y + {}^1/_2yCa^{2+} \rightarrow [PPV/PSS^{-1}/_2Ca^{2+}]_y + yTHT + yH^+ \quad (3)$$

Protons do not remain within the multilayer since they are present in much lower concentration than Ca^{2+}, and calcium exhibits a strong affinity for sulfonate sites in ion exchangers.

The progress of elimination was monitored by UV−vis absorption spectroscopy. As seen in Figure 7, the intensity of absorption bands between 300 and 400 nm increases as conjugation develops along the PPV backbone.[25b,43] At the very last stages of elimination (not observed here) these bands coalesce into a broad, red-shifted absorption thought to arise from exciton formation over several conjugated units.[44] The positive salt content, determined with $^{45}Ca^{2+}$ exchange as above, may be deduced from the exchange summarized in Figure 8. Virtually no salt ion is present in the as-constructed PXT/PSS multilayer (10.5 layer pairs, PXT on top). A small amount of elimination (ca. 3%) occurs during film processing at room temperature. After 1 h heating at 90 °C in aqueous solution the multilayer contains 35 × 10^{-10} mol cm^{-2} exchangeable (extrinsic) charges. Using the measured thickness of 230 Å for a similar film on silicon, assuming a density of 1.2 g cm^{-3} and a molecular weight per PXT/PSS repeat unit of 374 g mol^{-1}, there should be approximately 74 × 10^{-10} mol charge cm^{-2} in the nascent multilayer. After heating for 1 h at 90 °C the film is thus almost half eliminated. Since the elimination was carried out in water, there will probably be other side-reactions, such as displacement of THT by hydroxyl groups. This process will also remove positive charge from PXT but will not affect the conjugation length.

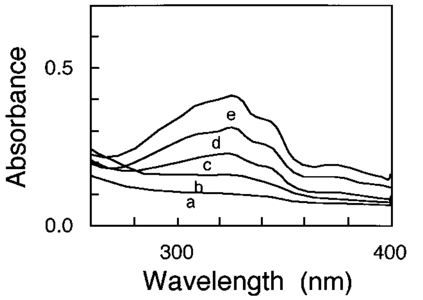

Figure 7. UV−vis absorption spectra of a 10.5 layer-pair PXT/PSS multilayer on quartz recorded after (a) 0 h; (b) 0.25 h; (c) 1 h; (d) 2 h; and (e) 6 h thermal elimination at 90 °C.

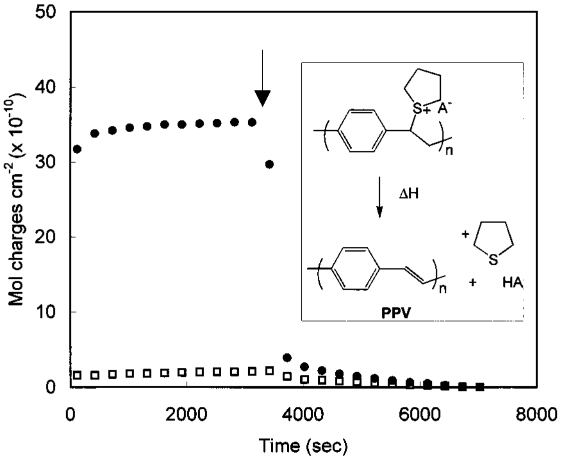

Figure 8. Cation content, in terms of areal charge density, of a 10.5 layer-pair (PXT on top) PEM following 0 h (squares) and 1 h (circles) elimination at 90 °C. The PEM was allowed to equilibrate with 10^{-4} M $^{45}Ca^{2+}$ and, at the point indicated, labeled Ca^{2+} was self-exchanged with an excess of unlabeled Ca^{2+}. Inset: thermal elimination scheme for PXV.

The heating times in Figure 7 range up to 6 h. We discovered that attempts at elimination beyond this time resulted in a decrease in the absorption intensity and a corresponding decrease in apparent charge content. We speculate that when the multilayer approaches complete elimination the charges on the PXT(PPV) are diminished to a point where there is no longer sufficient electrostatic interaction to hold the multilayer together and the structure disassembles, the PSS dissolving into the aqueous phase: weak intermolecular van der Waals forces are not enough to overcome the solvation energy for PSS and the unfavorable mixing free energy of PPV (neutral, hydrophobic) and PSS (charged, hydrophilic). This would represent the first example of thermally programmed PEM “deconstruction”. Presumably the same would happen with the PBV/PSS redox multilayer if it were exposed to a sufficiently negative potential for a long time. An interesting parameter to establish accurately would be the minimum charge density on a polyelectrolyte required to hold a multilayer together.

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(44) Obrzut, J.; Karasz, F. E. *J. Chem. Phys.* **1987**, *87*, 2349.

In contrast to Figures 7 and 8, elimination of PXT in multilayers for light-emitting device fabrication is accomplished under vacuum. There is no ion exchange possible and no prospect for dissolution of PSS. The negative charges are neutralized by protons.

In conclusion, by radiolabeling all possible charged components—polyelectrolytes and counterions—within a PEM, we have shown that, under the conditions employed, no salt ions reside within the multilayer, and charge is balanced by polymer segments. The surface charge, σ, which is reversed on each deposition step, has been determined directly and controls the increment of polymer added per cycle. Multilayer formation can be viewed as a method of "amplifying" σ by the number of layer pairs, and is thus an indirect method of establishing surface charge: multilayer charge density $= y(\sigma_{+\mathrm{ve}} + \sigma_{-\mathrm{ve}})$. We have shown that postdeposition modifications of internal charge, using, for example, electrochemistry or thermally eliminated sulfoniums, permits the introduction of small ions from solution. Active tuning of internal charge in PEMs would be useful in applications requiring controlled permeability.

Acknowledgment. The authors gratefully acknowledge support provided by Grants DMR 9414289 and DMR 9727717 from the National Science Foundation.

Supporting Information Available: Table of surface coverages of polyions on gold and figures of E-Rad cell for electrochemical and radiochemical measurements, buildup of a multilayer of PM2VP and PSS on gold, viologen repeat unit electrochemistry, and cyclic voltammetry of an eight-layer pair PEM of PBV/PSS (5 pages, PDF/print). See any current masthead page for ordering and web access instructions.

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