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Diffusion of Sites *versus* Polymers in Polyelectrolyte Complexes and Multilayers

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ABSTRACT

It has long been assumed that the spontaneous formation of materials such as complexes and multilayers from charged polymers depends on (inter)diffusion of these polyelectrolytes. Here, we separately examine the mass transport of polymer molecules and extrinsic sites – charged polyelectrolyte repeat units balanced by counterions – within thin films of polyelectrolyte complex, PEC, using sensitive isotopic labeling techniques. The apparent diffusion coefficients of these sites within PEC films of poly(diallyldimethylammonium), PDADMA, and poly(styrene sulfonate), PSS, is at least two orders of magnitude faster than the diffusion of polyelectrolytes themselves. This is because site diffusion requires only local rearrangements of polyelectrolyte repeat units, placing far fewer kinetic limitations on the assembly of polyelectrolyte complexes in all their forms. Site diffusion strongly depends on the salt concentration (ionic strength) of the environment and diffusion of PDADMA sites is faster than PSS sites, accounting for the asymmetric nature of multilayer growth. Site diffusion is responsible for multilayer growth in the linear *and* into the exponential regimes, which explains how PDADMA can mysteriously “pass through” layers of PSS. Using quantitative relationships between site diffusion coefficient and salt concentration, conditions were identified that allowed the diffusion length to always exceed the film thickness, leading to full exponential growth over three orders of magnitude thickness. Both site- and polymer diffusion were independent of molecular weight, suggesting that ion pairing density is a limiting factor. Polyelectrolyte complexes are examples of a broader class of dynamic bulk polymeric materials that (self-) assemble *via* the transport of crosslinks or defects rather than actual molecules.

Keywords: coacervate, layer-by-layer, exponential, linear, mechanism

INTRODUCTION

Polyelectrolyte complexes are made by mixing oppositely charged polyelectrolytes, either in bulk solution¹ or sequentially at interfaces.² Association between oppositely-charged repeat units is driven by the loss of counterions to solution³ and by dehydration (loss of water molecules).⁴ Diffusion in and among polymers, already known to be slow, becomes even slower during complexation due to extensive ion pairing between polyelectrolytes. Early work using luminescence quenching and fluorescence explored the kinetics of polyelectrolyte exchange in particles of nonstoichiometric polyelectrolyte complexes.⁵

When the mechanism for layer-by-layer assembly of “multilayers” of polyelectrolytes was first considered, it was immediately assumed that the slow (inter)diffusion of polyelectrolytes should place severe restraints on the kinetics of polymer assembly.² Hence, it is accepted that nonequilibrium structures should result from sequential adsorption of polyelectrolytes. These kinetic limitations lead to the familiar “fuzzy” layering seen in many multilayer systems.⁶ Within these systems, a polyelectrolyte repeat unit can be compensated either by an oppositely charged repeat unit (intrinsic site) or by a counterion (extrinsic site) (Scheme 1).

Scheme 1. Intrinsic sites are pairs, Pol⁺/Pol⁻, of cationic and anionic polyelectrolyte repeat units. In extrinsic sites the polyelectrolyte charge is compensated by a counterion. Nonstoichiometry of Pol⁺ and Pol⁻ requires additional counterions to balance the polyelectrolyte in excess. The structures are poly(diallyldimethylammonium), PDADMA, and poly(styrene sulfonate), PSS.

Later, with the discovery of multilayers which grow “exponentially” in thickness,⁷ some classes of polymers were assumed to diffuse more rapidly within a thin film of complex as it forms, allowing access to the entire film rather than just a surface region.⁸ This interpretation was revised to show that smaller chains could diffuse throughout the whole film,⁹ while larger ones were thought to cause restructuring in the underlying film.¹⁰ Because multilayers are essentially ultrathin films of polyelectrolyte complex¹¹ they provide the small diffusion lengths needed to model extremely small diffusion coefficients on a reasonable time scale. Thus, several polyelectrolyte complex systems, deployed using the multilayer format, have been used for quantitative measurements of diffusion coefficients.¹²

Many techniques have been employed to investigate diffusion within multilayers. Atomic force microscopy (AFM) was used to study salt-induced changes in surface morphology to follow diffusion at the surface.^{12a, 13} Using fluorescently-labeled polyelectrolytes, the mobility on top of, or within, the film can be measured by fluorescence recovery after photobleaching (FRAP).^{12b, e, 14} Neutron reflectometry (NR) uses deuterated polymer inserted within the film at defined layers,^{12d, e, 15} or within deuterated blocks,^{12c, 16} to study diffusion. Other techniques used in kinetic studies include neutral impact collision ion scattering spectroscopy (NICISS) which requires a heavy atom-labeled polymer,¹⁷ quartz crystal microbalance (QCM),^{12g-j, 18} attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR),¹⁹ as well as traditional FTIR.²⁰

This wide selection of techniques gives a wide range of polyelectrolyte diffusion coefficients, ranging from 10^{-9} to 10^{-20} $\text{cm}^2 \text{s}^{-1}$ due to the great number of variables, which include polymer composition, molecular weight, salt concentration, pH, and temperature. Contradictions were seen even for the same system. For example, the mean diffusion coefficient for polymers judged from the smoothing of topographical features in microscopy images of PDADMA and PSS films^{12a} was orders of magnitude faster than diffusion estimated from the mobility of layers of deuterated PSS observed by neutron reflectivity.¹⁵

Though little convergent data has resulted from the variety of polyelectrolytes and techniques employed, the most consistent result is the importance of the solution concentration of salt in which the complex is immersed. Higher salt concentrations accelerate diffusion, in line with earlier studies on the rates of complexation, compaction and interchange in complexes precipitated from bulk solution.²¹

The aim of the present work was to clarify the diffusion mechanism(s) by monitoring mass transport of both ions and polymer molecules. To achieve this, isotopic labeling was used to provide sensitive and unambiguous tracking of diffusing species within uniform, smooth starting films of polyelectrolyte complex.

EXPERIMENTAL SECTION

Materials. Wide molecular weight distribution PDADMA (PDADMA500, MW = 400 000 – 500 000 g mol⁻¹), poly(4-styrenesulfonic acid) (PSSH, MW = 70 000 g mol⁻¹) and deuterated sulfuric acid (D₂SO₄, sulfuric acid, 96 – 98 wt%) were from Sigma-Aldrich. PSS was neutralized with NaOH to give PSS79 (MW = 79 000 g mol⁻¹). Sodium chloride (NaCl, Fisher), sodium sulfate (Na₂SO₄, Fisher), concentrated sulfuric acid (J.T. Baker), and hydrogen peroxide (30% solution, Macron) were used as received. Protiated narrow molecular weight distribution (MWD) PSS (or H-PSS) was obtained from Scientific Polymer Products, Inc.

Table 1. Poly(styrene sulfonate) polymers used, mass- and number-average molar masses, and polydispersity indices (PDI = M_w/M_n).

Polymer	M_w (g mol ⁻¹)	M_n (g mol ⁻¹)	M_w/M_n
PSS8	7 950 ^a	7 200	1.11
PSS35	34 700 ^a	29 900	1.16
PSS127	126 700 ^a	108 200	1.17
PSS262	262 200 ^a	218 400	1.20
PSS588	587 600 ^a	557 600	1.05
D-PSS116	116 300 ^b	114 600	1.02

^a manufacturer-provided mass. ^b measured mass.

Deuterated polystyrene-d₈, (D-PS, Polymer Source, M_w = 56 700 g mol⁻¹, M_w/M_n = 1.09) was sulfonated to obtain D-PSS (deuterated PSS, D-PSS116) with M_w = 116 300 g mol⁻¹. Radioisotopes, ²²Na⁺ as ²²NaCl, and sulfur-35 labeled sodium sulfate were obtained from PerkinElmer. ²²Na⁺: half-life 950 days, positron, γ -emitter, $E_{\max}$ = 546 keV; provided as a solid of 100 μ Ci with a specific activity of 630 Ci g⁻¹ was dissolved in 1 mL of water to obtain the stock solution. ³⁵S in Na₂³⁵SO₄: half-life 87.4 days, β -emitter, $E_{\max}$ = 167 keV was provided as a stock solution of 1 mCi in 1 mL of water with a specific activity of 1494 Ci mmol⁻¹. Double-side polished silicon 100 wafers were obtained from Okmetic, Inc.. Deionized water (Barnstead, 18 M Ω E-pure) was used to prepare all solutions.

Sulfonation of Polystyrene. The sulfonation process was performed according to Coughlin et al.²² Briefly, 0.2 g of D-PS powder was mixed with 10 mL D₂SO₄ in a capped scintillation vial, which was placed in an oil bath pre-heated to 90 °C. The contents of the vial, equipped with a stir bar, were mixed vigorously. Stirring was stopped every hour and the vial was shaken to dissolve the powder stuck on the walls. The reaction was stopped when all the polystyrene powder was dissolved (which took around 4 h) and the solution was poured into ice water. The mixture was then dialyzed against water using 3 500 molecular weight cutoff dialysis tubing (SnakeSkinTM, Thermo Scientific) for about 48 h until the pH of the outer solution was above 3. The solution was then neutralized with NaOH and divided into 25 mL aliquots for lyophilizing to yield a white powder. The yield was around 90%. This procedure leads to 100% sulfonation with about 93% para and 7% meta substitution on the phenyl rings.²²

PEMU Buildup, Treatment and Characterization. PEMUs were built on double-side polished silicon wafers which were cleaned by soaking in 70:30 H₂SO₄:H₂O₂ “piranha” solution for 15 – 20 min, rinsed in deionized water and dried under a stream of nitrogen. Films used in the

diffusion and kinetic experiments were made with the aid of a robot (Stratosequence V, NanoStrata Inc.). Wafers were mounted on shafts rotating at 180 – 200 rpm and dipped consecutively in beakers containing around 50 mL of the polyelectrolyte solutions (10 mM polymer, with respect to the monomer units, in 1 M NaCl) for 5 min followed by 3×1 min dips in beakers containing deionized water. Each dip in polyelectrolyte solution followed by the rinses in water constitutes a “layer”. Films were built up to 20 or 40 layers depending on the experiment and dried with a light stream of nitrogen when finished. They were then cycled between 2 M NaCl for 30 min and 10 mM PSS in 1 M NaCl for 5 min according to our previously described technique to obtain stoichiometric homogeneous films – the starting platform for the diffusion experiments.²³ The notation (PDADMA/PSS)_n is used to refer to the films with “n” indicating the number of bilayers. Unless stated otherwise, PDADMA500 and PSS79 were used for the buildup and cycling of the films. Film thickness was measured with a Gaertner Scientific L 116 B Autogain ellipsometer equipped with a 632.8 nm laser at an angle of 70° and the refractive index was fixed at 1.55. Thicknesses were measured under dry conditions by performing the measurement in a chamber purged with dry nitrogen.

For the films built in the experiment comparing changes in the buildup technique, a manual process was used: after cleaning Si wafers, they were attached to cross-locking tweezers and dipped in solutions for the required duration. After immersion in polyelectrolytes, films were always rinsed for 3×1 min in beakers containing fresh deionized water.

After buildup, or after each layer in the buildup mechanisms experiment, films were dried with a light stream of nitrogen. For FTIR, they were held at 15° from the perpendicular to the incident beam (to avoid interference fringes) in a Thermo Nicolet Avatar 360 equipped with a DTGS detector. The spectra were acquired and analyzed using EZ-OMNIC software. During the layer-by-layer manual buildup experiment, the back of the double-side polished Si wafer was cleaned with 2.5 M KBr to remove any polyelectrolyte complex followed by rinsing with deionized water and drying. The dry thickness at each layer was obtained by ellipsometry.

Imaging of as-made and cycled films was performed using Scanning Electron Microscopy (SEM). An FEI Nova NanoSEM 400 at a voltage of 5 kV and a working distance of 5 mm was employed using a through lens detector with field immersion. A Cressington HR 208 sputter coater was used to coat samples with a 4 nm layer of iridium prior to imaging.

Radiolabeling of Extrinsic Sites. Solutions of radiolabel were prepared by diluting “hot” stock solutions in “cold” non-labeled salt solutions. $^{35}\text{SO}_4^{2-}$ solution was obtained by diluting 49 μL of the stock solution in 10^{-3} M Na_2SO_4 for a total volume of 50 mL with a specific activity of 1 Ci mol^{-1} . $^{22}\text{Na}^+$ was obtained by diluting 340 μL of the stock solution in 10^{-3} M NaCl to deliver a specific activity of 0.5 Ci mol^{-1} in a final volume of 50 mL. A concentration of 10^{-3} M ensured a large excess of ions in solution compared to ions in PEC films.

After immersion in polyelectrolytes, films were rinsed in deionized water (3×1 min) and dried with a gentle stream of N_2 . For radiolabeling, they were soaked in the “hot” solutions for 30 min and dried using a quick stream of N_2 . They were then counted by placing them, face down, on a 3.8 cm diameter, 3 mm thick plastic scintillator disk (SCSN-81, Kuraray). The disk was placed on the 5 cm diameter window of a PMT (photomultiplier tube, RCA 8850) inside a dark box, sandwiching a drop of immersion oil to ensure good optical contact. The PMT was connected to a high voltage supply (Bertan 313B) at 2130 V and a frequency counter (Philips

PM6654C) recorded counts. The data storage and initial manipulation was facilitated by a LabView software running on a computer connected to the counter. The gate time was fixed at 10 s and the pulse threshold at -20 mV. The counting was performed for around 15 min which provided a total number of counts for each data point that ranged between 3 500 and 700 000 with respective counting errors of 1.7% and 0.1%. The counting efficiency was around 46% for sulfate and 95% for sodium (. After counting, films were soaked in cold 10^{-2} M NaCl to exchange out the radiolabel for about 30 min, followed by a quick rinse in water and drying with N_2 . To translate counts to moles, calibration curves were built by dispensing 1 – 5 μ L of the same “hot” solution used for labeling on top of the plastic scintillator, covered with a bare Si wafer to ensure good spreading. The amounts were divided by the surface area of each film (calculated using ImageJ software, 1.50i) resulting in values in μ moles m^{-2} . The amounts were translated into fractions by dividing the values at each time point by the maximum value reached for each film. All experiments were performed at room temperature (23 ± 2 °C). Fitting of data was done using OriginPro 9.0.

RESULTS AND DISCUSSION

Starting multilayers from PSS and PDADMA were constructed from solutions containing 1.0 M NaCl. This well-studied system is known to provide nonlinear growth for the first few layers, then the thickness increment per layer becomes constant (“linear” growth).²⁴ While this behavior is presented as typical, studies of the morphology illustrate a non-ideal feature of layer-by-layer growth. The surface roughness increases with thickness to high values – on the order of 20% of the total thickness.^{12a, 25} The evolution of surface roughness, believed to be caused by strong, cyclic volume changes from water content,²⁶ is usually tracked with atomic force microscopy. Figure 1 depicts an SEM image of an as-made 40-layer film. Prior AFM measurements yield an rms roughness of 80 nm^{23, 26} for this 550 nm thick film. The SEM, however, shows greater detail and clear evidence of a history of cyclic stress. The actual morphology is far removed from cartoons typically showing alternating layers with a smooth surface.

Figure 1. (A) SEM image of an as-made (PDADMA/PSS)₂₀ multilayer prepared from 10 mM polymer solutions in 1 M NaCl. Multilayers are constrained by the substrate to grow in the z-direction only, resulting in ever-larger stress-induced wrinkling wavelengths as the film grows. (B) SEM image of the same PEMU cycled 6 times between 2 M NaCl for 30 min and 10 mM PSS in 1 M NaCl for 5 min. Scale bars are 1 μ m.

This as-made multilayer (a lower magnification image of Figure 1 is shown in Supporting Information Figure S1) does not yield a smooth morphology that would be preferred for modeling of mass transport. In addition, the multilayer composition is nonuniform: when PSS is added, the surface contains stoichiometric amounts of PSS and PDADMA while the bulk has excess PDADMA.²⁷

To produce a better-defined composition and starting material for subsequent diffusion studies, as-made multilayers were subjected to a recently-reported treatment – the film was cycled between 2 M NaCl (to mobilize and evenly redistribute all the excess PDADMA) and 1 M NaCl with 10 mM PSS79 (to complex with excess PDADMA). This procedure produced a stoichiometric thin film of PDADMA/PSS complex having an exceedingly smooth surface.²³ The smoothness is the result of salt-plasticized flow of complex in 2 M NaCl, which also erases

any “fuzzy” layering or structure of polyelectrolyte within the film. After this treatment, the film is simply a uniform film of PEC.

Kinetics of polyelectrolyte sorption

The association of oppositely-charged polyelectrolytes, Pol^+ and Pol^- , is driven mainly by the (entropic) release of counterions, A^- and C^+ , when the repeat units pair,²⁸ represented by

The process is reversible. If enough salt is added to solution, equation 1 reverses and the polyelectrolytes dissociate. In between full Pol^+Pol^- pairing and complete dissociation is a wide range of partial pairing, which gives rise to a rich spectrum of glassy, rubbery and viscous viscoelastic behavior.²⁹ Polyelectrolyte complexes are often assumed to yield stoichiometric, 1:1 ratios of Pol^+ and Pol^- , as charges “titrate” each other.³⁰ In fact, overcompensation or overcharging by the polymer in excess usually occurs,³¹ which was immediately recognized as an essential feature of the layer-by-layer (polyelectrolyte multilayer) assembly method.² Overcompensation, for example by Pol^+ , is represented by

We recently explored conditions for, and extent of, equilibrium overcompensation for the PDADMA/PSS PEC system and found the overcompensation level, σ , to be around 40% ($\sigma = 0.40$) for PSS or PDADMA, independent of the polymer concentration and film thickness.³² The time taken for equilibrium overcompensation throughout the entire thin film of PEC was found to be much longer than the time allowed for the addition of each “layer” in a multilayering experiment. For example, for the faster diffusing polymer (PDADMA), it took more than 3 hours to reach overcompensation equilibrium in a 550 nm film, while PSS, which is known to have slower kinetics,²⁷ took around 8 hours.

Table 2. Selected diffusion coefficients measured in polyelectrolyte complex films as a function of treatment conditions.

Polymer pair	[Salt] (M)/ Diffusing species/ Molecular weight (MW) (kDa)	D (cm ² s ⁻¹)	Method	Ref.
PSS/PDADMA	1.0 M NaCl/ Peak-valley structures	5.0×10^{-14}	AFM	12a
	1.0 M NaCl/ PSS/ 70	5.5×10^{-14}	QCM	12g
	1.5 M NaCl/ PSS/ 124	9.5×10^{-13}		12h
	1.0 M NaCl/ PVP ^e / 150–200	5.0×10^{-18}	Ion scattering	17a
	0.8 M NaCl/ D-PSS/ 112	$2 - 6 \times 10^{-17}$	NR	15
	1.0 M NaCl/ D-PSS/ 83.7	1.6×10^{-16}		16
	0.1 M NaCl/ PAH/ 55 – 65	3.0×10^{-15}	FRAP	12b
PSS/PAH ^a	1.0 M NaCl/ D-PSS/ 83.7	5.3×10^{-20}	NR	12c
	0.1 M NaCl/ PAH/ 55 – 65	$<1.0 \times 10^{-15}$	FRAP	12b
HA ^b /PDADMA	0.1 M NaCl/ PAH/ 55 – 65	5.5×10^{-12}	FRAP	12b
PDMAEMA ^c /PSS	1.6 M NaCl/ D-PSS/ 55.8	3.0×10^{-17}	NR	33
PDMAEMA/PMAA ^d	0.8 M NaCl/ D-PMAA/ 198/ pH 4.5	4.0×10^{-19}	NR	12e
	0.4 M NaCl/ D-PMAA/ 180/ pH 4.5	1.0×10^{-19}		12d
	0.01 M buffer ^f / D-PMAA/ 180/ pH 6.0	3.9×10^{-15}		34
	0.8 M NaCl/ PMAA/ 100/ pH 4.5	8.0×10^{-15}	FRAP	12e
	0.6 M NaCl/ PMAA/ 110/ pH 4.5	6.2×10^{-15} g		14a

^a PAH: poly(allylamine hydrochloride). ^b HA: hyaluronic acid. ^c PDMAEMA: quaternized poly(2-(dimethylamino)ethyl methacrylate). ^d PMAA: poly(methacrylic acid). ^e PVP: poly(4-vinylpyridine). ^f Phosphate/citrate buffer. ^g PDMAEMA is not quaternized.

Table 2 summarizes the literature reporting diffusion coefficients in PEMUs. In the present study, overcompensation kinetics were explored in more detail. Excess PSS is balanced by counterion C⁺. In the present case, C⁺ is exchanged with ²²Na⁺, which provides a highly precise and accurate method of measuring the PSS⁻Na⁺ “extrinsic” sites within the PEC (PSS*). Because kinetics experiments are performed on films immersed in solution, the “dry” thickness, *d*, must be converted to “wet” thickness, *w*. This was done using a known water content of about 40 wt% which yields a calculated wet/dry thickness swelling ratio of 1.66. Figure 2 illustrates the kinetics of overcompensation of a stoichiometric (Figure 1B) 347 nm_w (wet thickness) PEC film obtained from (PDADMA/PSS)₁₀ by adding PSS of various molecular weights. As seen previously,³² a steady state overcompensation level of 30 – 40% excess PSS is eventually achieved. The three higher molecular weights (127, 262 and 588 kDa) yielded the same overcompensation within error (40 ± 3%).

Figure 2. PSS overcompensation during the addition of narrow MWD PSS35 (○), PSS127 (◇), PSS262 (□), PSS588 (△) in 1 M NaCl to a stoichiometric 347 nm, w PEC film prepared by cycling in 2M NaCl then 1 M NaCl with 10 mM PSS as described in Experimental and reference 35 Overcompensation was measured with the radiolabeled ion $^{35}\text{SO}_4^{2-}$. Lines show the fits according to equation 3.

The kinetics of apparent PSS diffusion into the PEC film were modeled as diffusion into one face of a plate with the appropriate boundary conditions, which assume diffusion is limited by mass transport within the film and not in the solution adjacent to the PEC.³⁶ The fractional attainment f of equilibrium concentration C_∞ is given by³⁶

$$f = \frac{C_t}{C_\infty} = \frac{\sigma_t}{\sigma_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp \left[\frac{-D(2n+1)^2 \pi^2 t}{4l^2} \right] \quad (3)$$

where C_t (σ_t) is the PEC extrinsic site concentration (overcompensation) at time t (s), l (cm) is the measured film wet thickness, n are the Bessel roots, leaving D , the diffusion coefficient, as the only fit parameter. Further boundary conditions are: the starting film is planar with a uniform distribution of Pol^+ and Pol^- units; the starting film contains no small ions; the solution concentration of polyelectrolyte does not change throughout the experiment (the amounts of polyelectrolytes in solution are at least 1000 times those in the PEC). Equation 3 assumes no change in thickness during addition of polymer, whereas the thickness actually increased by an estimated 20% on equilibration. The fact that a single D fits the entire range so well may be fortuitous, since D may be increasing somewhat as the system becomes more swelled with water while l is simultaneously increasing. However, data fit at short time with this same D is likely more reliable since the dimensions and composition of the film have been minimally perturbed at low overcompensation.

Table 3. Diffusion coefficients of different narrow MWD PSS in a stoichiometric 347 nm,w PDADMA/PSS film obtained by fitting the data in Figure 2; and equilibrium percent overcompensation values.

PSS molecular weight (kDa)	Diffusion coefficient ($10^{-13} \text{ cm}^2 \text{ s}^{-1}$)	Percent overcompensation (± 3)
35	1.2 ± 0.5	30
127	1.0 ± 0.6	42
262	1.2 ± 0.3	37
588	1.2 ± 0.4	41

Fits to equation 3, shown in Figure 2, yielded apparent diffusion coefficients for PSS in PEC on the order of $10^{-13} \text{ cm}^2 \text{ s}^{-1}$ which were surprisingly independent of molecular weight. PECs are blends of Pol^+ and Pol^- , entangled at the molecular level, which suggests their transport might be described by reptation with diffusion that scales with molecular weight³⁷ according to $D \sim M^{-2}$ (the actual dependence of diffusion coefficient on molecular weight is found to be somewhat stronger,³⁸ $D \sim M^{-2.3}$). As will be demonstrated below, the reason for the independence of apparent PSS diffusion coefficient is that it refers to the transport of extrinsic sites and not the actual macromolecule. To distinguish between different diffusing species, D is used generally for a process that fits equation 3, D^* for diffusion attributed to extrinsic sites and D_{pol} for diffusion of polymer molecules. The coefficients listed in Table 3 are consistent with some of the previous studies on the same polymer pair^{12a, g} (see Table 2).

The addition of salt is well known to accelerate polymer mobility within complexes.^{5a, 12a} By breaking ion pairing between Pol^+ and Pol^- , segments of chains are decoupled from each other. This “doping” process, represented by equation 4 (the opposite of equation 1), also brings additional ions and water,⁴ representing additional free volume, into the material, plasticizing the PEC.³⁹

The rate of polymer addition to stoichiometric PEC film was studied as a function of the solution salt concentration. Figure 3 depicts the kinetics of PDADMA and PSS sorption into PEC for various [NaCl].

Figure 3. (A) Fraction of PDADMA*_{t=∞} ($\sigma_{t=\infty} = 38\%$), during the addition of PDADMA500 in different [NaCl] to 863 nm,w stoichiometric films. (B) Fraction of PSS*_{t=∞} ($\sigma_{t=\infty} = 47\%$), during the addition of PSS79 in different [NaCl] to 347 nm,w stoichiometric films. The lines are fits using equation 3 with diffusion coefficients listed in Table S1 and plotted in Figure 4. Precision of radiolabeling data is $\pm 2\%$. Precision of D fitting is $\pm 10\%$.

Thinner films and higher [NaCl] were employed to track the addition of PSS to PEC since its sorption kinetics were slower than those of PDADMA. The uptake of excess PSS was again measured using $^{22}\text{Na}^+$, while $^{35}\text{SO}_4^{2-}$ showed the excess of PDADMA sorbed. In Figure 3 the amounts of excess polymer added have been normalized to the maximum value at long times (σ_{∞} in equation 3). In separate experiments, it was found that overcompensation was independent of [NaCl] over the range used here. For example, Figure S2 in Supporting Information shows that with enough time, σ_{∞} for PDADMA reaches 35 – 40% for all [NaCl]. Figures 3 and S2 also reveal that for [NaCl] > 1.4 M the film starts to erode and polyelectrolyte is lost to solution after a while.

Apparent diffusion coefficients for PSS and PDADMA as a function of [NaCl] are presented in Figure 4 (and Table S1). Fitting of apparent PSS diffusion from 1.4 M NaCl in a

thicker film used in a previous study³² (860 nm, w) yielded $4.0 \pm 0.2 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$, close to the diffusion coefficient in the 347 nm, w film ($4.4 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$). For the PDADMA/PSS PEC the relationship between y , the fraction of Pol^+Pol^- ion pairs broken by salt (the doping level) is $y = 0.3[\text{NaCl}]$.⁴⁰ Thus, y is added as an axis in Figure 4.

Figure 4. (A) Apparent diffusion coefficients of PDADMA ($\diamond$) and PSS ($\blacktriangle$) in different concentrations of NaCl, with the corresponding doping level calculated using $y = 0.3[\text{NaCl}]$.⁴⁰ (B) Equivalence plot between diffusion coefficients of PSS* (PSS extrinsic site) and PDADMA* (PDADMA extrinsic site) in different concentrations of salt. Precision of D fitting is $\pm 10\%$.

Diffusion coefficients for PDADMA* (PDADMA extrinsic site) scale exponentially with $[\text{NaCl}]$ and y as follows:

$$D_{\text{PDADMA}}^* = (2.60 \times 10^{-14})e^{3.12[\text{NaCl}]} \quad (5)$$

$$D_{PDADMA}^* = (2.60 \times 10^{-14})e^{10.4y} \quad (6)$$

while for PSS* (PSS extrinsic site), the dependence is:

$$D_{PSS}^* = (3.41 \times 10^{-16})e^{4.85[NaCl]} \quad (7)$$

$$D_{PSS}^* = (3.41 \times 10^{-16})e^{16.2y} \quad (8)$$

The dotted lines in Figure 4A represent these empirical scaling relationships for this system. The theoretical underpinnings for this scaling are unknown but it is clearly a strongly nonlinear function of [NaCl] (or y) – extension of the “sticky reptation” theory of Semenov and Rubinstein may provide more insight.⁴¹ D^* for PSS and PDADMA converge at about 2.5 M NaCl or $y = 0.75$. This is the same value of y seen previously for the transition of PDADMA/PSS from solid-like to liquid-like (where storage and loss moduli are equal), defined as the transition between a polyelectrolyte “complex” and a “coacervate.”²⁹

For all measured [NaCl], diffusion of PSS is apparently slower. An alternative perspective is that the diffusion of PSS* may be matched to that of PDADMA* by adding more salt. The tie line showing individual [NaCl] for which the diffusion coefficients of PDADMA* and PSS* are equal is shown in Figure 4B. For example, PDADMA* in 1.0 M NaCl shows the same D^* (about $10^{-13} \text{ cm}^2 \text{ s}^{-1}$) as PSS* in 1.5 M NaCl. The difference of kinetics between PSS and PDADMA has been attributed by Guzmán et al. to differences in their charge density and chain length.^{12j}

Figure 4 also shows the reason behind the “asymmetric” growth of PDADMA/PSS multilayers.²⁷ It is customary to use the same [NaCl] in both polyelectrolyte solutions when constructing multilayers one layer at a time. Under this condition, PSS always apparently diffuses more slowly which means it is unable to compensate all the excess PDADMA in a growing multilayer on the time scale of the experiment. As a result, a buried zone of excess PDADMA accumulates within a multilayer.²⁷

Extrapolations of Figures 4A and B to [NaCl] = 0 provide thought-provoking apparent diffusion coefficients, $D_{y=0}$, for undoped PEC. These values are 2.6×10^{-14} and $3.4 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$ for PSS and PDADMA, respectively. While very small they are not zero and suggest slight mobility for the polymer, implying creep should be observed for long-term stresses placed on the material. The motions of segments can be modeled by self-exchange of neighboring Pol^+Pol^- pairs, as in Scheme 2.

Scheme 2. Self-exchange of neighboring polyelectrolyte pairs in the absence of salt is faster for PDADMA than for PSS.

In which case the diffusion coefficient is given by

$$D_{y=0} = \frac{k_{ex}\delta^2}{6} \quad (9)$$

where k_{ex} is the exchange rate (s^{-1}), δ is the distance between exchanging sites (the distance, in cm, between Pol^+Pol^- pairs). Using the $D_{y=0}$, PSS/PDADMA•9H₂O, with density equal to 1.1 g cm⁻³, gives 1.4×10^{21} Pol^+Pol^- cm⁻³ for an average separation of 8.9×10^{-8} cm (0.89 nm) between Pol^+Pol^- . The exchange rate would be around 0.26 s⁻¹ for PSS and 20 s⁻¹ for PDADMA. T_1 relaxation times of ¹³C from NMR on PDADMA/PAA PECs have been reported on this timescale⁴² but these experiments were performed with dry PECs, whereas a T_1 of around 1 s reported for a fully hydrated PAH/PAA PEC may be more comparable.⁴³

Tailoring the buildup mechanism: towards full exponential multilayers

A full picture of the kinetics for overcompensation, in which the diffusion rate is controlled by salt concentration, may now be used to define whether the amount of polyelectrolyte added on a “layering” step is in the kinetic or thermodynamic limit. Using the relationship between diffusion distance, Δ , and time of the adsorption step, $\Delta = \sqrt{2Dt}$, if the film thickness, l , is greater than the diffusion length the composition of the multilayer remains under kinetic control, i.e.

$$\begin{aligned} l &> \sqrt{2Dt} && \text{kinetic limit} \\ l &< \sqrt{2Dt} && \text{thermodynamic limit.} \end{aligned} \quad (10)$$

In polyelectrolyte multilayers, it is generally assumed that if a polyelectrolyte is added in the kinetic regime, it is unable to diffuse through the entire multilayer, and linear growth results. In contrast, if steady-state overcompensation occurs throughout the PEMU on each step, exponential growth occurs.^{8a, b} The mechanism of “in and out” diffusion leading to that effect was presented at first,^{8a, 44} then modified to show that exponential growth can occur without the polymer diffusing throughout the whole film.⁹⁻¹⁰ As a practical matter, many pairs of

polyelectrolytes show some type of nonlinear growth when they are thin enough and equation 3 applies, followed eventually by linear growth.

Three modes of buildup were used to explore three different regimes for PDADMA/PSS multilayering. The first was the *traditional* one where each polyelectrolyte was dissolved in the same concentration of NaCl (here 1.0 M NaCl) and each layer consisted of a 5-min dip in the polyelectrolyte solutions. The second was the *salt equivalency* one where PDADMA was dissolved in 1.0 M NaCl and PSS in 1.4 M NaCl, approximately matching diffusion coefficients according to Figure 4B (Table S1, Supporting Information). The layering time in the second method was maintained at 5 min. The third mode of buildup was intended to produce *exponential* buildup, in which the salt equivalency method was followed but the duration for each “layer” was prolonged to make sure the polymer overcompensated the entire film. For the last approach, the thickness of the film was measured after each layer and the dipping time, t , had to satisfy $l \leq \sqrt{2Dt}$. For simplification, D^* was taken as $1.5 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ for both polymers from Figure 4B.

Figure 5A summarizes the results of programming the three types of buildup. The “traditional” method produced nonlinearity up to about 12 layers, whereafter the growth turned linear, in agreement with extensive studies on this system.²⁷ The salt equivalency approach produced thicker films with “partial” exponential growth at the beginning but the growth also eventually became linear (Figure 5A). The exponential growth experiment presented some challenges: while films $< 300 - 400 \text{ nm}$ could be reliably measured *via* ellipsometry, which sufficed for the traditional and salt equivalency growth, exponential films quickly accumulated thickness beyond the range of the ellipsometer. Therefore, a hybrid technique for the exponential system was employed: thickness up to about 300 nm was measured using both ellipsometry and FTIR, while thicker films employed FTIR measurements of peak areas from the strong 1010 cm^{-1} aromatic band for PSS and the 1473 cm^{-1} PDADMA peak. Films around 100 nm thick were used to establish a conversion factor between ellipsometric thickness and FTIR peak area.

Figure 5. (A) Dry thickness measured with ellipsometry and calculated from FTIR peak areas, and FTIR PSS peak area ($990 - 1020\text{ cm}^{-1}$) during the buildup of multilayers using the traditional method (■ for thickness, □ for FTIR), the salt equivalency method where PSS was in 1.4 M NaCl and PDADMA in 1.0 M NaCl (● for thickness, ○ for FTIR), and the full exponential method (▲ for thickness, △ for FTIR). Precision is on average 2%. The inset shows the increase of dipping time as the film gets thicker in the full exponential method. (B) Log PSS peak area in films built using the traditional method (□), the salt equivalency method (○), and the full exponential method (△). (C) Thickness data (▲) using the “full

exponential” method with PDADMA dissolved in 1 M NaCl and PSS in 1.4 M NaCl, and increasing dip times based on the thickness of the previous layer. The dashed line shows the model describing the exponential buildup according to equation 11 with $l_o = 1.8$ nm and $k = 0.35$.

In exponential growth (Figure 5), added polymer overcompensates its oppositely charged partner in the *entire* PEC present in the multilayer, which means the thickness of the n th layer, $l_n = (1 + \sigma)l_{n-1}$, with σ the average overcompensation level, assuming the molar volumes of Pol^+ and Pol^- are the same. The total dry thickness after n layers are sorbed is given by⁴⁴ $l = \sum_1^n l_n$. This summation yields exponential growth according to

$$l = l_o e^{k(n-1)} \quad (11)$$

where l_o is the thickness of the first layer. We have found the following empirical relationship between k and σ : $k = 0.682\sigma + 0.062$. Exponential growth is modeled in Figure 5 using an average σ of 0.42 (i.e. 42%) consistent with Figure 2 and our previous work³² which gives a k of 0.35. Interestingly, the pre-exponential factor, which is the thickness of the first layer, would have a strong influence on the growth of the entire film (equation 11).⁴⁵ A value of 1.8 nm for l_o implies a monolayer PDADMA coverage of about 2.0 mg m⁻² if the density is assumed to be 1.1 g cm⁻³.

The inset in Figure 5A shows that for fewer than 13 layers, 5 minutes immersion was enough to maintain the condition $t \geq \frac{l^2}{2D}$. After 13 layers the dipping time was increased with the square of the thickness to ensure $t \geq \frac{l^2}{2D}$. The multilayer grew exponentially over the whole (“full”) range of thicknesses. A semilog plot of peak area or thickness versus time (Figure 5B and 5C) obeys “full” exponential growth for the entire buildup according to equation 11. Figure S3 (Supporting Information) shows the similar growth profile when PDADMA, instead of PSS, peaks are used. The fit holds over three orders of magnitude thickness.

Polymer vs. site diffusion

All diffusion modeling to this point was prompted by behavior that appeared to adhere well to Fick’s laws (i.e. equation 3), valid in a concentration gradient with no field-driven transport. For example, in the limit of short time (more specifically $f < 0.7$) the adsorbed amount scaled with $t^{1/2}$, as seen with QCM studies.^{12g}

As an alternative, direct measure of polyelectrolyte diffusion, deuterated PSS (D-PSS) was used to observe (self) exchange kinetics with non-deuterated PSS. Isotopic exchange methods are done in the near-absence of a gradient of composition (i.e. in a concentration gradient of D- versus H-PSS only) and yield reliable self-diffusion coefficients.⁴⁶ Overcompensated PDADMA/H-PSS127 films were immersed in solutions of deuterated PSS (D-PSS116) and monitored with FTIR to observe D-PSS exchange with H-PSS. FTIR provided a clear signal of isotopic exchange (see Figure 6A). The aromatic ring mode at 1130 cm⁻¹ decreased and the D-PSS band at 1080 cm⁻¹ increased as the D-PSS replaced H-PSS.

Figure 6. (A) Individual FTIR spectra of H- and D-PSS. The peaks used to monitor the exchange are in the red square. (B) Exchange experiment: FTIR spectra of a 350 nm,w film of overcompensated PDADMA/H-PSS127 immersed in D-PSS116 in 1.4 M NaCl up to 44 days. (C) H-PSS (1130 cm^{-1} , Δ) and D-PSS (1080 cm^{-1} , $\blacktriangle$) peak areas versus $t^{1/2}$.

Figure 6B shows the replacement of H-PSS by D-PSS over a period of more than a month. A similar experiment was performed by making the PEC film with D-PSS and exchanging with H-PSS (Figure S4, Supporting Information). It is immediately apparent that the kinetics of polymer exchange, limited by polymer diffusion within the PEC (Figure 6C), are far slower than the kinetics of overcompensation (Figure 3B), which have historically been attributed to polymer diffusion. Differences between diffusion coefficients, obtained by fits according to equation 3 (see Figure S5, Supporting Information), for the two kinds of experiments are quantitatively compared in Table 4. The kinetics of H-PSS127 overcompensation are taken from Figure S6 (Supporting Information). The apparent diffusion of PSS in the overcompensation experiment is almost three orders of magnitude faster than in the exchange experiment.

Table 4. Diffusion coefficients obtained from fitting the data of apparent PSS diffusion in overcompensation and exchange experiments.

PSS diffusion experiment ^a	Diffusion coefficient ($\times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$)
H-PSS127 overcompensation kinetics	1200
D-PSS116 exchange with film made with H-PSS127	2.1
H-PSS127 exchange with film made with D-PSS116	2.5

^aall in 1.4 M NaCl

We posit the difference in diffusion coefficients stems from the difference in diffusing species. Which diffusing species is actually observed depends on the experiment: the rate of polymer addition to an existing multilayer is controlled by transport of extrinsic sites through the film. These sites can move throughout the film by place-exchange reactions between Pol^+Pol^- ions pairs and extrinsic sites. *Site transport* is illustrated in Scheme 3A, which shows how additional Pol^- adds to a film. In the first step, a Pol^+C^+ unit on the incoming polyelectrolyte exchanges with a surface Pol^+Pol^- . This process is repeated in subsequent exchanges so that the Pol^+C^+ site can appear anywhere in the film. It is important to note that additional polymer can be added to the film using *minor perturbations* in the local pairing of Pol^+Pol^- units. There is no need for film-scale transport of polymer chains through the PEC.

Scheme 3. (A) Site-dominated diffusion: as the polymer approaches the surface, the polyelectrolyte complex network beneath it is rearranged in a way to propagate the excess charge brought in with the incoming polyelectrolyte. For simplification, only one site is shown to propagate through the complex. (B) Polymer-dominated diffusion: the polymer itself finds its way across the polyelectrolyte complex as the network around rearranges.

In contrast, Scheme 3B shows the much larger scale movements for one polymer molecule to entirely replace another. In *polymer-dominated* diffusion, the molecule travels through the PEC network, for example by reptation. The two types of diffusion are assigned coefficients D^* , representing site or apparent polymer diffusion, and D_{pol} , representing actual polymer diffusion.

With these two concepts in mind it is possible to reconcile some rather puzzling findings reported in the literature. For example, we estimated a polymer diffusion coefficient on the order of $10^{-14} \text{ cm}^2 \text{ s}^{-1}$ by estimating the rate at which surface features on a rough PEMU were smoothed under the influence of added salt,^{12a} as did McAloney et al.¹³ In contrast, subsequent neutron reflectivity measurements on the salt-induced spreading of deuterated layers within PDADMA/PSS PEMUs returned values on the order of $10^{-17} \text{ cm}^2 \text{ s}^{-1}$.¹⁵ In retrospect, it is likely that we were measuring *site diffusion* in the smoothing experiments and *polymer diffusion* in the NR measurements. Other literature results on D , summarized in Table 2, may now be re-evaluated with respect to the type of measurement. For example, NR results on deuterated materials generally provide D with the lowest values. Because NR in these experiments is based on the neutron contrast of deuterated polymers there is little doubt that polymer diffusion is

being tracked. On the other hand, measuring the amount of polymer added to a film as a function of time, using QCM or thickness increments for example,^{12g} would yield D corresponding to site diffusion.

Another key consequence is that during the time of a multilayering experiment, even in relatively high [NaCl], such as 1.4 M, the polymer diffuses so slowly ($D \sim 10^{-15} \text{ cm}^2 \text{ s}^{-1}$) that the diffusion distance for a 1-hour multilayering experiment is only 10% of the film thickness for a 200 nm film. Thus, site-dominated diffusion is responsible for overcompensation and the growth of most multilayers, *even into the exponential regime* for select systems such as PDADMA/PSS.

With polyelectrolytes of sufficiently low molecular weight¹⁶ or weak enough interactions (high enough salt concentration), it is possible that polymer diffusion may rival site diffusion, i.e. D_{pol} approaches D^* (it is unlikely that D_{pol} exceeds D^*). Such conditions approach those for polyelectrolyte coacervates,⁴⁷ which may be defined as polyelectrolyte complexes where the loss modulus G'' exceeds the storage modulus G' ²⁹ (although it is dangerous to categorize PEC types according to their viscoelastic properties, since they appear to be stiffer at higher frequency). A recent publication by Selin et al. explored the diffusivity of deuterated polyelectrolytes within multilayers.³⁴ These studies used a polyquaternary ammonium and a polycarboxylate polyanion, a combination shown to interact weakly compared to PDADMA and PSS.⁴⁸ Thus, polycations were able to access most of a ca. 120 nm thick film in less than 24 min. Consequently, their multilayers exhibited exponential growth up to about 10 layers when the dipping time was 24 min. In contrast, using mass uptake data the same work showed apparent polycation diffusion coefficients about 2 orders of magnitude higher, consistent with dominant site diffusion.³⁴ Given that all multilayering kinetics depend on conditions, probably the best way to discern systems that are mainly under the control of site- versus polymer- diffusion is molecular weight dependence: kinetics of systems building under site diffusion likely show no molecular weight dependence, whereas layering kinetics with a contribution from polymer diffusion should show a dependence on molecular weight.^{14a}

Combining equations 10 and 11, an expression for the critical number of layers, n_c , where exponential growth starts to transition to linear growth may be derived

$$n_c = 1 + \frac{1}{k} \left[\ln \left(\frac{\sqrt{2D^*t}}{l_0} \right) \right] \quad (12)$$

Note that D^* is the site diffusion coefficient for the *slowest* site (here PSS*), in which case a layer of excess PDADMA* builds up within the PEMU.²⁷ The implication is that *both* positive *and* negative sites must be able to diffuse throughout the film in all layering times to maintain exponential growth.

Assuming l_0 is constant at 1.8 nm, k is 0.35 as in Figure 5 and a typical time of 5 min per layer, n_c for the PDADMA/PSS system is around 7 layers in 0.5 M NaCl and 10 layers in 1.0 M NaCl, consistent with experimental observations.⁴⁹ Table S2 (Supporting Information) shows the n_c for a range of NaCl from 0.1 to 1.8 M, as well as the critical thickness ($l_c = \sqrt{2D^*t}$) – the thickness at which the growth turns from exponential to linear with 5 min deposition time. Strongly associated glassy systems like PAH/PSS⁴⁸ with exceptionally small diffusion coefficients (Table 2) show linear growth from the start of multilayering.

After the transition to linear growth, PSS can only compensate but not overcompensate as far as PSS* can diffuse into the film in the time allowed. The dry thickness increment per bilayer should be

$$\text{bilayer thickness} = \frac{(2 + \sigma)\sqrt{2D^*t}}{\text{swelling ratio}} \quad (13)$$

Calculated values for PDADMA/PSS, $t = 5$ min and D^* in 0.5 M and 1.0 M from Figure 4A (and Table S2, Supporting Information) give respective bilayer thicknesses of 22 and 63 nm compared to experimental values of 19 nm and 41 nm.⁴⁹

The thesis that site diffusion controls multilayer buildup also explains how a polyelectrolyte like PDADMA can mysteriously appear to “pass through” a layer or stratum of PSS without disrupting the layer. For example, PDADMA was previously shown to “diffuse faster” than PSS, leading to a buildup of excess PDADMA within a PEMU.²⁷ In fact, it is actually PDADMA* that diffuses, requiring minimal motion of a polymer chain as in Scheme 3A and preserving the layering of PSS. An interesting conclusion on multilayer structure, even for exponential or nonlinear PEMUs, is that they are probably *more* layered than previously suspected. A polyelectrolyte chain can adsorb near the surface and not have to move much as extrinsic sites are passed back and forth through it. Proton transport *via* the mechanism in Scheme 3A would be able to protonate/deprotonate deeply buried weak acid groups at a distance far greater than an electrostatic decay length.⁵⁰

Additional details on polyelectrolyte exchange properties may be gleaned from the self-exchange experiments. Figure 6B shows that not all polyelectrolyte was exchanged out of the film (or that there is an even slower portion of the exchange). Initially it was thought that the polymer next to the silicon substrate is more difficult to exchange because of interactions with the substrate. Experiments with different molecular weights of solution PSS suggested a different scenario. For example, Figure 7 shows attempted exchange of D-PSS116 (116 kDa) in a thinner multilayer with H-PSS of molecular weight ranging from 8 to 588 kDa. H-PSS in solution having lower molecular weight than D-PSS in the film would not exchange all the D-PSS out (Figure 7). It is known that polyelectrolytes of higher molecular weights displace those of lower molecular weight in PECs.⁵¹ From Figure 7 it appears that a requirement for substantial exchange is that the solution polymer has to be of equivalent (here, 127 kDa) or greater molecular weight than the PEC (PEMU) polyelectrolyte. The possibility of a small amount of non-exchangable polymer in Figure 7 is consistent with the recent conclusion of Selin et al. that polymer next to the substrate may be more firmly held.³⁴

Figure 7. (A) Decrease in D-PSS peak area during the diffusion of H-PSS8 (Δ), 35 ($\circ$), 127 ($\diamond$), and 588 ($\square$) into overcompensated 83 nm,w PDADMA/D-PSS116 in 1 M NaCl. (B) Fraction of D-PSS exchanged over time from panel A. Fits according to equation 3. Figure S7 shows individual fits. (C) Diffusion of H-PSS127 ($\diamond$) and H-PSS588 ($\square$) into the same film. The line represents a fit according to equation 3.

The amount of polymer that did exchange in Figure 7A was analyzed according to equation 3 to estimate polymer diffusion coefficients. As seen in Table 5, there is no significant

dependence of D on molecular weight (MW), a surprising result given the classical scaling of $D \sim MW^{-2}$ for entangled polymers.⁵² On the other hand, according to “sticky reptation” theory,⁴¹ the viscosity of PECs should not depend on molecular weight. Analysis of diffusion coefficients using this theory may also predict little dependence of diffusion on molecular weight.

Table 5. Diffusion coefficients D_{pol} from fits shown in Figure 7B of the exchange between incoming H-PSS and the outgoing D-PSS in a 83 nm,w overcompensated PDADMA/D-PSS116 PEC film.

PSS	Diffusion coefficient ($10^{-15} \text{ cm}^2 \text{ s}^{-1}$) ^a
Incoming H-PSS8	1.1
Incoming H-PSS35	0.7
Incoming H-PSS127	1.0
Incoming H-PSS588	0.6
Outgoing D-PSS during addition of H-PSS127	1.1

^a accuracy in D is $\pm 25\%$

The influence of salt concentration on polymer diffusion was not thoroughly assessed here. However, a comparison between Table 4 and Table 5 shows that using the same MW (PSS127), the diffusion coefficient decreases by about a half when the exchange is performed in 1.4 M NaCl versus in 1.0 M NaCl. The NR work of Xu et al. on deuterated layers of polyanions within PEMUs of PDMAEMA and PMAA clearly shows an increase of polymer diffusion rate with increasing [NaCl], although the dependence is more mild than that for PDADMA* or PSS* shown in Figure 4.^{12d}

The effect of molecular weight on uptake in the film agrees only partially with prior studies exploring this variable,^{12d, h, 16, 53} which usually show some dependence of the diffusion on MW. In the closest example, Zan et al.,^{12h} using QCM, found faster apparent uptake of PSS in a PDADMA/PSS multilayer only for $MW < \text{ca. } 10^5$. In a FRAP study by Xu et al., diffusion of PMAA in a PDMAEMA/PMAA system showed a $D \sim M_w^{-1}$ scaling.^{14a} In their extensive work on the mechanism of exponential growth, the Schaaf group reported that only short PLL chains in a HA/PLL multilayer actually diffused throughout the film.⁹ In the next section we support their conclusion that exponential growth can occur without high chain mobility.

Simultaneous Overcompensation and Exchange

Overcompensation and exchange must occur simultaneously, even if at different rates. To illustrate this, a stoichiometric 208 nm,d thick (PDADMA/H-PSS127) film was immersed in D-PSS116 in 1 M NaCl (Figure 8). The rate of H-PSS decrease, from *exchange* only, is much lower than the rate of D-PSS increase, which comes from both *overcompensation* (at short time, faster) and *exchange* (at longer times, slower). The overcompensation at any time is shown by the dotted line in Figure 8.

Figure 8. Normalized D-PSS peak area ($\square$) and H-PSS peak area ($\circ$) versus $t^{1/2}$ during the addition of 10 mM D-PSS116 in 1 M NaCl to a 208 nm,d stoichiometric PDADMA/H-PSS127 film (normalization is performed against the original value for H-PSS, and the maximum value for D-PSS). The braces above the plot show the transition from site-dominated diffusion (initial addition of D-PSS) to polymer-dominated diffusion (exchange of H-PSS by D-PSS) as well as the approximate time to add a layer (5 – 10 min) in a multilayering experiment. Percent PSS overcompensation (dashed line) is also shown for a similar film at the same concentration of salt. Precision is on average 3%. The dotted green line shows the slope for the site diffusion, while the solid red line shows the slope for the H-PSS polymer diffusion.

Three time regimes are shown in Figure 8. The shortest corresponds to the time taken to add a layer to the multilayer, which is on the order of a few minutes in the present case. The second regime defines the time for defects to permeate throughout this film under the conditions shown. The slowest time regime indicates the time taken for polymer molecules to diffuse throughout the film. This particular system illustrates very different time scales for each of the three processes. Figure 8 also provides a universal lens through which one can view multilayer buildup by comparing multilayering, site diffusion, and polymer diffusion times. For example, if the multilayering time is substantially shorter than the site diffusion time, *linear* growth should result. If the site diffusion time is comparable to, or smaller than, the multilayering time, exponential growth results. If it is fast enough, polymer diffusion may assist site diffusion in dispersing sites. In a “typical” multilayer growth, which starts with nonlinear (often loosely termed exponential) growth, at some point the film becomes thick enough for site diffusion to limit transport of sites throughout the film and the growth turns linear.

All experimental variables dictate the relative lengths of these time regimes. For example, weakly associating Pol^+Pol^- , high water content, higher temperature, low charge density,^{20b} and

high salt content favor faster site diffusion (and exponential growth). If chains are short enough, polymer diffusion will add to the site transport rate.

These arguments are in agreement with Porcel et al.,⁹ who pointed out that exponential growth does not necessarily require fast diffusion of polyelectrolyte. The detailed mechanism above explains why: overcompensation is controlled by site diffusion. Intriguingly, exponential multilayers that are grown not too far into the polymer diffusion time region in Figure 8 should also yield *layered* structures. Because each of these layers is increasingly thicker than the previous one, it is not possible to build up a periodic structure, for example with deuterated polymers, that would give Bragg reflections. However, it would be interesting to see these layers, perhaps on electron microscopy cross-sections. Scheme S1 (Supporting Information) depicts the addition of a layer, combining the compensation and overcompensation mechanisms, and the resulting thickness increment.

CONCLUSIONS

In combination with prior work on ion diffusion within PDADMA/PSS PECs,⁴⁰ it can be concluded that there are at least three types of diffusing species within complexes, all dependent on the salt concentration or doping level. As shown above, the polyelectrolytes themselves are the slowest, with diffusion coefficients on the order of $10^{-15} - 10^{-19} \text{ cm}^2 \text{ s}^{-1}$. Although multilayers are ultrathin, this rate of transport is usually too slow to allow access of the polymer to an entire PEMU during its construction. The diffusion of extrinsic sites is markedly faster, with D^* that ranges from 10^{-15} to $10^{-12} \text{ cm}^2 \text{ s}^{-1}$ in PDADMA/PSS. Ion diffusion is the fastest of all species,⁴⁰ with D_{ion} values on the order of $10^{-6} \text{ cm}^2 \text{ s}^{-1}$. The mechanism for multilayering, from the linear to the exponential regime, depends on site diffusion: if sites are able to diffuse throughout the multilayer on the time scale of an adsorption step, the film grows exponentially. If relaxation times correlate with diffusion it should be possible to observe relaxations on the order of 1 s in undoped complexes (from Pol^+Pol^- exchange) and $10^{-1} - 10^{-3}$ s in doped PEC (from Pol^+A^- or Pol^+C^+ exchange).

In a broader conceptual sense, the site diffusion mechanism is one representative of a way to (spontaneously) assemble soft matter without moving much actual material: functional groups just need to “flip” around as in Scheme 3A. The dynamics of material formation is related to the dynamics of crosslink migration, whether they are physical (ion pairing, hydrogen bonding) or chemical (for example disulfides and esters). Precipitating large volumes of complex is only possible because ion pairs are much more mobile than the polymers themselves.

ASSOCIATED CONTENT

Table of apparent diffusion coefficients, different buildup regimes shown with polycation FTIR peak area, additional exchange experiments and individual fits of the FTIR data. Scheme S1 details the mechanisms of compensation and overcompensation.

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Notes

The authors declare no competing financial interest

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