Influence of Molecular Weight on the Performance of Polyelectrolyte Multilayer Nanofiltration Membranes

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ABSTRACT: Polyelectrolyte multilayers (PEMs) are highly promising selective layers for membrane applications, especially because of their versatility. By careful choice of the types of polyelectrolyte and the coating conditions, the PEM material properties can be controlled to achieve desired separations. Less understood, however, is how the molecular weight (Mw) of the chosen polyelectrolytes (PEs) will impact layer build-up and thus separation properties. In this work, we investigate the influence of Mw on the performance of two types of PEM-based membranes. PEM membranes have been fabricated from low (15–20 kDa) and high (150–250 kDa) Mw poly(allylamine hydrochloride) (PAH), poly(sodium-4-styrenesulfonate)(PSS), and poly(acrylic acid) (PAA) to obtain PAH/PSS- and PAH/PAA-based nanofiltration membranes. For the linear growing PSS/PAH system, with low PE mobility, the Mw is found to influence the pore closure of the support membrane during coating but not its subsequent performance. In contrast, for the exponentially growing PAH/PAA system with a high PE mobility, much stronger effects of Mw are observed. For low-Mw PAH/PAA PEM membranes, separation properties are found that would be expected of a negatively charged separation layer, while for high-Mw PAH/PAA PEMs a positive separation layer is found. Moreover, molecular weight cutoff (MWCO) measurements show that the low-Mw PAH/PAA multilayers are much denser than their high-Mw counterparts. Here the higher mobility of the small PE chains is expected to lead to more optimal binding between the oppositely charged PEs, explaining the denser structure. Lastly, we find that PEM pH stability is lowest for low-Mw PAH/PAA multilayers which can again be attributed to their higher mobility. Clearly, the Mw can significantly influence the separation performance of PEM-based membranes, especially for more mobile PEM systems such as PAA/PAH.

KEYWORDS: polyelectrolyte multilayer, nanofiltration, micropollutants, tuning parameter, mobility, membrane technology

INTRODUCTION

The assembly of polyelectrolyte multilayers (PEMs) has been demonstrated to be a powerful tool to modify surfaces, finding multiple applications in the field of membrane engineering, drug delivery, and optics. Consequently, the formation of PEMs and the parameters that influence PEM material properties have been the focus of many investigations in the past years. Numerous parameters were reported to affect the properties of PEMs, including polyelectrolyte (PE) type, salt concentration, pH, and even PE molecular weight (Mw). Apart from the possibility of tuning PEMs by various parameters, also the fabrication of PEMs can be done using different methods, such as dip-coating, spray-coating, and electrodeposition. Dip-coating is the most commonly applied method and involves the layer-by-layer (LbL) deposition of polycations and polyanions to modify a charged surface. During coating, electrostatic interactions and an entropic driving force allow for the formation of a very thin polyelectrolyte layer (0.5–5 nm) on
top of a layer of opposite charge. Through the discussed parameters, the LbL technique allows one great control over the film thickness and material properties to modify substrates of different geometries.

In the field of membrane technology, PEMs are able to act as selective layers on the inner surface of hollow fibers resulting in excellent performance. The hollow fiber geometry provides advantages over other membrane geometries such as reduced fouling and pretreatment. Moreover, the assembly of PEMs on membrane supports has already led to promising nanofiltration membranes, forward osmosis membranes, and electro dialysis membranes. The technology has even been commercialized as hollow fiber nanofiltration membranes.

The great tuning potential of PEMs provides an additional advantage in the production of membranes. Depending on parameters such as PE type and salt concentration, the PEM-based membrane can be optimized to target specific applications. Salt concentration and PE type are generally reported as parameters of great influence on the properties of PEMs. Indeed, the effects of these parameters on PEMs coated on both ideal and porous surfaces have been reported by various studies. Surprisingly, other parameters such as PE molecular weight have been less explored in the literature. The influence of MW on the behavior of PEMs has been studied only for multilayers built on model surfaces and also there it has just been described by a few authors. To the best of our knowledge, the effect of PE molecular weight on PEMs assembled on porous membranes is yet to be explored.

The PE MW can certainly affect the formation of PEMs on model surfaces influencing properties such as layer growth, thickness, and mass. The influence of MW has been mainly explained by differences in mobility and layer interpenetration between PEs of low and high molecular weight. Generally, PEs of low MW are found to build multilayers that grow exponentially, because their higher diffusion coefficient allows faster transport of PE into the PEM bulk during layer assembly. Low MW was also correlated to a higher degree of layer interpenetration and the formation of complexes at the PEM surface. On the other hand, PEs of high MW are reported to grow layers in a linear mode, creating films generally showing low degrees of interpenetration between layers.

Yu et al. evaluated the effect of MW on poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) film growth and interpenetration at different pH conditions. PAH and PAA of low and high MW were used in coating solutions at pH 3.5, pH 8.5, and pH 10. At pH 3.5 and pH 10, PAH/PAA presented a linear growth behavior and an absence of layer interpenetration due to strong differences in charge density between PAH and PAA. On the other hand, when the PAH solution had a more intermediate pH of 8.5, interlayer diffusion was found to occur because of the low degree of ionization of PAA. It was concluded that the effect of MW on the growth of PAH/PAA multilayers depended on the degree of ionization and the deposition time. For instance, for low-MW PAA, adsorption is fast, such that interlayer diffusion was the controlling step for film growth. In contrast, for high-MW PAA, the adsorption step controlled the film build-up.

The polyelectrolyte MW was also found to affect the lateral chain mobility of PEMs. Xu et al. studied this effect on multilayers formed by poly(methacrylic acid) (PMAA) and poly(2-(dimethylamino)-ethyl methacrylate) (PC) assembled at pH 4.5. The ionic strength of the coating solution was increased to facilitate PE mobility. In this case, layer intermixing was almost not affected, but the lateral diffusion coefficient of PMAA scaled inversely with MW. Therefore, PMAA of higher MW had lower lateral diffusivity within the LbL film. However, the effect of MW on film mobility depends considerably on the choice of the PE pair. For instance, for PEMs composed of poly(acrylic acid) (PAA) and poly(1-lysine) (PLL) a low molecular weight is related to a higher film rigidity compared to PEs of medium and high MW.

These studies demonstrate that the PE molecular weight affects the growth, layer-interpenetration, and mobility of PEMs coated on model surfaces. However, this effect seems to be complex, depending on the coating conditions and on the type of PE composing the multilayers. For PEMs coated on porous surfaces, the effect of PE molecular weight has not yet been studied; however, it is expected that differences in layer interpenetration and mobility could affect the performance of PEM-based membranes. For instance, PEs of low MW having a higher diffusivity and being more likely to experience layer interpenetration could form less defined PE layers. This less defined layering could result in differences in retention compared to the more defined and structured layers formed by PEs of high MW. Here, we aim to study the effect of PE molecular weight on PEMs formed on membrane surfaces and the resulting membrane performance. The PEMs are composed of two different pairs of polyelectrolytes, PAH/PAA and PAH/poly styrenesulfonate (PSS).

The weak PE pair PAH/PAA and the weak/strong PE pair PAH/PSS have been widely used to form multilayers in different applications. PSS, a strong PE, when combined with PAH forms very stable multilayers on membrane surfaces, even when exposed to extremely acidic conditions, whereas PAH in combination with PAA has poor long-term stability at extreme acidic conditions. Between the two PE pairs a difference in multilayer growth behavior is reported. Where PAH/PAA multilayers typically show exponential growth, PAH/PSS multilayers show linear growth. Generally, PEMs which grow exponentially such as PAH/PAA are considered more mobile compared to linearly growing PEMs such as PAH/PSS.

In this paper we show for the first time that making use of different PEs and varying MWs can have a significant influence on the performance of PEM membranes. As such, careful selection of PEs and their size enables the fabrication of PEM membranes for specific applications. For this, we coated hollow fiber ultrafiltration membranes with PAH/PAA and PAH/PSS multilayers of both low (∼15 kDa) and high (∼200 kDa) MW. Membrane performance is examined by means of pure water permeability, salt retention, and molecular weight cut off (MWCO). Furthermore, we make use of optical reflectometry which enables us to in situ monitor multilayer adsorption on to model surfaces. In this way, we can examine growth type and, indirectly in combination with membrane performance, conclude on mobility in PEMs of low and high MW.

### EXPERIMENTAL SECTION

**Materials.** Polyelectrolytes of various $M_w$ and type were obtained from the following sources: Poly(allylamine) (PAH, $M_w = 15,000$ g mol$^{-1}$, 15 wt % in water) was purchased from Polysciences, Inc. Poly(4-styrenesulfonic acid) (PSS, $M_w = 19,000$ g mol$^{-1}$, dialyzed form) was purchased from Polymer Source, Inc. Poly(allylamine hydrochloride) (PAH, $M_w = 150,000$ g mol$^{-1}$, 40 wt % in water) was obtained from Nittobo Medical CO., LTD, Japan. Poly(acrylic acid)
the amount of adsorbed polyelectrolyte (in mg/m²) on a model can be found in the Supporting Information, Figure S1. 

di stagnant point, adsorption will be determined only by means of component polyurethane glue. This results in an e submerged in an aqueous glycerol solution containing 15% w/w bilayers was achieved. After dip coating, completed membranes were upon coating of either PAA or PSS depending on the type of system solution of 50 mM NaCl were performed. A bilayer was completed coated by immersing the hollow 

calculated using the following values:

\[ 
\text{permeability} = \frac{m_p}{p_m \cdot A \cdot t \cdot P_{mp}} 
\]

where \( m_p \) is the permeate mass in g, \( p_m \) the density of water in g·L⁻¹, \( A \) the membrane area in m⁻², \( t \) the time in hours, and \( P_{mp} \) the transmembrane pressure in bar.

Salt Retention. Single salt retention measurements were performed in cross-flow mode using the cross-flow setup mentioned above. Retention values of NaCl, MgCl₂, Na₂SO₄, and MgSO₄ were determined at concentrations of 5 mM for all mentioned salts. All measurements were performed at transmembrane pressures of 2 bar, while maintaining a cross-flow velocity of approximately 1 m·s⁻¹. The retention of salt was determined by means of conductivity, using a WTW ProfiLine portable conductivity meter.

\[
\text{retention} = \left(1 - \frac{C_p}{C_f}\right) \times 100\% 
\]

where \( C_f \) is the average conductivity of the feed between the start and end of the measurement and \( C_p \) is the conductivity of the permeate.

Molecular Weight Cutoff. The molecular weight cutoff of our membranes was determined by means of gel permeation chromatography (GPC, Agilent 1200/1260 Infinity GPC/SEC series) of feed and permeate samples. An aqueous feed solution of ethylene glycol, diethylene glycol, PEG200, PEG400, PEG600, PEG1000, PEG1500, and PEG2000 was used at a concentration of 1 g·L⁻¹. Measurements were performed in cross-flow mode at a transmembrane pressure of 2 bar and a cross-flow velocity of approximately 1 m·s⁻¹. A feed sample was taken half way into each measurement. The GPC was fitted out with two columns in series at a flow of 1 mL·min⁻¹. Suprema 8 × 300 mm Å, 10 µm followed by 30 Å, 10 µm. Both columns were obtained from Polymer Standards Service GmbH. The GPC was equipped with a refractive index detector.

Polyelectrolyte Multilayer Stability on Model Surfaces. Polyelectrolyte multilayer stability under acidic conditions was investigated on model surfaces. Multilayers consisting of PAH/PSS and PAH/PAA were dip-coated on a silicon wafer with a silicon oxide layer of 81 nm. As a first layer, PEI was used to ensure a stable polyelectrolyte layer. This means that the first bilayer consists of PEI/PSS or PEI/PAA depending on the used polyelectrolyte pair. After this first layer, 4 bilayers of the chosen polyelectrolyte pair were coated, resulting in a total of 5 bilayers. Coating conditions are similar to the coating conditions of the PEM membranes mentioned in Methods.

For investigating the stability, reflectometry was used. The coated wafers were placed inside the flow cell of the reflectometer upon which they were exposed to aqueous rinsing solutions of 50 mM NaCl at different pH values ranging from 4 to 1. The various pH conditions were all applied for 250 s in which usually a stable signal was obtained. After exposure to a pH condition, the flow cell containing the coated silicon wafer was flushed with an aqueous 50 mM NaCl solution at pH 5.8 upon which the pH was again lowered for the same sample. Note that the reflectometer was not used similar to the process explained in Reflectometry. For the here-described stability measurements a change in signal was used to obtain the stability of the dipcoated model surfaces. The way this change in signal was obtained is as described in Reflectometry.

Dry thickness of the coated wafers was determined using ellipsometry. For this a rotating compensator ellipsometer (MK-2000 V, J.A. Woollam Co., Inc.) was used. Coated wafers were stored in deionized water and blow dried using a nitrogen stream before measuring dry thickness. Measurements were performed under
multiple angles of incidence: 65°, 70°, and 75° in the range of 370–1000 nm. Data was fitted according to a Gauchy model, as shown in eq 4, using CompleteEase software. In the Gauchy model we fit the data assuming the PEM is a single layer.

\[ n(\lambda) = A + \frac{B}{\lambda^2} \]  

Because the coated multilayers are thin (<30 nm), the obtained data was fitted only for thickness. Both the A (1.49) and B (0.0045) parameters for similar multilayers were taken from the literature.45

■ RESULTS AND DISCUSSION

PEs of various Mw have been used. For the sake of clarity, from this point on we will be discussing between low and high Mw. Low Mw weight refers to 15 kDa PAH, 19 kDa PSS, and 15 kDa PAA, whereas high Mw refers to 150 kDa PAH, 200 kDa PSS, and 250 kDa PAA. First, we highlight the growth behavior of the various PE combinations on model surfaces by means of optical reflectometry. Second, the growth behavior of PEs on membrane supports is explored. Third, membrane performance will be discussed in terms of salt retention and MWCO. Lastly, we will cover the stability of low- and high-Mw PE layers which is investigated by means of optical reflectometry.

Reflectometry: Layer Growth on Model Surfaces. For monitoring layer growth on model surfaces in this study we turn to optical reflectometry. Reflectometry enables us to observe, in situ, the amount of PE that adsorbs to a model surface. Consecutive deposition steps, alternated with the exposure to solvent, reveal the amount of adsorption for each added PE layer. Experiments were performed using aqueous solutions with a PE concentration of 0.1 g/L, an ionic strength of 50 mM NaCl, and set to pH 5.5. For all systems the first layer grown on the silicon wafer is poly(ethylene imine) (PEI). PEI was chosen as a first layer to ensure a stable base, enabling a good adsorption of the first layer of anionic polymer.

In Figure 1a the adsorption of low- and high-Mw PAH/PSS multilayers as a function of increasing layer number are shown. A linear growth curve is observed for both Mw’s, which is typically seen for PAH/PSS multilayers.46,47 Slightly less adsorption is observed for the low-Mw PAH/PSS compared to high-Mw PAH/PSS; this difference seems to increase with increasing layers. Typically, multilayers containing strong PEs, i.e., PSS, grow in a linear fashion. The linear growth behavior is believed to be the result of reduced mobility of the PE. The Schlenoff group found that PSS showed a low mobility in PDADMAC/PSS multilayers.46 However, the fact that there is a slight difference in adsorption between low- and high-Mw PAH/PSS multilayers needs a different explanation. Spruijt et al. showed that long polymer chains have longer relaxation times compared to short polymer chains.86 An increase in relaxation time is the result of a lower mobility, but more mobility would be expected to lead to thicker PEM layers rather than thinner as observed here. If it is not mobility, it likely is simply a result of higher Mw polymers leading to higher adsorbed amounts when adsorbing. Longer polyelectrolytes form longer loops and tails and thus spread their charges and mass over a larger volume, allowing slightly more mass to adsorb with every adsorption step.50 It is important to realize that the reduced mobility at higher Mw can have other effects that are not immediately observed here, including less layer intermixing, in turn leading to a more defined layered structure.

Figure 1b shows the exponential growth behavior, which is typically seen, for PAH/PAA multilayers coated at pH values around 5.5.35 Picart et al. have shown that the exponential growth behavior observed in PEMs is a result of the diffusivity of at least one of the two PEs comprising the multilayer.31 The ability of I PE to diffuse deeply into, as well as out of the multilayer allows for exponential growth. Figure 1b showcases the difference between low-Mw PAH/PAA and high-Mw PAH/PAA multilayers, which appears after approximately 6 bilayers. The low-Mw PAH/PAA multilayers clearly show a higher amount of adsorption from this point on. This observation can be explained by the findings of Picart et al. As mentioned, diffusivity plays a key role in exponential growth of PEMs. It can be imagined that low-Mw PEs have the ability to diffuse deeper and easier into, and thus out of, the multilayer compared to high-Mw PEs. As a result, more low-Mw PE is
able to diffuse out of the layer when the multilayer is exposed to an oppositely charged PE solution. From this it logically follows that high-Mw PE will be more restricted to diffuse into the multilayer because of size restrictions and thus results in a lower amount of adsorption. Lastly, it should be noted that after approximately 5 bilayers high-Mw PAH/PAA seems to grow in a linear fashion instead of advancing in a more exponential regime. The different types of growth and differences in amount of adsorption between the two systems, and between high and low Mw for PAH/PAA, is expected to translate into a different type of retention behavior. As these PEM membranes will retain salts mostly based on Donnan and dielectric exclusion, the amount of excess charge present in the multilayer will have a major influence on the retention.

Layer Growth on Porous Supports. There are multiple reasons to expect a difference between layer growth on model surfaces and layer growth on porous support membranes. During reflectometry, polyelectrolyte transport toward the surface is purely determined by diffusion under controlled conditions. However, when multilayers are applied to hollow fiber membrane supports we have to take into account the presence of pores and the odd–even effect. In layer build-up on porous support membranes, swelling of the multilayer will cause the free volume of the pore to decrease. The degree of swelling will be different depending on the terminating layer, influencing the mobility of polyelectrolytes in the pore and thus layer build-up. According to the size or Mw of the polyelectrolyte this influence can be expected to be less or more pronounced. In this section we will discuss the PEM...

Figure 2. Pure water permeability vs MgSO₄ retention for low-Mw PAH/PSS-coated membranes (a) and high-Mw PAH/PSS-coated membranes (b). The red dotted line indicates the transition from the pore-dominated regime into the layer-dominated regime. Coating was performed at a PE concentration of 0.1 g/L, pH 5.5, and an ionic strength of 50 mM NaCl. Experiments were performed at 2 bar transmembrane pressure, approximately 1 m·s⁻¹ cross-flow velocity, and a constant temperature of 21 °C. Error bars: standard error; n = 4.

Figure 3. Pure water permeability vs MgSO₄ retention for low-Mw PAH/PAA-coated membranes (a) and high-Mw PAH/PAA-coated membranes (b). The red dotted line indicates the transition from the pore-dominated regime into the layer-dominated regime. Coating was performed at a PE concentration of 0.1 g/L, pH 5.5, and an ionic strength of 50 mM NaCl. Experiments were conducted at 2 bar transmembrane pressure, approximately 1 m·s⁻¹ cross-flow velocity, and a constant temperature of 21 °C. Error bars: standard error; n = 4.
growth on porous supports. For this, hollow fiber UF membranes were coated with the aforementioned PE pairs. Figure 2 shows the permeability versus MgSO₄ retention for both low- and high-Mw PAH/PSS-coated hollow fiber membranes. Using these graphs we are able to determine the layer dominated regime for each system, which means that the pores of the porous support membrane have closed, resulting in a multilayer on top of the porous support membrane. Pore closure is indicated by a drop in the odd–even effect of MgSO₄ retention in combination with a linear regime for the pure water permeability. Interestingly, just as with the layer growth, we see a reversed trend between PAH/PSS-coated membranes and PAH/PAA-coated membranes. Figure 2a clearly indicates sooner pore closure for the low-Mw PAH/PSS membranes at approximately 7 bilayers. For the high-Mw PAH/PSS membranes pore closure occurs at approximately 8.5 bilayers as can be seen in Figure 2b.

The reverse happens for PAH/PAA-coated membranes. Shown in Figure 3b, sooner pore closure for the high-Mw PAH/PAA-coated membranes is clearly observed at 7.5 bilayers. For the low-Mw PAH/PAA-coated membranes depicted in Figure 3a we observe a peak in MgSO₄ retention at 9.5 bilayers followed by a dip in retention until 12 bilayers, indicating full pore closure at 12 bilayers. One would expect sooner pore closure for a high-Mw PEM because of the bigger molecule size. However, the results show that this assumption holds only for PAH/PAA multilayers while for PAH/PSS multilayers the low-Mw PEM shows sooner pore closure. It is likely that the slightly higher mobility of low-Mw PAH and PSS plays a role with regards to layer growth on porous supports. Here the higher mobility, in a more confined environment such as membrane pores, allows for a better layer build-up compared to the less mobile high-Mw PAH and PSS. It could simply be more difficult for the longer and bulkier high-Mw PSS and PAH to enter the membrane pores. On the other hand, we see that for PAH/PAA multilayers sooner pore closer is obtained for the high-Mw PEs over low-Mw PEs. For PAH/PAA multilayers it seems that the bigger size in combination with the higher mobility of the system, regardless of Mw, allows for a more effective closure of the pores. For the low-Mw PAH/PAA multilayers it is likely that a too high mobility becomes a problem, as very mobile systems can lead to less well-defined layers and even to dewetting, probably requiring more material for full coverage.

The obtained results regarding layer growth on porous surfaces as shown in Figure 2 and 3 are in line with the reflectometry data. The linear growth of PAH/PSS multilayers is a result of a low amount of intermixing between the PAH and PSS layers. As a consequence, the PAH/PSS PEMs have a more distinct layer structure which is supported by the clear odd–even effect in pure water permeability, as can be seen in Figure 2. The odd–even effect is a result of the difference in swelling between the polycation and polyanion ending multilayer, resulting in a more dense or a more open layer. For both low- and high-Mw PAH/PSS multilayers the odd–even effect is clearly visible, although the high-Mw PAH/PSS PEM has an even more pronounced odd–even effect. This can be explained by means of mobility between the low and high Mw’s, where the low Mw has more mobility, and thus, it is probable that the low Mw has a slightly less defined layered structure. For the PAH/PAA PEMs shown in Figure 3 the odd–even effect in pure water permeability seems to be absent, indicating a high degree of intermixing which is typical for exponentially growing PEMs.

**Membrane Performance.** Up until this point we have considered layer growth on both model and porous surfaces, now membrane performance in terms of salt retention and MWCO will be discussed. Salt retention measurements have been performed for monovalent and multivalent salts. The combination of these salts give us more insight regarding overall membrane charge, layer intermixing and the retention mechanism(s) of PEM membranes. The amount of layers for the prepared PEM membranes was determined such that all PEMs are in the layer-dominated regime.
Figure 4 depicts the salt retention data obtained for both the PAH/PSS- and PAH/PAA-coated membranes. Figure 4a shows high retention for PAH/PSS-coated membranes toward all multivalent salts used. It should be noted that between the low- and high-Mw PAH/PSS-coated membranes there is no major difference in salt retention for all studied salts. For PAH/PSS multilayers one would expect a buildup of positive charge throughout the multilayer. However, the results indicate that salt retention in both low- and high-Mw PAH/PSS-coated membranes is mainly based on the dielectric exclusion mechanism. Here, a high retention for multivalent salts is independent of charge, as seen in Figure 4a where sodium sulfate retention is equal to magnesium chloride retention.

A completely different behavior is observed for PAH/PAA-coated membranes, as can be seen in Figure 4b. The low-Mw PAH/PAA-coated membranes show a clear Donnan exclusion type retention. The results indicate the membranes have an excess of positive charge. This is concluded from the high retention of magnesium chloride, the low retention toward sodium sulfate, while at the same time the sodium chloride retention lies between both values. Surprisingly, the high-Mw PAH/PAA-coated membranes appear to be overall negatively charged. Figure 4b shows that the high-Mw PAH/PAA-coated membranes retain sodium and magnesium sulfate up to 70%. However, retention of both sodium chloride and magnesium chloride appear to be low, which is not typical Donnan exclusion nor typical dielectric exclusion behavior. Because all membranes end on an anionic PE layer, it could be expected that the retention behavior would follow the trends of a membrane with a negative surface charge. However, the low-Mw PAH/PAA-coated membranes show retention behavior of a membrane with a more positively charged surface. This can be because it is easier for the low-Mw PAA to diffuse into the multilayer below or for PAH to diffuse out of the multilayer toward the surface upon exposure to the PAA coating solution, thus resulting in more positive charge at the surface of the multilayer and therefore membrane surface. For this system the difference in mobility between high and low Mw thus leads to very different separation behavior.

In Figure 5 the MWCO data is shown. The MWCO measurements show that between low- and high-Mw PAH/PSS there is a negligible difference, as also seen for the salt retention measurements. However, there is a major difference between low- and high-Mw PAH/PAA-coated membranes. The difference between the low- and high-Mw PAH/PAA-coated membranes is approximately 150 Da, meaning the low-Mw PAH/PAA membranes are more dense. This is expected if you consider the fact that the low-Mw PAH and PAA have a higher diffusivity and thus are able to form a more optimized multilayer, with a maximum amount of ionic cross-links formed by contact between anionic and cationic monomers. However, with a lower mobility at higher Mw, there will likely be more unconnected (extrinsically compensated) monomers and thus a lower ionic cross-link density and a higher MWCO.

Polyelectrolyte Multilayer Stability on Model Surfaces. Polyelectrolyte multilayer stability on model surfaces was investigated under different pH conditions ranging from pH 4 to pH 1. We investigated the tendency of multilayers to remain intact on the model surface under increasingly extreme pH conditions, which is very relevant for membrane cleaning and/or specific industrial applications. The stability in terms of layer thickness is depicted in Figure 6 for both PAH/PSS and PAH/PAA multilayers on a model surface. A combination of reflectometry and ellipsometry was used to obtain information regarding the multilayer stability on model surfaces. The obtained maximum signal after 5 bilayers during reflectometry measurements as shown in Figure 1 was assumed equal to dry thickness obtained by means of ellipsometry for 5 bilayers dipcoated on a model surface. The change in signal, e.g., a decrease for PAH/PAA, that followed from exposure to pH conditions during reflectometry stability measurements was converted to a percentage of the maximum signal obtained for data in Figure 1. This percentage was then converted to a percentage in thickness change using the ellipsometry data, which is shown in Figure 6.

Their is no clear difference between high- and low-Mw PAH/PSS multilayers, as can be seen in Figure 6a. For low and high Mw a slight swelling of the layer is observed at low pH values. When the pH is lowered, the weak PAH will gain charge, and charge allows for swelling in these multilayers. Moreover, it can be seen that at low pH both the PAH/PSS multilayers are stable, assuming that the increased layer thickness is caused by swelling.

Unlike PAH/PSS multilayers, PAH/PAA multilayers show an expected decrease in layer thickness, as can be seen in Figure 6b. Because both PAH and PAA are weak polyelectrolytes, upon changing pH toward extreme values their charge will alter. In this specific case of going toward a pH value of 1, PAA will become less charged. As a result, layer thickness decreases significantly when going from pH 3 to pH 2.

A noticeable difference is also seen between high- and low-Mw PAH/PAA multilayers with regard to the decrease in layer thickness. After exposing both high- and low-Mw multilayers to a pH of 2, low-Mw PAH/PAA multilayer thickness decreases more compared to the high-Mw PAH/PAA multilayer thickness. We believe this effect can be attributed to the size difference of the polyelectrolyte chains between high- and low-Mw polyelectrolytes, where the low-Mw polyelectrolyte chains are shorter and thus the ionic network, allowing for the formation of a multilayer, can be disrupted quicker upon the loss of charge due to lowering of the pH.
CONCLUSIONS

While many parameters that affect the material properties and thus the separation properties of PEM-based membranes have been investigated, the effect of Mw was still poorly understood. This study performed a detailed investigation into the effect of polyelectrolyte molecular weight on the resulting performance of PSS/PAH- and PAA/PAH-based PEM membranes.

PAH/PSS multilayers are known to grow in a linear fashion. We report on a slightly higher adsorption for high-Mw PAH/PSS multilayers, in line with the tendency for longer polymers to form loops and tails when adsorbing to a model surface. This simply results in more mass adsorbing during the growth of high-Mw PEMs. On the other hand we show opposite behavior for the more mobile and exponentially growing PAH/PAA PEMs. Here, more mass adsorbs during the growth of low-Mw PEMs because of the ability of low-Mw PAH and PAA to diffuse in and out of the PEM.

Furthermore, a difference in growth behavior between different PE pairs when fabricating PEMs on porous support membranes is observed. Unexpectedly, low-Mw PAH/PSS multilayers (7) reach a layer dominated regime sooner needing less coated bilayers compared to high-Mw PAH/PSS multilayers (8.5). In contrast, PAH/PAA multilayers show opposite growth behavior on porous support membranes with high-Mw PAH/PAA multilayers reaching the layer dominated regime at 7.5 bilayers.

In terms of performance, PAH/PSS PEM membranes show no difference when fabricated from either low- or high-Mw polyelectrolytes. A difference is seen for PAH/PAA PEM membranes where low-Mw PAH/PAA PEMs form denser membranes compared to their high-Mw counterparts. In addition to being more dense, low-Mw PAH/PAA PEM membranes show salt retention behavior indicating a positively charged membrane. On the other hand, the high-Mw PAH/PAA PEM membranes show salt retention which can be explained by a more negative charge being present in the PEM.

Both growth behavior and membrane performance can be linked to the variation in mobility of the polyelectrolytes. A combination of PAH and PSS forms multilayers resulting in performance and properties without a significant difference between low and high Mw. Here, we conclude mobility for PAH/PSS multilayers is similar at either low or high Mw. However, from pH stability measurements we observe a difference, upon exposure to pH 3, for PAH/PAA multilayers, indicating low PAH/PAA multilayers exhibit higher mobility compared to high-Mw multilayers constructed of PAH and PAA.

This work showcases the relevance of taking into account the polyelectrolyte Mw when constructing PEM membranes. More specifically, it is important to take into account the effect of Mw when constructing PEM membranes using a combination of 1 or 2 mobile polyelectrolytes. In general, this would be a PE pair that exhibits exponential growth behavior. We have shown that PEM membrane performance can be drastically altered when using either low- or high-Mw polyelectrolytes. This potentially could be very useful toward the development of new types of membranes designed to remove specific compounds, e.g., the novel asymmetric PEM membranes for micropollutant removal reported by te Brinke et al. which ideally have low ion retention and high micropollutant retention. The low-Mw PAH/PAA could act as an even denser separation layer, while still maintaining relatively low ion retention. In addition, we have observed a change in membrane charge between low- and high-Mw PAH/ PAA multilayers. This could be useful for applications where oppositely charged solutes need to be separated.

Overall, this study highlights that polyelectrolyte Mw is an important parameter to take into account in the production of...
PEM membranes, especially for more mobile PEM systems such as PAH/PAA. For these systems, the Mw also becomes an effective tuning parameter that allows fine-tuning of the separation properties toward specific applications.

**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsapm.1c00826.

Additional experimental details and results, including membrane module design, schematic illustration of experimental crossflow setup, and MWCO sieving curves (PDF)

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**Notes**
The authors declare no competing financial interest.

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