Factors Influencing the Interdiffusion of Weak Polycations in Multilayers

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ABSTRACT: One promising aspect of the electrostatic multilayer assembly techniques is the ability to consistently and predictably create controlled heterostructures that may be of interest for active devices, designed biomaterials, membranes, or other composite thin film structures. This promise is mitigated by the challenge of controlling diffusion and exchange processes that can take place in certain layer-by-layer assembled film systems and cause unanticipated or unwanted materials distributions and in extreme cases completely disrupt the assembly. To further understanding toward prediction and control of these processes, we investigate a series of polyamines and their interdiffusion and exchange within preassembled multilayer films to explore the role of polyion degree of ionization, hydrophobicity/hydrophilicity of the backbone, basicity of amine groups, and polyion topology in a polyelectrolyte interdiffusion and exchange process. Interdiffusion of these polyamines will be examined within a polyhexylviologen (PXV)/poly(acrylic acid) multilayer model system in which conditions favor exchange of the polyamine with PXV, a strong polycation containing quarternary ammonium groups along the backbone. Four amine-containing polycations were examined: linear and branched polyethylene imine (LPEI and BPEI), polyamidoamine (PAMAM) dendrimer, and poly(allylamine hydrochloride) (PAH). It was found that fully charged polycations in dilute aqueous solution are unable to diffuse through the multilayer film whereas partially charged polycations have the necessary mobility. Remarkably, despite strong differences in the nature of the polycation, as in the case of PAH, LPEI, and BPEI, for every polyamine there existed the same critical degree of ionization in solution below which interdiffusion was possible, which was seen to be near 70% in these exchange experiments with PXV. Only for the highly branched PAMAM dendrimer was this value different; the critical degree of ionization for PAMAM was observed to be 55%. Kinetics of the interdiffusion were significantly impacted by the polyion degree of ionization and molecular weight.

Introduction

The sequentially directed complexation of oppositely charged polyelectrolytes onto a substrate (called the layer-by-layer or LbL process) can be used to create structured polymer thin films[1] (polyelectrolyte multilayers or PEMs). These films are non-equilibrium structures that are highly sensitive to small changes in assembly conditions, making it possible to create films with a wide range of properties. LbL films have potential applications ranging from electrochemical devices such as fuel cells[2] to coatings on biomedical implants.[3] While it has been long known that the "layers" are somewhat interdigitated,[4] the adsorption of polyelectrolyte at each deposition step has typically been considered to result in kinetically "frozen" cross-links at and near the liquid−solid interface. However, from the start of observation of the nonlinearly growing systems of polysaccharides and other biomacromolecules,[5−7] it has become increasingly clear that interdiffusion and exchange of polyelectrolytes within LbL assemblies can be dominant processes that need to be well understood in order to rationally design films with desired properties. In a simple model of diffusion of polyelectrolytes within multilayer structures outlined by Lavalle et al.,[8] one of the requisites for this behavior was identified to be "permeability" of the multilayer. This is found primarily in weak polyelectrolyte systems assembled at low charge density, which are not tightly cross-linked. Additionally, the ability of weak polyelectrolytes to vary their charge density in response to changes in local environment may contribute to diffusion phenomena.[9,10] Many early PEM studies used strong polyelectrolytes, which explains why diffusion was not immediately identified as a frequently occurring phenomenon. Examples of highly stratified PEM heterostructures have been demonstrated.[11] These PEM assemblies, however, include strong polyelectrolytes and strongly charged weak polyelectrolytes, preventing diffusion.

Interdiffusion within LbL assemblies can cause not only the so-called "exponential" growth[5,6,12] but also the disruption of films during assembly or postassembly, or it may even lead to the ordering of elements due to enhanced film mobility.[13] Diffusion of polymer chains within a swollen LbL film is often coupled with reversible or irreversible exchange with chains that are already a part of the assembly.[14] This preference for one polyelectrolyte to be incorporated into the film's structure over another has also been observed during the formation of multilayers.[15] Exposure of a preassembled LbL structure to a polyelectrolyte solution can cause exchange of chains from solution to those in the film or cause chains to be transferred from the film into the solution, similar to the dissolution process that is observed by exposing LbL films to solutions with high ionic strength[16,17] or to the behavior of semisoluble polyelectrolyte complexes in solution.[19,20] Although many interdiffusion related effects have been observed, it has been difficult to predict which polymers will be able to interdiffuse in a multilayer and under which conditions they will be able to do so.

Heterostructured or otherwise stratified film architectures may be desirable for certain applications; at other times, a uniform film that is essentially a blend of the desired components may be called for. For certain applications, such as sequential drug delievery,[21] control of the film composition in the direction of film growth is crucial. In order to do this, diffusion must be understood and potentially stopped by compartmentalizing

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sections of the films.[21,22] The use of LbL films under physiological conditions calls for them to be exposed to solutions containing both salt and biomacromolecules, and therefore it is necessary to understand when this might lead to film deconstruction or otherwise alter the film's structure. Factors affecting the interdiffusion and ability to displace other polymer chains of a given polyelectrolyte include molecular weight,[23,24] hydrophobicity, charge density, and chain conformation.

We examined this idea earlier using the model system of redox-active poly(hexylviologen) (PXV)/poly(acrylic acid) (PAA) multilayers.[25] PXV is a good model polycation for these studies due to its being a strong polyelectrolyte, meaning that when exposed to solutions of varying pH its charge density remains constant. Also, it has a relatively large molecular weight (∼250 000 g/mol), which means that displacement of PXV within a multilayer is not due to the entropic gain from the release of smaller macromolecules or oligomers into solution. We learned that when exposed to a solution of linear poly(ethylene imine) (LPEI) the LPEI, which contains secondary amine groups along its backbone, is incorporated into the film and the PXV chains, which contain quarternary pyridinium charged groups, are ejected from the film structure. Exchange occurrs under PXV/PAA assembly conditions of pH 4 and 5. In these studies, we also found that higher molecular weight LPEI (250 000 as opposed to 25 000 g/mol) takes longer to exchange with the PXV, consistent with the proposed mechanism that the LPEI chains diffuse through the pre-existing multilayer structure. We attributed these results to the acid−base interactions between the secondary amine groups of LPEI and the carboxylic acid groups of PAA, which make the LPEI/PAA complex enthalpically favorable compared to complexation of PXV and PAA.

This exchange process appeared to be related to the difference in the various films' degree of ionization, which in turn determines the density of electrostatic cross-links that stabilize the multilayer. PAA in solution at pH 4 has a degree of ionization of approximately 10%.[10] However, PXV/PAA films assembled at pH 4 show only ∼20% ionization of the acid groups, which is lower than the polyamine containing films. This lesser ability of PXV to titrate the acid groups of PAA than the polyamines demonstrates weaker interaction between the bipyridine groups and the acid groups compared to that of amine groups and carboxylic acid groups. The hydrophobic nature of the alkyl chain likely contributes to lessening the interaction between the two polymers. The lower degree of acid ionization in PXV/PAA films indicates that there must also be a lower number of ionic cross-links, resulting in an LbL film with a looser network, thus making it easier for polymer chains to penetrate the film. Furthermore, the loss of charged anionic acid sites in the film at lower pH values leads to fewer "sticky" sites for the attachment of polyamine groups, thus, increasing the mobility of the polyamine chains within the film at lower pH. The enhancement of polyion chain mobility within the multilayer via the generation of multilayers with low ionic cross-link density and/or fewer charge sites, however, is not singularly sufficient for the interdiffusion and exchange processes; many multilayers are generated under conditions yielding low degrees of ionization but do not exhibit interdiffusion behavior. An additional consideration must also be the contribution to chain mobility resulting from the composition of the diffusing polymer component. The degree to which the polymer chain is hydrated during the adsorption and interpenetration processes impacts the localized polymer segment mobility. Furthermore, chain size (i.e., molecular weight) and topology (branched structure) directly impact the kinetics of diffusion.[24] The interdiffusing polymer's charge density, rigidity or flexibility, and solubility within the multilayer matrix are all potential factors in chain mobility.

The above two issues relate to the kinetic barriers that affect penetration and diffusion of polyion chains within the multilayer during the adsorption process. A third factor that appears to play a particular role in the interdiffusion and exchange between polyions within the film is the thermodynamic driving force for this exchange, whether it be due to chemical partitioning or specific chemical interactions. In the particular model system of interest here, this driving force is the difference in the relative affinity of the basic amine groups in the polyamine over the quaternized pyridinium groups in PXV due to strong acid−base interactions between acid and amine groups, as demonstrated by significant shifts in acid ionization in the presence of LPEI or other polyamine.

In this work, we explore multiple polycations possessing various pK_a values and molecular geometries in order to compare their mobility and capacity to exchange with PXV in PXV/PAA multilayers and then with one another in multilayers. We use FTIR and UV−vis absorption spectroscopies to probe these properties. Degree of ionization has been a well studied parameter in the formation of multilayers,[26−31] and here, we show that it is important in the interaction of free chains with multilayers as well. We find that there is a critical degree of ionization above which the polycation chains are unable to exchange with the PXV. This degree of ionization is similar in the three quasi-linear polymers regardless of the polycation's primary chemical structure. For PAMAM, the critical degree of ionization is somewhat lower due to the close proximity of the functional groups to one another.

Experimental Section

Materials. Linear and branched poly(ethylene imine) (LPEI, MW = 25 000 g/mol and BPEI, MW = 70 000 g/mol) and poly(acrylic acid) (PAA, MW = 90 000 g/mol) were purchased from Polysciences. Poly(amido amine) dendrimer (PAMAM G4, NH_2 surface, 22 wt % in methanol) was purchased from Dendritech. Poly(allylamine hydrochloride) (PAH, MW = 70 000 g/mol) was purchased from Sigma Aldrich. All materials were used as received. Poly(hexylviologen) was synthesized by refluxing 4,4′-bipyridine and 1,6-dibromohexane overnight in dry acetonitrile as described previously.[25] Molecular weight of the PXV was determined by NMR end group analysis to be ∼250 000 g/mol (NMR shown in the Supporting Information). Polymer solutions were made using DI water at a concentration of 20 mmol with respect to the repeat unit and adjusted to the required pH using HCl or NaOH. Si wafers were purchased from Silicon Quest. All silicon wafers were cleaned with methanol and Milli-Q water followed by a 5 min oxygen plasma etch (Harrick PCD 32G) to clean and hydroxylate the surface. Glass slides from VWR were cleaned by sonication for 10 min each in a series of solvents (dichloromethane, acetone, methanol, and then DI water) and then exposed to 5 min of oxygen plasma etch. VWR poly(propylene) weigh boats were used as substrates for freestanding film formation and were sonicated in water before use. ZnSe substrates were purchased from VWR and cleaned by sonication in ethanol and then with DI water.

Film Formation. LbL films were constructed as follows according to the alternate dipping method using an automated Carl Zeiss HMS series programmable slide stainer. Briefly, pretreated substrates were submerged in a polycationic dipping solution for 10 min followed by a cascade rinse cycle consisting of three deionized water rinsing baths (30, 60, and 60 s, respectively). Substrates were then submerged in a polyanionic solution for 10 min followed by the same cascade rinsing cycle, and the entire process was repeated as desired. After deposition, films were immediately removed from the final rinsing bath and dried thoroughly under a stream of dry nitrogen gas.

Characterization. FTIR measurements were performed using a Nicolet Magna 860 Fourier transform infrared spectrometer with a DTGS detector. Samples were examined in the transmission mode using ZnSe or silicon substrates or as freestanding films, which were made by depositing films onto poly(propylene) substrates and then peeling them off with tweezers as previously described.[32]To probe the exchange process, 25 layer pair films of (PXV/PAA), (PAH/PAA), or (PAMAM/PAA) were soaked in 20 mM LPEI, PAH, BPEI, or PAMAM solutions at different pH values, dried in a nitrogen stream, and then examined with FTIR. Films were exposed to the different polycation solutions for 4−5 days before observation with FTIR. (PXV/PAA) films were kept hydrated in DI water at pH 4 (matching assembly conditions) from the time assembled until exposed to polycation solution. Spectral characterization was performed with a StellarNet EPP2000 concave grating UV−vis−near- infrared spectrophotometer with combined incandescent and deuterium lamp sources.

The extent of carboxylic acid ionization was calculated from the ratio of the peak area at 1560 cm^{-1} ($-COO^-$ asymmetric stretching) to the sum of the peak areas at 1560 and 1710 cm^{-1} ($-COOH$ asymmetric stretching). We assume that the coefficient of extinction is the same for the protonated carboxyl at 1710 cm^{-1} and the deprotonated carboxyl at 1560 cm^{-1}.[9] In LPEI/PAA films, peaks at 1610 cm^{-1} (corresponding to $-NH^{2+}$) and 1650 cm^{-1} (corresponding to N−H deformation vibrations) overlap with the peak at 1560 cm^{-1} for the ionized carboxyl groups. To separate these peaks, Origin was used to fit Gaussian distributions to each peak.

Results and Discussion

We have previously demonstrated that LPEI, at pH 4 and 5, is able to exchange with the PXV in a PXV/PAA multilayer[25] and that the higher molecular weight LPEI (250 000 as opposed to 25 000 g/mol) takes longer to exchange with the PXV, consistent with the proposed mechanism that the LPEI chains diffuse through the pre-existing multilayer structure. To understand this phenomenon in a more general way, it is important to determine what conditions and aspects of the interdiffusing polyion species allow them to diffuse and exchange with polymer in underlying layers of an LbL film. By examining this behavior with the PXV/PAA model system and a range of polyamines, it is hoped that a greater understanding of this phenomenon can be achieved, particularly in the context of the competitive polyion exchange that has been observed in several heterostructure systems of practical interest. If these properties can be identified for a simple series of synthetic polyamines, it may be possible to predict how other polyelectrolytes will behave and contribute to developing predictive models of the polyelectrolyte multilayer assembly.

To probe how the primary chemical structure of the polycations influences their capability to exchange from solution with PXV in a pre-existing multilayer structure, four different polycations were examined. LPEI is a hydrophilic, weak polyelectrolyte with secondary amine chemical functionality. BPEI is similar except that due to its branched configuration has both primary and tertiary amine groups and is slightly more basic. PAH has a hydrophobic backbone with pendant primary amine groups and has a higher pK_a value than either of the PEI. PAMAM (generation 4, amine surface) is a highly branched, compact molecule with primary and tertiary amine groups. Films of 25 layer pairs of PXV/PAA assembled at pH 4 on silicon substrates were immersed in 20 mmol solutions of PAMAM, LPEI, BPEI, or PAH at different pH values. Published data from multiple literature sources were used to determine the solution degree of ionization for each polyamine. BPEI has a pK_a value of 6.5,[33,34] LPEI has a pK_a value of 5.5,[35,36] PAH has a pK_a value of 8.8,[10] and PAMAM has a pK_a of 6.9 for the primary amine groups and 3.9 for the tertiary amine groups.[37] The overall degree of ionization for PAMAM dendrimer was defined as the weighted average of the ionization of the primary and tertiary amine groups at each pH value (64 primary groups and 60 tertiary groups). It is important to note that for simplicity the degree of ionization referred here is that of the polyion in a dilute aqueous solution at the stated pH. It has been demonstrated that the degree of ionization of weak polyelectrolytes is shifted as the polyion is incorporated into the LbL film, For example, the incorporation of polyacids with polyamines has been shown to lead to a higher degree of ionization of the acid groups, i.e., to levels well above that expected at the pH of interest.[10] It is also likely that the degree of ionization of polyamines within the film will be higher than that in solution as the groups titrate each other to form the polyelectrolyte complex. We have also observed this effect, which is reported in the recent work with LPEI interdiffuion into PXV/PAA films.

As a model for exchange, 25 layer pair (PXV/PAA) films were used, which were constructed by alternating adsorption at pH 4 with no salt in either of the polyion solution. These multilayer thin films were immersed in a 20 mmol aqueous solution of each polyamine over a pH range of 3−10 for 5 days. In our previous publication, we observed the exchange of LPEI for PXV in films assembled at pH 4 in under an hour, but for films assembled at pH 5 the effect was observed by FTIR only after exposure to LPEI solution for over a day. An additional consideration is that the PXV/PAA films may swell differently on exposure to solutions of different pH values, which may influence diffusion rates. We therefore chose this longer period of exposure to the polycation solutions in order to eliminate such kinetic effects and to allow for observation of interchange even in the more kinetically hindered systems. It is noted that this time period is considerably longer than the usual time frame allotted to the construction−adsorption cycles of most LbL films. The samples were then rinsed in a stream of DI water for about 30 s, dried under nitrogen, and then examined by FTIR.

As an example of how the exchange with PXV in the multilayer was observed, Figure 1 shows the FTIR spectra of PXV/PAA films after being exposed to PAH solutions of various pH values for 5 days. It is possible to track the exchange and ejection of PXV from the film by the disappearance of the peak at ∼1640 cm^{-1} which corresponds to the aromatic carbon in the PXV chains and the appearance of peaks for the various amine groups. The characteristic PXV peak at 1640 cm^{-1} remains strong after exposure to pH 3, 4, and 6 solutions of PAH but has nearly disappeared after exposure to the pH 10 solution for 5 days. A shoulder at 1190 cm^{-1} corresponding to the aromatic amine of PXV also disappears only in the pH 10 case. Additionally, in the pH 10 spectra, a shoulder around 3000 cm^{-1} corresponding to unprotonated primary amines has appeared and the peak at 1190 cm^{-1}, which is due to aromatic amines, have nearly disappeared. For comparison, a spectrum of a PXV/PAA film soaked in DI water adjusted to pH 10 for over 24 h is included. It can be seen that the characteristic 1640 and 1190 cm^{-1} peaks remain strong even as the degree of carboxylic acid ionization changes. This confirms that the reduction in the 1640 cm^{-1} peak intensity in the other spectra is due to the ejection of PXV and not because it is covered by the increasing $-COO^-$ peak at 1560 cm^{-1}. UV−vis spectroscopy also shows the presence of PXV in the polycation solution after exposure (see Supplementary Information).

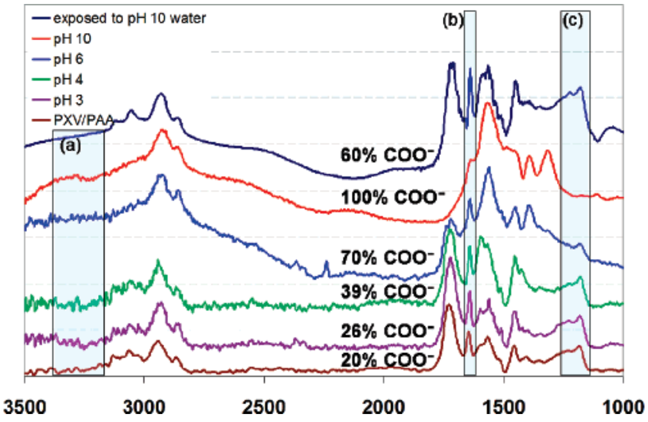

Figure 1. FTIR spectra of PXV/PAA multilayers after exposure to PAH solution at different pH values. For all of the pH values, there is an increase in carboxylic acid ionization compared to the ~20% ionizationfound in PXV/PAA films assembled at pH 4. In the pH 10 spectrum, there is a new shoulder at ~3300 cm^{-1}, and for primary amines, the aromatic carbon peak at peak at 1640 cm^{-1} has significantly decreased and the aromatic amine peak at 1190 cm^{-1} (c) has nearly disappeared. PAH can exchange with PXV at pH 10 but not at pH 3, 4, or 6. Absorbance is shown in arbitrary units, with spectra displaced along the *y*-axis for the sake of clarity. The percentage of charged carboxylic acid groups can be seen to increase after exposure to PAH of varying pH values. Exposure to high pH water also causes acid ionization but not to the same degree.

Another interesting observation is that the degree of ionization of the carboxylic acid groups is not as strongly influenced by exposure to high pH value water as that of high pH solutions of PAH. In all cases, whether or not exchange occurs, the carboxylic acid groups become more ionized, showing the ability of polyamines to titrate PAA. Exposure to pH 10 water changes the degree of acid ionization (to about 60%) but not as radically as that exposed to a PAH solution of pH 10 (100% ionization). This is further evidence for the acid−base exchange that occurs due to the presence of the polycation, which provides the major driving force for interdiffusion into the pre-existing film. The ability of weak polycations to change their ionization in response to their environment is no doubt an important factor in the displacement of PXV in favor of weak polyamines. One must assume that the polyamines are similarly undergoing changes in ionization by becoming more charged once within the film but that is more difficult to probe. Also, the observation that the starting degree of ionization of the polyamine changes the final outcome (and speed of exchange as discussed below) suggests the kinetic nature of this process. The more highly protonated polyamines adsorb to the multilayer surface, become kinetically fixed on the top surface, and repel additional polycation chains in solution from the surface before they are able to penetrate the multilayer structure and ionize a sufficient number of acid groups.

The results of the exchange experiment are summarized in Figure 2 along with the nominal solution state degree of ionization of the various polycations, obtained from titration curves. It is worth noting that significantly lower effective degrees of ionization have been observed in polyelectrolyte solutions, due to counterion condensation.[38] An x indicates the solutions for which exchange was seen to take place after 5 days of exposure. The criterion for determining whether exchange had taken place was the observation of a significant decrease of the peak in the FTIR signal at 1640 cm^{-1} along with other changes in the FTIR signals, as described above.

Each of the four polyamines is able to exchange with the PXV under appropriate pH conditions. LPEI was able to exchange with PXV at pH 3.5 and above, and BPEI exchanged at pH 4 and above. In the case of PAMAM, the exchange occurred at pH 4.5 and above. In the case of PAH, the exchange was observed at pH 8, 9, and 10 only. In all cases, exposure to a solution of the polycation was seen to increase the degree of ionization of the carboxylic acid groups within the film. Although hydrogen bonding has been reported in LbL films[39] and in those containing PAA,[40] it is unlikely to make any significant contribution here due to the degree of ionization of the PAA. These results show that there is a critical degree of solution state polycation ionization above which this process does not occur and the PXV chains are not displaced by the weak polycation. When highly charged, the chains are more highly extended and therefore adsorb more readily to the surface that is terminated with polyanion. This is seen elsewhere in the LbL literature as “molecularly thin” adsorbed layers of highly charged polyelectrolytes.[26,31,41] Highly charged polymers are also much more likely to become kinetically trapped at or near the surface of the film via ionic cross-links; the mobility of the chains within the LbL bulk film would thus be further limited for the most highly charged polymers due to charge interactions as well as extended chain size. For PAH, LPEI, and BPEI, this critical degree of ionization is ~70% ionization, and for PAMAM it is approximately 55% ionized.

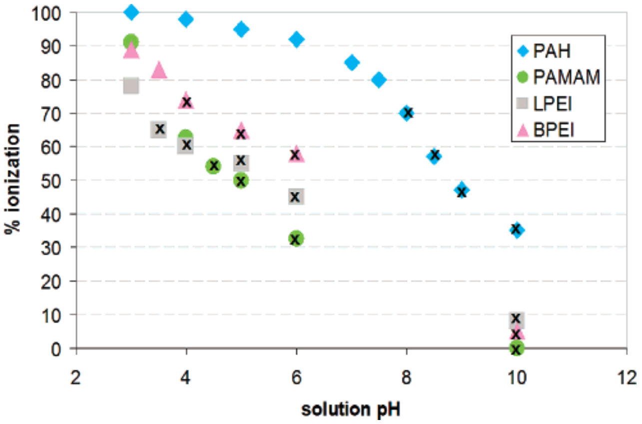

Figure 2. Degree of ionization of the various polycations in solution, taken from refs 23−28, determined by titration curves. The solutions that exhibited exchange with PXV in the $(PXV/PAA)_{25}$ multilayer are marked by an x. For each polycation, there seems to be a degree of ionization above which exchange is not able to take place. In the case of PAMAM, this critical degree of ionization is lower, probably due to PAMAM’s geometry and high charge density, which makes it more likely to adsorb to a charged surface.

These results indicate that the interdiffusion and exchange processes may occur for a range of polyelectrolytes of different chemical structures over appropriate time scales even if they are usually observed to form stable multilayers over the time frame of normal multilayer adsorption procedures. Although PAH is known to form stable, linear LbL films, it exhibits interdiffusion at lower degrees of ionization and slower rates when presented with a driving force for exchange. PAMAM dendrimer has a very different geometry and a combination of primary and tertiary amine groups. On the basis of the observation that these polycations were also able to diffuse within the PXV/PAA multilayer, we believe that diffusion and exchange must be related to a more general aspect of the polyelectrolyte shape, size, and ionization density. While we have demonstrated the displacement, specifically, of PXV from multilayer films in this work, we have reason to believe that exchange and diffusion can potentially impact any heterostructured LbL assembled film or any LbL film which is exposed to a polymer solution after assembly. The important factors

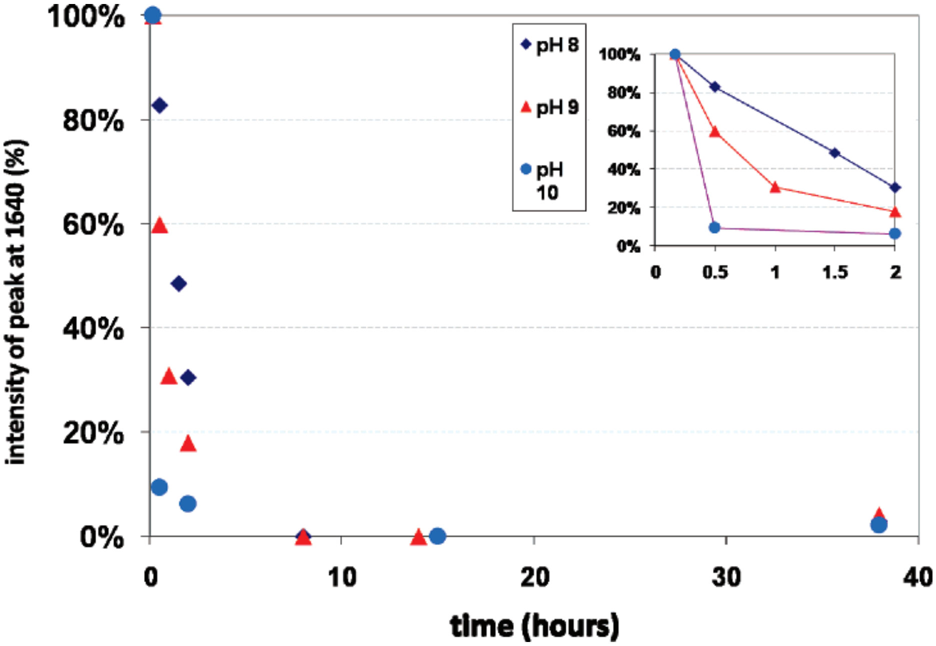

Figure 3. Kinetics of exchange of PXV with PAH. The decline of the characteristic PXV FTIR peak at 1640 cm^{-1} is plotted as a function of total exposure time to various solutions of PAH. The peak value declines more quickly for the higher pH solutions. Therefore, it can be said that the higher pH, and less ionized, PAH chains are able to exchange more quickly with PXV in solution.

seemingly are that the initial multilayer not have a high ionic cross-link density and that there be strong, preferential interactions between the polyelectrolyte presented in solution and the oppositely charged polymer within the initial multilayer film. It also seems that the polyelectrolyte in solution will be unable to diffuse into the original multilayer film if it is too strongly charged, likely due to strong electrostatic interactions that yield a kinetically hindered polyion chain at the surface. We propose that such conditions should be reproducible with any number of specific chemistries.

Our work indicates that partially charged polyamines are better able to diffuse through bulk LbL films than fully charged chains. The fully charged chains are much more likely to immediately adsorb onto the LbL surface. Once the surface PAA molecules are satisfied, charge reversal will occur and electrostatic repulsion will prevent PAH chains from penetrating the multilayer. PAMAM dendrimer is known to be a sticky molecule due to the high density of charged groups confined to a small volume. At pH 3 and 4, all of the PAMAM amine groups, including tertiary and primary, are charged, but at pH 4.5 and above, only the primary amines groups are charged. LPEI and BPEI are also more hydrophilic than the PAMAM and especially PAH. It seems to be a reasonable assumption that better solvated polymer chains will be able to more easily penetrate the LbL structure swollen in water. Hydrogen-bonded systems as well as some of these weak polyelectrolyte systems, such as LPEI/PAA, have been reported to show extremely thick per-layer pair thickness over the pH regime at which we see interdiffusion to take place.[42,43] Interdiffusion of the polymers likely contributes toward the superlinear growth that yields extremely thick films.

Post-treatment of LbL films by exposure to solutions at different pH values has been known to create morphological changes in the films, such as the creation of pores.[44] As mentioned above, exposure of the PXV/PAA multilayer to the polycation solutions does change the degree of ionization of the carboxylic acid groups in the film even in the cases for which no exchange takes place. Carboxylic acid ionization starts at about 20% in the PXV/PAA multilayers assembled at pH 4 but becomes 26% after exposure to pH 3 PAH solution, 39% after exposure to pH 4 PAH solution, 70% after exposure to pH 6 PAH solution, and essentially 100% after exposure to pH 10 PAH solution. Exposure to pH 10 water only yields a carboxylic acid ionization of about 60%. The carboxylic acid groups are much more readily deprotonated in the presence of 1°, 2°, or 3° amine groups rather than the quarternized bispyridyl functionality of the PXV. These acid−base interactions are strongly favored over the electrostatic PXV/PAA interactions due in part to the fact that the charged state of the carboxylic acid groups is very sensitive to the presence of polyamines, yielding many more ionized sites in the presence of basic polyamines.

These degrees of ionization are higher than the values of carboxylic acid ionization in the original film and are also higher than the degree of ionization of PAA in solution for each respective pH value.[10] A simple increase in the PAA ionization is not sufficient to cause the replacement of PXV in favor of a polycation, which could form more ionic bonds with PAA. The polycation itself must also possess a certain degree of mobility, which the strongly charged PAH chains do not.

The kinetics of PXV exchange with PAH was also probed. The FTIR spectra of $(PXV/PAA)_{25}$ were recorded at various times of exposure to PAH solutions at pH 8, 9, and 10, which had all previously been shown to cause exchange over the period of 5 days. For the complete time progression FTIR data, please see Supporting Information. The decline in intensity of the characteristic PXV peak at 1640 cm^{-1} is plotted as a function of time in Figure 3. The exchange process was followed over a period of 38 h. The starting value of the peak at 1640 cm^{-1} is considered to be the 100% value and the peak intensity after 38 h is considered to be the 0% baseline. Figure 3 then gives a comparison of how quickly the exchange takes place in the three films as opposed to an absolute percentage of PXV chains that has left the film. It can be seen that the intensity of the 1640 cm^{-1} peak drops of most quickly after exposure to pH 10 solution of PAH, then after exposure to pH 9 solution, and decreases the most slowly after exposure to pH 8 solution. In the case of exposure to pH 10 PAH solution, the 1640 cm^{-1} peak decreases to about 55% of its original value after 2 h and does not change significantly afterward over the course of 40

h. For the pH 9 case, a similar decrease is seen after 8 h of exposure time, and in the pH 8 case, 8 h of exposure reduces the peak to 63% of its original value, which also does not change significantly afterward until 40 h of total exposure time. At pH 10, PAH chains in solution are only 35% ionized, whereas the pH 8 solution PAH chains are 70% ionized. We observe that this does indeed make a significant difference in the polycation's ability to penetrate the film structure. We also see that the a plateau seems to be reached in the case of PAH exchanged with PXV in 10 h or less and there is likely an equilibrium reached that leaves some PXV in the multilayer. A comparison of the speed of exchange between the various polycations should provide more specific insight into the role that each specific type and basicity of the amine group plays and will be the focus of future studies.

Conclusions

In this work, we demonstrate that a number of weak polycations are capable of interdiffusion and exchange with the PXV and that this exchange appears to take place at or below a critical solution state polyion degree of ionization of approximately 70%. We have also shown that at lower degrees of ionization, the diffusion and exchage processes occur more quickly. Other factors that influence the kinetics of interdiffusion include polyion size and shape and the nature of the thermodynamic driving force behind the polyion exchange. For example, PAMAM dendrimer seems to be unable to exchange at an ionization greater than approximately 55%. We believe that the extreme lability of the carboxylic acid and amine groups contributes significantly to this process. These results may have a number of implications for biological applications of LbL films, as this weak polycation class includes many proteins, polysaccharides, and other biologically derived macromolecules. The exchange process may be relevant for both during the assembly of LbL films and postassembly conditions to which the films are exposed, such as a drug delivery or other biomedical devices, which would be subjected to physiological conditions. We are additionally able to conclude that there is a critical degree of ionization of the polycation chains below which these weak polycations are able to interdiffuse into our model system and replace the strong polycation. This critical degree of ionization is influenced by chain architecture, as it was found to be significantly lower for the dendritic polymer. The increased physical proximity of the functional groups of the PAMAM dendrimer makes adsorption more favorable, and diffusion occurs only when the dendrimers are less charged overall.

These results point to some parameters that can be chosen in order to control the inner structure of LbL films and more specifically heterostructures. The use of nondiffusive polycations/conditions can be applied as a general strategy for compartmentalizing film sections.

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Supporting Information Available: Molecular weight characterization of PXV by NMR, more FTIR data of specific exchange processes, and UV−vis data. This information is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Decher, G. *Science* **1997**, *277*, 1232−1237.
(2) Farhat, T. R.; Hammond, P. T. *Adv. Funct. Mater.* **2006**, *16*, 433−444.
(3) Hammond, P. T. *Adv. Mater.* **2004**, *16*, 1271−1293.
(4) Schmitt, J.; Grünewald, T.; Decher, G.; Pershan, P. S.; Kjaer, K.; Lösche, M. *Macromolecules* **1993**, *26*, 7058−7063.
(5) Elbert, D. L.; Herbert, C. B.; Hubbell, J. A. *Langmuir* **1999**, *15*, 5355−5362.
(6) Picart, C.; Lavalle, P.; Hubert, P.; Cuisinier, F. J. G.; Decher, G.; Schaaf, P.; Voegel, J. C. *Langmuir* **2001**, *17*, 7414−7424.
(7) Picart, C.; Mutterer, J.; Richert, L.; Luo, Y.; Prestwich, G. D.; Schaaf, P.; Voegel, J. C.; Lavalle, P. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 12531−12535.
(8) Lavalle, P.; Picart, C.; Mutterer, J.; Gergely, C.; Reiss, H.; Voegel, J. C.; Senger, B.; Schaaf, P. *J. Phys. Chem. B* **2004**, *108*, 635−648.
(9) Xie, A. F.; Granick, S. *Macromolecules* **2002**, *35*, 1805−1813.
(10) Choi, J.; Rubner, M. F. *Macromolecules* **2005**, *38*, 116−124.
(11) Nolte, A. J.; Rubner, M. F.; Cohen, R. E. *Langmuir* **2004**, *20* (8), 3304−3310.
(12) Lavalle, P.; Vivet, V.; Jessel, N.; Decher, G.; Voegel, J. C.; Mesini, P.; Schaaf, P. *Macromolecules* **2004**, *37*, 1159−1162.
(13) Yoo, P. J.; Nam, K.; Qi, J.; Lee, S.; Park, J.; Belcher, A.; Hammond, P. T. *Nat. Mater.* **2006**, *5*, 234−240.
(14) Jomaa, H. W.; Schlenoff, J. B. *Langmuir* **2005**, *21*, 8081−8084.
(15) Quinn, J. F.; Yeo, J. C. C.; Caruso, F. *Macromolecules* **2004**, *37*, 6537−6543.
(16) Kovačević, D.; van der Burgh, S.; de Keizer, A.; Cohen Stuart, M. A. *Langmuir* **2002**, *18*, 5607−5612.
(17) Dubas, S. T.; Schlenoff, J. B. *Macromolecules* **2001**, *34*, 3736−3740.
(18) Izumrudov, V.; Kharlampieva, E.; Sukhishvili, S. A. *Macromolecules* **2004**, *37*, 8400−8406.
(19) Michaels, A. S. *Ind. Eng. Chem.* **1965**, *57*, 32−40.
(20) Michaels, A. S.; Miekka, R. G. *J. Phys. Chem.* **1961**, *65*, 1765−1773.
(21) Wood, K. C.; Chuang, H. F.; Batten, R. D.; Lynn, D. M.; Hammond, P. T. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 10207−10212.
(22) Garza, J. M.; Schaaf, P.; Muller, S.; Ball, V.; Stolz, J. F.; Voegel, J. C.; Lavalle, P. *Langmuir* **2004**, *20*, 7298−7302.
(23) Sun, B.; Jewell, C. M.; Fredin, N. J.; Lynn, D. M. *Langmuir* **2007**, *23* (16), 8452−8459.
(24) Porcel, C.; Lavalle, P.; Decher, G.; Senger, B.; Voegel, J. C.; Schaaf, P. *Langmuir* **2007**, *23* (4), 1898−1904.
(25) Zacharia, N. S.; DeLongchamp, D. M.; Modestino, M.; Hammond, P. T. *Macromolecules* **2007**, *40*, 1598−1603.
(26) Schoeler, B.; Kumaraswamy, G.; Caruso, F. *Macromolecules* **2002**, *35* (3), 889−897.
(27) Schoeler, B.; Sharpe, S.; Hatton, A. T.; Caruso, F. *Langmuir* **2004**, *20*, 2730−2738.
(28) Glinel, K.; Moussa, A.; Jonas, A. M.; Laschewsky, A. *Langmuir* **2002**, *18*, 1408.
(29) Steiz, R.; Jaeger, W.; von Klitzing, R. *Langmuir* **2001**, *17*, 4471.
(30) Hoogeveen, N. G.; Stuart, M. A. C.; Fleer, G. J.; Bohmer, M. R. *Langmuir* **1996**, *12*, 3675.
(31) Shiratori, S. S.; Rubner, M. F. *Macromolecules* **2000**, *33*, 4213−4219.
(32) Lutkenhaus, J. L; Hrabak, K. D.; McEnnis, K.; Hammond, P. T. *J. Am. Chem. Soc.* **2005**, *127*, 17228−17234.
(33) Bloys van Treslong, C. J. *Recl. Trav. Chim. Pays-Bas* **1978**, *97*, 13.
(34) Shepherd, E. J.; Kitchener, J. A. *J. Chem. Soc.* **1956**, *4*, 2448.
(35) Weyts, K. F.; Goethals, E. J. *Makromol. Chem. Rapid Commun.* **1989**, *10*, 299.
(36) Smits, R. G.; Koper, G. J. M.; Mandel, M. *J. Phys. Chem.* **1993**, *97*, 5745.
(37) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A. *Angew. Chem., Int. Ed.* **1990**, *29*, 138−175; Park, S. Y.; Barrett, C. J.; Rubner, M. F.; Mayes, A. M. *Macromolecules* **2001**, *34*, 3384−3388.
(38) Muthukumar, M. *J. Chem. Phys.* **2004**, *120* (19), 9343−9350.
(39) Stockton, W.; Rubner, M. F. *Macromolecules* **1997**, *30*, 2717−2725.
(40) Granick, S.; Sukhishvili, S. A. *J. Am. Chem. Soc.* **2000**, *122*, 9550−9551.
(41) Park, S. Y.; Barrett, C. J.; Rubner, M. F.; Mayes, A. M. *Macromolecules* **2001**, *34*, 3384−3388.
(42) DeLongchamp, D. M.; Hammond, P. T. *Chem. Mater.* **2003**, *15* (5), 1165−1173.
(43) DeLongchamp, D. M.; Hammond, P. T. *Langmuir* **2004**, *20* (13), 5403−5411.
(44) Mendelsohn, J. D.; Barrett, C. J.; Chan, V. V.; Pal, A. J.; Mayes, A. M.; Rubner, M. F. *Langmuir* **2000**, *16*, 5017.

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