

Effect of Polyelectrolyte Molecular Weight on the Formation and Properties of Polyelectrolyte Multilayers

 Tin Klačić,*  Matej Masjar,  Davor Kovačević#

Division of Physical Chemistry, Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, HR-10000 Zagreb, Croatia

* Corresponding author's e-mail address: tklacic@chem.pmf.hr

Corresponding author's e-mail address: davor.kovacevic@chem.pmf.hr

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Abstract: Polymers whose repeating units bear an electrolyte group, so-called polyelectrolytes, are the main building blocks of polyelectrolyte multilayers (PEMs). These thin organic films are versatile nanomaterials with applications in many fields. The main reason for their widespread applications lies in the ability to fine-tune their properties simply by adjusting the experimental conditions of their preparation. One of these parameters is the molecular weight of polyelectrolytes utilized for PEM preparation. Although about three decades have passed since the preparation of the first PEM, consensus among scientists about the influence of polyelectrolyte molecular weight on the properties of PEMs still has not been achieved. For example, several studies have shown that PEM thickness increases with the increase of polymer molecular weight, others that PEM thickness decreases with polymer molecular weight, and third that molecular weight does not influence film thickness. To shed some light on these somehow contradictory findings, we report here the results of a study in which we explore the influence of polyelectrolyte molecular weight on the properties of PEM not as an independent parameter but as a variable related to the polyelectrolyte degree of charging. For that purpose, we prepared PEMs *via* the layer-by-layer assembly with two distinct molecular weights of poly(allylamine hydrochloride) and poly(acrylic acid) at pH = 5.0, 8.0 (with and without NaCl), and 10.0. In the end, we found that the thickness and, for the most part, the surface roughness of prepared films increased with higher molecular weights of polyelectrolytes in all examined conditions except at pH = 8.0. In that condition, the molecular weight of polymers did not affect the PEM properties because polyelectrolytes are highly charged at that pH and adsorb to a surface in a linear conformation. In other conditions, the impact of polyelectrolyte molecular weight on growth and properties of PEM has been explained by the packing of chain molecules at the film surface (pH = 5.0 and pH = 8.0 with NaCl) or by film erosion that was noticed during PEM build up (pH = 10.0).

Keywords: polyelectrolyte, polyelectrolyte multilayer, molecular weight.

INTRODUCTION

POLYELECTROLYTES are polymers composed of macromolecules in which a substantial portion of the constitutional units contains ionic or ionizable groups, or both.^[1] According to a charge of constitutional units, polyelectrolytes may be divided, on the one hand, into positively charged polycations and, on the other, into negatively charged polyanions. In addition, polyampholytes that bear both positive and negative charges also exist. From the point of view of electrolytic behavior, polyelectrolytes may be either strong or weak. Just like simple electrolytes of low

molecular weight, strong polyelectrolytes are completely ionized in solution, while weak polyelectrolytes ionize only partially. Therefore, the degree of charging (i.e. degree of ionization) of weak polyelectrolytes depends on the pH of a solution, and that of strong ones does not.^[2] The pH of a solution plays an important role in defining the conformation of weak polyelectrolytes. As the degree of charging increases, the conformation of weak polyelectrolytes gradually changes from collapsed globular to expanded rod-like due to an increased number of repulsions between monomer units of the same charge.^[3] The same is valid for increasing the concentration of simple electrolytes present

in polyelectrolyte solution but with the opposite trend. In the case of higher concentrations of background electrolyte, monomer units of polyelectrolyte are shielded with salt counterions, and polymer molecules adopt globular conformation. On the contrary, in the case of lower concentrations of background electrolyte, polymers are present in solution in linear conformation because charge screening is mostly absent.^[4,5]

Nowadays, polyelectrolyte molecules are building blocks of many interesting nanosystems, such as polyelectrolyte multilayers (PEMs). This type of organic thin film was prepared first by Decher and co-workers in the early 1990s through layer-by-layer (LbL) assembly.^[6] LbL method of PEM preparation consists of the alternative dipping of solid substrate in polycation and polyanion solution, often with rinsing and drying steps between them. Despite the opinion of many scientists that the LbL process is driven by electrostatic interactions and overcharging phenomena,^[7–10] there is more and more evidence that the driving force for that process is the change in entropy.^[11–13] More specifically, it is believed that PEMs are formed due to increased entropy caused by the unleashing of small counterions and water molecules associated with polyelectrolyte chains. The ion pairing between monomers of polycation and polyanion leads to the formation of so-called intrinsic charge compensation. In contrast, the association of small counterions to non-intrinsically compensated monomers is called extrinsic charge compensation.^[14]

So far, two regimes of PEM growth have been reported in the literature, namely linear and exponential. The former growth regime occurs when the increment in film thickness per deposited polyelectrolyte layer is constant. The latter corresponds to the exponential increase of PEM thickness with the number of deposited polymer layers. In general, it is considered that PEMs grow first exponentially and then linearly. However, if the transition point between exponential and linear growth is at a few deposited polymer layers the overall growth regime will be linear, and if the switch is at a greater number of deposited layers, the growth will be exponential. Two models have been proposed to explain the mechanism behind the exponential to linear growth transition.^[15,16] According to the first model, polymer islands are formed on the substrate surface at the initial stage of PEM growth. The islands expand as new polyelectrolyte material is adsorbed on the surface until they coalesce. The coalescence point represents the transition from exponential to linear PEM growth as the film surface area becomes constant. The other model of PEM growth is based on the polyelectrolyte diffusion in and out of the film. According to this model, the adsorption of polyelectrolytes at the beginning of PEM build up not only leads to complete coverage of the surface but also to diffusion of adsorbing species into the PEM. In this way, the

adsorbed amount of polyelectrolyte increases with each adsorption step. The switch from exponential to linear growth of PEM occurs when diffusion of polymers becomes forbidden. That can happen if the adsorption time is too low and the PEM thickness too high.

The potential application of PEMs nowadays ranges from sensors,^[17,18] membranes,^[19] flame retardants,^[20] and materials for corrosion protection^[21,22] to drug delivery capsules^[23–25] and antimicrobial coatings.^[26–28] One of the main reasons why PEMs have such a widespread application potential lies in the fact that their properties can be precisely controlled during the LbL build up by varying the conditions of their preparation. Some of the experimental conditions that are typically varied to obtain films of the desired properties are pH,^[29,30] ionic strength,^[31–33] and the type of background salt present in polyelectrolyte solutions.^[34–36] Besides the mentioned parameters, the molecular weight of polyelectrolytes also plays a significant role in PEM formation. Many studies that deal with the effect of polyelectrolyte molecular weight on the structure, growth, and properties of PEMs were conducted.^[37–49] However, the obtained results in those studies are in significant disagreement. For example, some authors reported that PEM thickness increases with the increase of polyelectrolyte molecular weight, most likely due to a rise in the entropic contribution of PEM formation.^[37–43] At the same time, others reported that it decreases with the increase of polyelectrolyte molecular weight as a consequence of more hindered diffusion of longer chain molecules than shorter ones.^[44–47] In addition, some researchers have even found that the molecular weight of polyelectrolytes does not affect the PEM thickness and structure.^[47–49] Therefore, it is difficult to predict the influence of polyelectrolyte chain length on the behavior of PEMs. Also, the reason behind the influence of polyelectrolyte molecular weight is still poorly understood, and it remains an open question. Maybe that is so because many of the previous studies have considered the molecular weight of polyions as the only independent variable. However, it is hard to expect that the effect of polyelectrolyte molecular weight is not associated with other variables that influence the conformation of polyelectrolytes, such as pH and ionic strength.

To shed some light on these somehow contradictory findings, we performed a detailed and systematic study with two well-known weak polyelectrolytes, poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA), whose structures are depicted in Figure 1a. Our goal was to better understand how the molecular weight of polyelectrolytes affects the growth and properties of PEMs. The experiments were designed so that 16 films representing different combinations of PAH and PAA were prepared on the surface of the silicon wafer. The combinations were chosen with regard to the molecular weight of the

polyelectrolytes and the conformation of the polymers in the dipping solutions that was adjusted by pH and ionic strength (Figure 1b). The prepared PEMs were characterized by ellipsometry. In particular, we focus on the PEM thickness and the development of film thickness with the number of adsorbed polymer layers. We also used atomic force microscopy (AFM) to evaluate the influence of polyelectrolyte molecular weight on the surface topography and roughness of PAH/PAA assemblies. It is anticipated that the results reported herein will lead to a better understanding of the effect of polyelectrolyte molecular weight on the growth and properties of PEMs.

EXPERIMENTAL

Materials

Poly(acrylic acid) of lower (PAA_l , $M_w = 1\,800\text{ g mol}^{-1}$) and higher (PAA_h , $M_w = 1\,033\,000\text{ g mol}^{-1}$) molecular weight were purchased from Sigma-Aldrich (USA). Poly(allylamine hydrochloride) of lower molecular weight (PAH_l , $M_w \approx 17\,500\text{ g mol}^{-1}$) was also purchased from Sigma-Aldrich (USA), and poly(allylamine hydrochloride) of higher

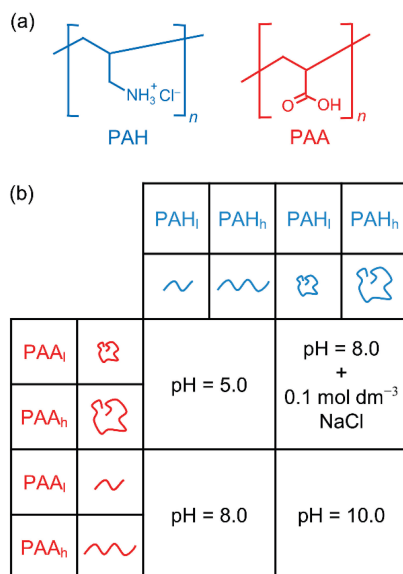


Figure 1. (a) Chemical structure of poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA). (b) Experimental design for preparing PAH/PAA multilayers based on different polyelectrolyte molecular weights and conformations. Poly(allylamine hydrochloride) of lower molecular weight is designated PAH_l , and higher PAH_h . Analogously, poly(acrylic acid) of lower molecular weight is denoted by PAA_l , and higher by PAA_h . The elongated (~) or globular (⊗) conformation of the polyelectrolytes was achieved by adjusting the experimental conditions (pH and ionic strength) as indicated in the figure.

molecular weight (PAH_h , $M_w = 140\,000\text{ g mol}^{-1}$) was obtained from Alfa Aesar (Germany). Potassium hydrogen phthalate, AgNO_3 , and NaCl (purity > 99.9 %) were purchased from Sigma-Aldrich (USA). HCl and NaOH solutions were obtained from Merck (Germany). Standard buffer solutions of pH 3.0, 5.0, 7.0, and 9.0 were purchased from Gram-mol (Croatia). Compressed nitrogen and argon (purity $\geq 99.999\%$) used for drying were purchased from Messer (Croatia). All the chemicals were used as received without any further purification. Ultrapure water was used in all the experiments. It was obtained by further purification of distilled water with a Milli-Q Advantage A10 Water Purification System (Merck Millipore, Germany) and had an initial conductivity lower than $0.055\text{ }\mu\text{S cm}^{-1}$.

Determination of PAA Functionalization Degree

The degree of functionalization (f) of PAA samples was determined by potentiometric acid-base titration of PAA solution ($V = 8.0\text{ mL}$) with standardized NaOH solution. PAA solution was prepared by dissolving the required mass of PAA in 25.0 mL of water so that the concentration of all monomers (c_M) was equal to 0.10 mol dm^{-3} . It should be noted that PAA was dried in an argon atmosphere at $60\text{ }^\circ\text{C}$ for about 200 minutes before the solution was prepared. The NaOH solution ($c \approx 1.0\text{ mol dm}^{-3}$) was standardized with potassium hydrogen phthalate solution ($c = 0.10\text{ mol dm}^{-3}$, $V = 25.0\text{ mL}$) by potentiometric acid-base titration. Before the solution of potassium hydrogen phthalate was prepared, this primary standard was dried at a temperature of $110\text{ }^\circ\text{C}$ for about 180 minutes. During the standardization of NaOH and titration of PAA solution, the electromotivity (*i.e.* electromotive force)^[50] of a combined pH microelectrode (6.0234.100, Metrohm, Switzerland) immersed in the reaction mixture was measured with a pH meter (913 pH Meter, Metrohm, Switzerland). The titrations were performed in a double-glass reaction cell thermostated at $25.0\text{ }^\circ\text{C}$ under the nitrogen atmosphere and under medium stirring of solution by a magnetic stirrer (728 Magnetic Stirrer, Metrohm, Switzerland) after each addition of titrant. The reaction cell and electrode were located in a homemade Faraday cage to reduce the impact of external electromagnetic fields on the results of measurements. Each set of titrations was repeated three times under the same experimental conditions. The analysis of electromotivity data was done in OriginPro 2015 software. The obtained f -values are expressed in the text as average values \pm standard deviation.

Determination of PAH Functionalization Degree

The degree of functionalization of PAH samples was determined by potentiometric titration of PAH solution

($V = 25.0$ mL) with standardized AgNO_3 solution. PAH solution was prepared by dissolving the required mass of polymer (predried in argon atmosphere at 60°C for around 200 min) in 100 mL of water so that the concentration of all monomers (c_M) was equal to 0.005 mol dm^{-3} . The AgNO_3 solution ($c \approx 0.05\text{ mol dm}^{-3}$) was standardized with NaCl solution ($c = 0.005\text{ mol dm}^{-3}$, $V = 25.0$ mL) by potentiometric titration. During the standardization of AgNO_3 and titration of PAH solution, the electromotivity of the cell consists of the chloride ion-selective electrode (MKS, Croatia) and the reference $\text{Ag}|\text{AgCl}|3\text{ mol dm}^{-3}\text{ KCl}$ electrode (6.0729.100, Metrohm, Switzerland) was measured with pH meter (913 pH Meter, Metrohm, Switzerland). The potentiometric titrations were performed in a homemade Faraday cage at 25°C and under stirring of the reaction mixture with the magnetic stirrer (728 Magnetic Stirrer, Metrohm, Switzerland) after each addition of titrant. Three titrations were carried out for each set of measurements. Obtained electromotivity data was analyzed in OriginPro 2015 software so that the mean value and standard deviation of concentrations and f -values were determined.

Substrate Preparation

Single-side polished silicon wafer discs (orientation: 100, type: P, doped with boron, Siltronic, Germany) of 15 cm diameter and $(675 \pm 25)\text{ }\mu\text{m}$ thickness were cut with a diamond needle (Krodat, Croatia) to plates of $1\text{ cm} \times 1\text{ cm}$ dimensions. The Si plates were used as a substrate for PEM preparation immediately after cleaning them in a "piranha" solution. „Piranha" solution was prepared by mixing 30 mL of concentrated H_2SO_4 (Gram-mol, Croatia) with 10 mL of H_2O_2 solution ($w = 30\%$, Gram-mol, Croatia). The cleaning procedure was carried out by soaking the plates in a freshly prepared "piranha" solution for about two hours. During that period, the temperature of the "piranha" solution was maintained at 90°C , and the solution was continuously stirred by means of a magnetic stirrer (RH basic 2, IKA, Germany). After taking the plates out of the "piranha" solution, they were rinsed thoroughly with deionized water and dried with a stream of nitrogen gas.

Polyelectrolyte Multilayer Preparation

Polymers were dried in argon atmosphere at 60°C for 200 min before preparation of polyelectrolyte solutions. Attenuated total reflectance (ATR) spectroscopy measurements confirmed that this process removed most of the water from the hygroscopic homopolymers without causing side reactions (description of ATR measurements, IR spectra of polymers, and assignments of IR bands are provided in Supplementary information). PAH and PAA solutions were prepared at 0.01 mol dm^{-3} monomer concentration. All polyelectrolyte solution concentrations were corrected taking into account the degree of

functionalization of the polymer. The pH of polymer solutions was adjusted to 5.0, 8.0, and 10.0 with NaOH solution ($c = 1.0\text{ mol dm}^{-3}$) using the pH meter (913 pH Meter, Metrohm, Switzerland) equipped with a combined pH microelectrode (6.0234.100, Metrohm, Switzerland), precalibrated with standard buffers (pH = 3.0, 5.0, 7.0, and 9.0). Part of the solutions was prepared with the addition of NaCl so that the final concentration of NaCl in solutions was 0.10 mol dm^{-3} (Figure 1b). From prepared PAH and PAA solutions, PEMs were built. The Si substrates were dip coated manually at $(25 \pm 1)^\circ\text{C}$ and 30 to 55 % humidity using the LbL method.^[6] Initially, the substrates were immersed for 5 minutes in the PAH solution ($V = 25$ mL) that was stirred with a magnetic stirrer (HI 190M, Hanna, Romania). The adsorption of PAH was followed by three 1-minute rinsing steps with 25 mL of MilliQ water and drying with argon. Next, the substrates were immersed in the PAA solution for 5 minutes under continuous stirring, followed by three 1-minute rinsing steps with 25 mL of MilliQ water and drying with argon. The process was repeated until PAH/PAA films with the appropriate number of layers (between 1 and 10) were assembled. For the sake of simplicity, PEMs will be written in the following text in the form $(\text{PAH}_x/\text{PAA}_y)_n$ when they have an even number of layers and $(\text{PAH}_x/\text{PAA}_y)_n\text{-PAH}_x$ when they have an odd number of layers. In such a notation, n denotes the number of PAH/PAA bilayers in the LbL film, and x and y are labels that can be l or h depending on whether the PEM is prepared from polyelectrolytes of lower or higher molecular weight.

Characterization of PEMs by Ellipsometry

PEM thickness was determined in the dry state with a null-ellipsometer (L116B-USB, Gaertner Scientific Corporation, USA) in a polarizer-compensator-sample-analyzer configuration. A He-Ne laser with 632.8 nm wavelength was used as a light source. The incidence angle of the radiation was 70° , and the angle of the polarizer was 45° . The measurements were carried out at a temperature of $(25 \pm 1)^\circ\text{C}$ and air humidity from 30 to 55 %. The measured quantities were changes in amplitude (Ψ) and phase (Δ) of the light reflected from the surface of the sample. The data modeling was performed using the Gaertner Ellipsometry Measurement Program (version 8.071) provided by the instrument supplier to extract the film thickness. The model used contained three phases: substrate, PEM, and atmosphere. Although the substrate consists of silicon and a native oxide surface layer,^[51] it was considered as a one-phase system, and its real and imaginary part of the refractive index was determined prior to PEM formation. The PAH/PAA multilayer was modeled as a homogeneous film with the real refractive index value chosen to be 1.55 and independent of film thickness. The choice of real part of

PEM refractive index was based on the value reported by Sun *et al.*^[45] Since the PEM did not absorb light, the imaginary contribution to the refractive index was taken to be zero. Furthermore, the real component of the refractive index of air in the model was fixed to 1.00. The obtained film thicknesses are presented as an average (with standard deviation) of 10 measurements at different locations on the sample surface.

Characterization of PEMs by AFM

A MultiMode 8 atomic force microscope (Bruker, USA) was used to examine the morphology, roughness, and thickness of the prepared PAH/PAA multilayers. The AFM measurements were performed on dry samples in air at $(25 \pm 1)^\circ\text{C}$ and air humidity ranging from 35 to 55 %. Before the measurements, several scratches were made vertically and horizontally on the surface of samples with sharp tweezers (EM-Tec 3C.AM, Micro to Nano, Switzerland) to determine the thickness of films by scanning at the border of the scratch. The tweezers were carefully pulled over the surface so that the substrate, which is much harder than PEM, was not damaged. The AFM images were acquired in tapping mode using NCHV-A silicon probes (Bruker, USA) with a nominal spring constant of 40 N m^{-1} , resonance frequency of 320 kHz, and a typical radius of curvature of 8 nm. The size of the scanned area was $5\text{ }\mu\text{m} \times 5\text{ }\mu\text{m}$. The scan rate and AFM image resolution were 0.5 Hz and 512×512 pixels, respectively. The mentioned parameters were adjusted using the software NanoScope 9.7 (Bruker). For each sample, scans of five macroscopically separated areas on the film surface were obtained. The resulting AFM images were processed using the NanoScope Analysis 2.0 (Bruker) software. Root-mean-square (RMS) surface roughness was obtained using the Roughness function in that software, and the coverage of the substrate surface with PEM was estimated using the Bearing analysis function. Images utilized for roughness and surface coverage analyses were flattened by a second-order fit correction. The surface roughness and coverage are expressed in the paper as average values with corresponding standard deviations of five measurements. The thickness of the PEMs was determined in Gwyddion 2.61 software after flattening (first-order fit) the AFM images taken in the scratch area. For that purpose, the Terraces function was applied. That function in Gwyddion software enabled us to calculate the mean value of film thickness and its standard deviation.

RESULTS

In the first part of this section, the properties of used polymers are presented, with the main focus on the PAH and PAA degree of functionalization, which is a significant parameter for PEM build up. In the second part, the growth

of PEMs, made of PAH and PAA of different molecular weights and conformations, is reported. The last two parts focus on the results of AFM measurements that provide insight into how polyelectrolyte molecular weight affects surface morphology, roughness, and porosity of PAH/PAA films.

Polyelectrolyte Degree of Functionalization

Polyelectrolyte synthesis does not always take place with 100 % conversion of reactants. Likewise, side reactions can occur during the synthesis of polyelectrolytes. Some polyelectrolytes are not stable, so their chemical nature gradually changes. All these processes reduce the functionality of the polyelectrolyte. Therefore, it is advisable to determine the degree of functionalization of polyelectrolyte. The polyelectrolyte functionalization degree, sometimes called the degree of substitution,^[52] represents the number of ionic or ionizable monomers, *i.e.* functional monomers, divided by the total number of monomers.

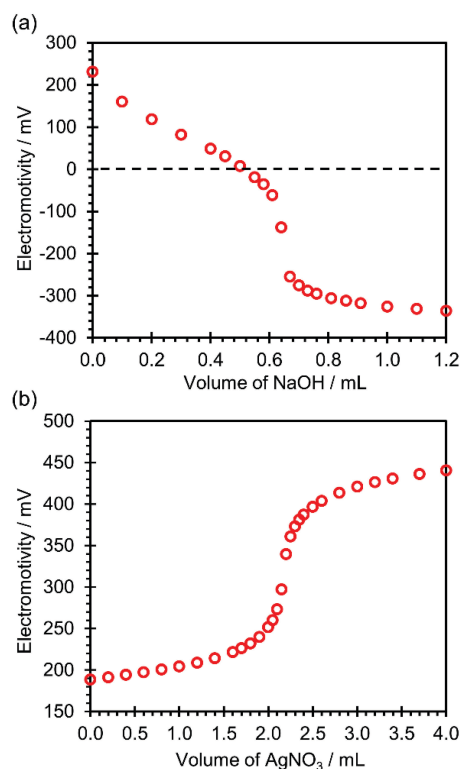


Figure 2. (a) Electromotivity of the combined pH microelectrode (glass and Ag/AgCl half cells) measured during the titration of PAAI solution ($c_M \approx 0.1\text{ mol dm}^{-3}$, $V = 8.0\text{ mL}$) with an aqueous solution of NaOH ($c = 1.009\text{ mol dm}^{-3}$) at 25°C . (b) Electromotivity of the cell composed of chloride ion-selective electrode and Ag/AgCl reference electrode measured during the titration of PAHI solution ($c_M \approx 0.005\text{ mol dm}^{-3}$, $V = 25.0\text{ mL}$) with a solution of AgNO_3 ($c = 0.0506\text{ mol dm}^{-3}$) at 25°C .

In this study, the functionalization degree of PAA samples was determined by potentiometric titration with standardized NaOH solution. Figure 2a shows an example of the result obtained by measuring the electromotivity of the combined pH microelectrode during the titration. Based on the results of the titration curve, the concentration of PAA monomers with functional -COOH group was determined. The degree of functionalization was obtained by dividing the concentration of functional monomers by the concentration of all monomer units. The values obtained were 0.837 ± 0.024 and 0.786 ± 0.004 for PAA of lower and higher molecular weight, respectively.

Titration using a chloride ion-selective electrode was performed to determine the degree of functionalization of PAH samples. For that purpose, PAH solution was titrated with the standardized solution of AgNO_3 . By adding Ag^+ ions to PAH solution, free Cl^- ions are precipitated in the form of AgCl , which results in a decrease in the concentration of Cl^- ions in the solution, and accordingly the electrode potential of the chloride ion-selective electrode changes. An example of titration curve is shown in Figure 2b. From the determined concentration of functional monomers and the concentration of all monomers, the degree of functionalization for PAH of lower molecular weight ($f = 0.863 \pm 0.001$) and higher molecular weight ($f = 0.945 \pm 0.002$) was obtained.

Growth and Thickness of PEMs

In the present work, two molecular weights of PAH (PAH_l and PAH_h) and PAA (PAA_l and PAA_h) were used to study the impact of polyelectrolyte molecular weight on the PEM growth. In order to relate the effect of molecular weight with the polyelectrolyte conformation, the growth behavior of PAH/PAA multilayers was explored by fabricating the PEMs under different pH and ionic strength conditions (Figure 1b). The LbL build up of various combinations of lower and higher molecular weight PAH and PAA is summarized in Figure 3.

The results indicate that at pH = 5.0 (Figure 3a) PAH/PAA multilayers of all molecular weight combinations grow exponentially, while at pH = 8.0 (Figure 3b) the growth is linear. At conditions of pH = 8.0 and high ionic strength (Figure 3c), as well as at pH = 10.0 (Figure 3d), films prepared with polyelectrolytes of higher molecular weight are subject to exponential growth, and films prepared with polyelectrolytes of lower molecular weight to linear growth. In addition, some PEMs prepared at pH = 10.0 ($\text{PAH}_l/\text{PAA}_l$ and $\text{PAH}_h/\text{PAA}_l$) lose their thickness during PAH adsorption (odd layers in Figure 3d). The thickest films were prepared from polyelectrolytes of higher molecular weight at pH = 8.0 with the addition of NaCl and at pH = 10.0. The thickness of these ($\text{PAH}_h/\text{PAA}_h$)₅ multilayers was about

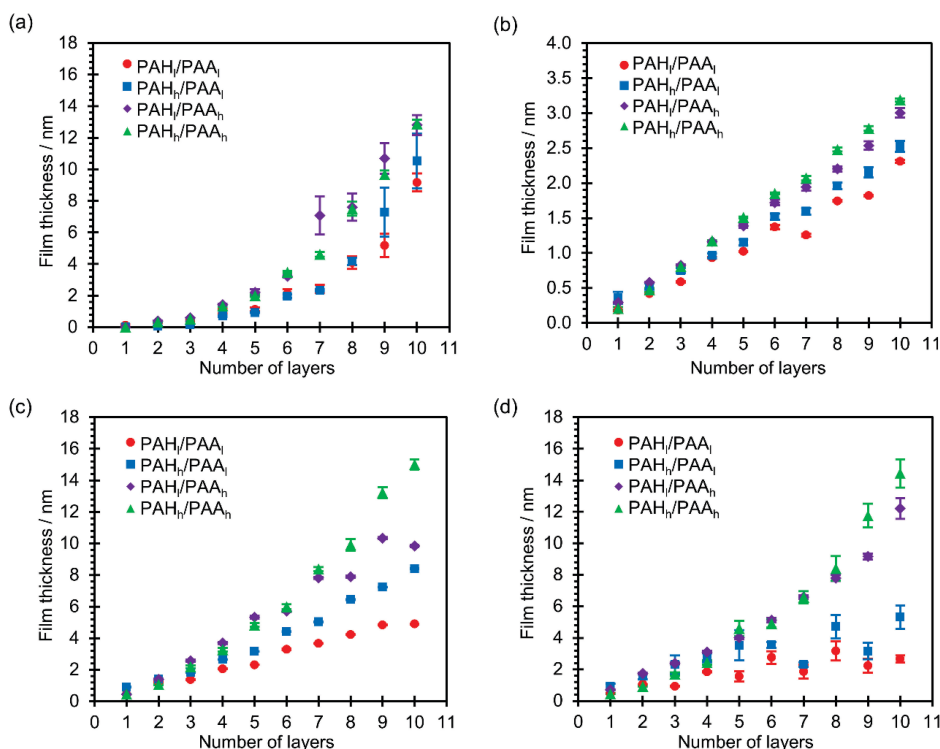


Figure 3. The influence of the molecular weight of the polyelectrolyte on the growth of the PAH/PAA multilayer prepared on the surface of the Si substrate at (a) pH = 5.0, (b) pH = 8.0, (c) pH = 8.0 in the presence of NaCl ($c = 0.10 \text{ mol dm}^{-3}$), and (d) pH = 10.0. The thickness of PAH/PAA multilayers was determined with an ellipsometer after each adsorbed polyelectrolyte

15 nm. In contrast to that, films with the lowest thickness were obtained at pH = 8.0 with all combinations of polyelectrolyte molecular weights. We observed, in general, that the thickness of PAH/PAA multilayers increases with the increase of polyelectrolyte molecular weights under all experimental conditions except at pH = 8.0. At this pH, the effect of polyelectrolyte molecular weight on the thickness of PEMs was negligible, and all the assembled films were ultra-thin with a total thickness lower than 4 nm. Under other conditions, the thinnest films were obtained with the PAH_i/PAA_i polyelectrolyte combination, while the thickest films were obtained with the PAH_h/PAA_h polyelectrolyte combination.

The thickness of the PAH/PAA multilayers was also determined by AFM imaging of the area around a scratch made by tweezers on the substrate surface (see the Experimental Section). Figure 4 shows the AFM thickness of the PAH/PAA films consisting of 10 layers that were prepared with polyelectrolytes of lower and higher molecular weight under different experimental conditions. The film thicknesses obtained using both ellipsometry and AFM are in good agreement. The close agreement between the ellipsometry and AFM results demonstrates that the choice of PEM refractive index ($n = 1.55$) for ellipsometry modeling was quite reasonable. The data in Figure 4 show that (PAH_h/PAA_h)₅ films prepared under all conditions are the thickest, and (PAH_i/PAA_i)₅ the thinnest. The thickness of (PAH_i/PAA_h)₅ multilayers at pH = 5.0 and pH = 10.0 is greater, and at pH = 8.0 without and with NaCl equal to the thickness of (PAH_h/PAA_i)₅ multilayers. At experimental conditions of pH = 5.0, pH = 10.0, and pH = 8.0 with NaCl, the thickness of PEMs increases with the molecular weight of polyelectrolyte. In contrast, at pH = 8.0, the film thickness is practically independent of polyelectrolyte molecular

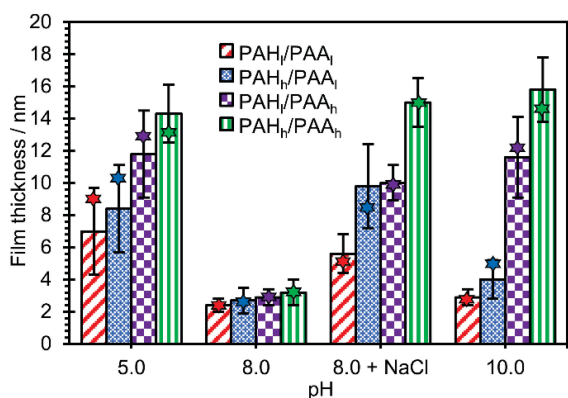


Figure 4. The influence of the polyelectrolyte molecular weight on the thickness of (PAH/PAA)₅ multilayer under different experimental conditions. The columns represent film thickness determined by AFM and the stars thickness determined by ellipsometry.

weight. Likewise, at pH = 8.0, the thickness of all films is much smaller compared to films of the same molecular weight combinations under other experimental conditions. The only (PAH/PAA)₅ multilayers that have thickness comparable to the PEMs prepared at pH = 8.0 are the ones fabricated at pH = 10.0 when PAA of lower molecular weight was used. As stated before, it has been observed that these films grow in a zig-zag trend (Figure 3d).

Surface Morphology and Roughness of PEMs

The surface of each prepared (PAH/PAA)₅ multilayer was imaged by atomic force microscope at five different locations. Figure 5 displays one representative AFM image of the PEM surface for all combinations of polyelectrolyte molecular weights and conditions explored in this study. By comparing the AFM images, it can be concluded that the influence of the molecular weight of the polyelectrolyte on the morphology of the PEM surface is complex and strongly depends on the conditions under which the film is prepared. While (PAH/PAA)₅ multilayers prepared at pH = 5.0 with lower molecular weight PAA have a granular texture of surface (Figures 5a and 5b), PEMs built up at the same pH but with higher molecular weight PAA exhibit porous morphology (Figures 5c and 5d). A granular surface form is also observed for (PAH/PAA)₅ films built up at pH = 8.0 in the presence of NaCl (Figures 5i-k). The only exception in this series is the film prepared with both polyelectrolytes of higher molecular weight (Figure 5l). This

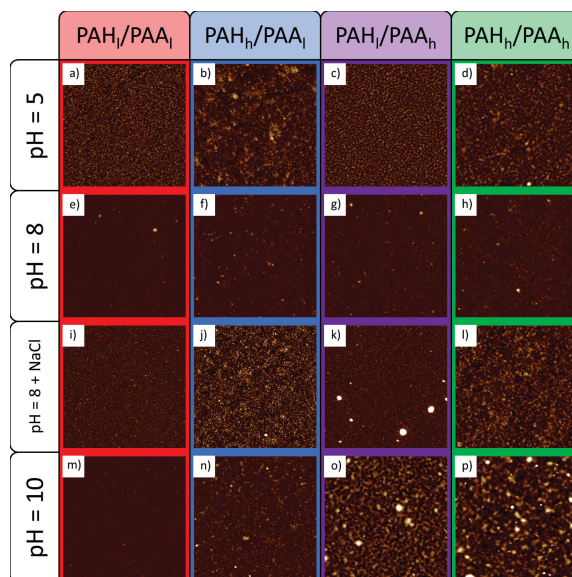


Figure 5. Surface morphology of (PAH/PAA)₅ multilayers prepared under different experimental conditions with polyelectrolytes of higher and lower molecular weight. The x and y scale on the AFM images is 5 μ m, and the z scale is 25 nm.

film has a surface that resembles an „orange peel“. The effect of the molecular weight of polyelectrolytes on the surface topography of (PAH/PAA)₅ multilayers formed at pH = 8.0 is not as significant as at other experimental conditions. All thin films prepared at this pH have a smooth surface with only a few polymer aggregates on the surface (Figures 5e–h). At pH = 10.0, the only clear increase in surface roughness of PEMs can be seen as polyelectrolytes of higher molecular weight are used. The surface topography changes from smooth in the case of (PAH_i/PAA_i)₅ film (Figure 5m) over the granular texture of (PAH_h/PAA_i)₅ assembly (Figure 5n) to porous-like for (PAH_i/PAA_h)₅ and (PAH_h/PAA_h)₅ multilayers (Figures 5o and 5p).

The surface roughness of PAH/PAA multilayers was determined by a detailed analysis of AFM images. Figure 6 depicts the surface roughness data of all prepared multilayer systems. As can be seen from the data, the featureless surface of (PAH/PAA)₅ thin films prepared at pH = 8.0 is the smoothest (RMS roughness parameter is less than 1 nm), and the influence of the molecular weight of the polyelectrolyte in that case is the smallest. The molecular weight of the polyelectrolytes also has a weak impact on the roughness of the PEMs prepared at pH = 5.0. At that pH, films prepared with PAH of lower molecular weight have a roughness of about 3 nm, and films prepared with PAH of higher molecular weight about 2 nm. Interestingly, in this case, the PEMs of the same roughness have different morphologies. It seems that the molecular weight of PAA regulates the morphological characteristic of the PEM surface formed at pH = 5.0, and the molecular weight of PAH controls the roughness properties of the surface. The situation is somewhat more complex with PEMs prepared at pH = 8.0 in the presence of NaCl, which all have a granular surface structure. (PAH_h/PAA_i)₅ and (PAH_i/PAA_h)₅ multilayers built up under these conditions have a significantly higher surface roughness ($R_q \approx 5$ nm) compared to (PAH_i/PAA_i)₅ and

(PAH_h/PAA_h)₅ multilayers ($R_q \approx 2$ nm). The surface roughness regularly increases with an increase in the molecular weight of the polyelectrolytes only in the case of PEMs prepared at pH = 10.0. For example, the surface roughness of LbL film built up at this pH with both polyelectrolytes of lower molecular weight is only 0.5 nm, and the one of PEMs prepared using both polyelectrolytes of higher molecular weight is ten times higher. The observed differences in the surface roughness of the films prepared at pH = 10.0 are consistent with the considerable differences in surface morphology of these films (Figures 5m–p).

Coverage of Substrate Surface with PEMs

From the AFM images shown in Figure 5, it was seen that the surface of some films appeared porous (e.g. Figures 5c, d, o, and p). However, this does not necessarily mean that these PEMs are porous. The porous film is the one for which the pore depth extends all to the substrate level. In that case, part of the substrate surface where pores are located is uncovered (without PEM). On the contrary, the surface of PEM can look like it contains pores, but the depth of pores does not extend to the substrate level. In that case, the film is compact and covers the surface of the substrate totally. In addition to providing information on the thickness of the PEM, AFM imaging of the area around a scratch made on the substrate surface is also a convenient method for exploring the porosity of films. Figure 7a shows an example of a porous surface of PAH/PAA multilayer in the scratch area. From the height profile of the PEM/substrate region (Figure 7c), it can be seen that in several places, the thickness of the film reduces to zero, *i.e.* it is equal to the substrate level. From this finding, we conclude that there is no PEM on the substrate in that part, which means the film is porous. In contrast, Figure 7b shows the surface of a compact PAH/PAA multilayer prepared with polyelectrolytes of the same molecular weight but at a different pH. On the height profile of that sample (Figure 7d), the thickness of the PEM is never in the plane of the substrate, which means that the film is continuous and covers the entire surface of the substrate.

By the described method, we investigated the effect of polyelectrolyte molecular weight on the coverage of the substrate surface with PEMs. We have found that in most of the explored conditions, the molecular weight of polyelectrolytes does not influence the surface coverage, which was 100 %. The only exception was observed for the (PAH/PAA)₅ multilayers obtained at pH = 5.0. For PEMs built up at this pH, we have established that the surface coverage increases by increasing the molecular weight of polyelectrolytes used to prepare PEM. Thus, (PAH_i/PAA_i)₅ and (PAH_h/PAA_i)₅ multilayers of granular surface topography covered (72 ± 1) % and (85 ± 1) % of the substrate surface,

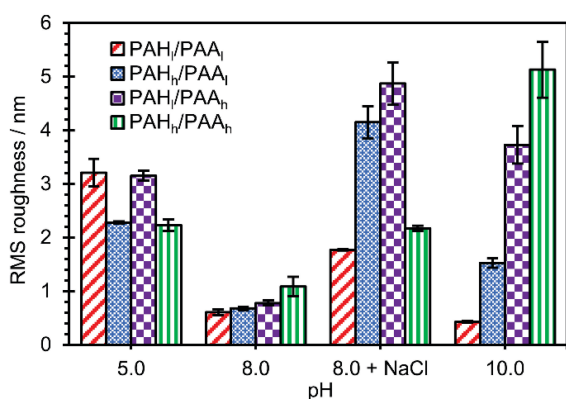


Figure 6. Influence of the polyelectrolyte molecular weight on the RMS surface roughness of (PAH/PAA)₅ multilayers prepared under different experimental conditions.

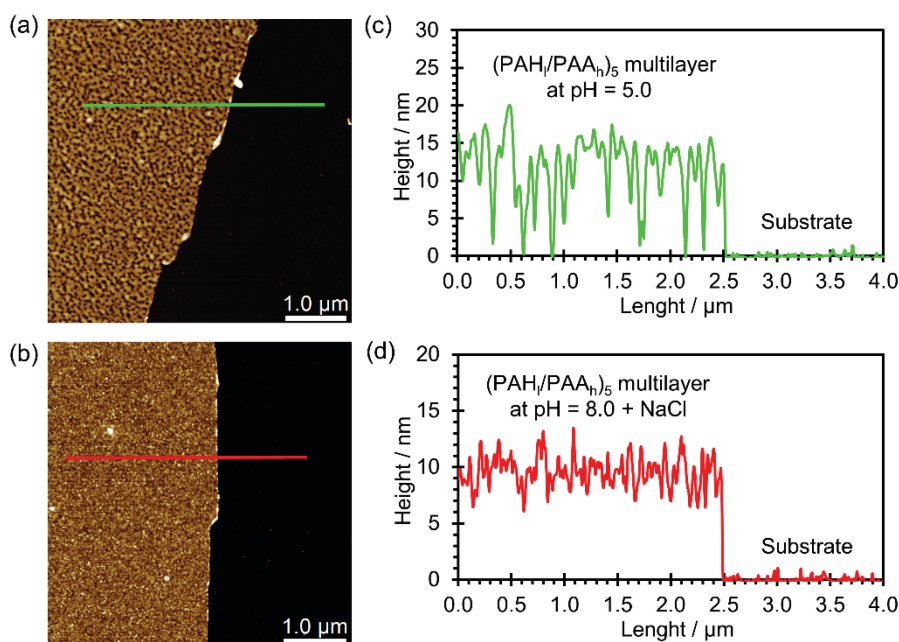


Figure 7. AFM image of the surface of: (a) porous $(\text{PAH}_i/\text{PAA}_h)_5$ multilayer prepared at pH = 5.0 and (b) compact $(\text{PAH}_i/\text{PAA}_h)_5$ multilayer prepared at pH = 8.0 in the presence of NaCl ($c = 0.10 \text{ mol dm}^{-3}$). (c) Height profile of the area marked with the green line in the AFM image under (a). (d) Height profile of the area marked with the red line in the AFM image under (b).

respectively. The surface coverage was even higher for porous PEMs prepared with PAA of higher molecular weight. It was $(88 \pm 1) \%$ in the case of $(\text{PAH}_i/\text{PAA}_h)_5$ multilayer and almost 96 % in the case of $(\text{PAH}_h/\text{PAA}_h)_5$ film. There seems to be a link between the morphology of the PEM surface and the coverage of the substrate surface with that film, as porous $(\text{PAH}/\text{PAA})_5$ multilayers have higher surface coverage than granular ones.

DISCUSSION

In order to explain the influence of the molecular weight of the polyelectrolytes on the properties and structure of PAH/PAA multilayers, all relevant parameters should be taken into account. One of them is the degree of functionalization of polyelectrolytes, which was determined by potentiometric titrations. The other is the degree of polyelectrolyte charging, which depends on the pH of the solution. Table 1 summarizes all the mentioned parameters for PAH and PAA used in this study.

In contrast to the molecular weight of PAH_h , which is eight times the molecular weight of PAH_i , the molecular weight of PAA_h is around 574 times greater than the molecular weight of PAA_i . Therefore, a more significant influence of the molecular weight of PAA on the PEM properties is expected than that of PAH. One should also keep in mind that the molecular weight of PAH_i is around ten times the molecular weight of PAA_i , and the M_w value of PAA_h is seven

times higher than the molecular weight of PAH_h . This difference in molecular weight of polyelectrolytes must induce somewhat different opportunities for assembly during PEM build up. Besides polymer molecular weight, PEM formation is also affected by the polyelectrolyte functionality. According to the results of potentiometric titrations, the highest proportion of non-functional monomeric units contains PAA_h , and the lowest proportion contains PAH_h (Table 1). PAH and PAA of lower molecular weight have similar degrees of functionalization, so when they are complexed on the surface, the best ionic pairing is expected.

Table 1. Weight-average molecular weight (M_w), degree of functionalization (f), and degree of charging (α) at pH = 5.0, 8.0, and 10.0 for the polyelectrolytes used in this research. The estimated conformations of the polyelectrolytes in the solution are indicated in parentheses next to α values.

	PAH _i	PAH _h	PAA _i	PAA _h
$M_w^{(a)}/\text{g mol}^{-1}$	17 500	140 000	1 800	1 033 000
$f/\%$	86.3	94.5	83.7	78.6
$\alpha(\text{pH} = 5.0)^{(b)}/\%$	95 (linear)		10 (globular)	
$\alpha(\text{pH} = 8.0)^{(b)}/\%$	70 (linear)		85 (linear)	
$\alpha(\text{pH} = 10.0)^{(b)}/\%$	30 (globular)		95 (linear)	

^(a) Molecular weights of polymers were provided by the supplier.

^(b) Values of α were taken from data published by Choi and Rubner.^[53]

Another parameter that correlates with the molecular weight effect is the charge density of a weak polyelectrolyte. Yu *et al.* applied infrared spectroscopy to determine the degree of charging of PAH and PAA with different molecular weights.^[46] They found that the degree of charging is independent of polymer molecular weight. Although it is independent of molar mass, the degree of charging affects the conformation that the polyelectrolyte will take in solution, as well as on the surface. A lower degree of charging means a lower amount of charged groups on the polymer chain. Due to the decrease in charge density, the electrostatic repulsion between the monomer units decreases, and the polymer chain adopts a loopy form. On the other hand, a higher degree of charging means a higher charge density on the polymer chain, which increases electrostatic repulsions between monomers, and the polyion takes on an elongated form. Based on the described „conformational theory of polyelectrolytes“, the influence of the molecular weight of polymer on the properties of the multilayer films prepared under different conditions will be discussed.

At pH = 5.0, PAH is highly charged ($\alpha \approx 95\%$), and PAA is very weakly charged ($\alpha \approx 10\%$).^[53] When almost fully ionized PAH chains and weakly ionized PAA chains are consecutively deposited on the silicon surface, the electrostatic assembly process is hampered, and the polymer chains cannot spread out flat over the substrate surface but instead adopt a conformational arrangement of globules. According to the „island“ model,^[15,16] the build up of PEM proceeds in two stages. In the first stage, the substrate is covered with isolated islands of polyelectrolyte complexes. In the second stage, the polymer islands interconnect, leading to a porous film morphology and eventually to an almost compact PEM as the LbL process goes on. It is obvious from AFM images of PAH/PAA multilayers fabricated at pH = 5.0 (Figures 5a-d) that, in our case, compact morphology of films was not achieved. Instead, applying lower molecular weight PAA led to PEMs of island patterns, and higher molecular weight PAA of porous structures. If compact films were obtained, a transition from exponential to linear growth of PEMs would be expected. However, the results in Figure 2a demonstrate that this transition did not occur, as PAH/PAA multilayers of all molecular weight combinations grow exponentially.

In addition, we noticed that the PEM thickness in the exponential growth phase depends on the molecular weights of polyelectrolytes. The use of higher molecular weight PAA resulted in films that increased in thickness more rapidly than PEMs fabricated using PAA of lower molecular weight. In this respect, the behavior of PAH/PAA multilayers appears to be the opposite of what was observed by Sun *et al.* for the exponentially growing PEMs fabricated from commercially available PAH and synthesized PAA of two well-defined molecular weights.^[45]

They reported that PEMs fabricated from high molecular weight PAA were thinner than those prepared using lower molecular weight PAA. However, the pH of the PAA assembly solution in their case was 3.5 and that of PAH 7.5. Although the degree of polyanion charging at pH = 3.5 is similar to that in our study ($\alpha \approx 5\%$), the degree of polycation charging at pH = 7.5 is significantly lower ($\alpha \approx 70\%$).^[53] Also, the adsorption step lasted 10 minutes in their case, which is enough time to promote the diffusion of polymers.

Nevertheless, the different behavior of PEMs made of higher and lower molecular weight PAA may be explained by the higher number of contact points per molecule for the former due to the longer chains. The cooperatively acting interactions of longer polymer chains induce a transition from individual islands to interconnected domains at a lower number of adsorbed polyelectrolyte layers in comparison to shorter chains. This lateral spreading of polyelectrolytes does not significantly affect the roughness of the PEMs regardless of the length of the polymer chains used (Figure 6). Meanwhile, the coverage of the substrate surface with PEMs increases by depositing polyelectrolytes of higher molecular weight.

Contrary to the behavior of PEMs prepared at pH = 5.0, the molecular weight of polyelectrolytes does not affect the properties of LbL films fabricated at pH = 8.0. As shown, PAH/PAA multilayers built up at this condition are uniform and of similar thickness and surface roughness regardless of used polymer chain lengths. We suspect that almost fully charged PAH and PAA at pH = 8.0 (Table 1) will strive to form 1:1 stoichiometric “zipped-up” structures on the surface. In that case, the net result would be the deposition of very thin polyelectrolyte layers, which are spread out flatly on the surface. Hence, longer polyelectrolyte chains, which are in the same elongated conformation on the surface as short ones, will only occupy more surface area without increasing the film roughness or thickness. The low thickness increase per adsorbed polyion layer that is not influenced by the molecular weight of polyelectrolyte (Figure 3b) and similar featureless surface topography of all films prepared at pH = 8.0 (Figures 5e-h) support this explanation. The results of a study carried out by Shiratori and Rubner also support this explanation. They found that the thickness increase of PAH/PAA multilayers fabricated at pH = 6.5 is independent of the molecular weight of the adsorbing polyelectrolytes over a range of 3000 to 1 000 000 g mol⁻¹.

We may conclude that in salt-free solutions at pH = 8.0 where both polyelectrolytes are highly charged, the impact of polymer molecular weight on PEM properties is inconsequential due to the adsorption of polyelectrolytes in flat form. With increasing salt concentration in the depositing solutions of the same pH value, higher mass adsorption is achieved, as indirectly demonstrated by ellipsometry and AFM measurements (Figure 4). The higher

polymer uptake is explained by the larger surface area available for adsorption due to the deposition of more coiled polyion chains. The adsorbed polyelectrolyte molecules have only a part of their segments intrinsically compensated on the surface. The other part of the polymer segments is extrinsically compensated and protrudes into the solution.^[31–33] When the molecular weight of polyelectrolytes is increased, the film thickness increases (Figures 3c and 4). That result is consistent with the explained surface structure of the multilayer. Namely, long-chain polymers will presumably form more loops and tails on the surface than short-chain polymers, and thus, the PEM surface area will be higher in the case of higher molecular weight polymers. However, to confirm the formation of loops and tails, as well as to achieve a more precise understanding of the polyelectrolyte conformation on the surface, a method such as single-molecule force spectroscopy could be applied in the future.

Kujawa and co-workers already examined the effect of polyelectrolyte molecular weight on the PEM properties at the high salt concentration ($C_{\text{NaCl}} = 0.15 \text{ mol dm}^{-3}$) but for the chitosan/hyaluronic acid system.^[40] These authors also found that thicker films are prepared by polyelectrolytes of higher molecular weights. According to them, this is attributable to an earlier transition from the exponential to the linear phase of PEM growth when polyelectrolytes of higher molecular weights are used. In the present work, PEMs prepared at pH = 8.0 and high ionic strength show different growth behavior depending on the molecular weight of the polyelectrolyte pair. According to the results of ellipsometry measurements (Figure 3c), films prepared with PAA of higher molecular weight are subject to exponential growth, and films prepared with PAA of lower molecular weight to linear growth. We can consider these results in the context of the „island“ model of PEM growth. While in the former case one can assume that substrate is covered with isolated islands of polyelectrolytes, in the latter case the film should be present on the substrate surface in compact form. However, our AFM data suggest, based on the surface coverage with PEM, that LbL films prepared both from polyelectrolytes of lower and higher molecular weight are compact and thus should enter the linear growth regime. In one of our previous studies,^[36] we prepared PAH_i/PAA_n multilayer in similar conditions as here (at pH = 7.5 in 0.10 mol dm⁻³ NaCl solution) and examined the surface of PEM by AFM after each adsorbed polyelectrolyte layer. We observed that the surface morphology of PEM alternately changed between the second and eighth layers from grain-like (PAA layers) to blob-like (PAH layers) island structures and then became more or less worm-like. In addition, we observed that the surface roughness of PEM changed in a zig-zag pattern as PAH and PAA layers were alternately adsorbed at the surface up to the ninth layer,

and then the roughness became constant. From those results, we can conclude that the switch from exponential to linear growth of PEM occurs at the 9th layer. This conclusion suggests that an extension of PEM thickness measurements to a higher number of adsorbed polyelectrolyte layers is needed to be sure that PAH_i/PAH_n and PAH_n/PAH_i multilayer growth is in a linear regime (Figure 3c).“

At pH = 10.0, the effect of polyelectrolyte molecular weight on the properties of PAH/PAA multilayer is most significant. Both the film thickness and surface roughness increase as polyelectrolyte molecular weight increases (Figures 4 and 6). The reason for such differences in film properties lies in the dissimilar stabilities of PAH/PAA multilayers prepared at this condition. While films prepared from PAA with higher molecular weight are stable and grow exponentially, films prepared with PAA of lower molecular weight show a certain amount of instability, which is manifested in thickness oscillations. More specifically, when PAH of lower or higher molecular weight is adsorbed on the film terminated with PAA of lower molecular weight, the thickness of the PEM decreases and again increases when a new PAA layer is deposited (Figure 3d). The resulting zig-zag growth of PEM is not so surprising because it was noticed earlier.^[38,54,55] According to Sui *et al.*,^[38] this non-monotonous PEM growth can be explained by the formation of polyelectrolyte complexes which are weakly attached to the film surface and can be easily removed during the adsorption or rinsing step. The formation of such quasi-soluble aggregates is strongly favored when employed polyelectrolytes have a large difference in molecular weights and when one of the polyelectrolytes is in high excess.^[56–58] Clearly, the latter condition is satisfied whenever a PEM is exposed to a polyelectrolyte solution. However, the former condition requires that the polyelectrolyte adsorbed on the surface has a lower molecular weight than the one in the solution, or vice versa.

Let us first consider the situation when PAH_i and PAH_n are adsorbed to PEM terminated with PAA_i. In our experiments, the average molecular weight of PAA_i was only 1 800 g mol⁻¹, which is around 10 times lower than the average molecular weight of PAH_i and 78 times lower than the average molecular weight of PAH_n. Therefore, both conditions for fabricating quasi-soluble complexes were satisfied when PAH_i or PAH_n was adsorbed to PEM capped with PAA_i. That reaffirms the idea that the formation of complexes in these conditions limited the system's growth. Effectively PAH/PAA multilayer plateaued in thickness and surface roughness after the adsorption of the third PAH layer (Figure 3d). Since only a few layers were required to limit the growth of the PEM, the formed films were extremely thin (less than 4 nm). Moreover, continuous adsorption and desorption of polymer materials have prompted smoothing of features on the PEM surface (Figures 5m and 5n).

Let us now consider the reverse situation at pH = 10.0, when a polymer of lower molecular weight (PAH_l or PAH_h) is adsorbed to PEM terminated with the polymer of higher molecular weight (PAA_h). In that case, stripping of polyelectrolyte molecules from surface is not likely to happen because polyelectrolyte of higher molecular weight is more strongly attached to the PEM surface than polyelectrolyte of lower molecular weight due to higher number of polymer-polymer contact points. Thus, PAH/PAA film can grow in a layer-by-layer fashion without limitations.

It is also interesting to compare the stability of PAH/PAA film at pH = 5.0 and pH = 10.0 when a PEM is built up from polycation of higher molecular weight (PAH_l or PAH_h) and a polyanion of lower molecular weight (PAA_l). At both of these pH values, one polyelectrolyte is of high and the other of low charge density. While at pH = 5.0, the PAH/PAA multilayer shows regular exponential growth (Figure 3a), the film made of the same polyelectrolytes is unstable at pH = 10.0 (Figure 3d). One of the explanations for such different behavior of PEM at pH = 5.0 and pH = 10.0 could be hydrogen bonding between PAH and PAA monomers. Our assumption is mainly based on the publication of Li *et al.*^[59] These authors investigated the formation of PAH/PAA complexes at equivalent monomer ratios in acidic, neutral, and alkaline media of different ionic strengths adjusted by adding NaCl. By imaging the samples with an optical microscope, they observed that complexes prepared in neutral and alkaline media gradually changed their shape from a fluffy precipitate to spherical coacervate droplets. However, this transformation was not observed in PAH/PAA complexes prepared at low pH, which retained the form of a precipitate up to a NaCl concentration of 4 mol dm⁻³. As the authors explained, in neutral and alkaline media, the dominant interactions between polyelectrolytes in the precipitate are electrostatic. The stability of the precipitate is disrupted by increasing ionic strength due to the screening effect of ions, and the precipitate turns into a coacervate. However, in an acidic medium, in addition to electrostatic interactions, hydrogen bonds are also formed between the protonated amino group of PAH and the non-protonated carboxyl group of PAA. Therefore, hydrogen bonds together with electrostatic interactions make the PAH/PAA multilayer prepared at pH = 5.0 more resistant to the “stripping” effect of polyelectrolytes than at pH = 10.0.

CONCLUSION

This investigation was directed toward evaluating the impact of polyelectrolyte molecular weight on the formation and properties of polyelectrolyte multilayers. Although the effect of polymer molecular weight on the formation and properties of PEMs has been explored extensively, as

pointed out in the Introduction section, there is still a lack of consensus in the literature. In most of the previous studies, the molecular weight of polyelectrolytes was explored as the independent parameter that affects PEM properties. However, we have shown here that the effect of polyelectrolyte molecular weight and its mechanism is strongly correlated with the polyelectrolyte charge density, which is intertwined with the conformation of polyelectrolyte in solution and at the surface. Considering the charge density of both polyelectrolytes, we can distinguish three cases. The first is when both polyelectrolytes are highly charged. The second case is when both polyelectrolytes are weakly charged, and the third case is when one polyelectrolyte is highly charged and the other weakly charged.

In conditions when both polyelectrolytes are highly charged, the molecular weight of the polymer should not influence the properties of the PEM due to the adsorption of polyions in flat conformation. In contrast, when both polyelectrolytes are weakly charged and in coil conformation, *e.g.* in conditions of high ionic strength, the film thickness and the surface roughness should increase with polyelectrolyte molecular weight. That should be so because longer polymer chains form more loops and tails on the surface than shorter chains. Consequently, the surface area available for adsorption of the next polyelectrolyte layer is higher in the case of longer-chain molecules than in shorter ones. The same outcome is expected when one of the polyelectrolytes is less charged and the other more charged. However, in that case, the molecular weight effect manifests itself through two mechanisms. The first mechanism considers the earlier crossover of PEM morphology from individual islands to interconnected domains when longer polymer chains are used in the LbL process. The second mechanism accounts for the zig-zag growth of PEM, which is induced by stripping polyelectrolytes off the surface in the form of quasi-soluble complexes. It is precisely this last mechanism that is interesting for application because it can be used to prepare compact ultra-thin films with extremely smooth surfaces.

In the end, it is interesting to note that we did not observe in any of the explored conditions that film thickness increases with the decrease of polyelectrolyte molecular weight. It is possible that the cause of this was limited diffusion of polymer molecules through PEM. Namely, the growth of PEM consists of two steps. One of them is the adsorption of polymer molecules from the solution to the PEM surface, and the other is the diffusion of these molecules from the surface to the PEM interior. As in our experiments deposition time was set to only 5 min, the diffusion of polyelectrolytes into the PEM was limited. Therefore, one of our future plans is to investigate the correlation between the deposition time and the polyelectrolyte molecular weight effect.

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PDF files with attached documents are best viewed with Adobe Acrobat Reader which is free and can be downloaded from [Adobe's web site](https://www.adobe.com/acrobat/).

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