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Review

Where Polyelectrolyte Multilayers and Polyelectrolyte Complexes Meet

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ABSTRACT: We summarize existing knowledge and present some new results on the relationship between polyelectrolyte multilayer (PEM) growth and phase behavior of polyelectrolyte complexes (PECs) in solution. Detailed understanding of competition between surface and solution as applied to PEMs requires selective labeling of polymers and/or the application of techniques that allow chemically specific monitoring of film components, such as in-situ ATR−FTIR spectroscopy. The trends observed with multilayers directly follow from the properties of PECs in solution. Effects of a number of parameters, such as the type of interacting polyelectrolyte chains, the ratio of their lengths, and ionic strength and pH of deposition solutions, on the likelihood of the multilayer stability or erosion are considered. Polycations with high density of primary amino groups and polyanions with SO_3^- or SO_4^- groups show the strongest interpolyelectrolyte binding, resulting in inhibited chain exchange within PECs and/or PEMs. With weakly bound polyelectrolyte pairs—polycations containing quaternary ammonium groups and carboxylate polyanions—water-soluble PECs are easily formed, often resulting in erosion of PEMs. For the latter case, we report a full phase diagram of polycation/polyanion/NaCl aqueous mixtures and show how ionic strength can be used to tune the deposition of PEMs at surfaces. In addition, we present that the phase behavior of PECs in solution also controls pH response of PEMs at surfaces. Better knowledge of the relationships between the PEMs and PECs allows rational prediction and control of deposition of a wide range of weak or permanently charged polyelectrolytes at surfaces.

Introduction

Alternating deposition of oppositely charged polyelectrolytes at a surface has recently become a widely used technique for surface functionalization and construction of polymer films.[1−8] The fundamentals and applications of these novel nanoscopically structured materials are summarized in several recent reviews.[9−13] The deposition procedure is temptingly simple and is often viewed as being applicable to virtually any pair of synthetic polyelectrolytes or charged biopolymers such as proteins, enzymes, or nucleic acids. Indeed, a variety of interacting macromolecules have been successfully used for the multilayer buildup.[7−13] In the euphoria of success, cases when polyelectrolyte multilayer (PEM) films could not be produced are rarely considered. Limitations of layer-by-layer technique were recongnized in cases when no interpolyelectrolyte binding occurred, such as for polymers whose charge density is lower than critical.[14,15] Disruption of interpolyelectrolyte binding also lies in the heart of salt-induced[16] and pH-induced dissolution of multilayers.[17−19] Other observations, however, were also made of removal of polyelectrolyte (PE) chains from the PEM when the substrate is brought in contact with PE solutions. Such chain removal has been reported by several authors[20−22] and is usually

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connected to solubilization of adsorbed chains through formation of a water-soluble PE complex (WPEC).[23] Competitive removal of polyelectrolyte chains from PEM to WPEC implies that chains remain strongly associated in both the PEM and WPEC, but redistribution of chains occurs, favoring WPEC and resulting in PEM erosion. One then concludes that strong intermolecular association between a pair of polyelectrolyte chains is not the only prerequisite for successful film deposition. A careful look at the literature shows that the reported cases of PEM erosion and inhibition of film growth are not rare for polyions with low charge density[24] and are often found when a combination of a weak polyacid at neutral/basic pH values and a positively charged protein or a synthetic polycation with quaternary ammonium groups are used for PEM deposition.[25,26] This deposition scenario differs from irreversible film growth, in terms of deposited amount, considered by theories of PEM growth[27] and recently reviewed by Dobrynin and Rubinstein.[28] Importantly, the exchange between PEM and WPEC is easy to overlook in experiments with no in-situ monitoring of the amount adsorbed with time. However, such exchange might drastically influence the composition and likely layering within PEMs and have severe consequences for properties and performance of PEM films. Understanding occurrences of PEM erosion is also important as it will eventually provide materials scientists with a “map” of PEM growth which will allow one to rationally avoid unstable regimes during film deposition.

This review presents a first step toward this goal, where we summarize existing knowledge and present some new results on the relationship between PEM growth and phase behavior of PE complexes (PECs) in solution. Where possible, we generalize and predict the likelihood of PE chain removal from PEM films during film growth for different types of polyelectrolytes and various ionic strength and pH conditions used for PEM deposition.

I. Correlation of PEM Growth and Phase Diagrams of PEC in Solution: Background

Cohen Stuart and co-workers[29] have clearly emphasized the connection between the phase behavior of PECs in solution and the deposition of PEMs. Specifically, using a polyelectrolyte pair of poly((dimethylamino)ethyl methacrylate) (PAMA) and poly(acrylic acid) (PAA), the authors observed overshoots in the total amount of polymers within the film at the step of polycation addition. Such overshoots reflected initial binding of polycation chains at the surface which was later followed by chain solubilization. The overshoot behavior developed when the concentration of salt increased to 5 mM which was required for acceleration of polyelectrolyte chain exchange or “plastification” of the PEM. In a later paper by Kovačević et al.,[30] a specific ion effect on erosion of multilayers (in the limit of small salt concentrations used) has been discussed. The authors stated that “the behavior of polyelectrolyte multilayers is governed by the same physics as that of corresponding polyelectrolyte complexes in solution”.[30] Furthermore, the relevance of the phase diagrams of PECs in solution was established in the context of PEMs. Schlenoff[21] has also described, for various molecular weights of polyelectrolytes, the competition between

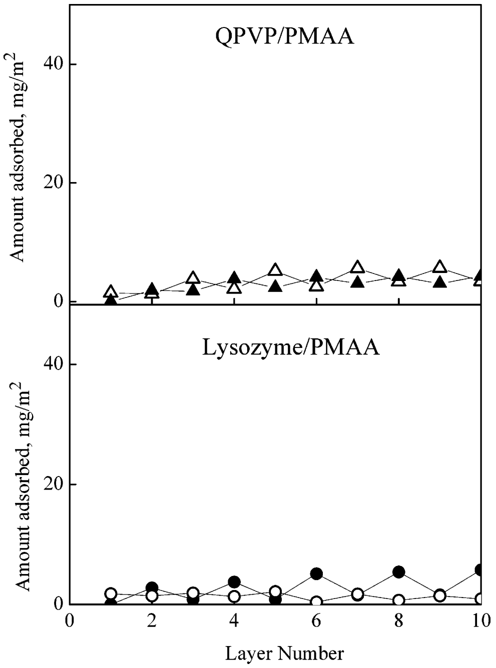

Figure 1. Layer-by-layer deposition of 10 layers in the QPVP/PMAA film (top panel) and lysozyme/PMAA system (bottom panel). Assembly of PMAA (open symbols) and QPVP or lysozyme (filled symbols) were performed for 30 min from 0.1 mg/mL solution in 0.01 M phosphate buffer at pH 8.

adsorption and solubilization of polyelectrolyte chains during PEM buildup.

Indeed, when a PEM is brought in contact with a solution of free polyelectrolyte chains (a situation routinely occurring during PEM buildup), erosion of multilayers can occur. In these conditions, one usually finds a large excess of polyelectrolyte in solution compared to an oppositely charged polymer within the film. For example, when film is deposited onto a substrate with 5 cm^2 surface area in a 50 mL beaker containing 1 mg/mL polymer solution, the total excess of polymer in solution to that residing at the film surface is 5 orders of magnitude (assuming the amount of oppositely charged polymer adsorbed within the outmost layer of the film is 1 mg/m^2). For polyelectrolyte systems in which chain exchange occurs at the experimental time scale, such excess of charged chains in solution is most favorable for the formation of WPECs.[31] When a polyelectrolyte chain is included within a WPEC, one expects gains in translational and configurational entropy due to an increase in the number of WPEC species in solution and greater mobility of dissolved polyelectrolyte chains, respectively. For many polyelectrolyte systems, specifically those containing highly hydrated carboxylate or phosphate polyanions and/or tertiary or quaternary ammonium polybases, water-soluble complexes are formed when the excess of negative charge is large, i.e., when the ratio φ of total positive-to-negative charge (in molar concentrations of repeat units) is relatively small, $\varphi < 0.5$.[30] The observation of chain removal during deposition of strongly charged polyelectrolytes within PEMs is a common phenomenon when polycations with tertiary or quaternary amino group and poly(carboxylic acid) chains are used.

Figure 1, top panel, shows data obtained in our lab where 98% quaternized poly(*N*-ethyl-4-vinylpyridinium bromide) (QPVP, with M_w of 330K, a polymerization degree DP$_{QPVP}$ of 1600) was assembled with poly(methacrylic acid) (PMAA with M_w of 150K, DP$_{PMAA}$ of 1700) at pH 8.4, when both components are strongly charged. A similar failure in film deposition occurs when one tries to self-assemble a globular protein lysozyme, Lys (M_w 14 600, pI 11.0) with PMAA at pH 8.4 where PMAA is fully ionized and Lys carries overall positive charge. As shown in Figure 1, bottom panel, Lys is completely removed from the surface to solution at the step of polyacid deposition, and adsorbed polyacid is in turn solubilized by Lys. In solution, strong binding between a positively charged protein and charged poly(carboxylic acid)s was found, with formation of WPECs in excess PMAA.[32] Also, solubilization of polyelectrolyte chains in an excess of proteins of opposite charge has been observed earlier.[33,34] In the literature, many other examples of multilayer erosion can be found,[20−22,24] illustrating a potential problem the multilayer technique might face if deposition needs to be performed at desired conditions and the use of specific polymer type is required.

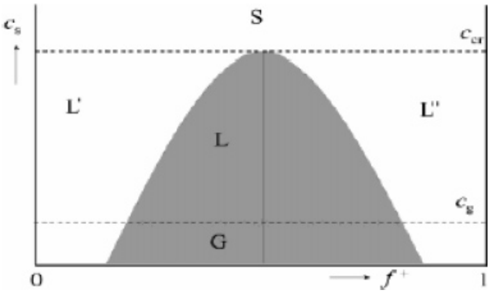

Figure 2. Schematic representation of the stability diagram of an adsorbed multilayer of oppositely charged polyelectrolytes (PAMA/PAA) (taken from ref 29).

A schematic stability diagram of multilayers was recently suggested by Kovačević et al.,[29] which takes into account the effect of the mole fraction of positively charged polyelectrolyte species, f^+, and concentration of low molecular salt on precipitation of polyelectrolyte complex. The diagram is shown in Figure 2. Erosion of PAMA/PAA PEMs at ionic strength of 5 mM (i.e., at ionic strength higher than "glassy ionic strength" c_g[29]) was explained by formation of negatively charged WPECs (region L′ in Figure 2) or positively charged WPECs (region L″ in Figure 2) during the deposition of polyanion or polycation, respectively. Importantly, the schematic diagram suggests that region L where PEC precipitate and stable multilayers are formed is bell-shaped, with wider precipitation range at lower salt concentrations.

However, phase separations in solutions of oppositely charged polyelectrolytes can be much more complicated. We studied phase separation in the QPVP/PMAA polyelectrolyte system in which polymer chain lengths differed by a factor of 1.8 (QPVP with M_w of 200K, DP 900; PMAA with M_w of 150K, DP 1400) in aqueous solutions at pH 8.4, where both polyelectrolytes were completely ionized. The phase diagram for this system is fan-shaped, as shown in Figure 3, and is in good agreement with our recent report on salt-induced phase separation of polyelectrolyte complexes in solution and its correletation with enhanced deposition of multilayers in salt solutions.[35] Phase diagrams similar to one shown in Figure 3 have been also found for other polyelectrolyte systems such as PAA/ionene,[23] PMAA/ionene,[36] DNA/poly(*N*,*N*′-dimethyldiallylammonium chloride) (PDADMAC),[37] DNA/QPVP,[37] RNA/PDADMAC, or RNA/QPVP.[38]

Results on compositional analysis of QPVP/PMAA solutions after separation of the precipitate are presented in Figure 4, top panel (see ref 35 for experimental details). At lower salt concentrations water-soluble complexes (region I) are formed for 5-fold excess (in molar units) of PMAA or QPVP ($f^+ = 0.167$ or $f^+ = 0.833$). Increased salt concentration triggers redistribution of polymer chains, and water-insoluble complex

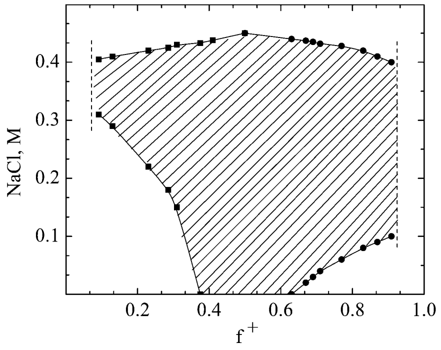

Figure 3. Phase diagram for QPVP/PMAA/NaCl mixtures in aqueous solution at pH 8.4 supported by 0.01 M phosphate buffer. Concentrations of polymers were 0.001 M, and degrees of polymerization of QPVP and PMAA were 900 and 1700, respectively.

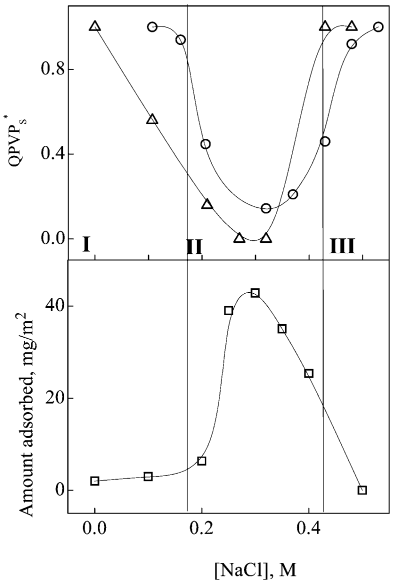

Figure 4. Top panel: Fraction of QPVP remaining in supernatants (QPVP*$_s$) of QPVP/PMAA mixtures for PMAA (M_w 350K, DP 4000) in excess of PMAA; $f^+ = 0.167$ (circles) and in excess of QPVP (M_w 330K, DP 1600), $f^+ = 0.833$ (triangles) plotted against concentration of the added salt. Bottom panel: Total amount adsorbed of nine-layer QPVP/PMAA films deposited from solution with various salt concentrations. Concentrations of polymers were 0.04 M (in monomer units) in the top panel and 0.1 mg/mL in the bottom panel. In all experiments, 0.01 M phosphate buffer at pH 8.4 was used.

and a water-soluble complex with a smaller fraction of PMAA or QPVP units coexist in region II. Mechanism for the salt-induced phase separation that considers the WPEC contraction due to screening of unbound PMAA (or unbound QPVP) charges by the added salt and cooperative chain rearrangements at the point of phase separation caused by high local ionic strength was recently proposed.[39] Importantly, salt-induced redistribution of polymer chains and separation of phases have direct consequences for multilayer growth. The amounts of polymers deposited at surfaces present mirror images of phase diagrams in solution (Figure 4, bottom panel) with larger amounts of polymers included within the film when phase separation occurs. Note that at even higher salt concentration (region III), QPVP/PMAA ionic pairs completely dissociate as a result of competition with low molecular weight ions, and both the PEC precipitate in solution and PEM dissolve.

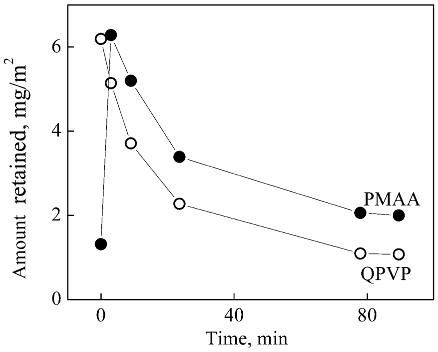

Figure 5. Time evolution of PMAA mass adsorbed (filled symbols) and QPVP (M_w 330K, DP 1600) mass adsorbed (open symbols) at the step of PMAA (M_w 350K, DP 4000) deposition onto an eight-layer QPVP/PMAA film from solutions at pH 8.4 which additionally contained 0.2 M NaCl.

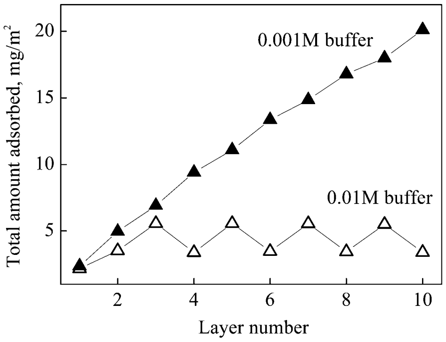

Figure 6. Evolution of total amount adsorbed during assembly of 10-layer QPVP (M_w 330K, DP 1600)/PMAA (M_w 25K, DP 290) films from 0.01 M (open symbols) and 0.001 M (filled symbols) buffer solutions at pH 8.4.

The application of in-situ ATR−FTIR for detecting PEM deposition allows the unique capability of chemical differentiation between PEM components. Figure 5 shows the results of separate monitoring of PMAA and QPVP during the QPVP/PMAA film buildup. The amount of PMAA deposited overshoots as a function of time, reflecting initial accumulation of PMAA at the surface, followed by overwhelming removal to WPECs. Observation that the balance between multilayer growth and polyelectrolyte chain removal is kinetically controlled was also made earlier by Schlenoff and co-workers.[21] Removal of QPVP included within the outermost layer starts immediately after PMAA addition and occurs at a similar time scale with PMAA adsorption. Enhanced deposition of polymer layers, illustrated in Figure 4 (bottom panel), is dictated by the phase diagrams of WPEC (Figure 4, top panel), which shows that formation of water-insoluble complexes is thermodynamically favorable at relatively high salt concentrations. The equilibrated amounts adsorbed depend on details of phase diagrams for a particular polycation/polyanion pair and may vary greatly between systems.

Interestingly, while multilayer formation is prohibited in 0.01 M phosphate buffer solutions, the film exhibits significant growth when concentration of counterions becomes very low (less than 0.003 M buffer or salt solutions). Figure 6 contrasts assembly of QPVP/PMAA films performed at different concentrations of phosphate buffer solutions at pH 8.4. In 0.001 M buffer solutions, robust film growth occurred, while at higher buffer concentration of 0.01 M multilayers were eroded. This result is consistent with earlier findings by Kovačević et al. on salt-induced acceleration of polyelectrolyte chain exchange.[29] Note that in our system an erosion-to-growth transition was observed for all ratios of polycation-to-polyanion chain lengths. Further in this paper we present results obtained in 0.01 M buffer solutions of polymers, where interchain interactions were weakened to promote exchange between polymer chains deposited within the film and those in solution.

II. Equilibrium and Dynamics in PEMs: Lessons from PECs

Below we consider effects of a number of parameters, such as the type of interacting polyelectrolyte chains, the ratio of their lengths, and ionic strength and pH of deposition solutions, on the likelihood of the multilayer stability or erosion.

II.1. Polyelectrolyte Type and Equilibrium and Dynamics in PEC. The type of polyelectrolyte has been shown to critically affect the binding energy and equilibration time of interacting polyelectrolytes in solution. For easily equilibrating PEC systems consisting of polyamines with tertiary or quaternary amino groups and polyacids with carboxylate or phosphate groups, it was shown that WPECs are thermodynamically stable structures, with a measurable chain transfer rate between molecularly dispersed complexes.[40] Here, we consider cases where all participating polymers are highly charged, i.e., either the case of strong polyacid and polybases or weak polyacids/polybases exposed to pH values significantly higher/lower than their pK_a/pK_b so that macromolecules can be considered as strong polyelectrolytes in these conditions. Binding of the two oppositely charged polyelectrolyte chains results in formation of multiple polymer/polymer contacts. A simplistic description of the binding constant K_n between two interacting chains having n polymer/polymer contacts is as a product of individual contacts $K_n = K_1^n$ (I), where K_1 is the binding constant of the interacting monomeric units.[41] The multiplicity of polymer−polymer contacts within polymer complexes, reflected by this equation, has major consequences for polyelectrolyte interactions.

First, according to this equation, in mixtures of the two types of interacting polymers A and B, where polymer A is monodisperse and of long chain length and type B polydisperse and of shorter chain lengths, strong selectivity in binding of the longest chains of type B within a PEC A/B is expected. Selective binding of this type was originally found for complexes stabilized by H-bonds.[42,43] For electrostatically associating polyelectrolyte chains, similar chain length selectivity was observed. Specifically, a polycation of high charge density (QPVP), DP of 500, and narrow molecular weight distribution showed selective binding with the longest chains in PMAA mixtures of various DPs, e.g., 4000, 500, and 50.[44]

The second type of selectivity of polyelectrolyte binding was observed in mixtures of three polyelectrolytes and reflects preferential binding based on different chemical nature of polymer chains. According to the equation (I), even small changes in the binding constant K_1 for individual polymer/polymer contacts should translate into large changes in mutual affinity of polymer chains. Experimentally, for WPECs of a quaternary ammonium polycation, QPVP, and polycarboxylate (PMAA) or polyphosphate polyanions (PP) with the same chain lengths, K_1 values, as estimated from the critical concentration of sodium chloride required for dissociation of WPECs, were very close.[45] In these systems with closely matched binding constants, when the polycation and the two polyanions are mixed together, the position of equilibrium was highly sensitive to the ratio of polyanion chain lengths, to the type of small ions in the buffer, and to the type of substituent in the QPVP chains. Specifically, QPVP preference to PP significantly increased as the radius of monovalent cation added as a chloride salt decreased from K^+ to Na^+ and Li^+ [45] and as the *N*-alkyl substituent in poly(*N*-alkyl-4-vinylpyridinium) was changed from propyl to ethyl and methyl.[46] Note also that in this system the same effect also could be caused by an increase in PP length[45] or by variation of temperature.[46]

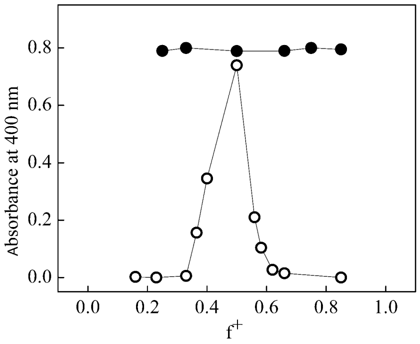

Figure 7. Turbidity of QPVP/PMAA (open circles) and PAH/PMAA (filled circles) mixtures measured as the absorbance of 0.04 M (repeat units) solutions at 400 nm as a function of the mole fraction of positively charged units f^+. The pH of 8.4 was supported by 0.01 M Trizma buffer. PMAA, QPVP, and PAH with M_w of 72K, 200K, and 70K, respectively, were used for the experiment.

Similar effects were also found in the system PMAA/QPVP/DNA.[47] However, in the latter case, the efficiency of monovalent cations to shift equilibrium toward formation of QPVP/DNA complex followed the opposite sequence; i.e., it was increased from Li^+ to $K^+$and further to Na^+, reflecting the strong affinity of Li^+ cations to native DNA. Similar but stronger effects of divalent cations, such as Ca^{2+} and Mg^{2+}, were also reported.[48]

Selectivity of binding of different ionenes to PMAA or DNA in the DNA/PMAA mixtures is efficiently controlled by the length and charge density of the ionene chains.[49,50] Thus, the increase in the ionene DP resulted in a steady increase in selectivity of interaction and ultimately in almost exclusive binding of one of the two polyanions. Ionenes with higher charge density exhibited preferential binding to PMAA, whereas ionenes with the lowest charge density selectively bound DNA. Quite recently, the fact of recognition and preferential binding of linear polycations with DNA of certain topology has been established in mixtures of polycations with linear and plasmid DNA.[51] Another interesting finding is selective binding of DNA by a polycation in mixtures of DNA and RNA.[38]

Recently, a quantitative approach to evaluate the binding constants K_1 and K_n was proposed on the basis of studies of the competitive reactions in three-component polyelectrolyte solutions.[48] Interestingly, for 3,3-ionene/DNA and 3,3-ionene /poly(acrylic acid) systems, K_1 values showed only a small difference (1.012 and 1.024 for 3,3-ionene/DNA and 3,3-ionene/poly(acrylic acid), respectively). However, for systems involving poly(styrenesulfonate) (PSS), much larger K_1 values were found. Specifically, for PSS/poly-L-histidine systems K_1 was ∼2, i.e., twice those for DNA/poly-L-histidine[50b] or DNA/3,3-ionene[50a] complexes. The large difference reflected irreversible binding of PSS with the polycation in the presence of DNA. This finding is in very good agreement with other reports that in mixtures of polyanions a polycation preferentially binds with macromolecules with sulfonate and/or sulfate groups such as, poly(vinylsulfonate),[52] PSS,[53] or poly(vinyl sulfate).[54] The presence of a small number of sulfate or sulfonate groups in the polycarboxylate polymer chains provided strong selective binding with a polycation in polyanion mixtures, even though the mixture contained polycarboxylate polyanions of much higher charge density.[55] The difference in free energy of association of a quaternized amine group with a sulfonate group and a carboxylate group was reported to be as large as 15 kJ mol^{-1} for the case of PEMs.[56] As a result of such strong interaction energy, ionic pairs of quaternized amine group with SO_3^- or SO_4^- are extremely stable in salt solutions. Water-insoluble stoichiometric PECs of PSS with QPVP involving even very short chains exhibited high stability in salt solutions. Specifically, the salt concentration required for QPVP/PSS dissociation for the case of QPVP oligomers of DPs 10 and 20 was 2.3 M NaCl and 3.4 M NaCl, respectively, which is 1 order of magnitude higher than that needed for destruction of complexes formed by QPVP oligomers with PMAA[57] or DNA.[58]

Strong binding of SO_3^-- or SO_4^--containing polyanions with polycations has a profound impact on kinetics of interpolyelectrolyte chain exchange. The first striking observation is significant acceleration of the substitution reactions or that transfer of polycations from carboxylate to SO_3^-- or SO_4^--contaning polyanions. The rate of chain exchange in PECs is enhanced in the presence of low molecular weight electrolytes due to screening and weakening of interpolymer electrostatic interactions.[40] In contrast to QPVP, transfer from WPEC QPVP/PMAA to added free PMAA chains that occurred at a measurable rate in 0.05 M NaCl solution; the competitive displacement of QPVP from WPEC by added PSS chains required 1 order of magnitude lower concentration of salt.[59]

On the other hand, the extremely high affinity of PSS to polycations imposes kinetic restrictions on interpolyelectrolyte exchange reactions or chain transfer between PECs of the same chemical identity. As a result, when a polycation and PSS solutions are mixed to provide large excess of polycation or PSS units, precipitation occurs in solution since equilibration through chain exchange is inhibited. Accordingly, it is commonly accepted that PSS is unable to form soluble complexes with polycations.[60,61] However, one of us showed that PSS-containing WPECs can be prepared in 0.12 M KCl solutions where interchain interactions are significantly weakened.[62]

Just as PSS is one of the strongest competitors for binding with polycations, polyamines containing primary amino groups are the strongest binders among polycations. When various polyamines were investigated for their binding with DNA, their association strength with DNA increased in a series: quaternized-, tertiary-, secondary-, primary-amine polycation[63] as amino groups became more sterically accessible. In addition, significant contribution of dispersive, nonelectrostatic interactions to the binding energy is likely to occur in the case of PSS and/or primary-amine polycations.

Figure 7 contrasts phase behavior of polycation/polyanion mixtures in solution for strongly bound and weakly bound polyelectrolyte pairs. In mixtures of PMAA with the primary amine polycation poly(allylamine) (PAH), insoluble complexes are formed in a wide range of polycation-to-polyanion ratios, even when excess of PMAA or PAH units is large. In contrast, solubility behavior of PMAA mixtures with the quaternized polyamine QPVP is drastically different: precipitation occurs in a narrow range when f^+ is close to 0.5, i.e., when equimolar charge ratio is achieved. Excess of PMAA or QPVP (at $f^+ <$ 0.35 and $f^+ >$ 0.6, respectively) results in formation of WPECs which are solubilized by either negative or positive charge in nonassociated polymer units. Consequences for PEM deposition are illustrated in Figure 1, top panel, which shows that chain deposition at the surface is greatly inhibited by exchange with solution and does not result in QPVP/PMAA film growth. In contrast, in the same conditions the irreversible deposition of polymer chains at surfaces occurs for strongly interacting systems such as PAH/PMAA or PAH/PSS (data not shown). For instance, construction of 12 layer films of PAH/PMAA results in 30 and 60 nm multilayers deposited for 5 and 30 min, respectively, from 0.1 mg/mL polymer solutions at pH 8.4 in Trizma buffer. Polyelectrolyte exchange with solution for weakly bound “exponentially” growing multilayers was also observed by others for films composed of macromolecules such as PGLu and hyaluronic acid.[64−66] In our group, we have recently observed competition and replacement reactions, when electrostatically associating chains replaced hydrogen-bonded polymers within hybrid PEMs.[67] Recently, Jomaa and Schlenoff demonstrated self-exchange of poly(carboxylic acid)s within a PEM as well as replacement of self-assembled PMAA with stronger binding PSS chains.[68] At the same time, formation of very strong and irreversible ionic pairs affords high stability to PAH/PSS films and makes this system a favorite choice for multilayer buildup. As described above, the trends observed with multilayers directly follow from the properties of PECs in solution.

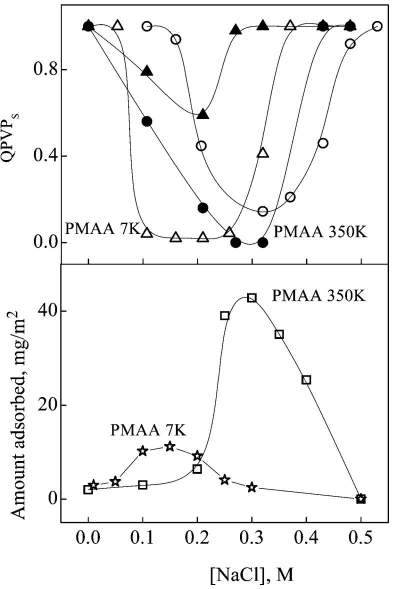

Figure 8. Top panel: Fraction of QPVP (M_w 330K, DP 1600) remaining in supernatants of QPVP/PMAA mixtures for PMAA (M_w 350K, DP 4000) in excess PMAA (open circles) and in excess QPVP (filled circles) and for PMAA with M_w of 7K, DP 80 in excess of PMAA (open triangles) and in excess QPVP (filled triangles) plotted against concentration of the added salt. Bottom panel: Total amount adsorbed of nine-layer QPVP/PMAA films deposited from solution with various salt concentrations for PMAA with 350K (squares) and 7K (stars). In all experiments, 0.01 M phosphate buffer at pH 8.4 was used.

II.2. Ratio of Polyelectrolyte Chain Lengths. For quickly equilibrating PEC systems, such as polycations containing quaternary ammonium groups and polyacids with carboxylate or phosphate groups, earlier works on WPEC suggested that mismatch in the polyelectrolyte chain lengths is critical for formation of water-soluble complexes.[23] However, more recent experiments by one of us showed that the formation of WPEC occurs for all ratios of polyelectrolyte chain lengths.[69,70] Figure 8 shows the results of phase separation in QPVP/PMAA mixtures in solution (top panel) and corresponding PEMs (bottom panel) for different ratios of QPVP-to-PMAA chain lengths.

Though the details of phase separations are different, water-soluble complexes exist at low salt concentration for all ratios of polycation/polyanion chain lengths from 24 to 0.5. Even when molecular weights of polyelectrolytes are close, there is a thermodynamic preference of formation of WPEC, and multilayer erosion occurs at low salt concentrations. This follows from the efficient inhibition of PEM deposition (Figure 1, top panel) due to solubilization of chains within WPEC in spite of the matched polyelectrolyte chain lengths (polycation/polyanion chain ratio close to 1.0).

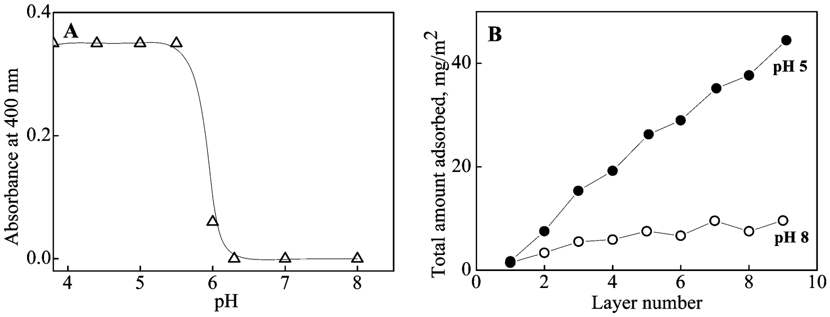

Figure 9. Panel A: Turbidity of QPVP/PMAA mixtures with $f^+ = 0.8$ measured as absorbance of 0.04 M solutions at 400 nm as a function pH. Panel B: Evolution of total amount of QPVP and PMAA adsorbed during nine-layer film assembly at pH 5 (filled circles) and pH 8 (open circles). The pHs were supported by 0.01 M phosphate buffer. In all experiment M_ws for PMAA and QPVP were 72K, DP 670 and 200K, DP 900, respectively.

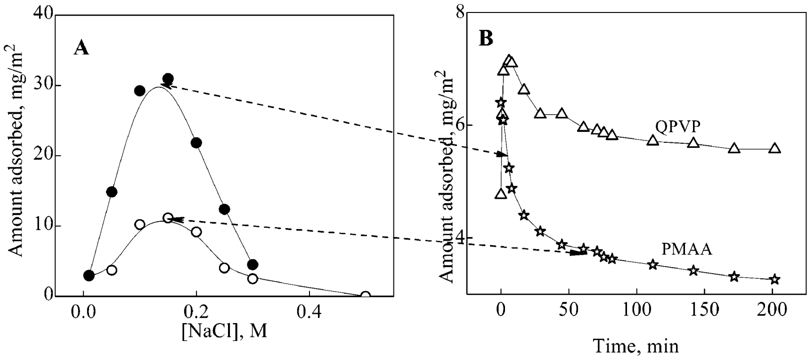

Figure 10. Panel A: Total amount adsorbed of nine-layer QPVP (M_w 330K, DP 1600)/PMAA (7K, DP 65) films deposited at pH 8.4 from solutions with various salt concentrations. The deposition time per layer was 5 min (filled symbols) and 1 h (open symbols). Panel B: Time evolution of PMAA (stars) and QPVP (triangles) amounts during deposition of QPVP on the top of the nine-layer film at 0.15 M NaCl concentration. Arrows show amount retained after 5 and 60 min.

II.3. Effect of Charge Density and pH. For the case of strongly interacting weak polyelectrolyte PAH/poly(carboxylic acid) pair where no chain exchange is expected as suggested by noticeable turbidity in the mixture of solutions (Figure 7), the dependence of multilayer thickness on pH was studied in detail by Rubner and co-workers.[71] Deposition of thicker PDADMAC/PAA multilayers at lower pH values was also reported by Dubas and Schlenoff.[16] However, with weaker bound polymer pairs, such as in the latter case, charge density of interacting chains can have a pronounced effect on the interpolyelectrolyte exchange rate. For example, a decrease in the number of positively charged pyridinium units in the chain of partly alkylated QPVP (a decrease in the degree of alkylation) resulted in acceleration of QPVP exchange by PMAA chains.[72] Also, in solution, drastic inhibition of chain exchange was found for the system QPVP/PMAA at lower pH values.[73] For multilayers, a recent study in our group showed that using lower pH deposition solutions eliminated solubilization of polyelectrolyte chains and dramatically improved the deposition of polycation/PMAA films.[74] Figure 9, panel A, shows that water-soluble complex with composition $f^+ = 0.8$ becomes insoluble when pH is lowered from 8 to 5. Correspondingly, deposition of chains at the surface follows the same pH trend. As shown in panel B in Figure 9, adsorption−desorption behavior at pH 8.4 is switched to robust multilayer growth at pH 5. The latter observations in solution and at the surface might look counter-intuitive after one considers the related data on increased exchange rates of polyelectrolyte chains in solution for polyelectrolytes with lower charge density.

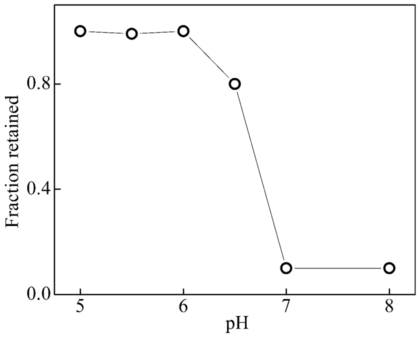

Figure 11. pH-triggered disintegration of a 10-layer QPVP/PMAA film deposited at pH 5 and exposed to higher pH values (in-situ ATR−FTIR results). In the experiment M_w for PMAA and QPVP were 150K, DP 1700 and 200K, DP 900, respectively.

Clearly, lowering charge density in a weak polyacid and lowering charge density in a polycation copolymer are not the same. Non-fully ionized poly(carboxylic acid)s bring significant nonelectrostatic contributions to the binding energy due to hydrogen bonding through protonated carboxylic acids and inhibit exchange and equilibration of polyelectrolyte chains. Note that a similar effect of lower ionization of PMAA with promoted PEM deposition at lower pH values was also demonstrated for protein/PMAA multilayer films.[26]

III. Kinetically Trapped PEMs

For systems with relatively fast equilibration times and exchange of polyelectrolyte chains, multilayer deposition at surfaces is not favored thermodynamically. In such systems, it seems unavoidable that strong interlayer mixing and chain removal will be triggered upon exposure to deposition solution containing one of the polyelectrolytes. However, loss of multilayer mass might be inhibited when not enough time is allowed for equilibration with solution. Panel A in Figure 10 shows the effect of deposition time on multilayer thickness. For the case of low molecular weight PMAA 7K, much thicker films are produced if only 5 min are allowed for equilibration with solution at each deposition step. An increase in deposition time resulted in evolution of multilayer thickness toward those predicted thermodynamically based on the shapes of QPVP/PMAA phase diagrams in solution. Panel B in Figure 10 illustrates how this behavior correlates with the overshoot in the amount of polymer deposited at the surface. Specifically, since binding of a polyelectrolyte at the film surface precedes the solubilization step, removal of previously adsorbed polymer chains is inhibited when polymer solution is replaced with pure buffer at early stages of desorption.

IV. pH-Triggered Decomposition of PEMs

pH-triggered behavior of PEMs is also controlled by the phase diagrams of polyelectrolyte pairs in solution. Note that hydrophilic poly(carboxylic acid)s, which are highly labile in interpolyelectrolyte exchange reaction and easily produce WPECs, are often used to build PEMs.[75−79] The capability of such films (wPEMs) to respond to such environmental stimuli as pH and ionic strength has been widely explored and exploited. Variations of the external pH may result in excess charge within wPEMs, which can be utilized, for example, to bind and release low molecular weight compounds such as dyes or drugs.[80−82] Such pH variations have also allowed Sui and Schlenoff to use wPEMs for controlling electroosmotic flow in microchannels.[83] One way for PEMs to respond to electrostatic stress within the film is through changes in film morphology. Sui and Schlenoff suggested a mechanism of dissipation of electrostatic stress within the film through migration of excess charge to the film surface via short-scale macromolecular rearrangements or charge “extrusion”.[84]

In the case of hollow wPEM capsules reversible porosity has also been used to design capsules with pH-gated permeability.[85,86] Nanoscale porosity can also be introduced in wPEM films and reversed via pH variations, making such films attractive candidates as erasable antireflection coatings.[87] Reversible pH-induced swelling transitions[88] have been also reported by Hiller and Rubner.

However, pH variations can also cause film instabilities of non-cross-linked wPEMs. Apart from conventionally expected film decomposition at extreme pHs,[18] which is a result of dissociation of polyelectrolytes, sections above emphasize that excess charge within the film can create conditions favorable for solubilization of polymer chains in solution. Figure 11 shows the pH-stability profile of QPVP/PMAA films which were self-assembled at pH 5 and then exposed to increasing pH values. We found that when negative charge within the film exceeds positive charge ∼3-fold, the PEM dissolves in a highly cooperative manner. Note that the 3-fold excess of PMAA charge corresponds to formation of WPEC. Dubas and Schlenoff have also reported that multilayers composed of a weak poly(carboxylic acid) and quaternary ammonium polycation are unstable during pH cycling.[16] This behavior, again, largely follows the phase diagrams of corresponding polyelectrolyte pairs in solution. We have earlier shown that stabilization of labile polyelectrolyte PEMs to pH variations can be achieved by shifting the total balance of charges toward unity, i.e., by raising the pH of wPEM in the presence of a polycation, which “buffers” accumulation of negative charge within the film.[25] An alternative strategy includes diluting pH-sensitive groups by using copolymer blends and the additional use of PSS polyanion which exhibits strong ionic pairing and enhances PEM pH stability.[83] Again, complexes involving PSS show precipitation in a wide range of polycation-to-polyanion charge f^+ (data not shown), suggesting high stability of PSS-containing multilayers during PEM buildup and pH response.

In summary, we demonstrated that deposition and pH response of PEM at surfaces are largely controlled by the phase behavior of polyelectrolyte complexes in solution. Detailed understanding of competition between surface and solution as applied to PEMs requires selective labeling of polymers and/or the application of techniques that allow chemically specific monitoring of film components, such as in-situ ATR−FTIR spectroscopy. We suggest that better knowledge of the relationships between PEMs and PECs would allow rational prediction and control of deposition of weak or permanently charged polyelectrolytes, proteins, and nanoparticles at surfaces and enable the design of PEM-based polymer films with predictable pH-response properties useful for a variety of applications.

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References and Notes

(1) Decher, G.; Hong, J.-D. *Makromol. Chem., Macromol. Symp.* **1991**, *46*, 321.
(2) Decher, G. *Science* **1997**, *277*, 1232.
(3) Schlenoff, J. B.; Dubas, S. T. *Macromolecules* **2001**, *34*, 592.
(4) Graul, W. G.; Li, M.; Schlenoff, J. B. *J. Phys. Chem. B* **1999**, *103*, 2718.
(5) Dubas, S. T.; Schlenoff, J. B. *Macromolecules* **1999**, *32*, 8153.
(6) Sukhorukov, G. B.; Möhwald, H.; Decher, G.; Lvov, Y. M. *Thin Solid Films* **1996**, *284*−285, 220.
(7) Kotov, N. A.; Magonov, S.; Tropsha, E. *Chem. Mater.* **1998**, *10*, 886.
(8) Fisher, P.; Laschewsky, A.; Wischerhoff, E.; Arys, X.; Jonas, A.; Legras, R. *Macromol. Symp.* **1999**, *137*, 1.
(9) Bertrand, P.; Jonas, A.; Laschewsky, A.; Legras, R. *Macromol. Rapid Commun.* **2000**, *21*, 319.
(10) Hammond, P. *Curr. Opin. Colloid Interface Sci.* **2000**, *4*, 430.
(11) *Multilayer Thin Films. Sequential assembly of nanocomposite materials*; Decher, G., Schlenoff, J. B., Eds.; Wiley-VCH: New York, 2003.
(12) Cooper, C. L.; Dubin, P. L.; Kayitmazer, A. B.; Turksen, S. *Curr. Opin. Colloid Interface Sci.* **2005**, *10*, 52.
(13) Sukhishvili, S. A. *Curr. Opin. Colloid Interface Sci.* **2005**, *10*, 37.
(14) Glinel, K.; Moussa, A.; Jonas, A. M.; Laschewsky, A. *Langmuir* **2002**, *18*, 1408.
(15) Steitz, R.; Jaeger, W.; Klitzing, R. *Langmuir* **2001**, *17*, 4471.
(16) Dubas, S. T.; Schlenoff, J. B. *Macromolecules* **2001**, *34*, 3736.
(17) Mendelsohn, J. D.; Barrett, C. J.; Chan, V. V.; Pal, A. J.; Mayes, A. M.; Rubner, M. F. *Langmuir* **2000**, *16*, 5017.
(18) Kharlampieva, E.; Sukhishvili, S. A. *Langmuir* **2003**, *19*, 1235.
(19) Kharlampieva, E.; Kozlovskaya, V.; Tyutina, J.; Sukhishvili, S. A. *Macromolecules* **2005**, *38*, 10523.
(20) Hoogeveen, N. G.; Cohen Stuart, M. A.; Fleer, G. J.; Böhmer, M. R. *Langmuir* **1996**, *12*, 3675.
(21) Sui, Z.; Salloum, D.; Schlenoff, J. B. *Langmuir* **2003**, *19*, 2491.
(22) Schoeler, B.; Kumaraswamy, G.; Caruso, F. *Macromolecules* **2002**, *35*, 889.
(23) Kabanov, V. A.; Zezin, A. B. *Pure Appl. Chem.* **1984**, *56*, 343.
(24) Serizawa, T.; Kawanishi, N.; Akashi, M. *Macromolecules* **2003**, *36*, 1967.
(25) Kharlampieva, E.; Sukhishvili, S. A. *Macromolecules* **2003**, *36*, 9950.
(26) Izumrudov, V. A.; Kharlampieva, E.; Sukhshvili, S. A. *Biomacromolecules* **2005**, *6*, 1782.
(27) Casrelnovo, M.; Joanny, J.-F. *Langmuir* **2000**, *16*, 7524.
(28) Dobrynin, A. V.; Rubinstein, M. *Prog. Polym. Sci.* **2005**, *30*, 1049.
(29) Kovačević, D.; Van der Burgh, S.; de Keizer, A.; Cohen Stuart, M. A. *Langmuir* **2002**, *18*, 5607.
(30) Kovačević, D.; van der Burgh, S.; de Keizer, A.; Cohen Stuart, M. A. *J. Phys. Chem. B* **2003**, *107*, 7998.
(31) Kabanov, V. A. Basic properties of soluble interpolyelectrolyte complexes applied to bioengineering and cell transformations. In *Macromolecular Complexes in Chemistry and Biology*; Dubin, P. L., Bock, J., Davis, R. M., Schulz, D. N., Thies, C., Eds.; Springer-Verlag: Berlin, 1994; p 151.
(32) Izumrudov, V. A.; Lim, S. H. *Polym. Sci.* **2002**, *A44*, 484.

(33) Kabanov, V. A.; Yaroslavov, A. A.; Sukhishvili, S. A. *J. Controlled Release* **1996**, *39*, 173.
(34) Zaitsev, V. S.; Izumrudov, V. A.; Zezin, A. B. *Polym. Sci. USSR*, **1992**, *34*, 54 (translated from: *Vysokomol. Soyedin., Ser. A* **1992**, *34*, 138).
(35) Izumrudov, V. A.; Kharlampieva, E.; Sukhishvili, S. A. *Macromolecules* **2004**, *37*, 8400.
(36) Zelikin, A. N.; Akritskaya, N. I.; Izumrudov, V. A. *Macromol. Chem. Phys.* **2001**, *202*, 3018.
(37) Izumrudov, V. A.; Wahlund, P.-O.; Gustavsson, P.-E.; Larsson, P.-O.; Galaev, I. Yu. *Langmuir* **2003**, *19*, 4733.
(38) Wahlund, P.-O.; Izumrudov, V. A.; Gustavsson, P.-E.; Larsson, P.-O.; Galaev, I. Yu. *Macromol. Biosci.* **2003**, *3*, 404.
(39) Izumrudov, V. A.; Lim, S. H. *Polym. Sci.* **1998**, *A40*, 276 (translated from: *Vysokomol. Soyedin., Ser. A* **1998**, *40*, 459).
(40) Bakeev, K. N.; Izumrudov, V. A.; Kuchanov, S. I.; Zezin, A. B.; Kabanov, V. A. *Macromolecules* **1992**, *25*, 4249.
(41) Papisov, I. M.; Litmanovich, A. A. *Adv. Polym. Sci.* **1989**, *90*, 139.
(42) Abe, K.; Koide, M.; Tsuchida, E. *Macromolecules* **1977**, *10*, 1259.
(43) (a) Papisov, I. M.; Nedyalkova, Ts. I.; Avramchuk, N. K.; Kabanov, V. A. *Vysokomol. Soedin., Ser. A* **1973**, *15*, 2003. (b) Bednar, B.; Li, Z.; Huang, Y.; Chang, L. C. P.; Morawetz, H. *Macromolecules* **1985**, *18*, 1829.
(44) Izumrudov, V. A.; Nyrkova, T. Yu.; Zezin, A. B.; Kabanov, V. A. *Vysokomol. Soedin., Ser. B* **1987**, *29*, 474.
(45) Izumrudov, V. A.; Bronich, T. K.; Saburova, O. S.; Zezin, A. B.; Kabanov, V. A. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 7.
(46) Izumrudov, V. A.; Ortega Ortiz, H.; Zezin, A. B.; Kabanov, V. A. *Macromol. Chem. Phys.* **1998**, *199*, 1057.
(47) Izumrudov, V. A.; Kargov, S. I.; Zhiryakova, M. V.; Zezin, A. B.; Kabanov, V. A. *Biopolymers* **1995**, *35*, 523.
(48) Izumrudov, V. A.; Zhiryakova, M. V.; Kargov, S. I.; Zezin, A. B.; Kabanov, V. A. *Macromol. Symp.* **1996**, *106*, 179.
(49) Zelikin, A. N.; Trukhanova, E. S.; Izumrudov, V. A.; Litmanovich, A. A. *Polym. Sci.* **2003**, *B45*, N9−10, 284 (translated from: *Vysokomol. Soedin., Ser. A* **2003**, *45*, 1595).
(50) (a) Trukhanova, E. S.; Izumrudov, V. A.; Litmanovich, A. A.; Zelikin, A. N. *Biomacromolecules* **2005**, *6*, 3198. (b) Zelikin, A. N.; Trukhanova, E. S.; Putnam, D. A.; Izumrudov, V. A.; Litmanovich, A. A. *J. Am. Chem. Soc.* **2003**, *125*, 13693.
(51) Bronich, T. K.; Hong, K. N.; Eisenberg, A.; Kabanov, A. V. *J. Am. Chem. Soc.* **2000**, *122*, 8339.
(52) Patchornik, A.; Berger, A.; Katchalski, E. *J. Am. Chem. Soc.* **1957**, *79*, 5227.
(53) (a) Izumrudov, V. A.; Bronich, T. K.; Zezin, A. B.; Kabanov, V. A. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 439. (b) Kabanov, V. A.; Zezin, A. B.; Izumrudov, V. A.; Bronich, T. K.; Bakeev, K. N. *Makromol. Chem., Suppl.* **1985**, *13*, 137. (c) Oupicky, D.; Konak, C.; Dash, P. R.; Seymour, L. W.; Ulbrich, K. *Bioconjugate Chem.* **1999**, *10*, 764.
(54) Kakizawa, Y.; Harada, A.; Kataoka, K. *Biomacromolecules* **2001**, *2*, 491.
(55) Izumrudov, V. A.; Chaubet, F.; Clairbois, A.-S.; Jozefonvicz, *J. Macromol. Chem., Phys.* **1999**, *200*, 1753.
(56) Dubas, S. T.; Schlenoff, J. B. *Langmuir* **2001**, *17*, 7725.
(57) Pergushov, D. V.; Izumrudov, V. A.; Zezin, A. B.; Kabanov, V. A. *Polym. Sci.* **1995**, *A3*7, 1081.
(58) Izumrudov, V. A.; Zhiryakova, M. V. *Macromol. Chem. Phys.* **1999**, *200*, 2533.
(59) Kabanov, V. A.; Zezin, A. B.; Izumrudov, V. A.; Bronich, T. K.; Bakeev, K. N. *Makromol. Chem., Suppl.* **1985**, *13*, 137.
(60) Zintchenko, A.; Rother, G.; Dautzenberg, H. *Langmuir* **2003**, *19*, 2507.
(61) Karibyants, N.; Dautsenberg, H.; Cölfen, H. *Macromolecules* **1997**, *30*, 7803.
(62) (a) Izumrudov, V. A.; Parashchuk, V. V.; Sybachin, A. V. *Polym. Sci.* **2006**, *A48*, 78 (translated from: *Vysokomol. Soedin., Ser. B* **2006**, *48*, 554). (b) Izumrudov, V. A.; Parashchuk, V. V.; Sybachin, A. V. *J. Drug Delivery Sci. Technol.* **2006**, *16*, 267. (c) Izumrudov, V. A.; Sybachin, A. V. *Polym. Sci.* **2006**, *A48*, 1098 (translated from: *Vysokomol. Soedin., Ser. A* **2006**, *48*, 1849).
(63) Izumrudov, V. A.; Zhiryakova, M. V.; Kudaibergenov, S. *Biopolymers (Nucl. Acid Sci.)* **2000**, *52*, 94.
(64) Lavalle, Ph.; Gergely, C.; Cuisinier, F. J. G.; Decher, G.; Schaaf, P.; Voegel, J. C.; Picart, C. *Macromolecules* **2002**, *35*, 4458.
(65) Picart, C.; Mutterer, J.; Richert, L.; Luo, Y.; Prestwich, G. D.; Schaaf, P.; Voegel, J.-C.; Lavalle, Ph. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 12531.
(66) Huebsch, E.; Ball, V.; Senger, B.; Decher, G.; Voegel, J.-C.; Schaaf, P. *Langmuir* **2004**, *20*, 1980.
(67) Kharlampieva, E.; Sukhishvili, S. A. *Langmuir* **2004**, *2*, 10712.
(68) Jomaa, H. W.; Schlenoff, J. B. *Langmuir* **2005**, *21*, 8081.
(69) Izumrudov, V. A. Polycomplexes for Bioseparation and Bioprocessing. In Galaev, I. Yu., Mattiasson, B., Eds.; *Smart Polymers for Bioseparation and Bioprocessing;* Taylor & Francis: London, 2002; pp 98−121.
(70) Izumrudov, V. A.; Gorshkova, M. Yu.; Volkova, I. F. *Eur. Polym. J.* **2005**, *41*, 1251.
(71) Shiratori, S. S.; Rubner, M. F. *Macromolecules* **2000**, *33*, 4213.
(72) Izumrudov, V. A.; Bakeev, K. N.; Zezin, A. B.; Kabanov, V. A. *Dokl. Acad. Nauk* **1986**, *286*, 1442.
(73) Izumrudov, V. A.; Rykunova, A. I.; Sinitsyn, A. A. *Vestn. Mosk. Univ., Ser. 2: Khim.* **1993**, *34*, 405.
(74) Izumrudov, V. A.; Sukhishvili, S. A. *Langmuir* **2003**, *19*, 5188.
(75) Müller, M.; Rieser, T.; Lunkwitz, K.; Berwald, S.; Meier-Haack, J.; Jehnichen, D. *Macromol. Rapid Commun.* **1998**, *19*, 333.
(76) Yoo, D.; Shiratori, S. S.; Rubner, M. F. *Macromolecules* **1998**, *31*, 4309.
(77) Chen, K. M.; Jiang, X. P.; Kimerling, L. C.; Hammond, P. T. *Langmuir* **2000**, *16*, 7825.
(78) Dubas, S. T.; Farhat, T. R.; Schlenoff, J. B. *J. Am. Chem. Soc.* **2001**, *123*, 5368.
(79) Cao, T.; Chen, J.; Yang, Ch.; Cao, W. *Macromol. Rapid Commun.* **2001**, *22*, 181.
(80) Chung, A. J.; Rubner, M. F. *Langmuir* **2002**, *18*, 76.
(81) Kharlampieva, E.; Sukhishvili, S. A. *Langmuir* **2004**, *20*, 9677.
(82) Burke, S. E.; Barrett, Ch. J. *Macromolecules* **2004**, *37*, 5375.
(83) Sui, Zh.; Schlenoff, J. B. *Langmuir* **2003**, *19*, 7829.
(84) Sui, Zh.; Schlenoff, J. B. *Langmuir* **2004**, *20*, 6026.
(85) Antipov, A. A.; Sukhorukov, G. B.; Leporatti, S.; Radtchenko, I. L.; Donath, E.; Möhwald, H. *Colloids Surf., A* **2002**, *198*−200, 535.
(86) Sukhorukov, G. B.; Fery, A.; Brumen, M.; Möhwald, H. *Phys. Chem. Chem. Phys.* **2004**, *6*, 4078.
(87) Hiller, J.; Mendelsohn, J. D.; Rubner, M. F. *Nat. Mater.* **2002**, *1*, 59.
(88) Hiller, J.; Rubner, M. F. *Macromolecules* **2003**, *36*, 4078.

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