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Cross-Linkable Polyelectrolyte Multilayer Films of Tailored Charge Density

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The layer-by-layer (LbL) deposition technique of anionic and cationic polyelectrolytes allows formation of thin and ultrathin nanostructured films with tunable properties and, therefore, functionality. Here, we report on the synthesis and characterization of new polyelectrolyte multilayer system consisting of anionic copolymer poly(sodium 3-(4-vinylbenzylsulfanyl)-propane-1-sulfonate)-*co*-poly(2-hydroxyethyl-vinylbenzyl sulfoxide) with different charge densities (21, 36, 65, 81, and 100%) and cross-linkable cationic poly(4-methyl-1-(4-vinylbenzyl)-pyridinium chloride. We study the impact of salt concentration on film thickness and roughness for the different charge densities and discuss the observed trends with regard to charge effects. Furthermore we covalently cross-link the films by an aldol reaction, which preserves the number of charged groups while being easily followed via UV−vis spectroscopy because of the characteristic absorbance band of the coupling product. Cross-linking increases film stability markedly. Thus the new multilayer system allows tuning of both ionic and covalent cross-linking in a quantitative fashion.

Introduction

The layer-by-layer (LbL) alternating adsorption of anionic and cationic species, mostly polyelectrolytes, is an attractive method to prepare ultrathin multilayer films on most various types of substrates.[1−6] The LbL deposition technique is enabled to control the films' structure and properties, by varying the chemical structure of the polyelectrolytes, for instance their charge density, the number of adsorbed layers, and the conditions of adsorption, thus providing a convenient way for their functionalization.[5,6] A further way to influence the properties of multilayer films is the use of polyelectrolyte blends[7−9] or of inorganic nanomaterials[10,11] for their construction. Multilayer films have been therefore intensively developed and increasingly studied with respect to diverse applications, e.g., for controlling wetting properties or interactions with biological systems,[12] as anticorrosion coatings,[13−16] free-standing membranes,[17−22] osmotic pressure sensors,[23] and micro- and nanocapsules.[24,25]

The sensitivity of the polyelectrolyte film to a variety of chemical and physical conditions, such as charge density or ionic strength of solution, provides the ability to tune mechanical properties, permeability, or stability of the

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films. Charge density of polymers is a major parameter to control structure and property of LbL films. In the case of weak polyelectrolytes, the charge density can be varied with pH, determining their degree of dissociation.[26] A potential limitation of systems based on weak polyelectrolytes is the polymer local charge density, which polymer chains adjust to accommodate different molecular environments. This difficulty is avoided when strong polyelectrolytes with fixed charge density are employed. In their case, the charge density can be controlled by "intramolecular dilution", either by fixing the distance between neighboring charged groups in the polymers via the use of complex constitutional repeat units[27−31] or by using copolymers of charged and uncharged monomers,[32−38] thus reducing the charge statistically by their relative contents.

The former strategy has the advantage to provide regular, extremely well-defined charge densities. However, the synthetic pathways to such polyelectrolytes are limited. Moreover, the mostly hydrophobic character of the uncharged spacer groups separating the charged moieties in such polymers give rise to strong hydrophobic interactions and complications.[27,28,30,31] Therefore, the control of the charge density by copolymerizing charged and uncharged monomers is not only a much more convenient but also more versatile strategy, as the appropriate choice of hydrophilic nonionic comonomers may circumvent the pitfalls of increasing hydrophobicity with charge reduction. However, care must be taken to use comonomer systems with reactivity ratios close to 1, in order to provide defined, true random copolymers under so-called azeotropic conditions, as otherwise broad mixtures of copolymers with strongly differing charge content are obtained. Particular useful in this respect have been copolymers of diallyldimethylammonium chloride and vinylamides,[33,34] or copolymers of 2-acrylamido-2-methylpropanesulfonate and acrylamides.[36,37] Still, it was found that the use of strongly hydrophilic comonomers may pose a problem for the LbL process, as with increasing share of the nonionic units (i.e., at low charge densities) in the copolymers, film growth is inhibited. This finding has been often justified by evoking a critical charge density for successful LbL deposition.[33,34] However, there is a high chance that the stoichiometric polyelectrolyte complexes formed by such strongly hydrophilic hybrid ionic−nonionic copolymers may be water-soluble and thus do not adsorb onto the substrate.

Here, we study a new polyelectrolyte multilayer system, which consists of the reactive polycation poly(4-methyl-1-(4-vinylbenzyl)-pyridinium chloride, PC, and polyanions with different charge densities, namely the copolymers poly(sodium 3-(4-vinylbenzylsulfanyl)-propane-1-sulfonate)-*co*-poly(2-hydroxyethyl vinylbenzyl sulfoxide) PA-*x*. The copolymer is obtained by copolymerization of ionic sodium 3-(4-vinylbenzylsulfanyl)-propane-1-sulfonate with the nonionic 2-hydroxyethyl-vinylbenzyl sulfoxide. As both monomers contain the same polymerizable group, the formation of random copolymers can be expected. Moreover, the nonionic comonomer is only moderately hydrophilic. Therefore, it is polar enough to be water-soluble, but the homopolymer is capable only of swelling in water without dissolving. These features were aimed at providing control over the charge-density of the resulting copolymers by adjusting the comonomer composition, without affecting on the one hand the overall hydrophobic/hydrophilic balance severely, while avoiding on the other hand the formation of water-soluble polyelectrolyte complexes at high contents of the nonionic comonomer. As the methyl substituent of the pyridinium moiety of PC is activated by the conjugated quaternary nitrogen atom, it is reactive toward carbonyl compounds to undergo aldol condensations.[39,40] This opens the possibility to cross-link the multilayer films with, e.g., dialdehydes without affecting the number of charged groups. Therefore, the newly used polyelectrolyte system allows varying simultaneously parameters such as the charge density and the degree of cross-linking in the multilayer films. Hence, we investigated the effect of charge density of polyanion and degree of cross-linking of polycation on film morphology, structure and properties. Film growth, its surface morphology and inner structure as well as film stability were studied by atomic force microscopy (AFM), ellipsometry and UV−vis spectroscopy in dependence on the preparation condition (ionic strength) and the polymers' chemical nature (degree of cross-linking and charge density of the chain).

Materials and Methods

Materials. 4-Vinylbenzyl chloride (technical ≥90%, Fluka) was passed through basic alumina before use. Sodium 3-mercapto-1-propanesulfonate (technical grade, 90% Sigma-Aldrich), 4-methylpyridine (γ-picoline, 99%, Acros), 2,6-ditert-butyl-4-methylphenol (99%, Acros), terephthaldialdehyde (99%, Sigma-Aldrich), piperidine (99.9%, Iris Biotech), sodium chloride (99.8%, Riedel-de

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Haën), zinc chloride (pure, Merck), basic Al_2O_3 (for chromatographie, Acros), and NaOH solution (1 M, Merck) were used as received. DMSO (dimethylsulfoxide), THF (tetrahydrofurane), *n*-hexane, methanol, and *N*,*N*-dimethylformamide (DMF) were analytical grade. Initiators V-50 (2,2′-Azobis(2-methylpropionamidine)dihydrochloride) and VA-044 (2,2′-Azobis[2-(2-imidazolin-2-yl) propane]dihydrochloride) were a kind gift of Wako Chemicals GmbH. Branched polyethyleneimine (PEI, $M_w \approx 25\,000$ g/mol) was from Sigma-Aldrich. Milli-Q water (18.2 MΩ cm) was used in all experiments. All aqueous polymer solutions were used after filtration. Dialysis tubes "ZelluTrans" (Roth, Germany) had a nominal molar mass cut off of 3500 D. The synthesis of sodium 2-benzylsulfanylthiocarbonylsulfanyl-ethanesulfonate,[41] (UV−vis in water: band at $\lambda_{max} = 425$ nm, extinction coefficient $\varepsilon = 49.3$ L mol^{-1} cm^{-1}), and polycation poly(4-methyl-1-(4-vinylbenzyl)-pyridinium chloride, PC,[40] were reported before.

Synthesis of Sodium 3-(4-Vinyl-benzylsulfanyl)-propane-1-sulfonate. Sodium 3-mercaptopropanesulfonate (12.11 g, 67 mmol) in THF (30 mL) and 82 mL of 1 M NaOH were refluxed for 30 min. 4-Vinylbenzylchloride (10.38 g, 68 mmol) and a small amount of 2,6-ditert-butyl-4-methylphenol in THF (56 mL) were then added dropwise within 25 min. The mixture was refluxed for 4 h and stirred at ambient temperature overnight, and then diluted with water (200 mL) and precipitated into acetone. The resulting suspension was filtrated and the filtrate concentrated under reduced pressure. The resulting precipitate was filtered off and dried in vacuo at 40 °C. Yield: 9.4 g (32 mmol, 48%) of sodium 3-(4-vinyl-benzylsulfanyl)-propane-1-sulfonate, a colorless powder that decomposes at 132 °C.

Elemental analysis: ($C_{12}H_{15}O_3S_2Na$, $M_r = 294.37$): Calcd: C, 48.96; H, 5.14; S, 21.78. Found: C, 48.84; H, 5.08; S, 21.62.

^{1}H NMR (200 MHz, in D_2O, δ in ppm) 7.36 (d, 2H, CH aryl); 7.23 (d, 2H, −CH aryl); 6.68 (dd, 1H, aryl−CH=); 5.77 (dd, 1H, aryl−C=CH (Z)); 5.22 (dd, 1H, aryl−C=CH (E)); 3.65 (s, 2H, aryl−CH_2−S), 2.85 (t, 2H, −CH_2−SO_3); 2.46 (t, 2H, S−CH_2−C) 1.90 (m, 2H, −CH_2−).

^{13}C NMR (75 MHz, in D_2O, δ in ppm) 138.6, 136.7, 129.7, 126.7, 114.6 (−C=aryl + alkene); 50.2 (CH_2−SO_3); 35.0 (aryl-CH_2−S); 29.7 (−S−CH_2−); 24.3 (−CH_2−).

MS (ESI) *m*/*z* (%) = 271.04 (100) (M^+-Na); *m*/*z* 148.9 (7.2) (M^+−S−$CH_2CH_2CH_2$−SO_3Na).

Synthesis of 2-(4-Vinyl-benzylsulfanyl)-ethanol. 4-Vinylbenzylchloride (38.87 g, 0.257 mol) was added during 60 min to a solution of 2-mercaptoethanol (21.17 g, 0.257 mol) and a small amount of 2,6-ditert-butyl-4-methylphenol in 250 mL of 1 M aqueous NaOH and 150 mL of THF, while refluxing. The mixture was refluxed overnight, diluted with 500 mL of water, and extracted four times with 500 mL of CH_2Cl_2. The organic phases were combined, dried over $MgSO_4$, and evaporated to give the product as colorless, waxy solid (mp 39 °C). Yield: 48.85 g (0.251 mol, 98%).

^{1}H NMR (200 MHz, in methanol-d_4, δ in ppm) 7.40,7.36 (d+d, 2H+2H, CH aryl); 6.71 (dd, 1H, aryl−CH=); 5.78 (dd, 1H, aryl−C=CH (Z)); 5.22 (dd, 1H, aryl−C=CH (E)); 3.74 (s, 2H, aryl-CH_2−S); 3.32 (t, 2H, −CH_2−O); 2.55 (t, 2H, S−CH_2−).

^{13}C NMR (75 MHz, in $CDCl_3$, δ in ppm) 137.9, 136.7, 136.6, 129.4, 126.7, 114.3 (−C=aryl + alkene), 61.2 (−CH_2−OH)), 35.7 (aryl−CH_2−S−); 33.4 (S−CH_2−).

MS (ESI): *m*/*z* (%) = 195 [M^+]; 117 [M^+ − SCH_2CH_2OH].

Synthesis of 2-(4-Vinyl-phenylmethanesulfinyl)-ethanol. Sodium periodate (30.87 g, 0.144 mol) in water (300 mL) was added at 0 °C dropwise 2-(4-vinyl-benzylsulfanyl)-ethanol (24.42 g, 0.126 mol) in methanol (400 mL). The mixture is stirred for 2 days at ambient temperature, filtered, and extracted 4 times with 400 mL of $CHCl_3$. The combined organic phases were dried over $MgSO_4$ and evaporated. The residue was crystallized from *n*-hexane after adding of a small amount of 2,6-ditert-butyl-4-methylphenol to give colorless crystals (mp 83 °C). Yield 15.82 g (80 mmol, 64%).

Elemental analysis: ($C_{11}H_{14}O_2S$, $M_r = 210.29$): Calcd: C, 62.83; H, 6.71; S, 15.25. Found: C, 62.72; H, 6.67; S, 15.25.

^{1}H NMR (200 MHz, in methanol-d4, δ in ppm) 7.48 (d, 2H, CH aryl); 7.36 (d, 2H, CH aryl); 6.77 (dd, 1H, aryl−CH=); 5.83 (dd, 1H, aryl−C=CH (Z)); 5.28 (dd, 1H, Aryl−C=CH (E)); 4.06, 3.96 (d + d, 2H + 2H, aryl−CH_2−S(=O)−); 3.99−3.96 (m, 2H, −CH_2−OH); 3.02, 2.84 (m + m, 2H + 2H, S(=O)−CH_2−).

^{13}C NMR (75 MHz, in MeOH-d4, δ in ppm) 139.0, 137.3, 131.8, 131.1, 127.5, 114.7 (−C=aryl + alkene); 58.4 (−CH_2−O); 55.7 (aryl−CH_2−S(=O)−); 54.9 (S(=O)−CH_2−).

MS (ESI): *m*/*z* (%) = 210 [M^+]; 117 [M^+ − S(=O)−CH_2-CH_2OH].

Synthesis of the Polyanions. In a typical polymerization procedure, sodium 3-(4-vinyl-benzylsulfanyl)-propane-1-sulfonate (3.599 g, 12.2 mol), 2-(4-vinyl-phenylmethanesulfinyl)-ethanol (0.2848 g, 1.2 mmol) and RAFT agent sodium 2-benzylsulfanyl-thiocarbonylsulfanylethanesulfonate (0.0446 g, 0.1368 mmol) were dissolved in 50 mL aqueous methanol (52 vol%). Then, 2 mL of a solution containing initiator V-50 (0.00454 g, 0.0167 mmol in water, 10 mL) was added. The mixture was purged with nitrogen for 15 min and then heated to 60 °C for 150 min. The polymer was isolated and purified by dialysis and lyophilized, to yield 1.16 g of polymer (colorless hygroscopic powder).

Multilayer Film Preparation by Spraying. The LbL films were assembled on silicon wafers (CrysTec) and on quartz slides (QSIL AG, Germany) from 1 mg/mL polymer solutions by the spray coating method.[42,43] The substrates were cleaned using RCA method (sonication in a 1:1 mixture of water and 2-propanol for 15 min),[44] followed by heating at 70 °C in a 5:1:1 mixture of water, 25% ammonia solution, and 30% hydrogen peroxide solution for 10 min. The freshly cleaned substrate was than precoated with one layer of PEI, which was allowed to adsorb onto the negatively charged surface during 20 min before rinsing with water.

The PEI-coated substrate was vertically placed in a home-made spray unit. The polyelectrolyte solutions containing precise concentrations of NaCl (0.02 M, 0.05 M, or 0.20 M) were filled into spray bottles (10 mL, NeoLab Migge GmbH, Germany) which were manually pressurized twice for each deposition step. After each step, the polymer was allowed to adsorb for 10 s before water was sprayed for 10 s (200 mL spray bottles "air boy", Carl Roth GmbH, Germany) to rinse the surface. The films were dried in a stream of nitrogen before characterization.

Cross-Linking. Cross-linking was performed on films deposited on quartz slides. The film coated substrate was immersed at room temperature into the solution of terephthalaldehyde (20 mg) in methanol (5 mL) adding piperidine (2 drops) as catalyst,[45] followed by rinsing with methanol and water and

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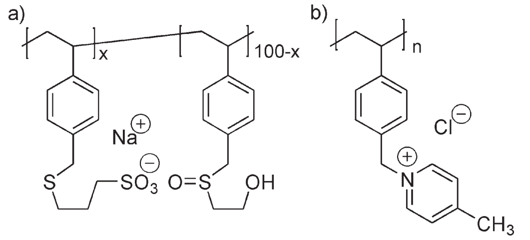

Figure 1. Polyelectrolytes used for the multilayer buildup: (a) anionic copolymers PA-*x* (*x* = 100, 81, 65, 36, and 21%); (b) reactive polycation PC.

drying with a stream of nitrogen. The progress of the reaction was monitored by UV−vis spectroscopy, following the evolving absorbance band of the newly formed chromophore.

To investigate the stability of films, we immersed multilayer-covered quartz slides into a ternary mixture of H_2O:DMF:$ZnCl_2$ (5:3:2, w/w/w).

Characterization Methods. Ellipsometry measurements were performed with a Sentech SE 850 spectroscopic ellipsometer at a constant incidence angle of 70°.

Atomic force microscopy (AFM) images were taken with a commercial AFM (DI Dimension 3100 Metrology) operating in Tapping Mode using Si_3N_4 cantilevers (Olympus) with a spring constant of 43.0−63.8 N/m. The surface mean roughness (R_a) was determined from the plain fitted and flattened images of 5 μm × 5 μm size using the DI NanoScope 7.20 software.

UV−vis spectra were recorded between 200 and 600 nm with 1 nm resolution using a Perkin-Elmer Lambda 19 UV−vis spectrometer, using a RCA-treated quartz slide for reference. When investigating the cross-linking process, absorbance spectra were recorded only above 300 nm, to protect the UV-light-sensitive newly formed chromophore.

Results

The new homopolymer poly(sodium 3-(4-vinylbenzylsulfanyl)-propane-1-sulfonate), and its copolymers with 2-hydroxyethyl-vinylbenzyl sulfoxide were synthesized for their use as strong polyanion PA-x with different charge densities *x*, expressed in mol % ionic monomer incorporated (Figure 1a). Accordingly, the charge density is adjusted by balancing the ratio of charged and uncharged monomers in the copolymerization (Table 1), independent of the pH of the solutions. Because of the similarity of the polymerizable moieties, the comonomers have similar reactivities, and thus are evenly distributed within the polymer chains (for the copolymerization diagram, see the Supporting Information, Figure S1). As intended, the balanced polarity of the nonionic comonomer has the effect, that the copolymers with markedly reduced charge density are still fully water-soluble, but that the complexation with the polycation PC results in thick precipitates, demonstrating the water-insolubility of their polyion complexes ("PIC", "symplex"). This contrasts, e.g., with the behavior of symplexes made from poly(diallyldimethyl ammonium chloride) and copolymers of anionic 3-acrylamido-2-methylpropanesulfonate (AMPS) and the strongly hydrophilic trismethylolmethylacrylamide.

Table 1. Anionic Polymers of Sodium 3-(4-Vinylbenzylsulfanyl)-propane-1-sulfonate and 2-Hydroxyethylvinylbenzyl Sulfoxide Synthesized

polymer	yield (%)	M_n[a] (g/mol)	sulfonate content in the reaction mixture (mol %)	sulfonate content in the polymer (= charge density)[b] (mol %)
PA-100	49	13 000	100	100
PA-81	51	7500	80	81
PA-65	26	6200	60	65
PA-36	20	5000	40	36
PA-21	30	7800	25	21

[a] Number average molar mass, as determined by vis-spectroscopy (based on the absorbance of the trithiocarbonate moiety of the RAFT agent used at λ = 425 nm and assuming exactly 1 RAFT end group per polymer [41,72]). [b] Mole fraction x of anionic sodium 3-(4-vinylbenzylsulfanyl)-propane-1-sulfonate in the copolymer, as determined from the C/S ratio by microanalysis.

The used polyanions are listed in Table 1. As cationic counterpart, we chose the reactive homopolymer PC (Figure 1b). Because of the conjugation with the quaternary nitrogen atom of the pyridinium moiety, the methyl substituent in 4-position is activated toward proton abstraction, and thus participates, for example, easily in aldol-type reactions catalyzed by mild bases.[45] However, this reactive group is inert toward radical attack and hence, the monomer is well-suitable for free radical polymerization. Moreover, chemical transformations at this reactive site do not affect the cationic charge, so that, for example, chemical cross-linking with bifunctional carbonyl compounds becomes possible over a wide range (theoretically, from 0 to 100% of γ-picolinium moieties may reacted), whereas the number of ionic cross-links is preserved. In contrast, the hitherto most used cross-linking reactions in LbL multilayers, namely the amide formation of carboxylic groups with amines,[18,46−49] or the unspecific decomposition of diazonium salts,[50−52] characteristically sacrifice ionic groups. Furthermore, the cross-linking products of the γ-picolinium moieties are strong chromophores and even fluorophores, if the carbonyl reagents are appropriately chosen.[39,40,45,53] This allows to follow positively and most conveniently the increase of coupling products. This differs from the typical photocross-linking reactions used in the past,[54−59] which conserve the number of ionic groups, but which allow only following the conversion of the reactive groups to nonidentified putative coupling products.

Here, the layer-by-layer (LbL) sequential adsorption of oppositely charged polyelectrolytes was performed by spray deposition. Spray coating is known to simplify and speed up the polyelectrolyte multilayer deposition as

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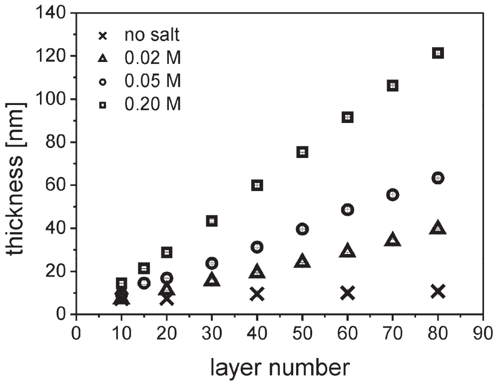

Figure 2. Plot of the ellipsometric thickness vs the number of layers of PEI(PA-100/PC)$_n$ films deposited by alternated spraying of polyelectrolyte solutions without added salt (×), and in the presence of 0.02 M (Δ), 0.05 M (○), 0.20 M (□) NaCl. The error bars are smaller than the size of the symbols.

compared to conventional dip coating.[42,43] Schlenoff et al.[42] used a spray deposition technique to construct poly(diallyldimethyl ammonium chloride)/ poly(sodium styrenesulfonate) multilayers and found similar buildup and composition of resulting films. Later, Izquierdo et al.[43] showed that spray deposition allows for achieving regular multilayer growth, even for extremely short contact times for which dipping fails to produce homogeneous films.

Multilayer Formation at Different Solution Ionic Strength. Polyelectrolyte multilayer films from aqueous homopolymer (100% charge density) solutions of varying salt concentrations were prepared via LbL spray assembly in order to analyze the influence of solution ionic strength on the film buildup. Figure 2 displays a plot of ellipsometric film thickness versus the deposited polyelectrolyte layer number. The driving force for the buildup process of multilayer assemblies is the alternate overcompensation of the surface charge after each deposition. As often reported for the absorption behavior of strong polyelectrolytes from pure aqueous solutions,[5,29,60,61] only very low thickness increment was observed, when the films were adsorbed from solutions without any added salt (see the Supporting Information, Figure S4). In contrast, linear buildup behavior was found for systems containing salt. The concentration of NaCl has a significant effect on the multilayer formation as the conformation of polyelectrolytes is highly dependent on the ionic strength of solutions. The increasing salt concentration leads to a more coiled conformation because of the screening of repulsive interactions within the chain, leading to thicker layers.[2,62,63]

To obtain detailed structural information about the LbL film deposited from different ionic strength solutions, we performed AFM measurements. Figure 3a displays the mean roughness (R_a) of multilayered films assembled from solutions containing 0.20 M, 0.05 M, 0.02 M NaCl, and without added salt as a function of layer number. If deposition is performed from solution without added salt, only marginal film growth was observed, so the roughness is very low (similar to substrate roughness) and independent from layer number as the thickness hardly evolves. The films deposited from 0.02 and 0.05 M NaCl solutions show a similar roughness increasing with the layer number. For adsorption from solutions with 0.20 M salt concentration, the roughness increased significantly in comparison to lower ionic strength solutions. AFM images of the 80-layer films show clear differences in the surface morphology between the four films deposited from varying salt concentration of polymer solutions (Figure 3b−e). In the absence of added salt, the film is very smooth with the mean roughness of 0.8 nm. With an increasing ionic strength of solution, the polyelectrolytes have more coiled conformation, leading to thicker, but also rougher layers, as commonly observed for polyelectrolyte multilayers.[6] The surface topography of films formed from solutions containing 0.02 and 0.05 M sodium chloride shows slightly topographical differences (Figure 3c, d) with the roughness for 80 layers of 1.6 and 1.9 nm, respectively. When 0.20 M sodium chloride solution is used, the surface of 80-layer film becomes much rougher than other samples ($R_a \approx 3.5$ nm).

Effect of Charge Density. Polyelectrolyte multilayers were prepared by adsorption of polyanions with different charge densities (PA-100, PA-81, PA-65, PA-36, and PA-21) from 0.20, 0.05, and 0.02 M NaCl solutions in order to analyze the influence of the ionic strength and the polyelectrolyte charge density, respectively, on the film properties. Thicknesses of the films were measured by ellipsometry and are displayed in figure 4. All three salt concentrations show a similar trend with respect to charge density: Only slight differences in the growth are observed between films from PA-100, PA-81, and PA-65. Virtually no differences are found at high ionic strength. But when lowering ionic strength, film thickness increases slightly as a function of decreasing charge density. In contrast, films deposited from PA-36 and PA-21 result in much thicker layers at all salt concentrations.

Figure 5a shows the thickness per adsorbed bilayer for the three salt concentrations studied. This behavior can be understood taking into account that secondary interactions for our system are expected to be comparable for the charged and uncharged monomers. Therefore, mainly charge-related effects should dominate the film buildup. In all cases, multilayer formation is observed, indicating that the polyelectrolyte charge density is above the critical value for charge reversal.[33] The assumption that charge effects are dominating is corroborated by the fact that the thickness scales for all charge densities with the square-root of the ionic strength, as illustrated in Figure 5b. This scaling exponent was already found in several studies[64−66] for multilayers built up from linear polyelectrolytes.

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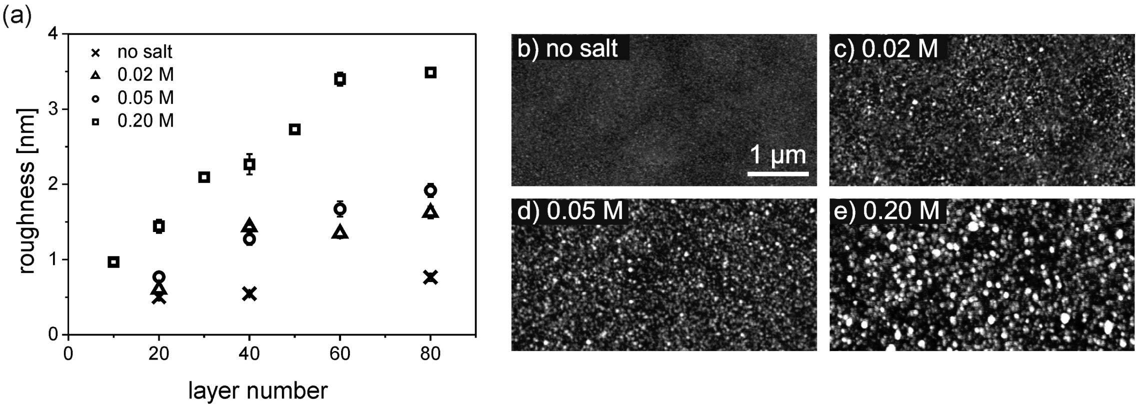

Figure 3. Roughness of the LbL films deposited from polyion solutions of different ionic strength measured by AFM: (a) dependence on layer number; (b−e) typical AFM height images (scale 0−20 nm) of PEI(PA-100/PC)$_{40}$ films, deposited from solutions (b) without added salt, (c) with 0.02 M, (d) with 0.05 M, and (e) with 0.20 M NaCl added.

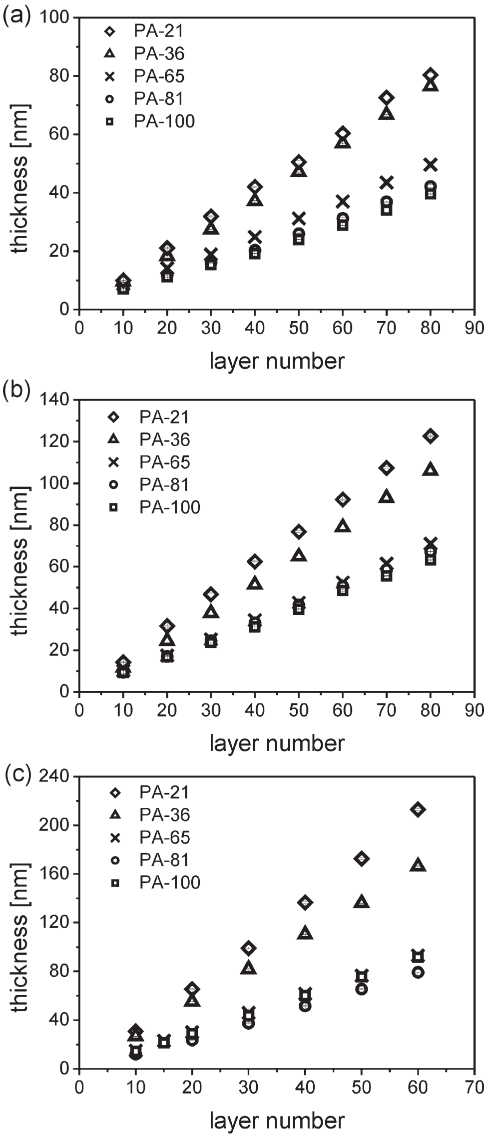

Figure 4. Plot of the ellipsometric thickness as a function of the layer number (with PEI as first layer) of films with different charge densities (PA-21 (◇), PA-36 (Δ), PA-65 (×), PA-81 (○), PA-100 (□)) adsorbed from solutions containing (a) 0.02 M sodium chloride, (b) 0.05 M sodium chloride, and (c) 0.20 M sodium chloride. The error bars are smaller than the size of the symbols.

The differences in layer thickness can therefore be attributed to the fact that self-repulsion of the polyelectrolytes decreases with decreasing charge density, giving raise to higher film thicknesses as charge density decreases. The Rubner group[67] describes a different mechanism whereby it takes more material for the surface charge overcompensation if the linear charge density of the polyelectrolyte is reduced. Both mechanisms could account for the trends observed in our measurements. The added electrolyte screens the self-repulsion, as reflected in the fact that at higher ionic strength the differences between 65 and 100% charge density are vanishing, whereas they become more pronounced at lower ionic strength. Although the trend of increasing thickness as a function of decreasing charge density can thus be rationalized, the pronounced increase in film thickness at a linear charge density below 36% especially at high ionic strength requires a more complex discussion. A possible reason for the qualitative change of the adsorption behavior is that the linear charge density of the polyelectrolytes approaches the Manning condensation threshold at this linear charge density, as proposed by Glinel et al..[34] The linear charge density of PA-36 (projected onto the backbone) is 6.9 Å, whereas the Bjerrum length in water is around 7 Å. Thus one expects that for charge densities above 36%, Manning condensation effectively reduces the linear charge density in solution to a similar value for the polyelectrolytes with 65, 81, and 100%, resulting in a similar effective linear charge density for these species. In contrast, for lower charge densities, this “masking” effect of counterion condensation diminishes. In several studies on multilayers formed from polystyrene-sulfonate and charge-diluted poly[(diallyl-dimethyl-ammonium chloride)-*rand*-(*N*-methyl-*N*-vinyl acetamide)] (P(DADMAC-*stat*-NMVA)), an opposite trend was observed.[33,66] Here, film thickness showed a pronounced decrease below a critical threshold of 40−50% DADMAC-content. The main difference between the system investigated here and P-(DADMAC-*stat*-NMVA) is the highly hydrophilic nature of both the ionic as well as the nonionic comonomers in P(DADMAC-stat-NMVA). This favors soluble polyelectrolyte complexes and acts against adsorption at low charge densities, thus preventing multilayer formation in this

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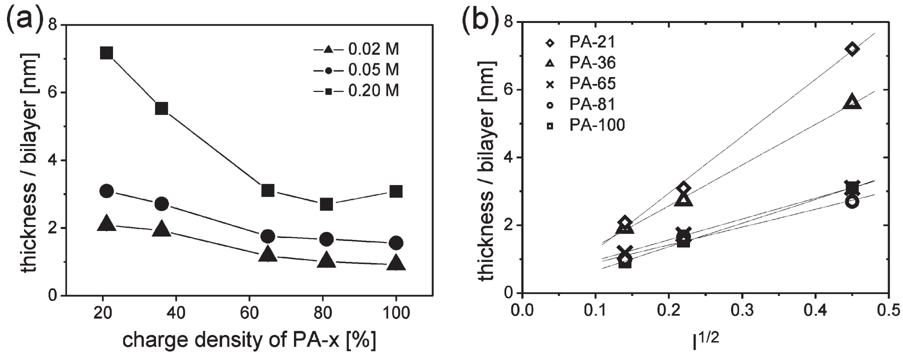

Figure 5. (a) Thickness per bilayer versus charge density of PEI(PA-x/PC)$_n$ films deposited by alternated spraying of polyelectrolyte solutions in the presence of 0.02 M (▲), 0.05 M (●), 0.20 M (■) NaCl. (b) Thickness per bilayer of films prepared from PA-100 (□), PA-81 (○), PA-65 (×), PA-36 (Δ), and PA-21 (◊) as a function of the square root of ionic strength (*I*). The lines are the fits to the data.

regime. Accordingly, the new system presented here might offer an access to low charge density regime.

The film roughness of these systems as a function of layer number was determined by AFM imaging, as shown in Figure 6. Here trends are less pronounced with regard to charge density. At high ionic strength, films show a nearly linear increase of the roughness with the number of added layers. Whereas the thicknesses of PA-65 and PA-100 films do not vary with the charge density, the film roughness is significantly influenced by it, decreasing with the increasing charge density. The mean roughness (R_a) of 60-layer for the fully charged system is 3.4 nm, while that of the 65% charged is 5.7 nm. This is in accordance with more coiled conformation of lower charged polymers in solution.[68] The roughness of 36% charged system remains almost constant about 3.0−3.1 nm over the studied range. With decreasing salt concentration, roughness decreases for all samples, which is as well in agreement with the picture that roughness is dominated by solution conformation of the polyelectrolytes.

Film Cross-Linking. The monomer units of the PC contain a CH-acidic methyl group, which offers the possibility of inter- and intramolecular cross-linking via a base-catalyzed condensation reaction without affecting the number of ionic cross-links (Figure 7).

The product of the cross-linking reaction shows a characteristic absorption at 365 nm, which offers the possibility to follow the process by UV−vis spectroscopy. Figure 8 shows the absorbance spectra of quartz-supported PEI(PA-65/PC)$_{25}$ multilayer film sprayed from solutions containing 0.20 M NaCl. Although before cross-linking the film is transparent between 300 and 600 nm, a new absorbance band of the coupling product is clearly visible after 1 h of reaction and grows with time, indicating the increasing number of cross-links in the film.

The inset in Figure 8 shows that the absorption increment decreases with time, approaching asymptotically a final maximum value after about 9 h. To verify the success of the cross-linking reaction, we immersed the sample in to the cross-linking mixture for additional 3 h. No changes in the absorbance maximum were observed.

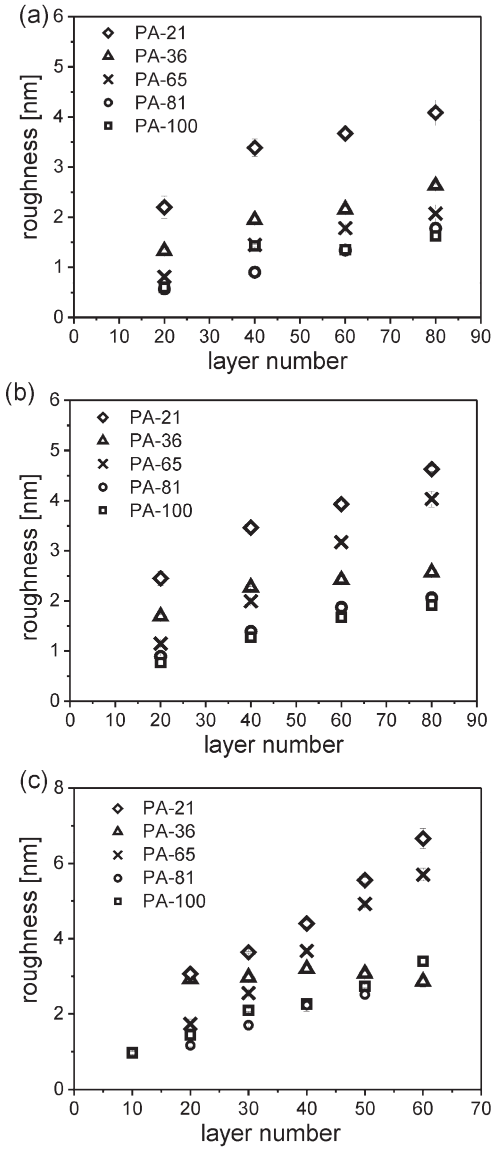

Figure 6. Surface roughness (R_a) determined by AFM measurements versus the layer number of films with different charge densities (PA-21 (◊), PA-36 (Δ), PA-65 (×), PA-81 (○), PA-100 (□)) adsorbed from solutions containing (a) 0.02 M NaCl, (b) 0.05 M NaCl, and (c) 0.20 M NaCl.

Film Stability. The stability of the cross-linked films relative to not cross-linked films, which are stabilized only by ionic bonds, was tested by immersion in a solution of

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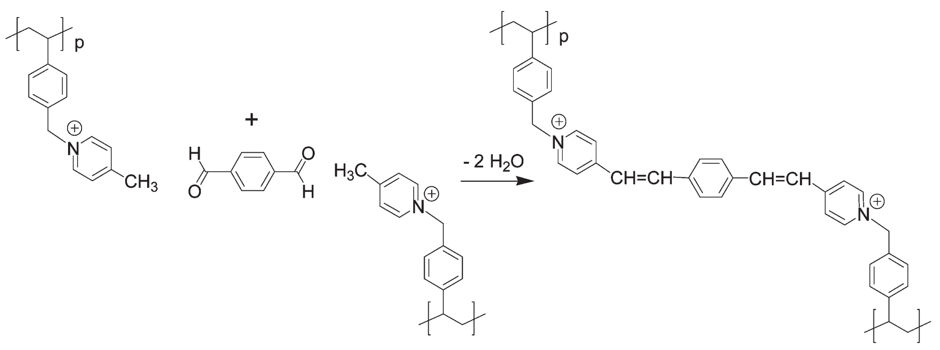

Figure 7. Scheme of the aldol reaction applied for cross-linking multilayer films (PA-*x*/PC)$_n$.

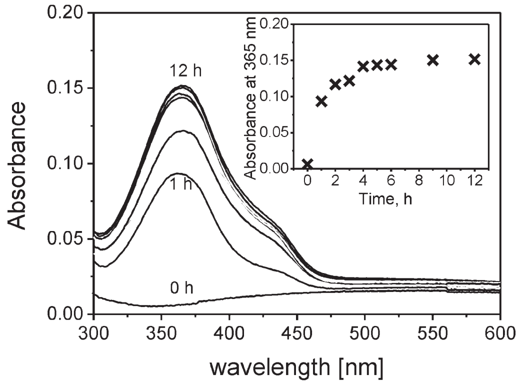

Figure 8. Evolution of the UV–vis absorption spectra of films PEI(PA-65/PC)$_{25}$ film deposited from solutions containing 0.20 M NaCl with increasing time of cross-linking. The inset shows the absorbance at 365 nm versus the time of cross-linking.

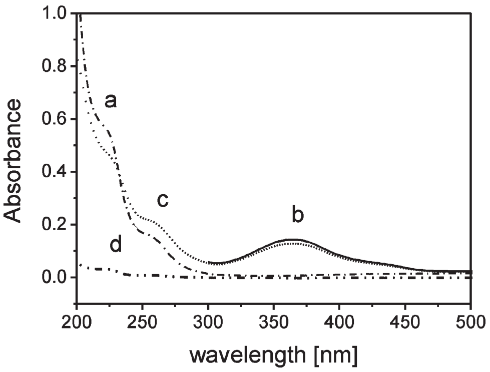

Figure 9. UV–vis spectra of films PEI(PA-65/PC)$_{25}$ sprayed from solutions containing 0.2 M NaCl: (a) before cross-linking (·-·-·-·), (b) after cross-linking (——), (c) after cross-linking and treatment by a ternary solution of H_2O–DMF-$ZnCl_2$ for 30 min (·······), and (d) not cross-linked film after treatment by the ternary solution for 10 s (·-·-·-·-·).

H_2O:DMF:$ZnCl_2$. This ternary system is known to dissolve similar polyelectrolyte complexes efficiently.[69] Figure 9 displays the UV–vis absorption spectra of PEI(PA-65/PC)$_{25}$ assembled on quartz. The adsorption spectra of the non-cross-linked multilayer films (Figure 9a) show characteristic peaks at 220 nm attributed to the benzylidene group of PA, and at 256 nm attributed to the pyridinium group of PC. After cross-linking, a new absorbance band at 365 nm appears, indicating the formation of the dicationic 1,4-bis-(pyridinioethenyl) benzene chromophore as coupling product of two cationic pyridinium units (Figure 9b).[53,70] Note, that for cross-linked film only the absorbance spectra were recorded from 300 nm upward, to exclude rigorously any possibly occurring photo induced side reaction, as the newly formed chromophore might be sensitive against intense UV light, inducing for instance a 2 + 2 photo cycloaddition.[71]

As can be clearly seen, the cross-linked samples are stable and no polymer desorption is detected, as demonstrated by the unchanged absorbance at 365 nm, when the film was treated in the ternary solvent 30 min (Figure 9c). In strong contrast, the absorbances at 220 and 256 nm of uncross-linked film nearly disappears after solvent treatment of only 10 s (Figure 9d), indicating the fast dissolution of the purely electrostatically stabilized LbL films, without any additional covalent bonds between the complementary polyelectrolytes.

Summary and Conclusions

The assembly of novel polyanions with variable charge density and cross-linkable cationic polyelectrolyte prepared by spray-coating was studied, with focus on film buildup and cross-linking of the films.

Investigating the influence of ionic strength and charge density on the film buildup, a linear film growth as a function of the number of deposition cycles was found in all cases. Film thickness increased with increasing ionic strength, exhibiting a scaling behavior of the thickness proportional to the square-root of ionic strength. For all ionic strengths studied, film thicknesses increase with decreasing charge density. This trend can be rationalized by decreasing self-repulsion of the polyelectrolytes. Interestingly, a qualitative change between the charge densities of 65, 81, and 100% as compared to linear charge densities below 36% is observed: Especially at higher ionic strength, film thickness varies only a little for the multilayers containing higher charge densities, whereas below 36%, an increase up to a factor of 2 is observed. A possible explanation for this behavior is that at this charge level, the linear charge density approaches

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one charge per Bjerrum length, the so-called Manning condensation threshold. Therefore, at higher charge densities, counterion condensation would reduce the effective charge of the polyelectrolytes to effectively the same value (strong screening).

Subsequently, we have studied cross-linking of the films by a base-catalyzed condensation. We took advantage of the fact that the cross-links in this system can be easily detected by UV/vis spectroscopy. The kinetics of the reaction could thus be quantified and we found a constant absorption after 4 h of reaction time. The reaction mechanism allows for both inter- and intramolecular cross-link formation. To check whether the stability of the films was improved because of intermolecular cross-links, we carried out stability tests on cross-linked and non-cross-linked samples, which show a stabilizing effect of the cross-linking procedure.

In conclusion, the system offers several advantages as compared to charge-diluted polyelectrolytes previously introduced in the literature: It combines a statistical copolymer nature that allows tuning of linear charge density with a hydrophobic backbone. This ensures multilayer assembly even for low charge densities, because the additional hydrophobic interactions and the corresponding lower solubility favor adsorption of the polyelectrolytes. This regime was previously often not accessible, although it is interesting from a fundamental point-of-view: Especially the case that charge densities approach or drop below the Manning condensation threshold gives rise to novel and more pronounced charge density effects than the regime of higher charge densities, because effects are no longer "masked" by counterion condensation. The data for the lowest charge densities reported here points toward such effects, and the synthetic approach could provide a good route toward even lower charge densities.

As well, the system reported here can be cross-linked. The cross-linking pathway offers two main advantages: First, the charge density of the charge diluted part is not affected in the process. Thus the system remains controlled in its anionic charge density even in the cross-linked state, which provides perspectives for studying the correlations between cross-linking and charge density on mechanical properties in the future. Second, cross-linking causes spectroscopic changes. A characteristic absorption wavelength is linked to the formation of cross-links. Therefore, cross-linking of the films can be directly followed by UV−vis spectroscopy. Thus the system gives perspectives for quantifying cross-linking kinetics and cross-link densities. Additionally, rupture of cross-links because of chemical degradation or mechanical strains could be directly detected in situ.

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Supporting Information Available: Details on the copolymerization behavior, exemplary ^{1}H NMR spectra of monomers and polymers, as well as film growth of layer-by-layer films made from PA-100 and PC from aqueous solutions without any additional salt (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.