Sustainable Membrane Production through Polyelectrolyte Complexation Induced Aqueous Phase Separation

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Nonsolvent induced phase separation (NIPS) is the most common approach to produce polymeric membranes. Unfortunately, NIPS relies heavily on aprotic organic solvents like N-methyl-pyrrolidone. These solvents are unsustainable, repro-toxic for humans and are therefore becoming increasingly restricted within the European Union. A new and sustainable method, aqueous phase separation (APS), is reported that eliminates the use of organic solvents. A homogeneous solution of two polyelectrolytes, the strong polyanion poly(sodium 4-styrenesulfonate) (PSS) and the weak polycation poly(allylamine hydrochloride) (PAH), is prepared at high pH, where PAH is uncharged. Immersing a film of this solution in a low pH bath charges the PAH and results in a controlled precipitation, forming a porous water-insoluble polyelectrolyte complex, a membrane. Pore sizes can be tuned from micrometers to just a few nanometers, and even to dense films, simply by tuning the polyelectrolyte concentrations, molecular weights, and by changing the salinity of the bath. This leads to excellent examples of microfiltration, ultrafiltration, and nanofiltration membranes. Polyelectrolyte complexation induced APS is a viable and sustainable approach to membrane production that provides excellent control over membrane properties and even allows new types of separations.

1. Introduction

Membrane technology is widely used in many applications, for example, in the production of drinking water, the treatment of waste-water, the separation of chemicals, and kidney dialysis. Most of the commercially available membranes are made from polymers using a technique now known as non-solvent induced phase separation (NIPS). NIPS began with the work of Loeb and Sourirajan which successfully produced reverse osmosis membranes that an asymmetric structure, i.e., a thin dense layer on top supported by a porous substructure. This was a big breakthrough in membrane technology because with NIPS it became possible to prepare defect-free asymmetric membranes in a continuous process with great control over the pore size and structure. The discovery of NIPS made membrane technology the important separation technique that it is today and NIPS is still the core technique to prepare membranes.

The NIPS process is a simple and elegant approach. First, a polymer is dissolved in a solvent that can mix with water in any quantity, typically a dipolar aprotic solvent, such as N-methyl-pyrrolidone (NMP). Then, the polymer solution is cast as a thin film and subsequently immersed in a so-called “non-solvent” bath, that is nearly always water. As the solvent (NMP) and nonsolvent (water) are miscible, they undergo an exchange such that the water diffuses into the polymer solution and the NMP diffuses out. The process continues until the polymer becomes insoluble and coagulates (phase separates) as a solid porous film. The final membrane morphology can be tailored to a great extent by manipulating parameters such as the type of polymer, the choice of solvent and nonsolvent, precipitation time, and composition of the coagulation bath. Over the past few decades, abundant knowledge has been generated in the field of NIPS based membranes for almost all the membrane based separation applications.

However, the NIPS process comes with a clear downside. It relies heavily on dipolar aprotic solvents (like NMP) which are unsustainable, harmful to the environment, and repro-toxic for humans. According to Razali et al., the membrane industry produces around 50 billion liters of waste-water each year that is contaminated with NMP and N,N-dimethylformamide (DMF). Due to the high costs of these solvents and environmental legislation, they have to be recycled, requiring an expensive closed cycle of process streams. Furthermore, the residual solvent must be fully removed from the membrane before it can be used for medical applications or the production of drinking water. Recently, the European Union has restricted the use of NMP throughout the EU. As a result, NMP cannot be used in a concentration ≥0.3% after May 2020, unless the manufacturers and consumers take appropriate risk management protocols. Therefore, there is a growing need to devise alternative strategies for the production of polymeric membranes in a way that is more environmentally friendly and sustainable.

Water is one of the most abundantly available solvents on earth. However, the traditional polymers that are used in NIPS...
are insoluble in water. Therefore, a different class of polymers called polyelectrolytes (PE) can be used because of their water solubility. PEs are charged polymers with either positive or negative charges on their repeating units, surrounded by small counter-ions. When two oppositely charged polyelectrolytes are mixed they can form a water-insoluble solid known as a polyelectrolyte complex (PEC).[11] The driving force for polyelectrolyte complexation is the increase in entropy due to the release of bound counter-ions. Polyelectrolyte complexation can lead to well-defined structures for encapsulation and drug delivery.[12] while polyelectrolyte complexes can also be processed into plastic-like materials, so-called saloplastics, with good material properties.[13] Furthermore, polyelectrolyte complexation can lead to well defined thin films, polyelectrolyte multilayers, as demonstrated by Decher and Hong by alternate deposition of polycations and polyanions.[14] This approach has gained widespread attention with thin multilayers being prepared in layer-by-layer fashion for several membrane applications such as nanofiltration,[15–17] reverse osmosis,[18] and gas separation.[19] Polyelectrolyte multilayer based membranes have excellent separation properties, demonstrating that polyelectrolyte based materials hold great promise for separation, yet they still require a membrane support that was prepared by NIPS.

Recently, De Vos showed that it is possible to prepare completely porous membranes entirely in water by using pH-responsive polyelectrolytes.[20] For pH-responsive PEs, water can act as both, a solvent and a nonsolvent depending on its solution pH. The weak polybase poly(4-vinylpyridine) is charged and soluble in water at low pH, but uncharged and insoluble in water at high pH. This phase transition can be controlled to form porous membranes with high water fluxes. De Vos also demonstrated a first example, where polyelectrolyte complexation leads to phase separation to produce freestanding membranes. Sadman et al. recently reported a similar approach based on polyelectrolyte complexation achieved by using salt concentration as a trigger.[21] Membranes with pore sizes ranging from microns to several hundred nanometers were prepared by dissolving a PEC in KBr salt solution to form a complex coacervate. This coacervate was then cast as a film and allowed to precipitate in deionized water following by immersion in a pH 1 bath. The resulting membranes were able to retain >99% of polystyrene beads of 100 nm size with a permeability lying in the ultrafiltration regime. Although the process eliminates the use of organic solvents, the downsides were that it is time-consuming because it requires extensive solution preparation and includes a two-step coagulation process. Moreover, the complex coacervates require an equilibration time ranging from 1 day to 1 month.[21] But most importantly, limited control over pore size and geometry was reported.

To truly replace NIPS with a more environmentally friendly process, it is essential to design an equally simple approach with the same degree of control over membrane structure. In this work, we employ polyelectrolyte complexation to prepare freestanding membranes using an aqueous phase separation (APS) technique. In our approach, pH is used to trigger complexation in a simple one-step process that allows membranes with tunable pore sizes to be prepared. Poly(sodium 4-styrenesulfonate) (PSS) and poly[allylamine hydrochloride] (PAH) are chosen as the strong and weak PEs, respectively, and because of their high charge density, they form smooth, dense, and stable complexes when mixed together.[22,23] At a pH above its pK_a, i.e., ≈9,[24] PAH is uncharged and the chains exist in their collapsed coiled state,[25] PSS, on the other hand, remains charged over the entire pH range and exists in an extended chain conformation due to the charge repulsion within the chains.[26] A homogeneous mixture of PSS and PAH is prepared at a high pH; here PAH is uncharged, which prevents it from complexing with PSS (Figure 1). This homogeneous solution is then cast as a thin film and immersed in a coagulation bath at low pH, which induces complexation and phase inversion. An aqueous cross-linking step is employed during phase inversion to improve the mechanical stability of the membranes. We will demonstrate that our APS approach is similar to NIPS in that the membrane pore size can be controlled through a number of simple parameters including the molecular weights of the PEs, the concentrations of PEs in the casting solution, and the salt concentration in the coagulation bath. APS allows many different classes of membranes to be made including microfiltration membranes that allow the treatment of oily waste-water, ultrafiltration membranes that can effectively concentrate protein solutions, and nanofiltration membranes that can remove small micro-pollutants from drinking water. The large degree of control over membrane structure makes our simple and scalable APS approach a viable alternative to the organic solvent-based NIPS approach and has the potential to allow the production of sustainable polymeric membranes for all applications.

### 2. Results and Discussion

In this work, a new APS approach is proposed that uses water as a solvent and nonsolvent for the polyelectrolytes. The phase separation is driven by a pH switch. A homogenous PE solution of PSS and PAH is prepared at high pH (pH = 14) in a monomer ratio of 1:2 (PSS:PAH). PAH is uncharged at high pH and this prevents it from forming a complex with PSS. The homogeneous solution is then cast on a glass plate and immersed in a low pH (pH = 1) coagulation bath. Here, the PAH becomes charged and complexes with PSS, inducing precipitation into a solid, porous polyelectrolyte complex film. Herein, the molecular weights of the PEs (low and high MW pairs), the concentrations of PEs in the casting solution, and the salt concentration in the coagulation bath are all explored as parameters to tune membrane pore size and structure. Porous structures can be formed without the need for cross-linking with reasonable mechanical properties. However, a strong benefit of the polyelectrolyte system used, i.e., PSS:PAH in a 1:2 ratio, is that there is an excess of primary amine groups which are free to be crosslinked to provide additional mechanical strength to the membranes. In this work, the excess of PAH is cross-linked using glutaraldehyde (GA) via a Schif base reaction (Figure S2, Supporting Information).[27] Importantly, this reaction can be performed in water and is therefore combined with the coagulation step, which in turn means that no additional processing steps are required during membrane fabrication. The GA concentration used is very low (0.05 w%) and this concentration is considered to be safe under standard lab safety conditions.[28] With this crosslinking step, the mechanical properties improve and therefore, this approach
is used throughout this work. The membranes prepared using low and high $M_w$ PE solutions are discussed separately (see Table 1), with membranes from the low $M_w$ PE solutions discussed first.

Figure 2a shows the cross-section and top surface scanning electron microscopy (SEM) images of the membranes prepared using low $M_w$ PEs as a function of casting solution concentration. These images immediately demonstrate that porous polyelectrolyte films can be formed by APS. The structure contains large macro-voids, but also a membrane matrix with a sponge-like morphology with inter-connected pores of 1–5 µm in size. The membranes have a relatively well-defined top layer of 1–2 µm in thickness where the smallest pores are found. All these membranes have an asymmetric structure, the most desired structure for membranes, where a thin layer with smaller pores is responsible for the separation behavior, while a thicker more open layer provides the mechanical strength.

The precipitation mechanism of APS is simple and has much in common with the traditional NIPS process. As discussed earlier, in NIPS, the polymer solution is immersed in a nonsolvent bath (typically water) to induce precipitation. The polymer is insoluble in water and therefore, precipitates as a membrane. The kinetics of phase inversion in NIPS largely govern the final morphology and pore structure of the resulting membrane.[6] Similarly, in APS (Figure 1), precipitation occurs when the high pH PE solution comes in contact with the low pH coagulation bath. At low pH, the weak polycation PAH becomes charged and complexes with the strong polyanion PSS. The resulting polyelectrolyte complex is insoluble in water and thus precipitates as a porous film. The precipitation of the PE film is a dynamic process, which progresses at different locations throughout the film. As in NIPS, the top layer is where the precipitation begins, which leads to the smallest pores. This first layer of precipitated polymer then slows down the exchange of $H^+$ and $OH^-$ between the bath and the film and thus the precipitation, leading to the formation of bigger pores deeper within the film.

It is known from the traditional NIPS process that higher polymer concentrations result in smaller pore sizes and lower overall porosity.[7] This is also seen in our work and is shown in the SEM images of Figure 2a where the pore size decreases with increasing PE concentration. The pore size distribution of these membranes was estimated by analyzing the top surface SEM images using ImageJ software with the results presented in Figure 2b. Membranes prepared using the 12 wt%
PE solution have relatively larger pores in the top surface; the average pore size is ≈0.23 μm and pore size distribution is broad and skewed toward larger pore sizes. The average membrane pore size decreases to ≈0.16 μm when the PE concentration in the casting solution is increased to 16 wt%. At 20 wt% PE, the average pore size is ≈0.08 μm, with the pores easier to see in the high magnification FE-SEM image, Figure S3, Supporting Information. The pore size distribution becomes narrower with the increasing concentration of PE in the solution (Figure 2b).

The changes in membrane pore size as a function of PE concentration can be related to the kinetics of the phase separation. Here, the kinetics are greatly influenced by the viscosity of the casting solution as this, in part, determines the rate of solvent and nonsolvent exchange. Therefore, the large differences in membrane microstructure as a function of PE concentration in the casting solution, observed in Figure 2a, can be related to the viscosity of the casting solutions. Figure 3 shows the dynamic viscosity of the low and high $M_w$ PE solutions as a function of PE concentration. For the low $M_w$ PE solutions, the dynamic viscosity gradually increases with the PE concentration from 10 to 16 wt%. After 16 wt%, there is a dramatic increase in the viscosity of the solution which most likely arises from an increase in chain entanglements. At 20 wt%, the dynamic viscosity is around 20 Pa s. This is almost eight times larger than the solution viscosity of 10 wt% PE (2.6 Pa s). Such a large difference in the casting solution viscosity has a significant impact on the precipitation kinetics. As the solution viscosity increases, the onset of precipitation is delayed; so-called delayed demixing. For NIPS, Smolders et al. found that instantaneous demixing leads to a more porous structure while delayed demixing results in a denser structure.[6] The increase in PE solution viscosity results in membranes that have relatively denser structures (Figure 2a, 20 wt% PE). A visual comparison of the phase inversion process for the membranes prepared using low $M_w$ PE solutions is made in Video S1 (Supporting Information). It was observed that membranes prepared using 20 wt% PE took approximately seven and a half minutes to fully precipitate. In comparison, the membranes prepared with 10 wt% PE fully precipitated in ≈4 min. The results obtained for PEC membranes are in accordance with what is already known about the relationship of viscosity and kinetics of phase inversion of traditional NIPS membranes.[6]

The pure water permeability of a membrane is a vital parameter that provides insight into membrane porosity, its substructure, and its hydrophilicity. Figure 2c shows the pure water permeability of the membranes with respect to PE concentration in the casting solution. As discussed previously, at lower PE concentration the resulting membrane has an open structure with high water permeability of ≈3200 L m⁻² h⁻¹ bar⁻¹ for the membranes prepared with 10 wt% PE. Increases in
the PE concentration result in membranes with smaller pores and hence lower water permeability values. The pure water permeability drops from \(1600 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}\) at 12 wt% PE to \(360 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}\) at 16 wt% PE. The trend continues up to 20 wt% PE, where the membranes have a water permeability of \(150 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}\). The water permeability values obtained for these membranes are in the range of typical microfiltration and ultrafiltration membranes.

The removal of oil droplets from waste-water is an important application for microfiltration and ultrafiltration membranes. Therefore, an oil-in-water emulsion was prepared and treated using the membranes discussed above. The oil (n-hexadecane) droplet retention increases from 74% to 100% when the PE concentration is increased from 10 to 20 wt% (see Figure 2c), in line with smaller and thus more selective pores. The lower oil retention of 74% at 10 wt% PE can also be attributed to the presence of significantly larger pores (see Figure 2a.b). The closed structure of the membranes at higher concentrations of PE retains the oil droplets (3–4 µm) while allowing only the water to permeate through. Such retentions also demonstrate that these membranes are in the range of typical microfiltration and ultrafiltration membranes.

In summary, for the membranes prepared using low \(M_w\) PEs, it is indeed possible to prepare highly permeable and selective PEC membranes using just a pH switch. Moreover, all these membranes have good mechanical properties and are easy to handle. Clearly, APS is a versatile process where a wide range of microfiltration membranes can be prepared simply by tuning the PE concentration in the casting solution for a given set of PE molecular weights. Another important parameter is the pH of the coagulation bath. As already shown, membrane formation greatly depends on the precipitation kinetics. Precipitation will occur faster if the pH of the coagulation bath is lowered further. This is because the driving force for complexation is the release of counter ions. At lower pH, this driving force increases because of the larger difference in pH between the PE solution and the coagulation bath. This results in faster precipitation. However, if the pH is reduced to 0.5, the precipitation occurs too fast and the resulting membranes become brittle. On the other hand, when the pH of the coagulation bath is increased above 1 (pH 1.5 and 2), the precipitation slows down to a degree which prevents the formation of a stable membrane.

Moving on to the high \(M_w\) PE, Figure 4a shows the SEM microstructure of membranes as a function of PE concentration. Again, porous PEC films are formed. At the lower PE concentrations, 8 and 10 wt% PE, macropores are observed in the cross-section images which disappear at 12 wt% PE. All the membranes are asymmetric with well-defined top layers containing the smallest pores. The top surface FE-SEM images reveal that the pores become smaller as the PE concentration in the casting solution is increased from 8 to 10 to 12 wt%. Again, the pore size distribution was estimated from the top surface images using ImageJ software. Membranes prepared using 8 wt% PE solution had an average pore size of \(4.5 \text{ nm}\) with a broad distribution skewed toward higher pore size (Figure 4b). As the PE concentration increases, the pore size distribution becomes narrower and the average pore size decreases to \(3.8 \text{ nm}\) for 10 wt% PE and further to \(1.9 \text{ nm}\) for 12 wt% PE. These pore sizes identify these membranes as dense ultrafiltration membranes, with relevant applications in water treatment, but also, for example, concentration of proteins in food applications.

As discussed earlier, there is a direct relationship between the PE solution concentration and the solution viscosity. The dynamic viscosity of the 8 wt% PE solution was measured to be 9.8 Pa s. This increased to 22 Pa s for 10 wt% PE and further to 41.4 Pa s for 12 wt% PE (see Figure 3). Such a drastic increase in the solution viscosity causes a delay in demixing during the phase inversion process, resulting in a sponge-like structure with a dense top layer. This can also be seen in the SEM cross-section images of the membranes in Figure 4a where the morphology gradually shifts from finger-like macropores (8 and 10 wt%) to a sponge-like structure with a denser top layer (12 wt%). A higher PE concentration in the casting solution leads to the formation of a denser top layer which hinders the formation of finger-like macropores. Video S2 (Supporting Information) shows the phase inversion kinetics of these membranes.

Figure 4c shows the pure water permeability and BSA retention of the membranes prepared using the three PE concentrations. Pure water permeability decreases as a function of PE concentration. Membranes prepared with 8 wt% PE had the highest permeability among this set (24.5 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\)) with \(>85\%\) BSA retention. Some BSA molecules permeate through primarily because of the existence of pores \(>10\) nm (see Figure 4b). Also, the average pore size of the membrane (\(4.5 \text{ nm}\)) is larger than the hydrodynamic radius of BSA (4.3 nm). At 10 wt% PE, the permeability drops to 17 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\) with BSA retention increasing to \(>92\%\). Similarly, at 12 wt% PE, \(>98\%\) of BSA was retained by the membrane while having a pure water permeability of 12.5 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\). The average pore size of this membrane was estimated to be \(1.9 \text{ nm}\) (Figure 4b). It can be concluded that the membranes separate BSA molecules based on the size-exclusion mechanism.
The high retentions also demonstrate that little to no defects were present in these membranes.

Comparing the results for the membranes prepared with low and high $M_w$ PE solutions, there is an association between membrane morphology and the molecular weights of the PEs. This can also be correlated to the dynamic viscosities of the casting solutions prepared using different $M_w$ of PEs but having the same PE concentrations (Figure 3). For example, at a fixed concentration of 12 wt% PE, the low $M_w$ PE solution had a dynamic viscosity of 3.3 Pa s while the high $M_w$ PE solution had a dynamic viscosity of 41.4 Pa s. This substantial difference is due to the large difference in the molecular weights of the PEs used. Chain entanglement is greater for high $M_w$ PEs and this causes the dynamic viscosity of the solution to increase. These results show that by simply tuning the $M_w$ of the PEs, it is possible to fabricate membranes that can be used for microfiltration and also ultrafiltration applications.

To reduce the membrane pore size even further, NaCl was added to the coagulation bath. It is known from the literature that the addition of salt increases the mobility of PE chains in polyelectrolyte complexes.\cite{13,31} Figure 5a shows the cross-section and top surface SEM images of the membranes prepared at different concentrations of NaCl in the coagulation bath. In all cases, asymmetric films are formed, but now the membranes have dense top layers with no observable pores. While the top surface is dense for all of these membranes, cross-sectional images reveal that the substructure changes significantly as a function of NaCl concentration in the bath. Membranes prepared using 1 M NaCl showed relatively larger voids in the substructure. Also, the voids are located near the top surface. As the NaCl concentration in the coagulation bath increases, the voids in the substructure reduce in size, making the membranes more compact. For comparison, full cross-section images of two different membranes are shown in Figure S4 (Supporting Information). This shows that the membranes become denser with the addition of NaCl in the coagulation bath due to the increased PE chain mobility. Videos of phase inversion at different NaCl concentration are shown in Video S3 (Supporting Information). It can be observed that the membranes coagulated in the 4 M NaCl bath become opaque faster. These results show that it is not only the PE concentration and the molecular weight that is important in controlling the membrane structure, but NaCl concentrations in the coagulation bath is also a tuning parameter. The ability to control PE mobility during APS is also where this approach goes beyond the traditional NIPS process where such a tuning parameter simply does not exist.
Pure water permeability and retention tests were also performed on these membranes. The membranes were tested against a cocktail of micropollutant molecules (Table S1, Supporting Information). These small organic molecules stem from medicine and pesticide usage and end up in the environment through waste-water streams. The micropollutant mixture has both charged and uncharged molecules. In addition, the molecular weight of these molecules is in the range of 216–624 g mol\(^{-1}\). This mixture of micropolllutants was selected because it covers positive, negative, and neutral molecules and also contains hydrophilic and hydrophobic molecules so that an assessment of charge and size-based separation can be made.\(^{[16]}\)

Good approaches to remove the micropolllutants are urgently needed. These molecules are notoriously difficult to remove due to their small size and their widely varying molecular properties, and they are only removed with reverse osmosis (RO) membranes or dense nanofiltration class membranes.

Figure 5b shows that the water permeability decreases as the membranes become more compact due to the addition of NaCl in the coagulation bath. While the permeability decreases with increasing NaCl in the coagulation bath, the average micropolllutant retention increases sharply from being extremely low at 0 \(\text{M} \) of salt up to a significant 80% at 4 \(\text{M} \) of salt (Figure 5b). A detailed graph showing the retentions of all the eight micropolllutants as a function of NaCl concentration in bath is presented in Figure S6 (Supporting Information). Membranes prepared in 4 \(\text{M} \) NaCl had a permeability of \(\approx 2 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}\) with the highest retentions for the eight micropolllutants tested (Figure 5c). Retentions of 100% are reached for bromothymol blue, again a clear indication that no defects are formed in the membranes prepared using this APS approach. Looking more closely at Figure 5c, one can see that both the charged and uncharged molecules were largely retained by the membranes. This demonstrates that the separation of organic molecules is most likely achieved due to the size-exclusion mechanism with some additional charge based effects.\(^{[32]}\) Since the membranes themselves are positively charged (Figure S7, Supporting Information), the high retention (>98%) of the positively charged Atenolol molecule is expected.

As mentioned earlier, typically reverse osmosis and dense nanofiltration membranes are used to remove micropolllutants from waste-water and drinking water. A downside of these membranes is that they also have very high ion retention, retaining not only the micropolllutants but also all salts in solution. This leads to a complex and difficult to treat waste stream, containing high concentrations of micropolllutants and salt. Moreover, the clean water often needs to be remineralized before use. When studying the salt retention of our membranes, we found low...
salt retentions, 0–10% for MgSO₄. With our new APS approach to membrane production, we also use new materials (polyelectrolyte complexes) that, especially as dense membranes, might have different separation properties compared to that of common commercial membranes. Indeed the properties seen here (high micropollutant retention and low salt retentions) would be desirable for applications such as drinking water production, where removal of organic molecules without the removal of essential salts is wanted. Our new membrane materials might also come with new challenges as polyelectrolyte complexes are known to plasticize at high ionic strengths. To study this, the membranes prepared in a 4 m NaCl coagulation bath were immersed in 1 m NaCl and 1 m KBr solutions for 5 d. We found that the water permeability of these membranes is not affected by such a long exposure to these highly saline solutions (see also Figure S8 in the Supporting Information). The polyelectrolyte complex membranes are thus stable and resistant to plasticization by NaCl and KBr at least up to concentrations of 1 m.

3. Conclusion

In this work, we have proposed a new approach that allows sustainable membrane production with excellent control over membrane structure. The APS technique employs a combination of strong and a weak polyelectrolyte (PE) that, on one hand, can form a polyelectrolyte complex at low pH conditions and on the other hand, can be mixed at high pH to form a homogeneous one-phase solution. The phase separation that occurs when immersing a film of the high pH homogeneous polyelectrolyte solution in a low pH bath leads to the formation of membranes with desired structures and excellent properties. Here asymmetric membranes with tunable pore sizes are prepared based on PSS and PAH as polyanion and polycation. To guarantee the stability of the membranes, an aqueous cross-linking step was applied during the phase inversion process. By utilizing tuning parameters such as polyelectrolyte concentration and molecular weight, the membrane pore size was tuned from micrometers down to just a few nanometers. This allowed the production of microfiltration membranes that are well suited to remove dispersed oil from waste-water and ultrafiltration membranes that are able to concentrate dilute protein solutions. This large degree of control over pore size is very similar to that found for the traditional solvent-based NIPS method. A higher viscosity of the casting solution, obtained by using both, higher polyelectrolyte concentrations and higher PE molecular weights, led to slower phase inversion kinetics and thus denser top layers, just like in NIPS. But with APS we can also go beyond the standard tuning parameters associated with NIPS. Indeed, it was observed that adding NaCl to the coagulation bath results in even denser membranes due to the higher mobility of polyelectrolytes during complexation. The membranes prepared using 4 m NaCl in coagulation bath showed high retention (80%) toward small and notoriously difficult to retain micropollutants but extremely low salt retentions. Such membranes would be highly desirable for many applications where it is important to retain organics without retaining salts. More importantly, this demonstrates that APS is not just a sustainable alternative to NIPS, it also allows for the production of membranes with new separation properties that opens up the possibility of new separation processes. With the demonstrated control over pore size and membrane structure and allowing for the production of membranes with excellent separation properties, the completely water-based APS process is truly an alternative to the now dominant solvent-based NIPS approach. The similarities between APS and NIPS are a real advantage and current NIPS-based membrane production lines could also be used for large scale APS. Furthermore, the many types of polyelectrolytes that could potentially be used for this approach, in combination with the new tuning parameters associated with APS (salt concentration, pH), will allow optimization of this process towards many applications.

4. Experimental Section

Materials: PSS sodium salt was purchased from Sigma-Aldrich (Netherlands) as 25 wt% (Mₘ 200 kDa) and 30 wt% (Mₘ 1000 kDa) aqueous solutions. PAH in powder form (Mₘ 17.5 kDa) was purchased from Sigma-Aldrich (Netherlands). PAH as 40 wt% aqueous solution (Mₘ 150 kDa) was purchased from Nittobo Medical Co. Ltd., Japan. Sodium hydroxide (NaOH) pellets (>98%), glutaraldehyde (GA) (50 wt% aqueous solution), sodium chloride (NaCl) (>99.5%), hydrochloric acid (HCl) (ACS reagent, 37%), glycerol solution (86–89%), n-hexadecane (99%), oil red EGN (analytical standard), sodium dodecyl sulfate (SDS) (>99%), albumin from bovine serum (BSA) as lyophilized powder (>98%), citric acid in powder form (99%), and MgSO₄ (>99.5%) were purchased from Sigma-Aldrich (Netherlands). The micropollutants atenolol (>98%), azatrace (analytical standard), bezafibrate (>98%), bisphenol-A (>99%), bromothymol blue (>95%), naproxen (analytical standard), phenolphthalein (analytical standard), and sulfamethoxazole (analytical standard) were all purchased from Sigma-Aldrich (Netherlands). Deionized water was obtained from a Milli-Q Ultrapure water purification system. All the chemicals were used without any further purification.

Preparation of Polyelectrolyte Casting Solutions: Two sets of casting solutions were prepared using different molecular weights (Mₘ) of PSS and PAH (Table 1). Low Mₘ PE solutions (PSS 200 kDa, PAH 17.5 kDa) and high Mₘ PE solutions (PSS 200 kDa, PAH 17.5 kDa) were prepared under the following conditions. First, PAH powder (Mₘ 17.5 kDa) was dissolved in deionized water under continuous stirring to obtain a 30 wt% aqueous solution. The pH of this solution was measured using a handheld pH meter (pH 110, VWR). Since PAH is a weak polyelectrolyte with a pKₐ value of 9.9, it stays positively charged in aqueous solutions at pH 3. Therefore, when this PAH solution is mixed with the strong polyelectrolyte PSS it forms a PEC. This complex cannot be further processed for membrane fabrication. Hence, a homogeneous PE solution is required which can be processed and cast as a membrane. In order to prepare this homogeneous mixture, PAH needs to be deprotonated so that it does not complex with PSS. Therefore, 5 m NaOH solution was added to PAH solution such that the ratio of wt% NaOH to wt% PAH monomer was constant at 0.7. For example, to prepare a 15 g solution having 10 wt% PAH, 3.91 g deionized water and 6.09 g of 5 m NaOH solution was added to 5 g of PAH stock solution (30 wt%). Following this procedure, PAH solutions of various concentrations (10–20 wt%) were prepared (Table 1). On the other hand, PSS (30 wt%, Mₘ = 200 kDa) was diluted with deionized water to prepare a set of solutions having the same PE concentration as PAH, i.e., (10–20 wt%). The two polyelectrolyte solutions of equal concentrations (e.g., 10 wt% PSS and 10 wt% PAH) were then mixed in a 1:2 monomer ratio (PSS:PAH). The monomer ratio was calculated based on the molecular weights of individual monomers. To obtain a 10 wt% PE casting solution, 7.87 g of 10 wt% PSS was added to 7.13 g of 10 wt% PAH. It is important to mention that casting solutions with other monomer ratios (PSS:PAH) such as 1:0.5, 1:1, 1:3, 1:4, and 1:5
were also prepared in this study. However, these ratios did not result in sufficiently stable membranes. The ratio 1:2 was chosen because the membranes prepared with this ratio exhibited the best mechanical stability. Furthermore, it has been shown by Rieger and Essler that PAH charges substantially overcompensate the PSS charges in PSS-PAH films, which indicates that the two polyelectrolytes naturally form nonstoichiometric complexes.\(^{[3]}\)

Similarly, casting solutions of high \(M_w\) PEs were prepared under the following conditions. First, a set of PAH solutions having different concentrations (8–12 wt%) was prepared by diluting aqueous PAH (40 wt%, \(M_w = 150 \text{ kDa}\) with deionized water followed by addition of 5 M NaOH. In this case, the NaOH:PAH wt% ratio was kept constant at 0.5. For instance, to prepare a 15 g solution having 10 wt% PAH, 6.90 g deionized water and 4.35 g of 5 M NaOH was added to 3.75 g PAH stock solution (40 wt%). Likewise, PSS (25 wt%, \(M_w = 1000 \text{ kDa}\)) was diluted with deionized water to obtain a series of solutions having the desired concentrations (8, 10, and 12 wt%). The two PE solutions (8 wt% PSS and 8 wt% PAH) were then mixed in PSS:PAH monomer ratio of 1:2 to obtain a homogeneous casting solution having 8 wt% PE. Following the same method, casting solutions containing 10 wt%, and 12 wt% PEs were prepared by mixing the corresponding PE solutions in 1:2 (PSS:PAH) monomer ratio.

**Viscosity Measurements:** The viscosity of all the PE casting solutions was measured using a HAAKE Viscotester 550 Rotational Viscometer (ThermoFisher Scientific, USA). The PE casting solution (\(\approx 15 \text{ mL}\)) was poured into the spindle cylinder (SV-DIN), which was then mounted on the viscometer. The dynamic viscosity was measured as a function of shear rate (2.5–250 s\(^{-1}\)). Two samples of each PE solution were tested for their dynamic viscosity at 293 K and the average value at a shear rate of 2.57 s\(^{-1}\) is reported here.

**Membrane Fabrication:** Each solution prepared using low \(M_w\) PE was cast on a glass plate using a casting knife (gap = 0.4 mm). The glass plate was then immediately immersed into an acidic water bath at pH = 1 containing 0.05 wt% glutaraldehyde (GA) as a cross-linker. The pH of the coagulation bath was adjusted by adding HCl. At pH = 1, the PAH becomes fully ionized and complexes with PSS. The resulting PEC precipitates as a white solid film. Casting solutions prepared using high \(M_w\) PEs were cast in a similar manner using a casting knife (gap = 0.6 mm). The coagulation bath was the same as mentioned above. In addition, these PE solutions were also cast and then immersed in coagulation baths (pH = 1, 0.05 wt% GA) containing different concentrations of NaCl ranging from 1 to 4 M.

The resulting films were removed from the coagulation bath and washed with deionized water to remove any excess salts and/or PE. The membrane samples for permeability tests were stored in deionized water. The membrane samples for SEM were kept in 20 wt% glycerol for 2 h followed by drying under ambient conditions in order to prevent the pores from collapsing.

**Membrane Characterization:** The surface and cross-sectional morphology of the membranes were analyzed using scanning electron microscopy SEM (JSM-6010LA and JSM-7610F, field-emission electron microscope, JEOL, Japan). For cross-sectional images, the membrane samples were first immersed in liquid nitrogen before carefully fracturing them to preserve the pore structure. All the samples were vacuum dried at 30 °C for 24 h before coating them with a 5 nm thick layer of platinum using a Quorum Q150T ES sputter coater (Quorum Technologies Ltd., UK). The membrane pore sizes were measured from the top surface SEM images using the ImageJ software. From the data, histograms were produced for each membrane. For the low \(M_w\) PE membranes, a total of 32 bins each with a size of 0.05 \(\mu m\) was used. For the high \(M_w\) PAH membranes, a total of 40 bins each with a size of 0.5 nm was used. The zeta potential of the membranes was measured using a SurPASS electrokinetic analyzer (Anton Paar, Graz, Austria). Zeta potential values were calculated by measuring the streaming current versus pressure in a 5 \(\times 10^{-3} \text{ m KCl solution using Equation (1)}\):

\[
\zeta = \frac{dI}{dP_{\text{ELE}}} \eta x_e R
\]  

where \(\zeta\) is the zeta potential (V), \(I\) is the streaming current, \(P\) is the pressure (Pa), \(\eta\) is the dynamic viscosity of electrolyte solution (Pa s), \(x_e\) is the dielectric constant of the electrolyte solution, \(\kappa_p\) is the vacuum permittivity (F m\(^{-1}\)), \(x_b\) is the bulk electrolyte conductivity (S m\(^{-1}\)), and \(R\) is the resistance (\(\Omega\)) inside the streaming channel.

**Pure Water Permeability and Retention Tests:** Samples were prepared by cutting the membranes into circular disks of 25 mm diameter. Pure water permeability tests were conducted using a dead-end cell setup (Figure S1 Supporting Information). Deionized water from a MilliQ water purification system was used as the feed solution. The samples were first compacted at 4 bar of pressure until a constant flux was achieved. The permeate mass was measured as a function of time using an electronic weight balance that was connected to a computer. Pure water permeability, \(P\) (L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\)), was then calculated using Equation (2):

\[
P = \frac{J_w}{\Delta p}
\]

where \(J_w\) is the pure water flux (L m\(^{-2}\) h\(^{-1}\)) calculated by measuring the change in permeate volume (L) per unit membrane area (0.38 cm\(^2\)), per unit time (h). \(\Delta p\) is the transmembrane pressure difference (bar). Three samples from each membrane were tested and the average value with the standard deviation is reported.

Three different types of retention tests were conducted based on the pore sizes of the membranes. Retention tests for microfiltration membranes were conducted using an oil in water emulsion. The emulsion consisting of n-hexadecane (100 mg L\(^{-1}\)) in sodium dodecyl sulfate (463 mg L\(^{-1}\)) was prepared according to the procedure reported by Dickhout et al.\(^{[34]}\) The average oil droplet size was 3–4 \(\mu m\). An oil-soluble dye, oil red EGN, was added (0.02 g L\(^{-1}\)) to the emulsion during stirring as a marker for oil droplets. Retention tests were conducted on three different membrane samples at 0.4 bar pressure on a dead-end cell. The cell containing the membrane and the vessel containing feed emulsion was stirred to maintain emulsion stability. Permeate samples were collected and analyzed using UV–vis spectrophotometer (Shimadzu UV-1800, Japan) at \(A_{512} = 521 \text{ nm (maximum absorbance wavelength of oil red EGN). Retention, } R(%) \text{ was calculated using Equation (3)}\):

\[
R = \left[ 1 - \frac{C_p}{C_f} \right] \times 100
\]

where \(C_p\) and \(C_f\) are the concentration of species at the permeate and feed side, respectively. In a dead-end cell, the feed concentration is constant by changing above the membrane surface because of the constant enrichment. Therefore, \(C_f\) was taken as a mean of initial feed concentration and retentionate concentration.

Ultrafiltration membranes were characterized by a protein retention test. BSA (1 g L\(^{-1}\)) was dissolved in a 0.1 M citrate buffer at pH 5.5. The solution was then filtered through the membranes in a dead-end permeation cell. Permeate and retentate was analyzed by UV–vis spectrophotometer at \(A_{280} = 280 \text{ nm (retention was calculated using Equation (3)}}\).

Nanofiltration separation performance was characterized using a mixture of eight different micropollutants (Table S1, Supporting Information). The micropollutant mixture (3 mg L\(^{-1}\) of each compound) was prepared in deionized water and the pH of the solution was adjusted to 5.8 using 0.1 M NaOH. The mixture was filtered through the membranes in a dead-end cell for a minimum of 24 h to ensure a steady-state retention. Permeate samples were collected and analyzed using UHPLC (ThermoScientific, USA). The separation was done on ACCLAIM RSLC C18 2.2 \(\mu m\) column (ThermoScientific, USA). First, a calibration curve was made by analyzing different concentrations of feed solutions (Figure S5, Supporting Information). The retention was then calculated using Equation (3). Three samples of each membrane were tested for micropollutant retention measurements to ensure reproducibility. MgSO\(_4\) retention tests were conducted using 5 \(\times 10^{-3} \text{ m MgSO}_4\) feed solution. The feed, retentate, and permeate conductivity was measured using a handheld conductivity meter (WTW Cond 3210).
Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

aqueous phase separation, membranes, microfiltration, nanofiltration, polyelectrolyte complexes

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