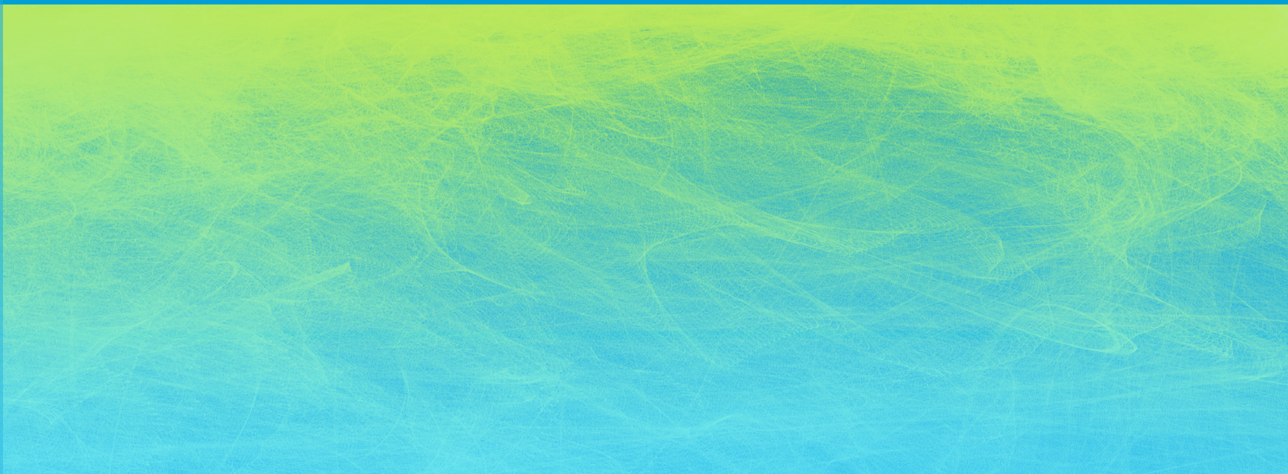
Aqueous Phase Separation

a novel and sustainable approach for membrane preparation



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Aqueous Phase Separation: a novel and sustainable approach for membrane preparation.

PROEFSCHRIFT

ter verkrijging van

de graad van doctor aan de Universiteit Twente,

op gezag van de rector magnificus,

prof. dr. ir. A. Veldkamp,

volgens besluit van het College voor Promoties

in het openbaar te verdedigen

op vrijdag 27 augustus 2021 om 14.45 uur

Door

Wouter Martinus Nielen

Geboren op 14 april 1993

In Best, Nederland

Dit proefschrift is goedgekeurd door:

Promotor

prof. dr. ir. W.M. de Vos

Cover design: Carolien Kaal

Printed by: Ipskamp printing

ISBN: 978-90-365-5210-3

DOI: 10.3990/1.9789036552103

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Chapter 1

Introduction

1.1 Membrane separations

Climate change is currently one of the world's most pressing issues as our current way of life is unsustainable and changes must be made to mitigate its effects.[1-2] Related global issues include, but are not limited to, depletion of fossil fuels[3-4], increasing contamination of surface and ground water,[5-6] and global water scarcity.[7-9] To mitigate and overcome these issues it is essential to reduce energy demand and develop methods to reduce and remove pollution. In this transition membrane technology can play an important role.[10-12] In regards to energy production and demand, membranes can be used in fuel cells to efficiently generate electrical energy directly from hydrogen without emissions.[13-14] Additionally membranes can improve many existing processes in the chemical industry through process intensification.[15-18] Traditional separation methods such as distillation require a lot of energy and membranes can be integrated into or used to replace the traditional process, achieving similar yields while reducing the cost and energy consumption.[15-18] To prevent the increasingly more contaminated surface and ground water from negatively affecting health and environment it is best to reduce pollution and prevent it from reaching surface waters. Conventional water purification techniques are often not designed to effectively remove the wide variety of contaminants, especially small micropollutants such as medicinal waste, pesticides, and industrial chemicals from waste water.[5, 19] As human consumption is only increasing the amount of these micropollutants will also increase requiring a redesign of water treatment systems. Again membranes offer an excellent solution as with various membranes techniques it is possible to effectively retain and remove over 90% or even 98% of all micropollutants.[20-22] Besides pollution the total amount of fresh water is also a problem, while over 70% of the earth's surface is water only 2.5% of that is fresh water and demand is ever increasing.[7, 23] Desalination through reverse osmosis (RO) is a viable solution which has been investigated since the 1950s.[24-25] With the use of RO membranes, potable water can be produced from brackish and highly saline water at the cost of electrical energy to generate the pressure required to overcome the osmotic pressure of salt water.[23-27] Although RO is more energy intensive than producing potable water from fresh water it is essential in arid regions where fresh water is limited. Besides the previously mentioned applications membranes are also extensively used in medical applications and food processing.[10-12] The reason membranes are suitable for a wide variety of applications is that membranes can be easily produced with different selectivities and separation properties.

1.2 Membrane types and structures

A membrane is in essence a selective barrier which can selectively separate a feed mixture of different compounds into a retentate and a permeate stream. Examples include the removal of microbes, proteins, or salt from water. Based on their separation mechanism and structure, membranes can be sorted into different categories such as porous membrane and dense membranes. In Table 1.1 an overview is given of the properties of the four different membrane types typically used in water treatment.

Table 1.1. Overview of different membrane types used in water treatment and their typical properties, operation pressure, and potential applications.[10-12, 28]

	Microfiltration	**Ultrafiltration**	**Nanofiltration**	**Reverse osmosis**
Permeability ($L\cdot m^{-2}\cdot h^{-1}\cdot bar^{-1}$)	>1000	10–1000	1–20	0.5-2
Pore size (nm)	>100	100–2	2–1	<1
Operation pressure (bar)	0.1–2	0.5–7	3–20	30–100
Retains	Particles, bacteria	Proteins, viruses	Divalent salts, Small organic molecules	Monovalent salts

1.2.1 Porous membranes

Porous membranes mainly separate based on size exclusion. This means that particles larger than the pore size of the membrane are retained while smaller particles or molecules pass through. Microfiltration (MF) membranes have the largest pore size of approximately 2–0.1 μm which makes them suitable to remove small particles like bacteria, while smaller particles like viruses can still permeate though the membrane. The permeability of MF membranes is relatively high as seen in Table 1.1, however whatever is retained by the membrane can foul the membrane. For MF membranes fouling is a significant issue as bacteria can accumulate on the membrane surface and grow into biofilms which reduce the water permeability.[29] To overcome this membranes can be modified to reduce the adhesion of bacteria, but periodic chemical and/or physical cleaning of the membrane is still required.[30]

Ultrafiltration (UF) membranes have a smaller pore size of 100–2 nm and they are best suited to retaining small particles such a viruses and proteins. UF membranes are therefore widely used in the medical industry for applications such as kidney dialysis and also in the food processing industry.[10, 31] The smaller pore size also results in a higher resistance to water leading to lower permeabilities; to compensate UF membranes are typically operated at higher pressures than MF membranes. As with MF membranes fouling is a common problem. For UF membranes with the smallest pore sizes, typically referred to as tight ultrafiltration membranes, the separation mechanism becomes more complex, similar to the separation mechanisms of nanofiltration membranes.

Nanofiltration (NF) membranes are on the border between porous and dense membranes. While ceramic membranes still have defined pore sizes as mentioned in Table 1.1, the pores of polymeric nanofiltration membranes are typically so small they are often referred to as having dense separation layers. Therefore the water permeability of NF membranes is very low compared to MF and UF membranes. As mentioned with the tight UF membranes the separation mechanism for NF membranes is complicated.[32] The reason is that the for membranes with a pore size in the nm length scale, ionic and electric interactions become significant. Besides size exclusion, Donnan exclusion and dielectric exclusion play an important role in determining the separation properties of NF membranes.[33-34] NF membranes are often charged and therefore solutes with an opposite charge as the membranes can permeate more easily than those with the same charge. Depending on the membrane these so-called Donnan effects can be quite pronounced, where for instance a negatively charged membrane can have a very high retention for Na_2SO_4 but a very low retention for $CaCl_2$ while for positively charged membranes it is the opposite.[35] Dielectric exclusion is caused by the electrostatic interactions between the solute and the membrane material where favorable interactions lead to an increase permeance of the solute and vice versa.[34] The overall retention of the NF membrane is often determined by a combination of these mechanisms.

1.2.2 Dense membranes

Dense membranes have as the name implies a dense layer without a discernible pore size, which are typically used for applications such as: reverse osmosis (RO), ion exchange, and gas separation. For dense membranes there are many different possible transport models but in essence it comes down to the affinity of the membrane with the solvent/solute; i.e. how easily is the solute absorbed into the membrane, and at what the speed the solvent/solute can move inside the membrane to the other side.[24, 36] RO membranes are widely used in desalination as the selective layer of the membrane retains almost everything except water. However, to overcome the osmotic pressure difference between that of a brine and pure water high operation pressures are required. While energy intensive, a high operating pressure can actually be desired as it results in an increased salt rejection. This is because the permeation of water is linearly dependent on the applied pressure while the permeation of salt is dependent on the concentration difference between the feed and the permeate.[24-25] Ion exchange membranes are membranes with a very high charge density and are typically used to separate different ionic species in solution.[37] Gas separation membranes are as the name implies used to separate different gas molecules such as N_2, H_2 and CO_2.[38]

1.3 Non-solvent induced phase separation for membrane preparation

For polymeric membranes the non-solvent induced phase separation (NIPS) method is the predominant production method which was developed by S. Loeb and S. Sourirajan in the early 1960s and is generally regarded as one of the major breakthroughs in membrane development.[39-40] The success of the NIPS method is due to its simplicity and scalability, which allows for the production of defect-free membranes on a large industrial scale using hollow fibre spinning or roll-to-roll processes. To prepare membranes with the NIPS method a polymer e.g. polyvinylidene difluoride (PVDF) or polyether sulfone (PES), is dissolved in a solvent e.g. *N*-methyl-2-pyrrolidone (NMP), dimethylacetamide (DMAc), or dimethyl formamide (DMF) which is cast as a thin film or spun as a hollow fiber and then submerged in a non-solvent bath, typically water.[10-11, 40-41] After the polymer solution is submerged, a solvent exchange occurs which results in coagulation and precipitation of the polymer forming a membrane structure, as schematically depicted in Figure 1.1.

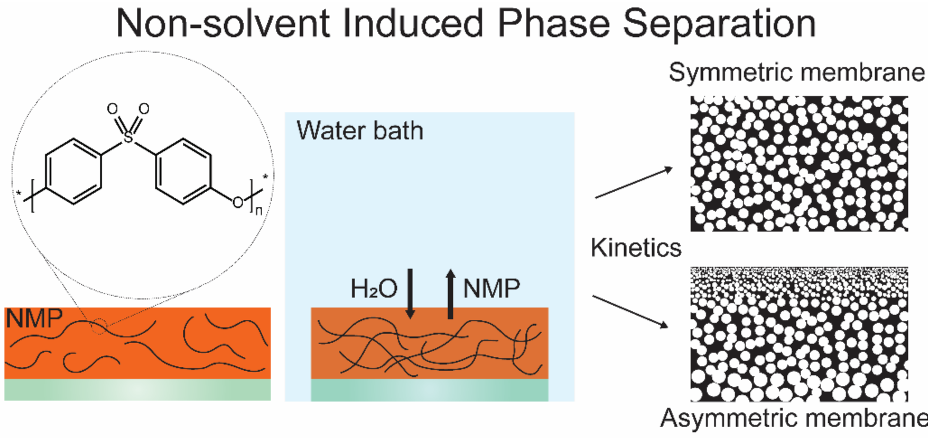

Figure 1.1. Depiction of non-solvent induced phase separation of a PES in NMP polymer solution cast onto a flat support and submerged in a coagulation bath of water. The kinetics of the phase separation determine the final structure of the prepared membrane.

During coagulation/precipitation of the polymer, thermodynamic as well as kinetic factors play a role in determining the final structure and therefore the properties of the membrane. A ternary phase diagram is often used to help describe the phase separation process as seen in Figure 1.2. In the ternary phase diagram the ratio of polymer, solvent, and non-solvent are depicted at each point of the phase separation process, starting at point A which is the initial casting solution. After the cast film is submerged in the non-solvent bath the phase separation process begins as depicted by the line from A to D. As the non-solvent diffuses into and the solvent out of the cast film, a point is reached (B) where it becomes thermodynamically unfavorable for the polymer to remain in solution and precipitation can begin. Point B lies on the binodal boundary which is used in the ternary phase diagram to indicate where the polymer solution starts to transition from a single phase into two phases. After passing the binodal boundary the polymer solution is unstable but not yet phase separated, during this time the polymer chains can still move and prefer interactions with other polymers over interactions with the solvent/non-solvent mixture. This leads to the formation of polymer rich phases, which will become the membrane, and polymer lean phases, which will become the pores. Next is the spinodal boundary which indicates the point where the phase separation becomes irreversible and after which the polymer starts to solidify (C). While the polymer solidifies the exchange between solvent and non-solvent continues as the non-solvent is washed from the membrane but no structural changes occur (D).

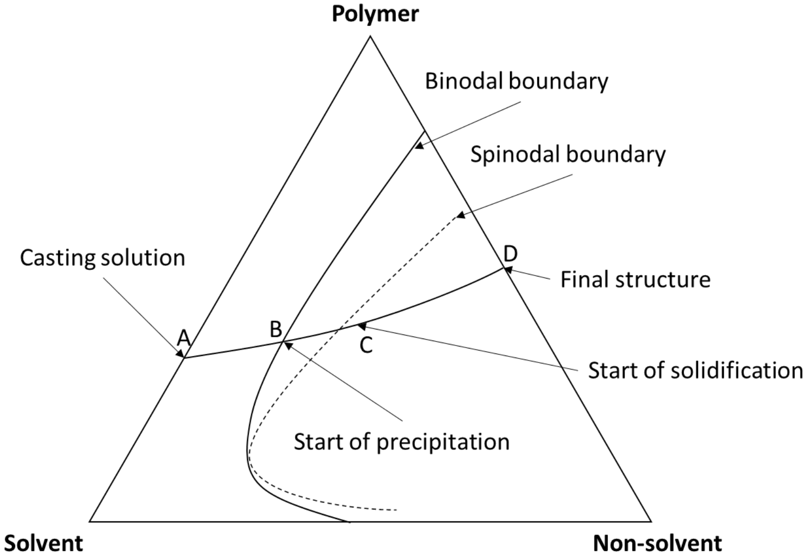

Figure 1.2. Ternary phase diagram representing the NIPS process. Adapted from Baker, R. W. 2012.[10]

The membrane structure depends on the path the solution takes through the phase diagram. It is important to note that not every part of the membrane follows the exact same path. As the phase separation starts at the interface it alters the diffusion rates of the (non-)solvent which results in different exchange kinetics and thus a different structure deeper into the membrane. By tuning the onset and speed of the phase separation it is possible to prepare all kinds of membranes from open and symmetric membranes, such as MF, all the way to dense asymmetric membranes such as RO. Commonly used parameters to control the NIPS process are listed here:

1. *Choice of polymer and solvent.* Different polymers can precipitate differently and have different material properties. Factors like the solubility of the polymer and the miscibility of the solvent with the non-solvent can greatly affect the resultant membrane structures.[12]
2. *Non-solvent bath composition.* A common method to control the phase separation is the addition of solvent to the non-solvent bath. This reduces the driving force for separations and can be used in combination with other parameters to either obtain denser or more open strucutures.[42-44]

3. *Polymer concentration*. Solution viscosity is strongly affected by concentration which in turn affects the kinetics of phase inversion. Typically a high polymer concentration leads to dense structures and a low polymer concentration to more open structures.[45-46]
4. *Additives*. Additives can be used in both the polymer solution as the non-solvent bath. The addition of e.g. surfactants or small polymers can be used to tune the porosity and pore size. For instance hydrophilic polymers such as polyethylene glycol and polyvinylpyrrolidone are commonly used to enhance porosity and suppress macrovoid formation.[47-50]
5. *Temperature*. Polymer solubility and viscosity are temperature dependent which in turn affects the phase separation and allows further tuning of membrane structure.[51-52]

Often a combination of these parameters is used to precisely tune the membrane structure. The control over structure through these parameters is one of the great advantages of the NIPS process as it allows to tailor make membranes for specific applications.[10] Yet for all of its advantages the NIPS process also has some disadvantages as it uses large amounts of aprotic solvents like, NMP, DMF, and DMAc, which have severe health hazards and lack sustainability. Therefore it is relevant to investigate alternative methods for membrane fabrication. In the recent decades this has received the attention of multiple research groups around the world, all of which have investigated the possibility of using alternative, safer and more sustainable solvents.[28, 53-54]

1.4 Recent advances in sustainable membrane production

While membranes are typically used as a sustainable alternative for conventional separation methods there is still room for improvement in the membrane production process. In 2015 a study by Razali et. al. estimated that yearly over 50 billion waste water contaminated with hazardous solvents is produced which is expected to increase every year.[55] The increased global attention to sustainability has led to increasing efforts to find alternative methods for membrane production as current methods rely heavily on unsustainable toxic solvents.[53-54, 56] An additional motivator in the search of alternative solvents is the European Union which through its Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) legislation is restricting the usage of organic solvents like NMP in industry.[57-58] To improve the sustainability and safety of membrane production a lot of researchers have looked to various alternative solvents which, while having similar properties as the conventional solvents, are less hazardous and/or more sustainable.[28, 53] Examples include: conventional non-toxic solvents like dimethyl sulfoxide (DMSO),[59] plant-derived solvents like methyl lactate or ethyl lactate,[60] ionic liquids,[61-62] and, new synthetic solvents.[63-64] The membranes prepared with these solvents typically have performances comparable to membranes prepared using conventional methods. Yet, while promising these alternative methods still have down sides. Solvents like DMSO and ionic liquid are safer to use but offer little improvement in regards of the sustainability of membrane production. Plant derived and bio renewable synthetic solvents are in that aspect more preferable alternatives, as they safer as well as more sustainable. Still most of these alternative solvents are quite expensive, making it less tempting for industry to use them. An ideal solution would be to not use organic solvents at all, which is actually possible using the aqueous phase separation approach.

1.5 Aqueous phase separation

The Aqueous Phase Separation (APS) method goes a step further than other alternatives methods by using water as both the solvent and non-solvent instead of organic solvents.[65] This is achieved by using stimuli-responsive polymers which can be made water-soluble and also precipitated in water using a trigger like a pH or salinity switch. These responsive polymers are polyelectrolytes which are highly charged polymers with ionizable groups on their repeat units.[66-67] A distinction is made between strong polyelectrolytes, which remain charged regardless of the pH, and weak polyelectrolytes whose charged state is dependent on the pH.[66-67] In the APS method there currently exist three different approaches to prepare membranes using polyelectrolytes.

In the first approach a single weak polyelectrolyte is dissolved at a pH where it is charged and water-soluble. Then, in the non-solvent bath a pH switch is induced causing the polyelectrolyte to lose its charge and precipitate into a solid membrane. In essence this is quite similar to conventional NIPS using the same principles but a different solvent and polymer combination as seen in the APS ternary phase diagram in Figure 1.3. The first example of this APS approach is described in Chapter 2 in which the polybase poly-4-vinylpyridine (P4VP) is made water-soluble in acidic conditions and precipitated in alkaline conditions to prepare membranes as schematically depicted in Figure 1.4.[68] This APS approach also works with polyacids for which an opposite pH switch, from alkaline to acidic, is used to induce precipitation which is described in chapter 3–6.[69-70] It has been shown that while different solvents and polymers are used than in regular NIPS a lot of the parameters to control the membrane are the same.[71] This includes polymer concentration, use of additives and solvent to non-solvent ratio, which in this system is the pH of the polymer solution and the coagulation bath. As the polymers remain water-soluble in certain pH conditions after precipitation often a crosslinking step is employed to enhance the chemical and mechanical stability of the membrane.[68-71]

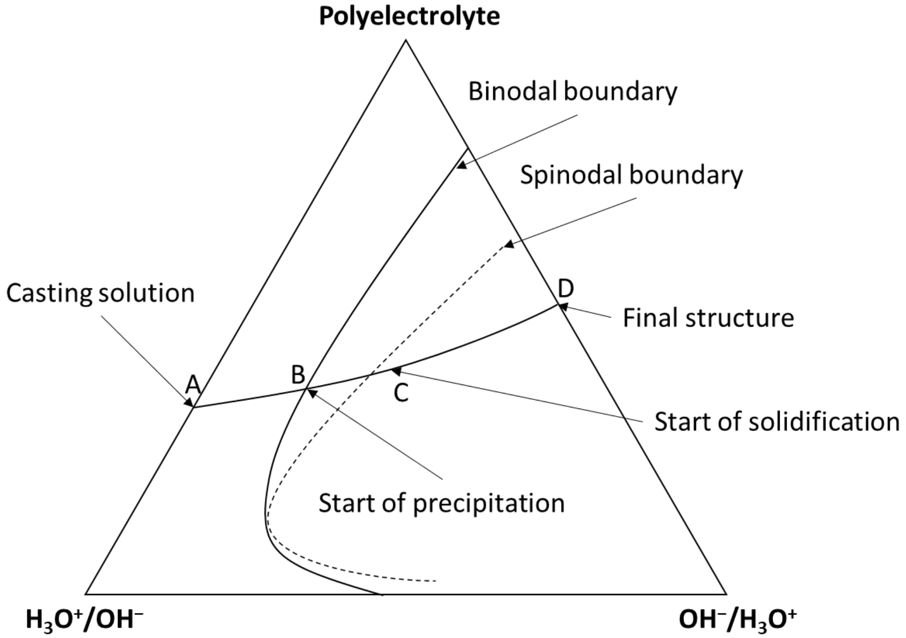

Figure 1.3. Ternary phase diagram of the APS system. The type of polyelectrolyte determines which pH is the solvent and non-solvent. For a polybase H_3O^+ makes the polymer water soluble and OH^- insoluble while for polyacids it is the opposite.

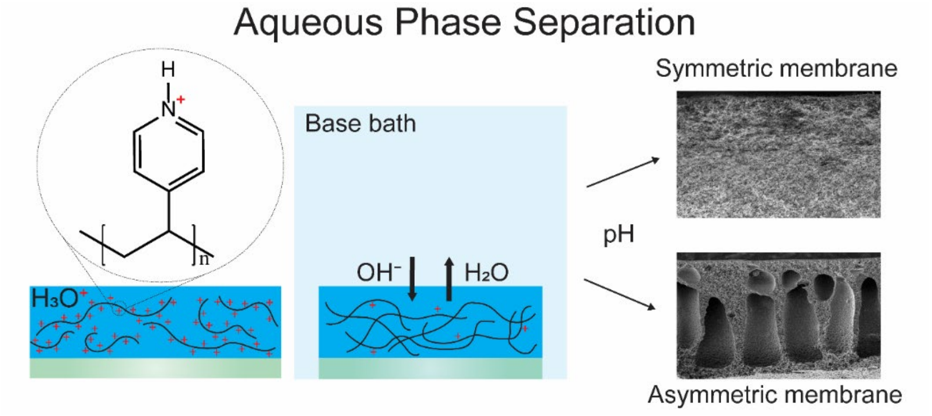

Figure 1.4. Depiction of aqueous phase separation of a poly-4-vinylpyridine in acidic water polymer solution cast onto a flat support and submerged in a coagulation bath of water. With the pH of the bath and the casting solution the final structure of the prepared membrane can be controlled.

The second approach uses the complexation of oppositely charged polyelectrolytes to form a membrane. When oppositely charged polyelectrolytes are mixed in solution an insoluble, solid complex can form under the right conditions. The complexation is driven by the release of bound counterions which increases the entropy of the system.[72] A successful way to control when this complexation occurs is by pairing a weak polyelectrolyte with a strong polyelectrolyte. By using a weak polyelectrolyte that is water-soluble even when uncharged, a solution can be prepared of both polyelectrolytes without complexation. An example system is schematically depicted in Figure 1.5. In this case the weak polybase polyallylamine hydrochloride (PAH) is mixed with the strong polyelectrolyte polystyrene sulfonate (PSS) at a high pH where PAH is uncharged.[73] In the non-solvent bath with a low pH PAH becomes charged which leads to the complexation between the polyelectrolytes and precipitation thereof forming a membrane.[73-75] As with the first approach the pH of the polymer solution and the coagulation bath as well as polymer concentration are parameters that allow control over the structure and properties of the membrane. In addition it has been found that the mixing ratio as well as the molecular weight of the two polymers are important parameters.[73, 76] In combination these factors can be used to prepare open membranes as well as dense membranes. Interestingly with the PAH-PSS system, the open membranes have large macrovoid structures while the membranes with a dense top layer do not, which is the opposite of what is typically observed with the first APS approach.

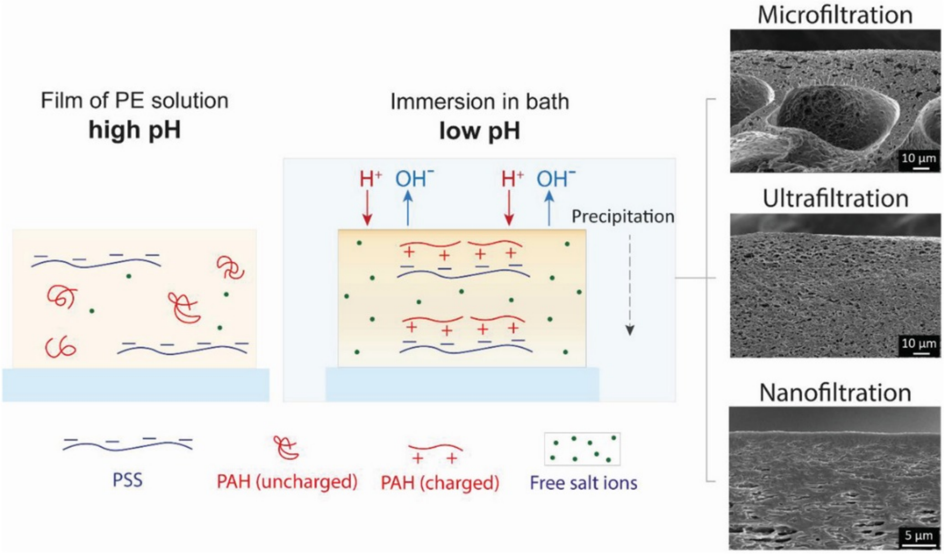

Figure 1.5. Schematic depiction of membrane preparation using pH responsive polyelectrolyte complexation. Adapted from Baig et al.[73]

The third approach is similar to the second approach as it also uses the complexation of oppositely charged polyelectrolytes, except in this approach two strong oppositely charged polyelectrolytes are used. As the complexation of oppositely charged polyelectrolytes is driven by entropy gain from the release of counterions an extreme ion concentration can be used to reduce the gain in entropy and therefore prevent complexation.[77] As schematically is depicted in Figure 1.5 such a solution can be precipitated in a low salinity bath as the reduction in salt concentration induces complexation between the polymers.[78-81] In this approach high salinity water is the solvent and water the non-solvent which is an advantage of this approach over the others as it does not use any hazardous chemicals at all. As with the previous approaches similar parameters as in conventional NIPS can be used to control the membrane formation and the ratio between the two polyelectrolytes can be used to control the membrane properties.[78-81] Besides water filtration, membranes prepared this way are also interesting for organic solvent filtration as polyelectrolyte complexes are insoluble in organic solvents that are problematic for conventional membranes.[82]

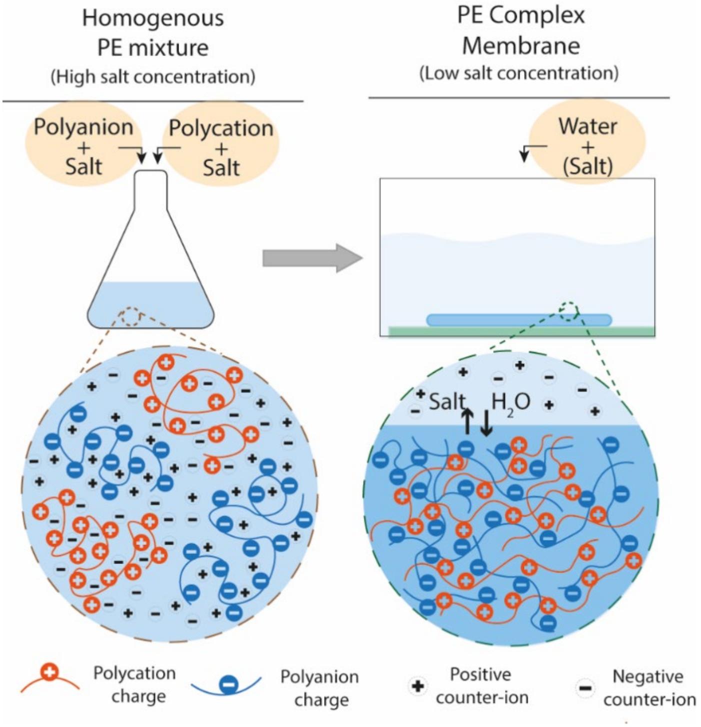

Figure 1.6. Schematic depiction of aqueous phase separation using a salinity switch. Adapted from Durmaz et al.[78]

1.6 Thesis outline

This thesis investigates a single polyelectrolyte based APS approach, as depicted in Figure 1.4, as an alternative, more sustainable method for membrane preparation which avoids/significantly reduces the use of toxic organic solvents. The goal is to highlight the viability of this method by showing that different types of membranes, open microfiltration as well as dense nanofiltration membranes, can be produced with excellent permeability and retention performances in a more sustainable way.

Chapter 2 discusses how the weak polybase poly-4-vinylpyridine (P4VP) can be used to prepare both MF and NF membranes.[68] P4VP can be dissolved in an acidic solution in which the tertiary amine groups of the polymer are protonated resulting in a positively charged polymer. After being cast into a thin film the polymer is precipitated in an alkaline bath which removes the positive charge of the polymer and causes precipitation thereof. It was found that the membrane structure could be controlled by the type and concentration of acid used in the polymer solution as well as the pH in the alkaline coagulation bath.

With crosslinking the mechanical stability of the membrane is improved and additionally the crosslinking extend could be used to modulate the permeability and the pH responsiveness of the membrane.

In Chapter 3 the preparation of membranes using the alternating copolymer poly(styrene-alt-maleic acid) PSaMA is presented.[69] PSaMA is a weak polyacid which combines the responsive monomer maleic acid with the hydrophobic styrene monomer. The advantage of this polymer compared to P4VP is that the resultant membranes have significantly better mechanical stability due to the hydrophobic styrene groups. Additionally, crosslinking of PSaMA does not lead to permanent charges being introduced in the membranes which overcomes several issues that membranes prepared with P4VP have. The PSaMA membranes showed excellent separation performances as well as mechanical stability up to 20 bars of applied pressure for the NF membranes.

In Chapter 4 it is shown how different types of salts can be used to influence the APS process. It is known from existing literature that salt type can influence the precipitation of charged polymers in solution.[70] Quite famous is the Hofmeister series that describes how some salts can stabilize proteins/polymers in solution while other salts induce precipitation more easily.[83] We find that the success of APS is strongly dependent on both the type and concentration of salt used throughout the process. For example, LiCl can be used to create more open structures while $CaCl_2$ significantly densifies the membrane structure.

In Chapter 5 it is reported how parameters like polymer concentration affect membrane formation and how the sustainability of APS can be further improved by reducing the amounts of acid used. It is found that when low concentrations of acid are used in the coagulation bath the membranes are more prone to form defects in the top layer.[71] By using an increased polymer concentration in the casting solution the formation of these defects is suppressed which allows the preparation of NF membranes with good retentions.

Chapter 6 further discusses membranes prepared with PSaMA and examines their resistance to several organic solvents as well as their pH stability and responsiveness. It is demonstrated that crosslinked membranes prepared with PSaMA are stable in various organic solvents, and show relevant pH responsive behavior in aqueous conditions. However the membranes do lose some of their stability at higher pH conditions and in NMP.

Chapter 7 is the outlook which discusses several interesting way to continue developing the single polyelectrolyte APS method. In previous chapters most work is done using the P4VP and PSaMA polymers as these polymers are suitable for the APS system as well as commercially available. In this chapter several recommendations are made for new polymers that can potentially help to further improve the performance of single polyelectrolyte APS membranes. In addition the preparation of APS hollow fibers is discussed which is an important step towards making the APS method more widely applicable.

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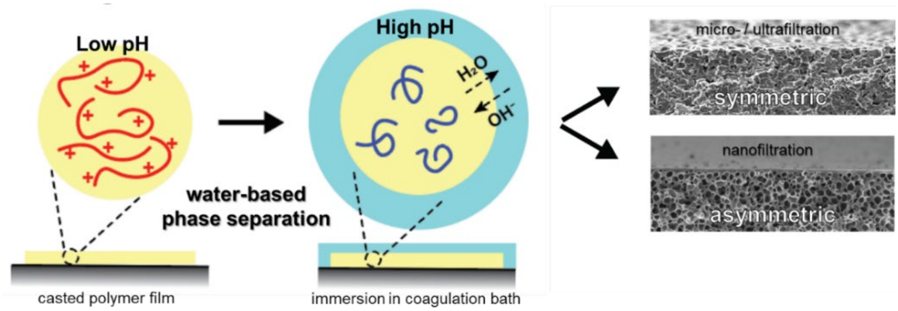
Chapter 2

Stimuli-responsive membranes through sustainable aqueous phase separation



This chapter has been published as:

Stimuli-Responsive Membranes through Sustainable Aqueous Phase Separation. Willott, J. D.; Nielen, W. M.; de Vos, W. M. ACS Applied Polymer Materials, 2020, 2 (2), 659-667.

Abstract

Polymeric membranes are used on huge scales for kidney dialysis, wastewater treatment, and drinking water production. However, almost all polymeric membranes are fabricated by a process reliant on the use of unsustainable, expensive and reprotoxic dipolar aprotic solvents. In this work, we propose an aqueous phase separation approach to preparing porous membrane films. Poly(4-vinyl pyridine) (P4VP), a pH-responsive polymer, is first dissolved at low pH where the polymer is charged and subsequently cast as a thin film. Switching to a high pH where the polymer is uncharged and insoluble, results in controlled phase separation and solidification of the polymer into porous membrane structures. This approach gives a large degree of control over membrane structure, leading to symmetric porous microfiltration membranes and asymmetric dense nanofiltration membranes. Moreover, the use of a pH-responsive polymer, leads directly to a pH-responsive membrane, where the degree of responsive behaviour can be tuned by the degree of crosslinking. Such responsive behaviour allows effective cleaning of the membrane, without the use of harsh chemicals. This work outlines an approach toward preparing membranes in a more sustainable fashion, an approach that allows control over the membrane structure and one that naturally leads to advanced membranes with responsive properties.

2.1 Introduction

Membrane technology received its great breakthrough in the early 1960s with the invention of non-solvent induced phase separation (NIPS).[1] NIPS made it possible to fabricate, in a continuous process, defect-free polymeric membranes with symmetric and asymmetric structures.[2-3] Because of this breakthrough, membranes are now used on massive scales for the production of drinking water, in kidney dialysis, for the separation of chemicals for biomedical applications, for the separation of gasses, and for the treatment of waste water.[4] Each year this amounts to tens of millions of square metres of membrane material and tens of billions of US dollars.[4] But all this comes at a price. The NIPS process is heavily reliant on the use of dipolar aprotic organic solvents like N-methyl-pyrrolidone (NMP), N,N-dimethylacetamide (DMAC), and N,N-dimethylformamide (DMF).[3] These solvents are expensive, flammable, and most significantly harmful to humans (reprotoxic) and the environment.[5] Therefore, residual solvent must be removed from the membranes by post-treatment, and due to high costs and environmental legislation the solvents must be recycled. REACH legislation first implemented by the European Union in 2008,[6] imposes strict time and concentration (in air) limits for NMP, DMAC and DMF. As of October 2017, the REACH committee agreed to further restrict the exposure limit for NMP with legislation coming into effect in 2020.[7] It is highly likely that similar restrictions will be extended to include other aprotic solvents like DMAC and DMF. Finding alternatives to avoid the use of these solvents is key to the future development and success of the synthetic membrane industry.

In the traditional NIPS process,[3] the aprotic solvent has two important properties: one it acts a good solvent for the chosen polymer(s), and two it is strongly miscible with water (the typical non-solvent). When a thin film of the polymer casting solution is immersed in the non-solvent water, solvent diffuses out of the film and mixes with the water, while the water diffuses into the film. The gradual change in solvent quality leads to a controlled precipitation of the polymer into a porous film. A major advantage of this approach is the control it gives over membrane structure, as the speed of the precipitation process and the rates of solvent and non-solvent movement (kinetics) together with the type of demixing event (thermodynamics) that occur during phase separation govern the final membrane porosity and structure.[3] In more recent years, some attention has been focussed on the preparation of membranes without the use of dipolar aprotic solvents.[8-11] Unfortunately this has simply not lead to a real alternative to NIPS, one that gives the same control over the membrane structure without requiring toxic solvents.

For certain responsive polymers, a transition from soluble to insoluble is possible in a completely aqueous environment, for example, by changes in pH or ionic strength for polyelectrolytes.[12-13] Poly(4-vinyl pyridine) (P4VP) is one such polymer. P4VP is a weak polyelectrolyte that consists of monomers with basic pyridine groups that have an effective pK_a value of 4.5–5.0 when free in solution.[14-15] Because of the basicity of the pyridine groups, the hydrophilicity of P4VP increases significantly upon lowering pH, which makes P4VP water-soluble under acidic conditions.[16] For higher pH values, the polymer charge is neutralised and P4VP is insoluble in water. Salt concentration also affects the fraction of charged monomer residues and hence the aqueous solubility of the polymer. In this work we propose that the use of pH-responsive polymers such as P4VP could lead directly to an alternative to NIPS, where water is employed as both the solvent and non-solvent for the polymer. We term this pH-induced phase separation process aqueous phase separation (APS) and will demonstrate that APS provides a clear route to produce membranes with a variety of structures without harmful aprotic organic solvents.

P4VP is already an often studied polymer for membrane modification due to its desired responsive properties, typically by one of two approaches.[17-18] In the first method, porous support membranes (prepared by NIPS) are coated with P4VP,[19-20] while in the second approach, asymmetric isoporous membranes are fabricated via a NIPS based process utilising the self-organising properties of P4VP-containing diblock copolymers; where P4VP forms the walls of the pores.[21-23] Pore-filled P4VP membranes exhibit pH-responsive filtration properties, where the water flux decreases drastically below approximately pH 4, slightly lower than the effective pK_a of P4VP in free solution. Here, at low pH, the pyridine groups are protonated and the P4VP-phase swells to fill the pore volume, thus reducing the effective pore volume of the membrane. Due to the pH-tuneable charge density of the P4VP-coated membranes, charge-selective separation has also been reported for diblock copolymer membranes.[21] Similarly, this responsive behaviour can be used as an effective cleaning step, where a change in membrane surface properties allows easy detachment of fouling agents. This means that membrane cleaning can be achieved using much lower quantities of chemical cleaning agents.

In this work, the soluble to insoluble transition for P4VP that is present with varying pH (that also exists for many other weak polyelectrolytes), is exploited to prepare porous membranes in a water-based approach. The membranes consist entirely of P4VP and are made using the aqueous phase separation (APS) approach in which water acts as both the solvent and the non-solvent for the polymer. Membranes can be prepared with great control over their properties, and we study in detail the membrane properties of a microfiltration and a nanofiltration type membrane prepared in this way. The P4VP, that makes up the membranes, retains its pH- and salt-responsive properties and variations in crosslink density can be used to control the extent of the responsive behaviour. This work thus provides a clear approach for the preparation of membranes with advanced properties without the need for toxic solvents.

2.2 Results and Discussion

This section is divided into three main parts. First, the aqueous phase separation (APS) process used to prepare the P4VP membranes is presented and discussed together with covalent crosslinking steps used to improve the chemical and mechanical properties of the membranes. Secondly, the preparation, morphology and performance of symmetric porous membranes is discussed. Third, the preparation of asymmetric membranes with dense top layers supported by porous support substructures is discussed along with some performance characteristics. We will show that the water-based APS process is well-suited to preparing membranes with a variety of structures and that it can offer a sustainable alternative to the solvent based NIPS process.

2.2.1 Membrane fabrication by aqueous phase separation

Flat sheet P4VP membranes were prepared by the novel aqueous phase separation process, in which a thin film of polymer solution at low pH is immersed in an alkaline coagulation bath. The APS process is shown schematically in Figure 2.1. P4VP is a weakly basic polyelectrolyte with an effective pK_a of 4.5–5.0[14-15] that dissolves in aqueous solutions at low pH due to protonation of the pyridinyl nitrogens within the repeating units. At high pH, the charge of P4VP is neutralised and the polyelectrolyte precipitates. This switch in polymer solubility as a function of pH can be exploited to prepare membranes. For the specific APS approach used in this work, a thin film of acidic P4VP solution is cast onto a non-woven mesh supported by a glass plate and then immersed in an alkaline coagulation bath. After immersion, an immediate exchange takes place where the alkaline bath neutralises the acidic casting solution and thus the charge of the polyelectrolyte. In the bath, the polyelectrolyte begins to precipitate and at a given point the polyelectrolyte solidifies forming the membrane matrix. The composition of both the polymer casting solution and coagulation bath were fine-tuned in order to achieve the optimal membrane cross-section structures and homogeneity (uniformity across the membrane surface area). The polymer concentration, acid type and amount, as well as the pH of the coagulation bath were all varied systematically. The importance of these factors will be discussed in the following sections and akin to the traditional NIPS process, the polymer concentration and phase separation time are important in governing the final structure of the P4VP membranes.

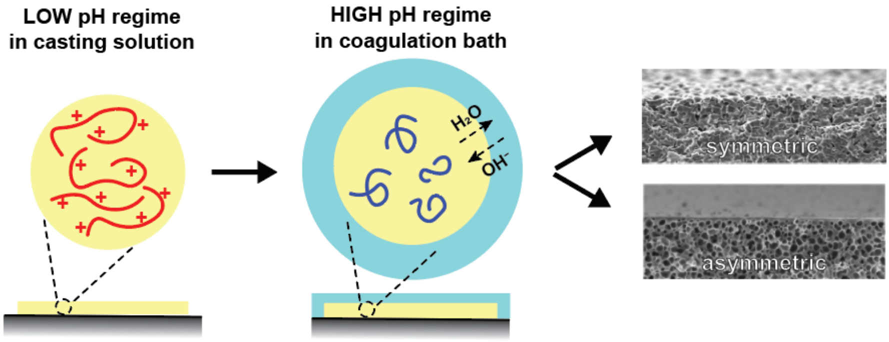


Figure 2.1. Schematic depiction of the aqueous phase separation (APS) approach. First, the polymer (P4VP) is dissolved in one pH regime (low pH for P4VP) and cast into a thin film. Next, the thin film is immersed in a coagulation bath at a second pH regime (high pH for P4VP). The fluid film precipitates and solidifies into the membrane structure. Control over the precipitation allows for the formation of both symmetric and asymmetric films.

2.2.2 Symmetric membrane preparation, morphology and performance

Before the most successful membranes were obtained (Figure 2.2), many parameters were explored. Polymer concentration was one factor studied in the preparation of the symmetric membranes. Polymer concentrations in the casting solution less than 17 wt% resulted in membranes that were inhomogeneous or patchy. Here the solution viscosity is too low and the cast film breaks apart in the coagulation bath during precipitation. Polymer concentrations of 20, 22 and 25 wt% produced much more homogeneous membranes and 20 wt% was found to produce the most consistent and reproducible membranes. Above 25 wt% of polymer, the casting step became difficult due to the high viscosities of the casting solutions.

Another factor investigated was the difference in pH between the casting solution and the coagulation bath. In principal, this pH difference drives the exchange of H^+/OH^- occurring within the cast polyelectrolyte film that in turn leads to the precipitation of the polyelectrolyte. Therefore, this factor will determine the precipitation speed of the polymer and thus the structure of the resultant membrane. Varying the acidity of the casting solution by changing the amount of hydrochloric acid had little effect on overall membrane structure and homogeneity (for a given bath condition). However, the addition of acetic acid (a weak acid) to the casting solution, in combination with hydrochloric acid, substantially improved the cross-section structure and reproducibility of the membranes. It is believed that the buffering capacity of acetic acid assists in controlling the phase separation process. Acetic acid is a green solvent,[24] that can be produced in a sustainable fashion in biorefineries and that can be easily recovered from water streams.[25] The final casting solution composition used to prepare the symmetric membranes is presented in Table 2.2 found in the Experimental section.

Varying the alkalinity of the coagulation bath, had a much more noticeable impact on overall membrane cross-section structure and homogeneity. At bath pH values of 12.5 and 12.7 (NaOH concentrations of 0.032 and 0.05 M), the precipitation was slow (>15 min) and the membrane surface was inhomogeneous. The precipitation was faster (~3 min) at higher bath pH values; as expected, since the driving force for precipitation is greater at higher bath pH (for a given casting solution composition). However at bath pH values of 13.3 and 13.5 (NaOH concentration of 0.2 and 0.316 M), the faster precipitation of the polyelectrolyte also produces inhomogeneous membranes. The optimal coagulation bath pH, for the selected casting solution, was found to be pH 13.0 (NaOH concentration of 0.1 M) and these conditions led to symmetric films.

Figure 2.2a,b,c presents the scanning electron microscopy (SEM) cross-section (a,b) and top surface (c) images of the film/membrane prepared using the optimised casting solution and coagulation bath conditions. The membrane is symmetric with a porous nodular structure. The mean pore size was measured by capillary flow porometry and was 0.78 ± 0.04 µm, which means that the membrane resides in the microfiltration category. During pure water flux measurements on the non-crosslinked membranes, the water flux decreases as a function of transmembrane pressure (discussed in detail later). This behaviour can be attributed to pore or structural compaction due to the water pressure experienced by the membrane. To overcome these performance issues, the symmetric P4VP membranes were chemically crosslinked to improve their mechanical strength. Three different crosslinking extents were achieved by varying the concentration of crosslinking reagent present during the crosslinking reaction from 0.5 to 2.0, and lastly 4.0 v/v%, for 'low', 'medium', and 'high' crosslink extents, respectively. Increasing the crosslinker concentration resulted in membranes with progressively smaller mean pore sizes as measured by porometry from 0.78 ± 0.04 µm for the non-crosslinked membrane, to 0.50 ± 0.05 µm for membrane crosslinked with 0.5 v/v crosslinker ('low' crosslink extent), and to 0.23 ± 0.03 µm for the membrane formed with 4.0 v/v% crosslinker ('high' crosslink extent).

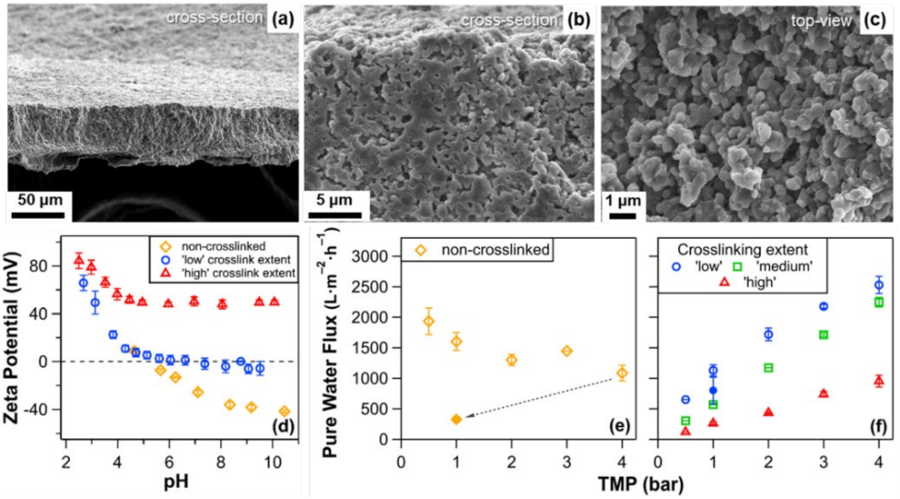


Figure 2.2. Top panel: scanning electron microscopy images of the non-crosslinked P4VP symmetric membrane: (a,b) cross-section view at magnification of ×1000 and ×3000 respectively and (c) top-view at magnification of ×10,000. Bottom panel on left: (d) zeta potential measurements as a function of pH (5 mM KCl) for the non-crosslinked membrane (□) and the 'low' (□) and 'high' (□) crosslink extent membranes. Symbols are the average and error bars the standard deviation of two distinct measurements. Bottom panel on right: pure water flux of (e) the non-crosslinked (□) membrane and (f) membranes crosslinked to varying extents: 'low' (□), 'medium' (□), and 'high' (□) as a function of transmembrane pressure (TMP). All water flux measurements were performed from 0.5 bar TMP progressively up to 4 bar TMP. The dashed arrow (e) and the solid symbol in (f) represent the pure water flux measured at 1 bar TMP after 4 bar TMP was reached. For all water flux data, the symbols are the average of three distinct measurements on separate membrane samples and the error bars are the standard deviation of those measurements.

The crosslinking reaction occurred between two pyridine groups in the P4VP membrane and is therefore a quaternisation reaction. Therefore, with every successful crosslink, two positively charged quaternary pyridine groups are formed, which is seen in Figure 2.2d through zeta potential measurements performed on the membranes. Quaternary amines are known for their high chemical stability and are stable against oxidative cleaning agents such as hypochlorite.[26] It is also possible that in some cases only one end of the crosslinking molecule reacted, which would result in grafting of the crosslinker molecules. This scenario would not result in crosslinking, but the membrane charge would still increase as one pyridine group would become quaternised. From Figure 2.2d, the non-crosslinked P4VP membrane has a pH-dependent zeta potential; negative at high pH and increasingly more positive with decreasing pH. The non-crosslinked membrane dissolves at pH values <4.0 (below the effective pK_a of P4VP) and is also solubilised by alcohols (ethanol and isopropanol) due to favourable hydrogen-bonding interactions.[16] For the 'low' crosslink extent membrane, the surface charge is more positive at higher pH values compared to the non-crosslinked membrane suggesting quaternisation of the pyridine groups. The 'high' crosslink extent membrane has a positive zeta potential (on average +50 mV), from pH 10 to pH 4; suggesting substantial quaternisation and therefore significant crosslinking. For both the 'low' and 'high' crosslink extent membranes, at pH values <4.0, the pyridine residues that have not undergone crosslinking become charged (below the effective pK_a of P4VP) and consequently the measured zeta potential increases substantially (pH-responsive surface charge). Significantly, all of the crosslinked membranes no longer dissolve in acidic water and alcohols, because the covalent crosslinking maintains the structural integrity of the membrane. Across the pH range studied, no visible swelling of any crosslinked membranes was observed. As will be shown in the next section, varying the degree of crosslinking is an important control parameter to tune the water permeance and magnitude of the responsive properties of the P4VP membranes.

Figure 2.2ef present the pure water flux as a function of transmembrane pressure (TMP) for the non-crosslinked and crosslinked P4VP membranes, respectively. The non-crosslinked membrane experienced irreversible structural (pore) compaction as shown by the drastic decrease in flux with increasing applied pressure beyond 0.5 bar. Importantly, for all the chemically crosslinked membranes, pure water flux increases as a function of pressure. The flux increase is linear as a function of applied pressure for the 'low', 'medium' and 'high' crosslink extent membranes and thus no structural compaction was observed over this pressure range (up to 4 bar, which is beyond the standard operating pressure for these class of membranes[4]). The pure water permeance of the crosslinked membranes is 930 ± 510, 580 ± 50, and 250 ± 80 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$ for the 'low', 'medium', and 'high' crosslink extents respectively. These values are expected for membranes in the ultra- to microfiltration range.[4] Increasing the extent of crosslinking results in a progressive decrease in the pure water permeance, which is not surprising as the swelling of the polyelectrolyte matrix is reduced at higher crosslink extents, leading to smaller pore sizes.

An important application for microfiltration and ultrafiltration membranes is the removal of suspended oil from industrial waste water.[27] In addition to the pure water permeance measurements, the separation of oil droplets from water was investigated for the 'high' crosslink extent membrane using a SDS-stabilised hexadecane-in-water emulsion. The mean oil droplet size was 3–4 μm.[28] The retention of hexadecane droplets was high at 96.6 ± 1.2% (data from three distinct measurements). Fouling experiments using the same oil-in-water emulsion revealed the self-cleaning capability of the P4VP membrane in response to a simple pH switch; data presented in Table 2.1. Fouling resulted in a drastic decrease in water flux with a water permeance recovery of only ~20%. Cleaning of the membrane by soaking in a pH 7 solution of 5 mM NaCl was largely ineffective with the water permeance recovery only slightly improving to be ~40%. After cleaning in an acidic solution of pH 3 (5 mM NaCl) the water permeance recovery substantially increased to be ~90%. Switching to pH 3 results in an increase in the surface charge (see zeta potential measurements in Figure 2.2d) of the crosslinked P4VP membrane and therefore its hydrophilicity; this combination of effects is most likely responsible for the desorption of the hydrophobic oil droplets (i.e. self-cleaning response). These data (Table 2.1) nicely demonstrate the pH-responsive self-cleaning ability of the P4VP membrane prepared by APS and are in line with the cleaning behaviour of P4VP pore-filled membranes.[29]

Table 2.1. Self-cleaning response to pH of the 'high' crosslink extent P4VP membrane.

Membrane condition	Water permeance ($L{\cdot}m^{-2}{\cdot}h^{-1}{\cdot}bar^{-1}$)	Water permeance recovery
Fresh	210 ± 20	
Fouled	40 ± 10	~20%
Post pH 7 clean	85 ± 10	~40%
Post pH 3 clean	190 ± 25	~90%

The pH and salt responsive water permeance was studied for the 'low' crosslink extent membrane. Figure 2.3a presents the pH responsive water permeance measured for

0.005 M NaCl solutions (the water flux was measured at a TMP of 1 bar, before these measurements the membranes were compacted at 4 bar for 30 min to prevent it from affecting the measurement). At pH 9.0 and pH 5.5 (pH > effective pK_a of P4VP) the permeance is the same as in pure water (within error), as expected for the weakly basic P4VP since the polymer and hence overall membrane charge from P4VP protonation is low. At pH 4.25 the permeance increases slightly (from ~900 to ~1000 $L{\cdot}m^{-2}{\cdot}h^{-1}{\cdot}bar^{-1}$), while at pH 3.0 (pH << effective pK_a of P4VP) the permeance increases substantially compared to that measured at pH 5.5 (from ~1000 to ~1600 $L{\cdot}m^{-2}{\cdot}h^{-1}{\cdot}bar^{-1}$, an increase of ~85%). At low pH, the weakly basic pyridine groups are protonated and the increased electrostatic repulsion between the charges together with swelling due to counterion and solvent absorption results in an increase in the effective pore size of the membrane, and thus the higher permeance values. Importantly, crosslinking restricts the amount of swelling and the membrane and water permeance is stable. This pH-induced swelling of the membrane is similar to the swelling response of crosslinked spin-coated P4VP thin films reported by Harnish and coworkers.[30] Figure 2.3b shows the influence of ionic strength on the permeance at a fixed pH of 3.0 (measured at TMP of 1 bar). With an increase in ionic strength from 0.005 M to 0.05 M, the permeance does not change. However, at 0.5 M, the permeance drops, which can be attributed to greater charge screening at higher ionic strengths that results in a reduction in the swelling and hence a decrease in the effective pore size of the membrane.

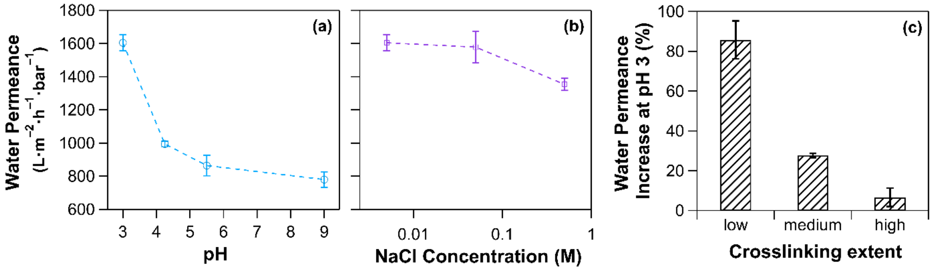


Figure 2.3. Water permeance of the 'low' crosslink extent P4VP membrane to (a) changes in pH at fixed NaCl concentration of 0.005 M, and (b) changes in ionic strength at fixed pH of 3.0. All measurements were performed at 1 bar of TMP from high to low pH and from low to high NaCl concentration. (c) pH-triggered permeance increase (%) observed for pH 3.0 (in 0.005 M NaCl background electrolyte) compared to pure water as a function of crosslinking extent. All data are the average of three distinct measurements on separate membrane samples and the error bars are the standard deviation of those measurements.

The influence of crosslinking extent on the magnitude of the pH-response of the membrane upon switching to pH 3 was also investigated. Figure 2.3c shows the percentage increase in water permeance observed at pH 3.0 (in 0.005 M NaCl) compared to the permeance measured in pure water for the three different crosslinking extents. At 'low' crosslink extent, the permeance increases by ~85% at pH 3. The magnitude of the pH-triggered increase in permeance is much less for higher crosslinking extents; ~28% and ~7% increase in permeance for the 'medium' and 'high' crosslink extent membranes, respectively. The degree of crosslinking can thus be used to tune the responsive properties of the membrane. This provides a useful additional tuning parameter to optimize membranes produced by APS towards a specific application.

Clearly with the APS approach used here we can prepare porous membranes that show good separation properties. Moreover, the chemical and mechanical stability can be guaranteed by crosslinking, which even allows additional control over membranes properties including the responsiveness of the membrane. Still, an important feature of the traditional NIPS process is its excellent control over membrane structure, allowing a variety of membranes to be produced with a single approach. It becomes important to show that also APS allows this control over membrane structure, by preparing asymmetric and much denser membranes.

2.2.3 Asymmetric membrane preparation, morphology and performance

For the preparation of asymmetric membranes, the polymer concentration in the casting solution was 20 wt%; the same amount used for preparing the symmetric membranes. The major differences between the preparation of the symmetric and the asymmetric membranes is that for the latter, the pH of the coagulation bath was higher and the amount of acetic acid in the casting solution was greater.

As discussed earlier, increasing the pH difference between the casting solution and the coagulation bath increases the driving force for precipitation and therefore shorter precipitation times should be expected. This is indeed the case for when the pH of the coagulation bath is increased progressively from pH 13 up to pH 14 (0.1 M up to 1 M NaOH). However, when using the same casting solution used to prepare the symmetric membranes, increasing the bath pH results in inhomogeneous films in which more than half of the cross-section structure is completely dense. These films were unsuitable to be used as membranes. To overcome this issue, changes in the composition of the casting solution were made. The first result to note is that varying the concentration of hydrochloric acid in the casting solution did not improve the structure of the resultant films. Next, it is important recall from the preparation of symmetric membranes that the addition of acetic acid to the casting solution significantly improved the structure and homogeneity of the films. Therefore, casting solutions with no hydrochloric acid and only acetic acid were prepared and studied. The lowest acetic acid concentration that resulted in a homogeneous (single fluid phase) casting solution was 8 wt%. However, the resultant films had very thick (>20 µm) dense top layers. Increasing the concentration of acetic acid in the casting solution results in films with progressively thinner dense top layers and indeed this trend can be observed by following the SEM images in Figure 2.4. For 20 wt% acetic acid (Figure 2.4a,b) the thickness of the top layer is approximately 15 µm. For 30 wt% acetic acid (Figure 2.4c,d) the thickness of the top layer decreases to approximately 10 µm. At 40 wt% acetic acid (Figure 2.4e,f) the thickness of the dense top layer decreases further to approximately 2 µm, which is importantly within the thickness range seen for the separation layers of typical nanofiltration membranes. It is postulated that the buffering capacity of acetic acid acts to control the phase separation process. Consequently, at higher acetic acid concentrations, increasingly more porous films are formed.

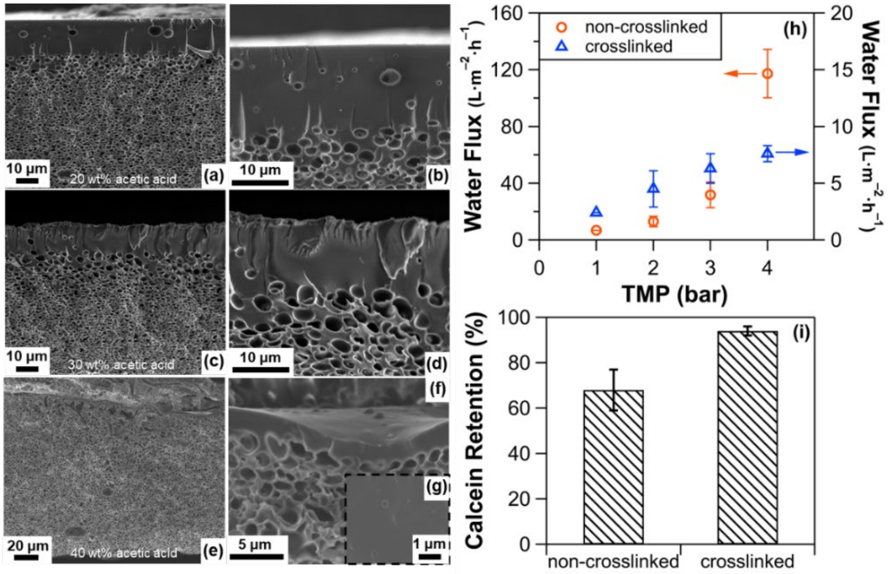


Figure 2.4. SEM cross-section images of asymmetric membranes prepared in a 1 M NaOH coagulation using casting solutions with an increasing concentration of acetic acid (a,b) 20 wt%, (c,d) 30 wt%, (e,f,g) 40 wt%. Left images of the pair are cross-sections at ×1000 magnification for (a,c) and ×500 magnification for (e). Right images of the pair are higher magnification at ×2500 for (b,d) and ×5000 for (f). The inset (g) is a top surface image of that membrane at ×10000 magnification. (h) Pure water flux as a function of TMP and (i) Calcein retention (at TMP of 3 bar) for the non-crosslinked and crosslinked 40 wt% acetic acid membranes. All data are the average of three distinct measurements on separate membrane samples and the error bars are the standard deviation of those measurements.

The asymmetric membrane prepared using 40 wt% of acetic acid in the casting solution was selected for further studies since the thickness of the dense top-layer was low (~2 µm by Figure 2.4f) and SEM images (Figure 2.4g) show that the top of the film was defect-free (within the resolution of the SEM). The pure water flux of the non-crosslinked and crosslinked 40 wt% acetic membranes were measured as a function of transmembrane pressure and the results are presented in Figure 2.4h. Starting with the non-crosslinked membrane, the water flux increases with higher pressures and this behaviour is linear up to 2 bar of applied pressure. Beyond 2 bar of pressure, the increase in water flux is no longer linear and the size of the error bars increases substantially. This reveals that the membrane suffers from structural instabilities, and most likely defects form in the top layer, at increased pressures. To address this problem, the asymmetric films were also subjected to chemical crosslinking. After crosslinking, the flux increases linearly with pressure, see Figure 2.4h. The pure water permeance of the crosslinked membrane is 2.2 ± 0.2 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$ (average for three distinct measurements on separate membrane samples). The combination of the SEM images (Figure 2.4e,f,g) and water permeance value for the 40 wt% acetic acid membrane suggests that it resides in the nanofiltration category; albeit the water permeance is lower than many commercially available nanofiltration membranes. To further study the performance of this membrane, the retention of the small organic molecule Calcein (Mw of 623 Da) was studied; see Figure 2.4i. The average retention of Calcein for the non-crosslinked and crosslinked membranes was 68 ± 9% and 94 ± 2%, respectively supporting the claim that these membranes have the qualities of nanofiltration membranes. The results in this section nicely show the adaptability of the APS approach. With APS it is possible to not only prepare symmetric porous membranes but also asymmetric membranes with dense separation layers, all from a single polymer and significantly without the need for aprotic organic solvents.

2.3 Conclusions

Production of polymeric membranes is currently dominated by NIPS, a simple and powerful approach to prepare membranes with great control over membrane structure. However, NIPS is heavily reliant on unsustainable, expensive and toxic aprotic solvents such as NMP. We propose, as an alternative, a novel water-based phase inversion approach (termed APS) that provides similar control over membrane structure. Moreover the very nature of this approach, produces membranes with responsive properties that allow for easy membrane cleaning.

The APS approach was used to prepare P4VP membranes with a porous symmetric structure exhibiting pure water permeance (250–900 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$) and retention characteristics for the ultra- to microfiltration ranges. Covalent crosslinking was used to improve chemical and mechanical stability. Irreversible structural compaction was observed for the non-crosslinked symmetric membranes under applied water pressure, but importantly this problem was eliminated through covalent crosslinking that furnished membranes with stable pure water permeance up to 4 bar of transmembrane pressure. With higher crosslink extents, the measured pore size and pure water permeance progressively decreased showing that crosslinking degree can be used to tune membrane performance. An excellent retention of n-hexadecane droplets (~97%) from a hexadecane-in-water emulsion was found. Moreover, the membranes were found to be self-cleaning in response to pH, due to the responsive properties of P4VP, with a water permeance recovery of >90% after immersion in a pH 3 solution. Indeed, pH and salt responsive permeance behaviour of the crosslinked symmetric membranes was found with higher permeant fluxes observed below pH 4 where P4VP becomes charged. The magnitude of the permeance increase triggered at low pH decreased with higher crosslinking extents showing again that the crosslinking is an adjustable parameter to tune membrane properties; in this case its degree of responsiveness. It was also demonstrated that APS provides substantial control over membrane structure. By tuning the acetic acid content in the casting solution, stable asymmetric membranes could also be prepared with water permeance (2.2 ± 0.2 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$) and retention (96% Calcein) values characteristic for nanofiltration membranes.

The APS approach presented here is a simple and scalable approach that gives a large degree of control over membrane structure. It thus demonstrates all the advantages of traditional NIPS, but in a much more sustainable fashion without requiring toxic aprotic solvents. Moreover, the APS approach naturally results in responsive membranes, with the degree of crosslinking determining the extent of the responsive behaviour. We thus see the APS approach as an important tool toward more sustainable membrane preparation. While we have shown that APS works for P4VP we expect that this approach can be extrapolated to many other responsive polymers, allowing for many novel and sustainable membranes to be prepared in the near future. Performing APS with, for example, polyacids will allow water-based chemical crosslinking methods to be used; a step towards making APS a completely aqueous approach.

2.4 Experimental Methods

2.4.1 Materials

Poly(4-vinyl pyridine) (P4VP, $M_W = 200$ kDa) was purchased from Scientific Polymer Products Inc. (Ontario, Canada) and used without further purification. Hydrochloric acid (fuming, 37%, ACROS Organics), acetic acid (glacial, ≥99.9%, Merck Millipore), sodium hydroxide (≥97%, Merck Millipore), potassium chloride (≥99%, VWR International), sodium chloride (≥99%, Akzo Nobel), n-hexane (≥96%, Merck Millipore), 1,4-dibromobutane (99%, Merck), sodium dodecyl sulfate (SDS, ≥99%, Merck), n-hexadecane (≥99%, Merck Millipore) and the fluorescent molecule Calcein (Sigma Aldrich/Merck) were used as received.

2.4.2 Membrane preparation and crosslinking

P4VP was added to a solution of water and acid (hydrochloric acid and/or acetic acid) and stirred for several hours (using a magnetic stirrer bar) until fully dissolved; making the homogeneous membrane casting solutions. Final compositions used herein are given in Table 2.2.

Table 2.2. Composition of the final membrane casting solutions.

	concentration (wt %)			
	for symmetric membranes	for asymmetric membranes		
P4VP	20	20	20	20
Water	67	60	50	40
Hydrochloric acid [a]	6.5	—	—	—
Acetic acid	6.5	20	30	40

[a] in terms of 100% HCl

To prepare all the membranes, the given polymer casting solution was poured onto a non-woven fabric (poly(phenylene sulfide)) supported by a glass substrate and a thin film of polymer was formed using a manual film applicator with a gate height of 300 µm. Immediately afterwards, the cast polymer film was carefully transferred, through gentle submersion by hand, to the bottom of an alkaline coagulation bath (pH 12.5–14.0, 0.032–1 M NaOH) where the phase inversion process took place forming the symmetric or asymmetric membranes. The membranes were left in the coagulation bath for 30 min. The precipitated and solidified polymer film was transferred to a deionized water bath (pH 5.5) for rinsing and storage.

A selection of the membranes was subjected to a chemically crosslinking process. To achieve this, the membranes were first dried overnight in air, then transferred to a sealable glass vessel and lastly immersed in a solution of hexane containing the crosslinking agent 1,4-dibromobutane: at concentrations of either 0.5, 2.0 or 4.0 v/v% to achieve the ‘low’, ‘medium’, or ‘high’ crosslink extent symmetric membranes, respectively. The asymmetric membranes were crosslinked with 4.0 v/v% of the crosslinking reagent. The solution was heated to 50 °C with slow stirring using a magnetic stirrer bar; a temperature sensor was immersed in the solution to control the heating. The crosslinking reaction was allowed to proceed for 1 h. Afterwards, the crosslinked membranes were rinsed with hexane, followed by ethanol, and lastly deionized water before being placed in a deionized water bath (pH 5.5) for storage. While the crosslinking approach used is simple and successful, we do acknowledge that the crosslinking agent and solvent used is toxic. However, importantly, the quantity of solvent and crosslinker used is very small and its usage does not lead to a polluted waste water stream, which is the case for the solvents used in the traditional NIPS process. In a continuation of this work, alternative crosslinking strategies using greener molecules and solvents are being explored.

2.4.3 Morphology characterisation

Scanning electron microscopy (SEM, JEOL JSM-6010LA and JEOL JSM-7610F, operated at an acceleration voltages of 5 kV and 2 kV, respectively) was used to study the morphology of the polymeric membranes. For cross-section analysis, the samples were fractured in liquid nitrogen, mounted in cross-section holders with adhesive carbon tape and dried overnight in a vacuum oven at 30 °C. Before SEM analysis, the samples were coated with a 10 nm conducting layer of chromium using a Quorum Technologies Q150T sputter coater.

2.4.4 Water Permeance

The flux ($L \cdot m^{-2} \cdot h^{-1}$) of pure water and various pH-controlled salt solutions through the P4VP membranes (Ø 25 mm) were measured at different transmembrane pressures, ranging from 0.5 to 4 bar, at 20 °C, using a dead-end filtration setup. Transmembrane pressure (TMP) is defined as the difference in pressure between the feed and permeate side of the membrane. At each pressure, data was collected for at least 15 min after a steady-state flux was achieved. Water permeance ($L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$), defined as the flux divided by the TMP, was calculated for each measurement. The reported flux and permeance values are the average of at least two measurements and the standard deviation of the repeats gives the error bars. For each measurement, the free-standing membrane was placed on top of a non-woven fabric to provide additional mechanical support. The non-woven fabric had a mesh size of >100 µm and therefore a significantly higher permeance ($\sim 7.5 \times 10^6$ $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$) than the P4VP membranes. Consequently, it was assumed that the non-woven support had no influence on the obtained permeance results. To investigate the pH and salt response of the P4VP membranes, dead-end filtration measurements were performed with 0.005 M (pH 3.0, 4.25, 5.5, and 9.0), 0.05 M (pH 5.5), and 0.5 M (pH 5.5) sodium chloride solutions in addition to the pure water (pH 5.5). Here, pH adjustments were made using a minimal volume of 1 M HCl or 1 M NaOH solutions.

2.4.5 Oil retention, membrane self-cleaning and Calcein retention

To study retention for the symmetric porous membranes, an oil-in-water emulsion of hexadecane-in-water stabilised by sodium dodecyl sulfate (SDS) was used. A stock emulsion was prepared and then diluted immediately before the filtration measurements. The stock emulsion was prepared by mixing 2 g of hexadecane and 0.02 g of Oil Red O dye with a 463 mg/L SDS aqueous solution using a dispersing mixer (IKA® T25 digital Ultra-Turrax with S25N 18G element) for 10 min at 14000 rpm. Before filtration measurements, the stock emulsion was diluted to contain 100 mg/L of hexadecane. The mean oil droplet size of the emulsion was 3–4 µm.[28] The concentration of SDS was chosen to be below the critical micelle concentration (CMC) to avoid micelle formation (CMC of SDS is ~2400 mg/L). Separations were performed at TMP of 0.5 bar. The separation was allowed to stabilise for 15 min before collection of the permeate; to ensure that adsorption to the membrane does not affect the separation data. Subsequently, approximately 10 mL of permeate was collected. Feed, retentate and permeate were analysed by ultraviolet–visible spectroscopy at 521 nm (UV-1800 Shimadzu). Oil retention was determined using the following relationship:

$$\text{Retention (\%)} = \left(1 - \frac{A_p}{\left(\frac{A_r + A_f}{2}\right)}\right) \times 100 \qquad (2.1)$$

where A_P, A_r, and A_f are the absorbance values measured for the permeate, retentate, and feed respectively. A calibration line was made from the stock emulsion by series dilution. For this concentration range (0 to 2000 mg/L), the Beer–Lambert Law applied. Here the relationship between the absorbance of the solutions and concentrations of the absorbing species was linear. The reported retention value is the average of four measurements (two measurements on two different membrane) and the error bar is the standard deviation of the four measurements.

To investigate membrane self-cleaning performance, fouling experiments were performed using the same oil-in-water emulsion. First, the pure water flux was measured for 30 min. Next, the fouling experiments were performed using 100 mg/L of the emulsion for 30 min. The fouled membrane was removed and placed in the cleaning solution, either pH 7 or pH 3 5 mM NaCl, for 15 min with slow stirring. Afterwards, the pure water flux was measured again. The self-cleaning capacity is expressed as water permeance recovery, which is calculated from the pure water permeability before and after the fouling experiments. Water permeance recovery (%) = $(P_{initial}/P_{fouled}) \times 100$, where $P_{initial}$ is the water permeance of the fresh membrane and P_{fouled} is the water permeance of the fouled membrane.

Calcein (also named Fluorexon, M_W = 623 Da) retention was measured for a selection of the asymmetric P4VP membranes. A feed concentration of 10 µM was used. Filtrations were performed for 2 h and then the permeate was collected and analysed. The initial 2 h of filtration before collection of the permeate was performed to help eliminate the effect of Calcein adsorption to the membrane on the reported retention values. The feed, retentate and permeate were measured using a fluorometer (Qubit 4 fluorometer, Invitogen). For the concentration range studied, fluorescence intensity was directly proportional to the concentration of Calcein and therefore the retention was calculated using Equation 1.

2.4.6 Porometry

Membrane pore size distribution was characterised using a Porolux™ 500 capillary flow porometer (IB-FT GmbH, Berlin, Germany) for the symmetric porous membranes. Before each measurement, the membranes (Ø 25 mm) were immersed for 15 min in perfluorotributylamine (Fluorinert™ FC-43, 3M Belgium). Measurements were performed from 0.1 to 6.0 bar of applied nitrogen pressure. Reported values for mean pore size are the average of at least two measurements with the standard deviation of the repeats used for the error bars.

2.4.7 Zeta Potential

Membrane zeta potential was studied using a SurPASS™ electrokinetic analyser (Anton Paar, Graz, Austria). Zeta potential was calculated by measuring the streaming current as a function of pressure, in 5 mM potassium chloride solution, using the following expression:

$$\zeta = \frac{dI}{dP}\frac{\eta}{\varepsilon\varepsilon_0}\frac{l_s}{a_s} \tag{2.2}$$

where ζ is the zeta potential (V), I is the streaming current (A), P is the pressure (Pa), η is the dynamic viscosity of the electrolyte solution (Pa·s), ε is the dielectric constant of the electrolyte, ε_0 is the vacuum permittivity (F·m^{-1}), and l_s (m) and a_s (m^2) are the length and cross section, respectively, of the streaming channel.

2.5 Acknowledgements

Lieke van Ginkel is thanked for some performance tests on the asymmetric membranes. The authors acknowledge funding support from the “Vemieuwingsimpuls” programme through project VIDI 723.015.003 (financed by the Netherlands Organisation for Scientific Research, NWO) and from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (ERC StG 714744 SAMBA).

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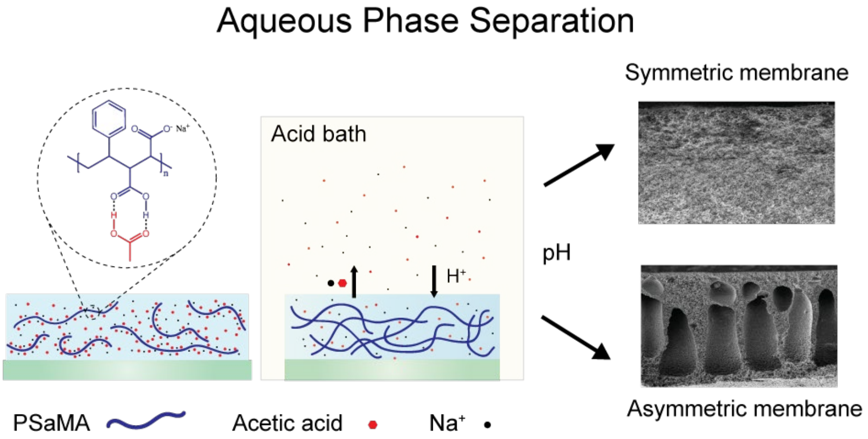
Chapter 3

Aqueous phase separation of responsive copolymers for sustainable and mechanically stable membranes.



This chapter has been published as:

Aqueous Phase Separation of Responsive Copolymers for Sustainable and Mechanically Stable Membranes. Nielen, W. M.; Willott, J. D.; de Vos, W. M. ACS Applied Polymer Materials, 2020, 2 (4), 1702-1710.

Abstract

Membranes are often used in environmentally friendly applications and as a sustainable alternative to conventional processes. Unfortunately, the vast majority of polymeric membranes are produced via an unsustainable and environmentally unfriendly process that requires large amounts of harsh reprotoxic chemicals like N-methyl-2-pyrrolidinone (NMP) and dimethylformamide (DMF). In this Chapter we investigate an aqueous phase separation (APS) system that uses weak polyelectrolytes, whose charge is dependent on the pH (weak polyelectrolytes), to produce membranes. Specifically the copolymer polystyrene-alt-maleic acid (PSaMA) is used. PSaMA contains responsive monomers, required for the aqueous phase separation, and also unresponsive hydrophobic monomers that provide mechanical stability to the resultant membranes. This Chapter demonstrates that by controlling the precipitation of PSaMA it is possible to prepare a wide range of membranes, from microfiltration membranes capable of treating oily waste water, to dense nanofiltration-type membrane with excellent micropollutant retentions and high mechanical stability. Whereas similar materials in Chapter 2 could only withstand 4 bar, the membranes presented here demonstrate stable operation up to 20 bar. The only solvents used in this APS system are water and the green solvent acetic acid, thus making our APS process significantly more sustainable and environmentally friendly compared to conventional membrane fabrication methods.

3.1 Introduction

Membrane technology is widely used for the production of drinking water, biomedical applications, waste water treatment and chemical separations.[1-3] Polymeric membranes, by far the most widely used membranes, are predominantly made using the well-known non-solvent induced phase separation (NIPS) approach; a technique known for its versatility, low cost, and scalability.[1-5] However, the solvents used in NIPS like N-methyl-2-pyrrolidinone (NMP) and dimethylformamide (DMF), are expensive and reprotoxic, and over 50 billion liters of contaminated wastewater is produced annually.[6] Recently, the use of NMP became restricted throughout the European Union by the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) legislation, and consequently the need to find suitable alternatives becomes even more pressing.[7] Efforts to find alternatives to the conventional NIPS approach have been made. These include studies that aim to use less toxic solvents like dimethyl sulfoxide (DMSO), ionic liquids or super critical CO_2 and other works that use temperature induced phase separation.[8] However, all these approaches lack the versatility of NIPS, where extensive control over membrane structure and pore size is the key to its success. More recently, de Vos proposed an aqueous phase separation (APS) approach similar to NIPS that is based on the use of responsive weak polyelectrolytes, whose charge depends on the solution pH.[9] In this APS approach, water-soluble responsive polymers are dissolved in water and then precipitated also in water using a simple pH switch. The APS approach is schematically depicted in Figure 3.1 for a weak polyacid. For APS, instead of a solvent exchange between NMP and water as seen in NIPS, a solvent exchange between alkaline and acidic water takes place. By using a polymer that is only soluble in either alkaline or acidic conditions, i.e. a weak polyacid or weak polybase respectively, the system can undergo phase separation forming porous membranes.

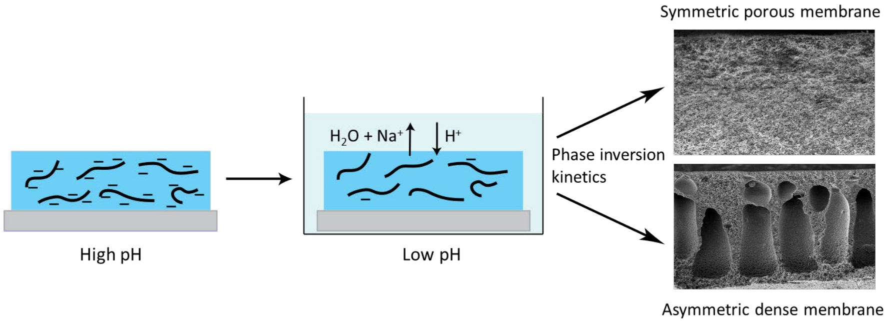


Figure 3.1. A schematic representation aqueous phase separation using a weak polyacid.

In Chapter 2 we demonstrated the simplicity and versatility of the APS approach using the weak polybase poly(4-vinyl pyridine) (P4VP) by preparing both symmetric and asymmetric structures.[10] P4VP is dissolved in water with a low pH where P4VP is charged and therefore water-soluble. A thin film of the polymer solution is then placed in a coagulation bath with a high pH where P4VP loses its charge, becomes water-insoluble and then precipitates. By adjusting the polymer casting solution composition and the coagulation bath conditions different membrane structures were obtained. A problem that was encountered was that the crosslinking steps required to improve the mechanical and chemical stability of the membranes resulted in quaternization of the amine groups and thus permanent charges were formed in the membrane leading to swelling. This swelling results in poor mechanical properties and unstable membrane performance above 4 bars of applied pressure.[10]

For APS to become a suitable sustainable alternative to NIPS membranes with strong mechanical properties are essential. Ideally, one would use a responsive polymer which has high mechanical stability, that can be precipitated at mild conditions and that does not require crosslinking or can be easily crosslinked under mild conditions. For this copolymers are expected to provide an ideal platform as a responsive monomer, required for APS, can be combined with a monomer that provides good mechanical properties. Examples of such copolymers are the commercially available polystyrene-co-maleic acid partial isobutyl ester (PScMA) and polystyrene-alt-maleic copolymer acid (PSaMA). In these copolymers the maleic acid monomer is the responsive unit that allows the polymer to dissolve in alkaline water and to precipitate in acidic water. Moreover, these carboxylic acid groups can be easily crosslinked in water using mild conditions.[11] The styrene and isobutyl groups are expected to provide improved mechanical stability to the resultant membranes as they are unresponsive and hydrophobic and thus will reduce swelling.

The aim of this Chapter is to demonstrate the potential of APS with copolymers as a sustainable alternative to conventional NIPS. For the first time copolymers will be used in an APS approach. The behavior of the copolymers will be systemically evaluated using different acid concentrations, acid types, and additives in the polymer casting solution as well as the coagulation bath. By tuning these variables the phase inversion kinetics will be controlled which in turn will allow us to prepare different types of membranes, from microfiltration type, to nanofiltration type membranes, with improved mechanical properties.

3.2 Experimental section

3.2.1 Materials

Poly(styrene-alt-maleic acid) sodium salt solution 13% (M_w 350,000, PSaMA), poly(styrene-co-maleic acid) partial isobutyl ester (M_w 65000 g·mol^{-1}, PScMA), polyethylene glycol (M_w 200 g·mol^{-1}, PEG 200; M_w 400 g·mol^{-1}, PEG 400; M_w 600 g·mol^{-1}, PEG 600; M_w 1500 g·mol^{-1}, PEG 1500; M_w 2000 g·mol^{-1}, PEG 2000), polyethyleneimine, branched (M_n 600 g·mol^{-1}, PEI 600) were purchased from Sigma Aldrich. N-(3-Dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC), N-Hydroxysuccinimide (NHS), atenolol, atrazine, bezafibrate, bisphenol A, bromothymol blue, naproxen, phenolphthalein, sulphamethoxazole, Oil Red EGN, n-hexadecane, magnesium sulfate, magnesium chloride, sodium sulfate, sodium dodecyl sulfate (SDS), sodium hydroxide, glacial acetic acid, sodium phosphate monobasic dihydrate, phosphoric acid 85%, and hydrochloric acid 37% were bought from Sigma Aldrich. Ethanol 100% technical grade, was bought from Boom B.V. N-hexane 99+% was purchased from Acros organics. Sodium chloride (Sanal® P) was received from AkzoNobel. Deionized water (DI, 1.0 µS·cm^{-1}) was used for the preparation of coagulation baths, Milli-Q water (Millipore, 0.6 µS·cm^{-1}) was used to prepare solutions. The PSaMA solution was dried for 16 hours at 100 °C to obtain the solid polymer which was used without further purification. All other chemicals were used as received.

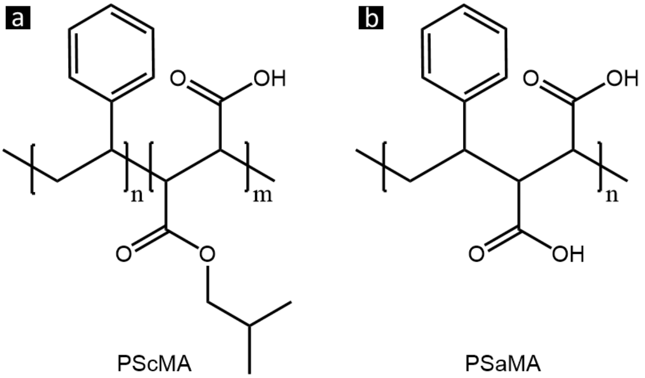


Figure 3.2. Chemical structures of (a) poly(styrene-co-maleic acid) partial isobutyl ester (PScMA), and (b) poly(styrene-alt-maleic acid) (PSaMA).

3.2.2 Membrane preparation

The polymer casting solutions were prepared by dissolving the polymer and additives in water, a typical solution consists of 18 g PSaMA (20% w/v), 36 mL acetic acid (40% v/v) and 36 mL H_2O (40% v/v). The solutions were stirred until dissolved, followed by filtration through a Bekaert 25 µm Bekipor ST25 AL 3 steel filter. The solutions were left for at least 24 hours to allow air bubbles to leave the solution. The polymer solutions were cast onto a glass substrate using a steel casting knife with a 0.3 mm gap height. The films were then submerged in an acidic coagulation bath containing either HCl, H_3PO_4, acetic acid, formic acid, malonic acid, NaCl or a combination thereof which induces the phase separation. After 5 minutes the formed porous film was transferred to a bath with 0.1 M HCl to wash salt and/or acids from the film. After a washing step of at least 30 minutes the membranes were washed twice more in 0.1 M HCl. After the washing procedure, the membranes were crosslinked using EDC, NHS, and PEI. The crosslinker concentrations were based on the estimated amount of carboxylic acid groups per surface area of the membrane calculated using Equation 3.1:

$$C = \frac{h \cdot A \cdot w \cdot a}{M_w} \tag{3.1}$$

where C is the number of acid groups, h the casting height of the membrane, A the surface area of the membrane, w the fraction of polymer in the casting solution, a the amount of acid group per polymer chain, and M_w the molecular weight of the polymer. A ratio of 1 : 1 : 0.4 : 0.33 of carboxylic acid groups : EDC : NHS : PEI was used in the crosslinking reactions. The pH of the crosslinking mixture was set to approximately 5 using HCl. After crosslinking the membranes were washed twice, for 30 minutes each, in DI water and then stored in DI water.

3.2.3 Membrane performance tests

The performance of the membranes was studied using dead-end filtration cells with a pressurized vessel supplying the feed water. The free standing membrane (38 mm^2 permeable surface area) was supported by a polyphenylene sulfide nonwoven fabric and pure water permeability and its ability to reject oil droplets, salts, PEG, or micropollutants was studied. Pure water permeability was measured by allowing the membrane to compact for one hour after which the average permeability was recorded. Oil retention was measured using a stock oil in water emulsion, made by dissolving 0.2 g of oil red EGN in 6 g hexadecane, any undissolved solids were filtered off.[12] Then a 0.2% w/w oil-in-water emulsion was prepared by the addition of 0.463 g·L^{-1} SDS which was mixed for 15 minutes at 14000 rounds per minute. For oil filtration tests, the stock solution was diluted 20 times using 0.463 g·L^{-1} SDS. The diluted emulsion was stirred continuously during the measurement. The oil droplet retention was measured at 0.5 bar. The first 10 minutes of permeate was discarded after which samples were collected. Absorbance of the feed, retentate and permeate was measured using UV-vis spectroscopy at λ = 523 nm. The retention was calculated using the following equation:

$$R = \left(1 - \frac{C_p}{\frac{C_f\ +\ C_r}{2}}\right) \cdot 100\% \tag{3.2}$$

where R is the retention and C_p, C_f, and C_r is the absorbance of the permeate, feed and retentate. Salt retention was measured at 4 bar of applied pressure using a 5 mM salt solution ($MgSO_4$, $MgCl_2$, Na_2SO_4, or NaCl). The feed solution was stirred above the membrane and the conductivity of the feed, retentate, and permeate was measured. The retention was calculated using Equation 3.2 where C_p, C_f, and C_r is the conductivity in the permeate, feed and retentate. The molecular weight cut-off of the membranes was measured using a 1 g·L^{-1} poly ethylene glycol solution with the following PEG molecular weights: 200, 400, 600, 1500, 2000 g·mol^{-1}. Samples were analyzed via gel permeation chromatography (Agilent 1200/1260 Infinity GPC/SEC series, Polymer Standards Service data center and column compartment) using Milli-Q eluent containing 50 mg·L^{-1} NaN_3, at 1 mL·min^{-1}, through two Polymer Standards Service Suprema 8x300 mm columns in series: 1000 Å, 10 μm followed by 30 Å, 10 μm. Concentrations were calculated via refractive index detection. Using Equation 3.2, the retention for the different PEG molecules was calculated, where R is the retention and C_p, C_f, and C_r is the concentration in the permeate, feed and retentate. Micropollutant retention was measured at 3 bar of applied pressure using a 3 $mg \cdot L^{-1}$ solution of atenolol, atrazine, bezafibrate, bisphenol A, bromothymol blue, naproxen, phenolphthalein and sulfamethoxazole. After two days of stirring the solution pH was set to 5.8. To account for absorption of the micropollutants the samples were taken after 24 hours of continuous permeation at which point a steady state between absorption and desorption can be assumed.[13] The samples were analyzed using ultra-high performance liquid chromatography (Dionex Ultimate 3000, water/acetonitrile gradient, 0.1% phosphoric acid, 0.8 $mL \cdot min^{-1}$) through a Thermo Scientific Acclaim RSLC 120 C18 column (2.2 µm, 2.1x100 mm), micropollutant concentrations were determined via UV/Vis detection at 225 nm, bromothymol blue at 430 nm. Micropollutant retention was determined using Equation 3.2.

3.2.4 Scanning electron microscopy (SEM)

The crosslinked membranes were washed twice in ethanol and twice in n-hexane for 30 minutes to remove water from the membrane and to prevent pore collapse during drying. Non-crosslinked films were only washed in n-hexane as PSaMA dissolves in ethanol. After drying of the films, they were submerged in liquid nitrogen and fractured, mounted on a sample holder. The samples were further dried in a vacuum oven at 30 ^{o}C for at least 4 hours, after which using a Quorum Q150T ES 10 nm chromium was sputtered onto the samples. Images were taken with secondary electron imaging (SEI) using Jeol JSM-6010LA, and JSM-7610F scanning electron microscopes.

3.2.5 Nuclear magnetic resonance imaging (NMR)

0.1 g of PScMA was dissolved in 0.5 mL deuterated dimethyl sulfoxide and ^{1}H NMR spectra were recorded using a Bruker 400 MHz NMR spectrometer. Integrals of the intensity of characteristic peaks for each monomer were used to calculate an approximate average monomer distribution.

3.2.6 Dynamic viscosity measurements

The dynamic viscosity was measured using a HAAKE Viscotester 550 Rotational Viscometer with a SV-DIN rotor and cup, rotating at shear rates from 2.6 to 258 s^{-1} at 20 ^{o}C.

3.3 Results and discussion

3.3.1 Selection of polyelectrolyte system

For APS with acidic polyelectrolytes, ideally a weak polyacid is used that precipitates under mild acidic conditions. As previously stated copolymers are expected to provide a versatile platform for APS since a responsive monomer can be combined with a hydrophobic monomer. Polystyrene-co-maleic acid partial isobutyl ester (PScMA) is one such polymer (see Figure 3.2a in the experimental section for chemical structure of PScMA). In this random copolymer the maleic acid monomers provide the pH-responsive behavior required for APS, while the styrene and partial isobutyl ester groups make the polymer more hydrophobic. This was hypothesized to result in precipitation at mild pH conditions. Using ^{1}H NMR, the monomer distribution was estimated to be approximately 1.5 : 1 mole ratio of styrene : maleic acid, with approximately half the acid groups having an isobutyl ester (see Figure S3.1 for further details). Dissolution of the polymer proved to be difficult with strong alkaline conditions of pH 14 required. Upon precipitation in the mildly acidic conditions of pH 3, no stable polymer film was formed with the film fracturing into small pieces indicating inhomogeneous phase separation. This is not entirely surprising as the monomer distribution of PScMA is not homogeneous and the isobutyl ester is partially hydrolyzed in the strong alkaline conditions of the polymer casting solution. This inhomogeneous monomer distribution leads to the formation of hydrophilic and hydrophobic domains in the polymer chain. Supramolecular interactions between these domains most likely causes the film to fall apart. To overcome these issues, the alternating polystyrene-alt-maleic copolymer acid (PSaMA) was selected as a suitable alternative since it has a 1:1 ratio of hydrophilic and hydrophobic monomers, contains no hydrolysable ester groups, and has a significantly higher molecular weight (see Figure 3.2b in experimental section for the chemical structure of PSaMA). As PSaMA has less hydrophobic groups the polymer readily dissolves in water. Slightly more acidic conditions are required to induce precipitation of PSaMA compared to PScMA. As expected stable and dense films were formed by precipitating PSaMA solutions at pH 1, as shown by the SEM image presented in Figure 3.3a. The polymer concentration and the coagulation bath pH were varied systematically but no porous structures were obtained. In conventional NIPS it is not uncommon to add low molecular weight hydrophilic polymers such as short-chain polyethylene glycol (PEG) molecules into the polymer casting solution to improve the morphology.[14-16] In this APS system, a similar effect is observed as porous films are formed when PEG is mixed into the polymer casting solution, see Figure 3.3b. However, the largely macrovoid structure is mechanically weak and a large number of pinhole defects were observed in top layer, Figure 3.3c, making these films unsuitable to be used for membrane applications.

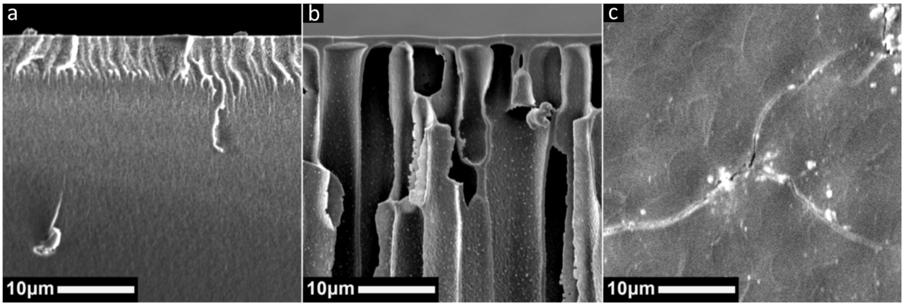


Figure 3.3. SEM images of (a) cross section of a film made by precipitating 16.6% w/v PSaMA at pH 1, a completely dense film is observed. (b and c) cross section and top layer of a film made by precipitating 16.6% w/v PSaMA with 25% v/v PEG 200 in pH 0.5, a thin dense top layer is observed which is supported by marcovoids. In the top layer several defects can be observed which are most likely formed during drying of the film.

Instead of adding short-chain PEG molecules, it is also possible to control precipitation kinetics by changing the polymer casting solution composition so that the solution is moved closer to the precipitation point. In conventional NIPS this can be achieved by adding non-solvent to the polymer solution which in this APS system means the addition of acid. For this, weak acids were deemed to be more suitable than strong acids as they can be easily mixed into the solution while strong acids will induce local precipitation when added, making it more difficult to obtain homogenous polymer solutions. Acetic acid was chosen as it is a green solvent which can be produced in biorefineries and is easily recovered from waste water streams.[17-18] Acetic acid is also an ideal acid for this system as its pK_a value is 4.75, this means that even at high concentrations acetic acid does not lower the solution pH below pH 2. Therefore, acetic acid brings the polymer solution close to the point of phase separation without actually causing precipitation of the polymer. However, when 20% v/v of acetic acid was added to a 20% w/v PSaMA solution, a gel-like phase was formed. It is interesting that when a higher concentration of acetic acid is used a translucent solution is formed and further increases in acetic acid concentration result in a decrease in solution viscosity. Dynamic viscosity measurements reveal that a 30% v/v acetic acid, 20% w/v PSaMA solution has a viscosity approximately 20-fold higher than a 20% w/v PSaMA solution without acetic acid, as depicted in Figure 3.4. When the acetic acid concentration is increased further to 40% v/v, the solution viscosity is approximately halved. Further increasing the acetic acid to 50% v/v further lowers the viscosity further but the effects are not as pronounced as the difference between the solutions with 30% to 40% v/v acetic acid.

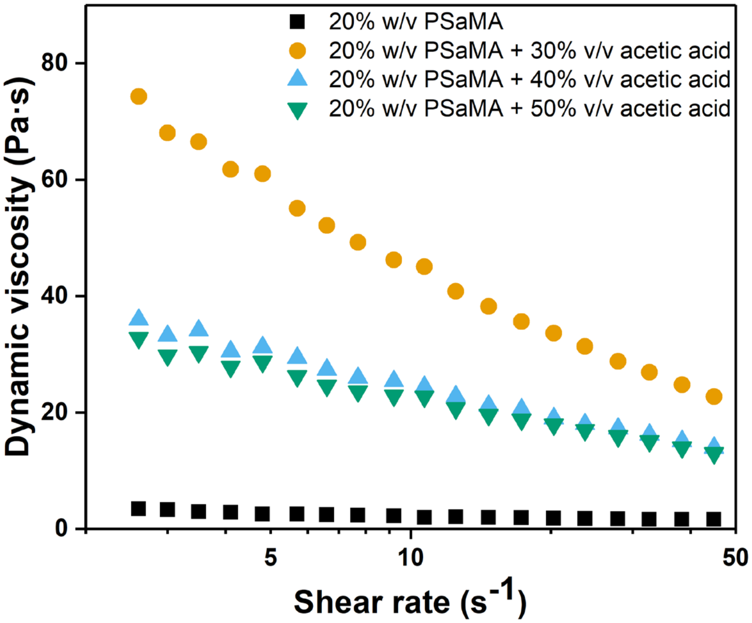


Figure 3.4. Dynamic viscosity for 20% w/v PSaMA solutions with different concentrations of acetic acid, for different shear rates at 20 °C. Data was taken from a single measurement.

The viscosity behavior presented in Figure 3.4 shows that acetic acid behaves as a non-solvent at low concentrations and conversely as a solvent at higher concentrations for PSaMA. To explain this behavior, it is hypothesized that the decrease in solution pH by the addition of acetic acid causes partial protonation of the acid groups on the PSaMA. These protonated acid groups can then form interpolymer hydrogen bonding pairs which causes complexation/gelation of the polymer. Because acetic acid is a weak acid it mostly exists in its associated form and therefore it can also form hydrogen bonding pairs with the protonated acid groups of the polymer. At higher concentrations, acetic acid disrupts the interpolymer hydrogen bonds through competitive binding which in turn prevents the formation of a polymer complex and thus results in a solution. Further increases in the acetic acid concentration decreases the interpolymer hydrogen bonding and this results in the observed decrease in solution viscosity. Through its acidity acetic acid is a non-solvent for PSaMA, but at a higher concentrations acetic acid aids in the solvation of PSaMA through favorable hydrogen bonding interactions. However, it is expected that at even higher acetic acid concentrations the amount of water in the solution will be too low to dissolve PSaMA. Together this means that the acetic acid concentration is an additional parameter to control the phase inversion kinetics. In conventional NIPS, an approach to increase the porosity of the membrane is to add solvent to the coagulation bath to delay polymer demixing.[3] For this APS system, the same effect can be achieved by adding acetic acid to the coagulation bath, which is discussed in the following section.

3.3.2 Formation of porous membranes

When the 20% w/v PSaMA solution with 40% v/v acetic acid is submerged in the coagulation bath the change in environmental pH causes protonation of the acid groups. This results in a decrease of the hydrophilicity of PSaMA as it loses its charge while at the same time the hydrogen bonding capacity is increased. This makes it thermodynamically unfavorable for PSaMA to remain in solution and thus it precipitates. By the addition of acetic acid in the coagulation bath, interpolymer hydrogen bonding is suppressed and therefore acetic acid can be used to tune the solvent quality for both the polymer solution and the coagulation bath. Upon addition of 2M acetic acid to the coagulation bath a slow and delayed demixing is observed (see Supporting Information for a short movie of the phase separation process), which results in the formation symmetric porous films, see Figure 3.5a,b,c. From SEM top-section image analysis the pore size is on average 106 ± 37 nm indicating it is a microfiltration membrane, see Figure S3.2a for pore size distribution data. Besides acetic acid 0.1M NaCl was also used in the coagulation bath as it helped to provide stable films. It is expected that salt can affect the phase separation as it is known that salt concentration can have a strong effect on polyelectrolyte conformation.[19] However, this was not further investigated. To ensure PSaMA does not re-dissolve during the membrane performance tests, the membranes were crosslinked in water using a small amount of low molecular weight branched PEI, EDC and NHS, which links the amine groups of PEI to the carboxylic acid groups of PSaMA.[11] Branched PEI was chosen as the crosslinker because it has multiple primary amine groups and it is also much safer to use than smaller molecules with multiple primary amine groups. After crosslinking, besides the chemical stability also the mechanical stability of the porous membranes was visibly improved. Pure water permeability measurements show a permeability of approximately 6500 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$ which is in line with commercial microfiltration membranes.[1-2] To study membrane retention an oil-in-water emulsion stabilized by SDS, was prepared with an average droplet size of 3–5 µm.[12] Due to the dead end filtration setup, the membrane rapidly fouls resulting in a significant drop in water permeability. Therefore, retention was measured during the first 15 minutes of permeation to measure the actual performance of the membrane and not that of the fouling layer that forms. It is expected the retention will remain stable or even improve over time as an additional oil "cake" layer is formed on top of the membrane. The membranes were found to retain over 98% of the oil demonstrating their function as a microfiltration membrane.

Further investigations on the effect of acetic acid concentration in the coagulation bath revealed that the at 2.5 M and 3 M acetic acid obtained membrane structures were similar. However when an acetic acid concentration of 1.5 M or lower was used in the coagulation bath the films were mechanically unstable and could not be removed from the casting substrate intact, indicating a much weaker structure. As the change in pH is the main driving force to precipitate PSaMA the pH of the coagulation bath was systemically investigated. With only a slight increase of the HCl concentration from 0.04 M to 0.05 M, a significant reduction in membrane pore size and pure water permeability was observed (Figure 3.5c,d). Analysis of the SEM images show that the average pore size is 31 ± 13 nm, indicating that it is an open ultrafiltration membrane, see Figure S3.2b for pore size distribution data. Further increases in the HCl concentration in the coagulation bath resulted in the formation of a dense top layer with macrovoids and pinhole defects. When a HCl concentration of 0.03 M or lower was used in the coagulation bath, highly porous symmetric structures were formed with high permeabilities however, these membranes lacked mechanical stability. Here, a greater than 50% drop in permeability was observed within one hour of filtration indicating significant structural collapse. This shows the sensitivity as well as the versatility of the APS process. By controlling the acid concentration different open membrane structures can be prepared in a simple way without the use of harsh chemicals.

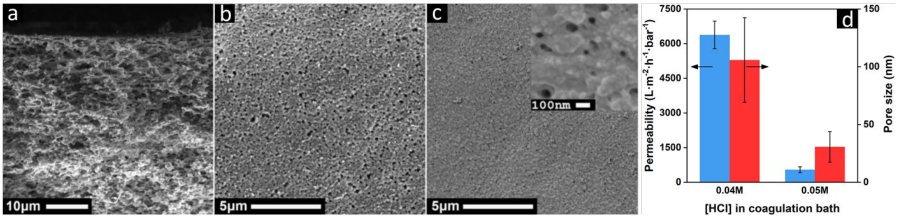
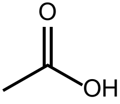
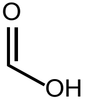
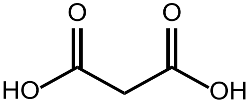
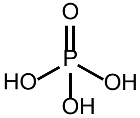


Figure 3.5 (a and b) SEM images of the cross section and top layer of a membrane made by precipitating a 20% w/v PSaMA solution with 40% v/v acetic acid, in a coagulation bath with 2 M acetic acid, 0.1 M NaCl, and 0.04 M HCl. (c) SEM images of the top layer of a membrane made by precipitating a 20% w/v PSaMA solution with 40% v/v acetic acid, in a coagulation bath with 2 M acetic acid, 0.1 M NaCl, and 0.05 M HCl. (d) Pure water permeability and average pore size of the membranes shown in a–c. Permeability was measured in a dead-end filtration setup at 1 bar, the data shown is the average of at least 3 different membranes with the error bars showing the sample standard deviation. The average pore size is determined using imageJ software, the error bars display the population standard deviation, see Figure S3.2 for pore size distribution.

3.3.3 Formation of membranes with dense top layers

Acetic acid was chosen for the coagulation bath as it is also used in the polymer casting solution, but there are other weak acids that could be used. To investigate the effect of the type of acid used in the coagulation bath on membrane formation, several other weak acids with different pK_a values than acetic acid were investigated, shown in Table 3.1.

Table 3.1. Chemical structure and pKa values of the selected acids

	Acetic acid	Formic acid	Malonic acid	Phosphoric acid
Chemical Structure				
pK_a values[20]	4.76	3.75	5.7, 2.8	12.32, 7.09, 2.15

Formic acid, malonic acid, and phosphoric acid were chosen as these acids can all form hydrogen bonding pairs with protonated carboxylic acid groups in a similar fashion to acetic acid. Formic acid has a similar structure to acetic acid while malonic acid and phosphoric acid are diprotic and triprotic acids respectively, and so can potentially form hydrogen bonding pairs with multiple protonated carboxylic acid groups. Moreover, due to the lower pK_a values of these acids, additional HCl in the coagulation bath was not needed in order to precipitate PSaMA. For all acids, a 2 M concentration was used which resulted in asymmetric structures with dense top layers and macrovoid defects in the support structure (Figure 3.6a-f). The high viscosity of the solution, as seen in Figure 3.4, was expected to suppress macrovoid formation yet the support structure is dominated by them. It is therefore expected that a dense selective layer is formed which by impeding the diffusion of acid slows down the phase inversion and causing the formation of macro voids. This is confirmed by the observation that for all three acids, the initial onset of the phase separation is near instant instead of the delayed onset that was observed when acetic acid was used in the coagulation bath, yet it takes quite a while before the separation is complete (see Supporting Information for a short movie of the phase separation process).

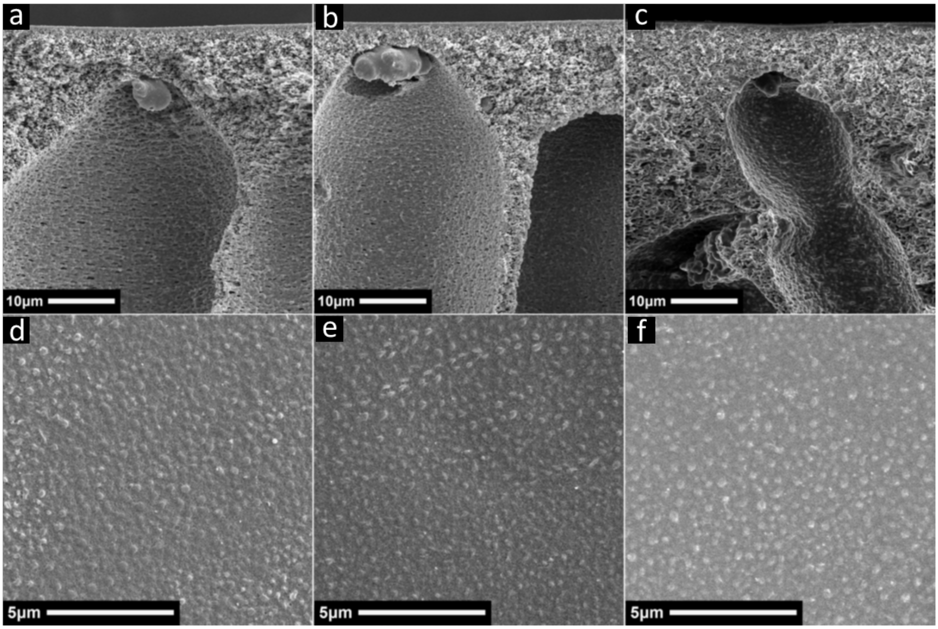


Figure 3.6. SEM images of the cross section and the corresponding top surfaces of membranes made with 2 M formic (a,d), 2 M malonic(b,e), or 2 M phosphoric acid (c,f) in the coagulation bath using 20% w/v PSaMA with 40% v/v acetic acid as casting solution. The structures appear to be similar regardless of the acid that is used in the coagulation bath.

The membranes prepared with phosphoric acid in the coagulation bath were studied in more detail by changing the coagulation bath acid concentration. It was observed that at all phosphoric acid concentrations a dense top layer without visible pores is formed (Figure 3.7d,e,f) and when a concentration lower than 2 M is used the overall structures are similar (Figure 3.7a and Figure S3.3). However, when a phosphoric acid concentration higher than 2 M is used in the coagulation bath significant changes in the support structure are observed. At 2.5 M, as seen in Figure 3.7b, the macrovoid defects are almost completely suppressed and at 3 M the thickness of the top layer increases from approximately 300 nm to approximately 10 µm (Figure 3.7c). A possible explanation for this behavior is that at 2.5 M the phosphoric acid concentration is high enough to diffuse through the dense selective layer fast enough that in combination with viscosity of the solution (Figure 3.4) marcovoids are suppressed. At 3 M concentration the ability of phosphoric acid to form hydrogen bonding pairs with two different carboxylic acid groups could possibly cause severe densification of the membrane structure which therefore creates a very thick dense layer. Further research is required to confirm this and to determine whether this effect also applies to other weak acids like malonic acid that can also from hydrogen bonding pairs with multiple carboxylic acid groups. For the membranes prepared with 0.5–2.5 M phosphoric acid in the coagulation bath the pure water permeability and $MgSO_4$ retention were measured. All membranes have similar performance with high $MgSO_4$ retentions (>94%) and relatively low water permeability (0.35 ± 0.1 $L{\cdot}m^{-2}{\cdot}h^{-1}{\cdot}bar^{-1}$). Based on the $MgSO_4$ retention data, the membranes can be compared to nanofiltration membranes prepared by classical processes such as layer-by-layer deposition of polyelectrolytes or interfacial polymerization on top of porous NIPS-based polymeric membranes.[21-22] The advantage of this APS system compared to layer-by-layer deposition or interfacial polymerization is that the APS membranes are prepared in a single step followed by submersion in a crosslinking solution. This approach can be easily configured to a roll-to-roll process that will most likely result a significant time reduction to produce these APS membranes. Although the water permeability is currently low, APS is currently still in its infancy and there remain plenty of opportunities for optimization, for example in the polymer solution, the coagulation bath or in the selection of polymer. The simplicity in preparation and the possibility to prepare open porous microfiltration and ultrafiltration membranes as well as nanofiltration membranes with dense top layers by just changing the type of acid and the acid concentration shows again that APS is a promising sustainable alternative to the traditional NIPS process.

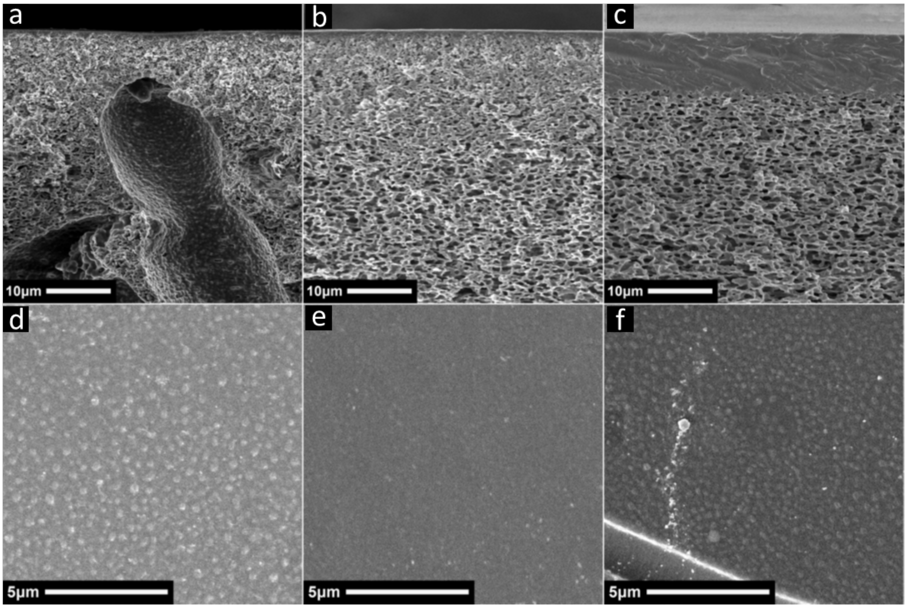


Figure 3.7. SEM images of the cross section and the corresponding top surfaces of membranes made with 2 M (a,d), 2.5 M (b,e), or 3 M phosphoric acid (c,f) in the coagulation bath using 20% w/v PSaMA with 40% v/v acetic acid as casting solution. Increasing the phosphoric acid concentration form 2 M to 2.5 M results in a suppression of macrovoids. Further increasing the concentration to 3 M increases the thickness of top layer from approximately 300 nm to approximately 10 µm, which cracks upon drying.

3.3.4 Detailed dense membrane separation performance

The membranes prepared with 2 M phosphoric acid in the coagulation bath were studied in greater detail. In Figure 3.8a, retentions for different monovalent and divalent salts are compared at 4 bar of applied pressure. In addition the retention of NaCl was measured at 10, 15 and 20 bar. As expected, the retention is lowest for NaCl which can be attributed to its small size and monovalency. The higher retention for $MgCl_2$ compared to NaCl is also expected as Mg^{2+} is divalent and has a larger hydrated diameter than Na^+. The difference between $MgCl_2$ and Na_2SO_4 can be attributed to Donnan exclusion as the negative charge of PSaMA gives the membrane an overall net negative charge.[23] At higher pressures, namely 10, 15 and 20 bar, the NaCl retention increases and permeability remains constant indicating that the solution-diffusion mechanism applies and the separation is not based on pore size exclusion.[1-2] The membranes show excellent stability under high transmembrane pressures as the water permeability remained stable at 0.32 ± 0.04

$L\cdot m^{-2}\cdot h^{-1}\cdot bar^{-1}$ over the course of five days under pressures ranging from 10 to 20 bar; showing that no membrane densification occurs. In addition, after the membrane performance at 20 bar transmembrane pressure was measured, it was measured again at 10 bar transmembrane pressure which showed the same performance as before. Molecular weight cut-off (MWCO) measurements were performed to assess the capability of this membrane to retain small organic molecules. The retention of differently sized uncharged polyethylene glycol (PEG) molecules was analyzed and PEG molecules with a molecular weight of 232 ± 27 Dalton or larger were retained ≥90% as shown in Figure S3.4. MWCO measurements using PEG molecules is a model system and therefore additional experiments were performed where the retention of a mixture of charged and uncharged small organic molecules was studied, see Figure 3.8b. These so-called micropollutant molecules were chosen for their range of low molecular weights (215–624 $g\cdot mol^{-1}$) and different charges which provides a better representation of the membrane performance under more realistic conditions.[13] An average retention of 92% shows that these membranes are capable of removing a diverse range of micropollutants from water and this performance is on par or even better compared to what is obtained with conventional membranes in the literature.[24] The retention for the largest micropollutant, bromothymol blue, is more than 99.9%, which importantly shows that the top separation layer of this membrane is defect free. Differences in retention of the different micropollutants can be attributed to their difference in charge, size, geometry and affinity to the membrane material.[24]

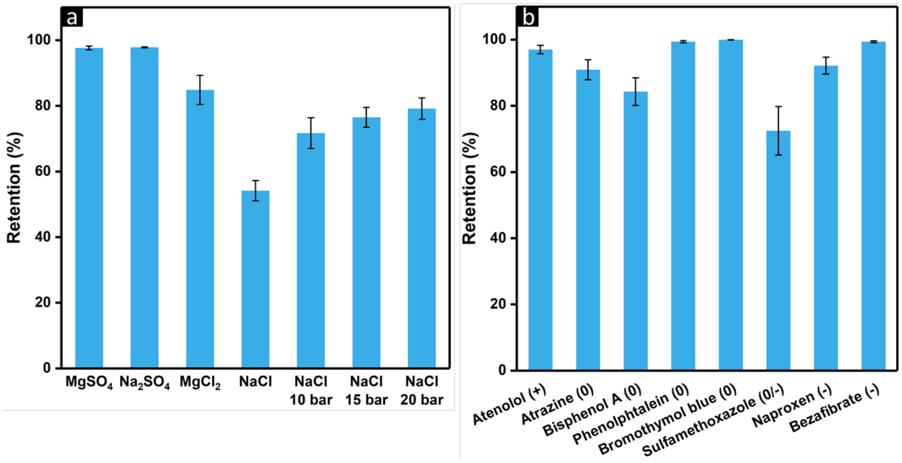


Figure 3.8. Retention of salt (a) and micropollutants (b) by membranes made with 2 M phosphoric acid in the coagulation bath using 20% w/v PSaMA with 40% v/v acetic acid as casting solution. All measurement were performed using dead-end filtration cells using either 4, 10, 15, or 20 bars of pressure for the salt retention and 3 bars pressure for the micropollutant retention. The pH of the micropollutant mix was set at 5.8, in this regime the micropollutants either have a positive (+), negative (–), or no charge (0), with sulfamethoxazole being partially charged. Data shown is the average of at least 3 different membranes with the error bars showing the sample standard deviation.

3.4 Conclusion

A simple aqueous phase separation (APS) approach based on a pH switch with responsive copolymers has been used to prepare a wide range of mechanically stable membranes without using unsustainable and toxic organic solvents like NMP and DMF. Similar to the classical NIPS process, the phase inversion kinetics can be controlled by changing the composition of the polymer casting solution and the coagulation bath. By controlling the pH as well as the type and concentration of acid used in the casting solution and coagulation bath, microfiltration, ultrafiltration, and nanofiltration membranes with dense top layers have been successfully prepared. This clearly showcases the simplicity and versatility of the APS approach. The open porous membranes can be used to effectively treat oily water streams, >98% rejection, while the membranes with thin dense separation layers show excellent retentions towards small notoriously difficult to remove micropollutants with an average rejection >92%. Besides possessing excellent retention performance, the nanofiltration type membranes have significantly improved mechanical stability, in comparison to similar materials in Chapter 2,[10] with consistent performance up to 20 bar of applied pressure. Here, the carboxylic acid groups within the PSaMA copolymer are easily crosslinked using mild conditions in water, which provides greater mechanical stability and also chemical stability for the membranes in non-acidic media while maintaining an overall green and sustainable fabrication process. This research shows that aqueous phase separation can be used to prepare different types of highly performing membranes and therefore has the potential to become a viable alternative to the classical NIPS process.

3.5 Acknowledgements

The authors acknowledge funding support from the "Vemieuwingsimpuls" programme through project VIDI 723.015.003 (financed by the Netherlands Organization for Scientific Research, NWO), and from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (ERC StG 714744 SAMBA).

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3.7 Supporting Information

3.7.1 NMR

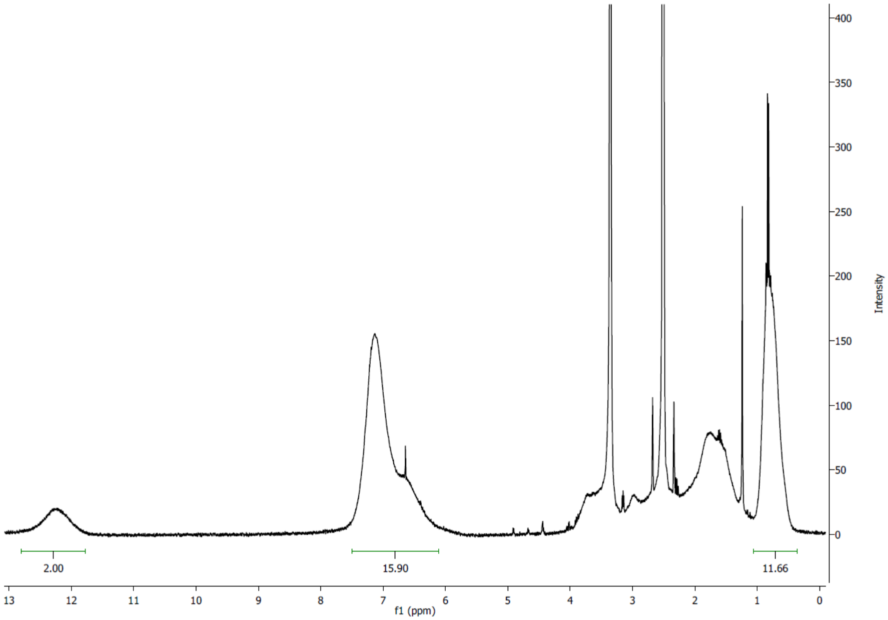


Figure S3.1. ^{1}H NMR (400Hz) of polystyrene-co-maleic acid partially isobutyl ester (PScMA). Integrals of the intensity of maleic acid (2H) at 12 ppm, styrene (5H) at 7ppm, and isobutyl ester (6H) at 0.7 ppm were used to calculate an approximate average monomer distribution. Dividing intensity by the number of protons per group gives an approximate ratio of 1:3:1 of Maleic acid:styrene:isobutylated maleic acid.

3.7.2 Pore size distribution

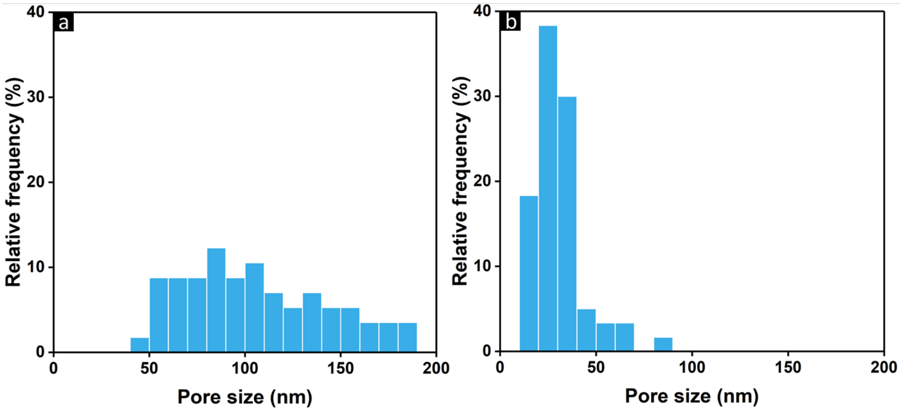


Figure S3.2. Pore size distribution of membranes made by precipitating a 20% w/v PSaMA solution with 40% v/v acetic acid, in a coagulation bath with (a): 2 M acetic acid, 0.1 M NaCl, and 0.04 M HCl, (b): 2 M acetic acid, 0.1 M NaCl, and 0.05 M HCl.

3.7.3 SEM images

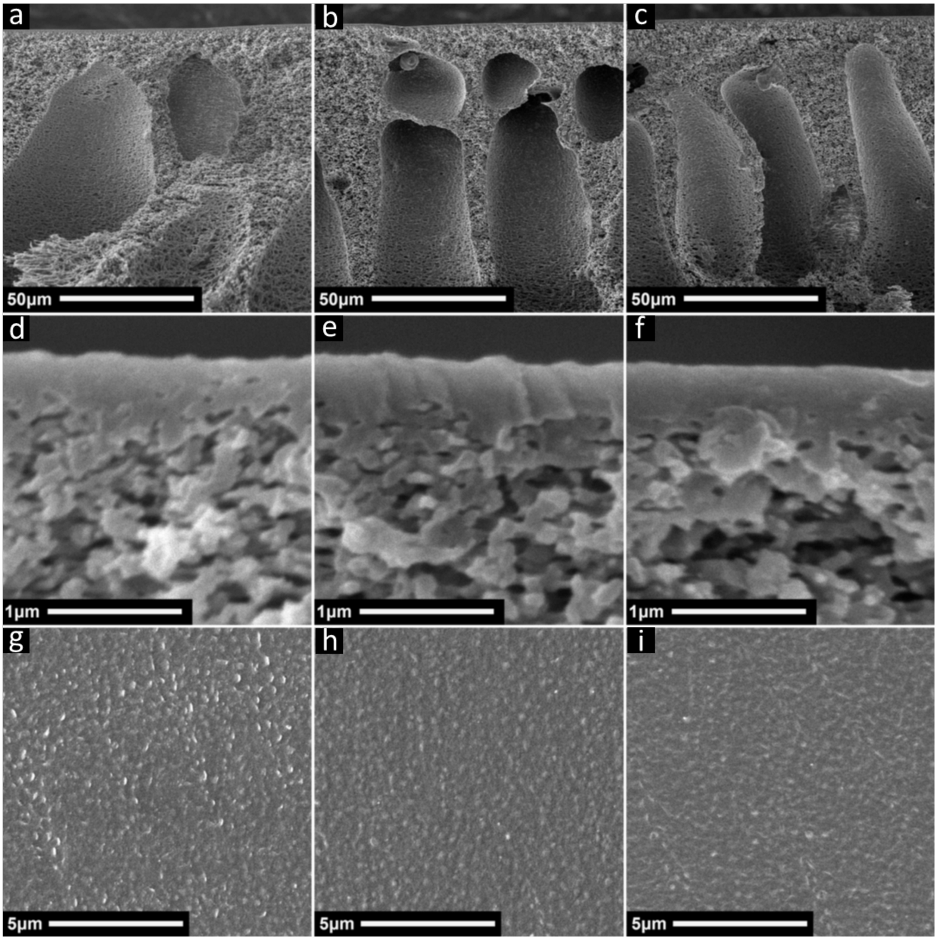


Figure S3.3. SEM images of the cross sections and the corresponding top surfaces of membranes made with 0.5 M phosphoric (a,d,g), 1 M phosphoric (b,e,h), or 1.5 M phosphoric acid (c,f,i) in the coagulation bath using 20% w/v PSaMA with 40% v/v acetic acid as casting solution. Besides the slightly differently shaped macrovoids of the membrane prepared in 0.5 M phosphoric acid, the structures appear to be similar regardless of the acid concentration used in the coagulation bath.

3.7.4 Molecular weight cut-off

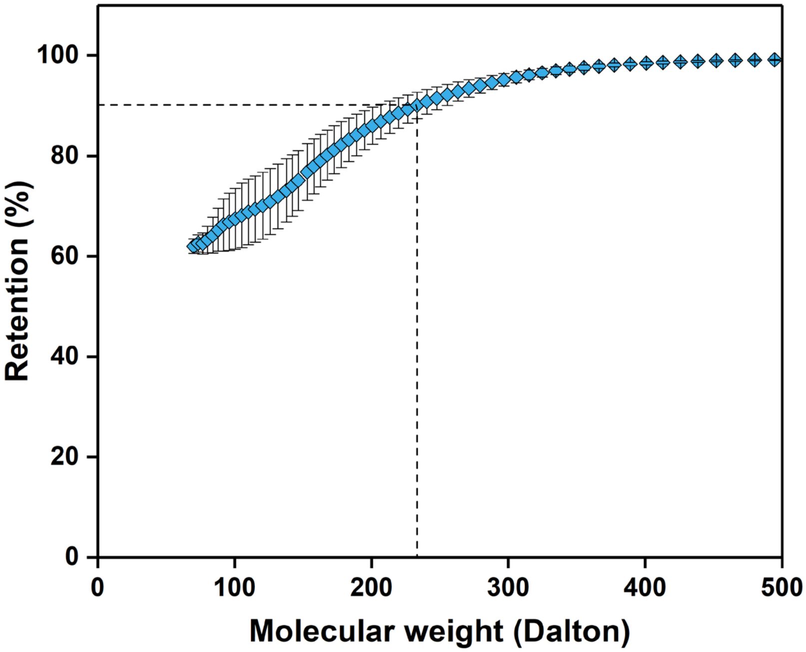


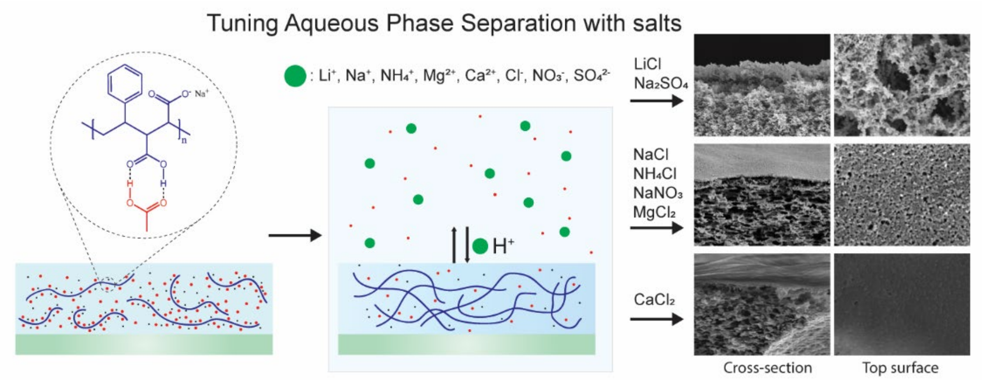
Figure S3.4. Retention of PEG chains based on their molecular weight of membranes prepared with a 20% w/v PSaMA solution with 40% v/v acetic acid in a coagulation bath with 2 M phosphoric acid. The molecular weight cut-off is determined at which molecular weight ≥90% of the PEG is retained, as indicated by the dashed line. The data shown is the average of at least 3 different membranes with the error bars showing the sample standard deviation.

3.7.5 Movie

Video S3.1. Available at https://pubs.acs.org/doi/10.1021/acsapm.0c00119. The movie is sped up 10 times, indicated by the timer (hh:mm:ss). A 300 µm thin film of 20% w/v PSaMA with 40% v/v acetic acid, on the left precipitates in a 2M acetic acid solution with 0.1M NaCl and 0.04M HCl, on the right in 2M phosphoric acid. The precipitation of 20% w/v PSaMA with 40% v/v acetic acid in 2 M formic and malonic acid is not recorded but is nearly identical to the precipitation in 2 M phosphoric acid.

Chapter 4

Ion specific effects on aqueous phase separation of responsive copolymers for sustainable membranes



This chapter has been published as:

Ion specific effects on aqueous phase separation of responsive copolymers for sustainable membranes. Nielen, W. M.; Willott, J. D.; Esguerra, Z. M.; de Vos, W. M. Journal of Colloid and Interface Science, 2020, 576, 186-194.

Abstract

Hypothesis

Salt identity and concentration affects the preparation of membranes via the aqueous phase separation approach. The phase inversion process and morphology of the resultant membranes is expected to vary as function of these two parameters.

Experiments

Polymeric membranes based on the responsive copolymer polystyrene-alt-maleic acid (PSaMA) are prepared using the aqueous phase separation approach and the influence of salt identity (Na_2SO_4, LiCl, NaCl, $NaNO_3$, NH_4Cl, $MgCl_2$, $CaCl_2$) and concentration on resultant membrane morphology and separation performance is investigated. Complementary stability experiments of PSaMA solutions are performed to help understand the intricate aqueous phase separation process.

Findings

Specific ion effects are observed during membrane formation by the aqueous phase separation approach. At equal ionic strengths, Na_2SO_4 and LiCl lead to the formation of more open membrane structures compared to NaCl, $NaNO_3$, NH_4Cl, and $MgCl_2$, while $CaCl_2$ results in membranes with dense top layers. These ion-specific effects are likely caused by a combination of ion mobility and interaction potential between the ion and the polyelectrolyte. Overall, in this Chapter it becomes clear that salt identity and concentration are key parameters in the APS process, and they can be optimised to tune membrane structure from open microfiltration to dense nanofiltration membranes.

4.1 Introduction

In a world that strives for improved sustainability, membranes play an important role in optimising separation processes because they are often more energy efficient than conventional techniques like distillation or extraction.[1-2] A lot of current research is focused on improving membrane performance, yet a very important issue that is often overlooked is the need for sustainability within the membrane fabrication process.[3] The production of polymeric membranes is most commonly based on the non-solvent induced phase separation (NIPS) method, which uses large quantities of reprotoxic organic solvents such as *N*-methyl pyrrolidinone (NMP) and dimethylformamide (DMF).[4] Finding suitable alternatives to these solvents is becoming a pressing issue as the European Union has restricted the use of NMP as of May 2020.[5] Indeed in recent years, alternative membrane fabrication processes that use more benign solvents have been proposed; including ones that use ethyl lactate, ionic liquids, supercritical CO_2 and even water.[6-11] The complete replacement of toxic solvents with greener alternatives for membrane production is still in its infancy, however in several cases, membranes prepared using these greener solvents have achieved performances comparable to those produced by the classical NIPS approach.

Among these alternative methods, Aqueous Phase Separation (APS) stands out because of its versatility and its lack of reliance on organic solvents.[11-14] As of now there exist three different APS approaches: 1. Where a single pH-responsive, weak polyelectrolyte, is dissolved in water in its charged state and precipitated using a pH switch;[11-12] 2. Where a weak polyelectrolyte is initially mixed with an oppositely charged strong polyelectrolyte at a pH where the weak polyelectrolyte is uncharged, and then a switch in pH induces complexation between the two polymers and thus phase separation;[13] and 3. Where two oppositely charged strong polyelectrolytes are mixed at high salt concentration, which prevents complexation, and switching to low salinity induces complexation of the polymers.[14] The main advantage of all three APS methods is that it is possible to produce membranes in a more sustainable and environmental friendly fashion without the reliance on toxic solvents such as NMP and DMF.

Apart from the solvent and polymers used, APS is very similar to NIPS. In both cases the polymer(s) are dissolved in a solvent where the polymer-solvent interactions are favourable and the resultant solution is homogeneous. When a cast film of this polymer solution is submerged into a non-solvent bath, a solvent exchange occurs and this results in unfavourable polymer-solvent interactions causing the phase separation. As with NIPS, a low driving force for phase separation results in more symmetrical, open membrane structures and a high driving force results in more asymmetric membranes with denser top layers.[2] When considering APS with a single acidic polyelectrolyte, H_2O can be seen as the solvent and H_3O^+ as the non-solvent. At a pH > pK_a, the polymer is charged and polymer-solvent interactions are favourable resulting in a stable single-phase solution. An important difference between this APS system and NIPS is that the introduction of the non-solvent changes the polymer itself instead of changing the solvent-polymer interactions. Here, H_3O^+ protonates the weakly anionic polymer which causes it to lose its negative charge. The reduction in charge makes it thermodynamically unfavourable for the polymer to remain in solution as polymer-polymer interactions are now more favourable than polymer-solution interactions and thus the polymer precipitates. A very important kinetic parameter of this system is the rate at which the polymer loses its charge. Using a larger concentration of H_3O^+ results in a larger driving force to protonate and therefore precipitate the polymer and vice versa. This can be compared to the solvent to non-solvent ratio in NIPS, where the addition of solvent to the coagulation bath can be used to slow down the kinetics of the phase separation.

Since APS is water-based and relies on polyelectrolytes it can readily make use of additional tuning parameters that are rarely used in conventional NIPS, the salt type and concentration. It is well-established that the behaviour of polyelectrolytes in solution can be controlled by salt concentration.[15] Moreover, it has been known for a long time how specific salts (or ions) can precipitate/stabilise polyelectrolytes from/in solution ('salting-out' and 'salting'-in, respectively)[16-17] i.e. specific ion effects, but to the best of our knowledge this effect has yet to be studied in the context of synthetic membrane formation. From the perspective of well-defined colloidal systems[18] such as negatively charged silver iodide sols[19] and anionic polystyrene latex particles,[20-22] individual cations and anions can be ordered from those that have the greatest salting-out effect (i.e. lowest critical coagulation concentration, CCC, for the colloidal solutions) to those that have the least (i.e. highest CCC). This leads to the following series for cations: $Ca^{2+} \sim Mg^{2+} > NH_4^+ > K^+ \sim Na^+ > Li^+$, and anions: $SO_4^{2-} > F^- > Cl^- > NO_3^- > SCN^-$. Sequences of such data are known as *lyotropic series* or *Hofmeister series*. Throughout the literature, the position of individual ions in these series is variable, for example the position of NH_4^+ can shift due to its hydrogen-bonding capacity.[23] Moreover, completely inverted (or reversed) series are found depending on the given experiment and experimental conditions such as pH,[24-25] ionic strength/concentration,[26] solute/surface charge and polarity,[27] and temperature;[28] as elegantly discussed in the following review articles.[29-30] Beyond these effects, the physical properties of ions (e.g. ionic size, polarizability, hydration strength and 'hydrophobicity') are also important.[31] At present, the scientific community is yet to uncover the fundamental origins of specific ion effects, but seemingly the general consensus is now that they result from the complex interplay of a number of interactions in solution i.e. ion–solvent, ion–solute, ion–ion, solute–solvent, solute–solute, and solvent–solvent interactions.[32]

In this Chapter, the focus lies on studying the influence that different types of salt and concentrations thereof have on the formation of polymeric membranes prepared using polystyrene-alt-maleic acid (PSaMA). This copolymer is used since it contains both responsive, maleic acid, and unresponsive, styrene, monomers which allows for the preparation of mechanically stable membranes as shown in Chapter 3.[11] The ion specific effects of different mono- and divalent salts on membrane formation will be systematically evaluated at different concentrations. As PSaMA is a polyanion it is expected that cations will primarily have a more significant influence on the phase inversion behaviour. Divalent cations are expected to have a stronger effect due to their potential to form ionic crosslinks, which may increase polymer-polymer interactions and therefore accelerate the phase separation process. Moreover, an increase in salt concentration will increase charge screening and therefore reduce repulsion between the negative charges of the polymers. By investigating how salt affects the phase separation, additional control over membrane morphology can be achieved which in turn leads to membranes with improved performance.

4.2 Experimental section

Poly(styrene-alt-maleic acid) sodium salt solution 13% (M_w 350,000 g·mol^{-1}, PSaMA), polyethylene glycol (M_w 200 g·mol^{-1}, PEG 200; M_w 400 g·mol^{-1}, PEG 400; M_w 600 g·mol^{-1}, PEG 600; M_w 1500 g·mol^{-1}, PEG 1500; M_w 2000 g·mol^{-1}, PEG 2000), polyethyleneimine, branched (M_n 600 g·mol^{-1}, PEI 600) were purchased from Sigma Aldrich. N-(3-Dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC), N-Hydroxysuccinimide (NHS), magnesium sulfate, magnesium chloride, sodium sulfate, sodium dodecyl sulfate (SDS), glacial acetic acid, and hydrochloric acid 37% were purchased from Sigma Aldrich. Ethanol 100% technical grade, was purchased from Boom B.V. N-hexane 99+% was bought from Acros organics. Sodium chloride (Sanal® P) was purchased from AkzoNobel. To prepare coagulation baths, deionized water (DI, 1.0 µS·cm^{-1}) was used and Milli-Q water (Millipore, 0.6 µS·cm^{-1}) was used in the preparation of PSaMA solutions. The received PSaMA solution (Sigma Aldrich) was dried for 16 hours at 100 ^{o}C and used without further purification. Other chemicals were used as received.

4.2.2 Turbidity experiments

Turbidity measurements were performed using a Turb® 430 IR – WTW portable turbidity meter. Solutions were prepared directly in the cuvettes (d: 25 mm, h: 40 mm) by mixing the salt (0.1–1 M ionic strength) into the polymer solution. Ionic strength (*I*) is calculated using Equation 4.1.

$$I = \frac{1}{2}\sum_{i=1}^{n} c_i z_i^2 \tag{4.1}$$

Where c is the molar concentration of the ion and z the charge number thereof. After a homogenous solution was obtained, a vacuum was applied to remove air bubbles and then the solution was left for a least 12 hours. Turbidity is measured in formazin nephelometric units (FNU) which is based on scattered light from dispersed colloidal particles of a formazin standard (where the particles have a turbidity of 1 FNU and are made in water by mixing 1.25 mg·L^{-1} of hydrazine sulfate with 12.5 mg·L^{-1} of hexamethylenetetramine).[33]

4.2.3 Membrane preparation

The membranes were prepared in similar fashion as the method described in Chapter 3 with the vital details reported below.[11] To prepare the polymer casting solutions PSaMA (20% w/v) was dissolved in water (40% v/v) with acetic acid (40% v/v). After a homogenous solution was obtained via stirring, it was filtered through a Bekaert 25 µm Bekipor ST25 AL 3 steel filter. For degassing, the solution was allowed to rest for at least 24 hours. The polymer solution was cast on a glass substrate using a steel casting knife with a 0.3 mm gap height. The film was then submerged in an acidic coagulation bath containing 2 M acetic acid, 0.04 M HCl, and either one of the following salts; NH_4Cl, NaCl, LiCl, $NaNO_3$, Na_2SO_4, $MgCl_2$, $CaCl_2$ at varying ionic strengths. Cast films were left in the coagulation bath for 5 minutes followed by three washing steps of 30 minutes using 0.1 M HCl. Crosslinking of the membranes was achieved with an aqueous carbodiimide based crosslinking method with branched low molecular weight PEI using the same method as in Chapter 3.[11, 34] Post crosslinking the membranes were rinsed with and stored in DI water.

4.2.4 Membrane performance tests

Membrane performance was studied with dead-end filtration cells using a pressurized feed vessel following the same protocol as in Chapter 3.[11] The pure water permeability of the membranes (surface area of 38 mm^2) as well as their retention of oil droplets, salt and small molecules was measured. The details of these measurements can be found in the Supporting Information.

4.2.5 Scanning electron microscopy (SEM)

Membrane samples for SEM analysis were prepared after the membranes were washed twice in ethanol and twice in n-hexane for 30 minutes and then dried. The samples were fractured after immersion in liquid nitrogen and subsequently mounted on a sample holder. The samples were stored in a vacuum oven at 30 ^{o}C for at least 4 hours, after which 10 nm chromium was sputtered onto the samples using a Quorum Q150T ES. Imaging was performed using Jeol JSM-6010LA scanning electron microscope.

4.3 Results and discussion

In this Chapter, the influence of different salts on the precipitation of PSaMA for sustainable membrane production is investigated in three parts: 1. Ion specific effects were studied in a model system using turbidity measurements; 2. It is shown that by using different types of salt and/or salt concentrations in the coagulation bath, different membrane structures can be obtained; 3. The separation performance of a selection of the membranes prepared is investigated.

4.3.1 Ion specific effects on turbidity of PSaMA solutions.

To understand the influence that different types of salt have on the solution stability and precipitation of PSaMA, it is important to understand how the different salts interact with PSaMA. This is achieved by measuring the turbidity of PSaMA solutions containing different types and ionic strengths of added salt. The turbidity of the solutions is studied as it provides a clear indication of which salts strongly induce phase separation and which salts do not, which is akin to the salting-out and salting-in effects first described by Hofmeister for salts and proteins.[35] The turbidity was measured for a series of PSaMA solutions prepared with different salt concentrations using ionic strengths ranging from 0 M to 1 M with the results presented in Figure 4.1a. As electrostatic interactions are expected to play a significant role in the ion specific effects, molar ionic strength is used throughout this Chapter to allow for a fair comparison between the mono- and divalent ions. Due to ease of preparation a 13% w/v PSaMA solution is studied in Figure 4.1a. The general trend is that when more salt is added, the turbidity increases and this signifies phase separation. Significant differences are observed depending on the type of salt. The large turbidity increase seen for divalent cations was expected as these salts can most likely form ionic crosslinks between the polymer chains by coordinating with two different carboxylic acid units. The different monovalent cations have a lower, but nonetheless distinct effect on solution turbidity as the ionic strength increases. For cations, the trend observed in Figure 4.1a directly follows the stability of negatively charged carboxyl-functionalised polystyrene latex particles in water,[20] i.e. the salting-out efficiency of cations on PSaMA is Ca^{2+} > NH_4^+ > Na^+ (Li^+ was not studied by López-León et al., but it is typically found close to Na^+ in the lyotropic/Hofmeister series).[20] For the anions, the salting-out effect on PSaMA is greater in Cl^- than in NO_3^-, which follows the trend observed by López-León et al.[20] However, the behaviour of PSaMA in the presence SO_4^{2-} (i.e. little to no salting out effect) is different which is since monovalent and divalent ions are compared based on ionic strength in this Chapter rather than molar concentration which López-León et al. did.

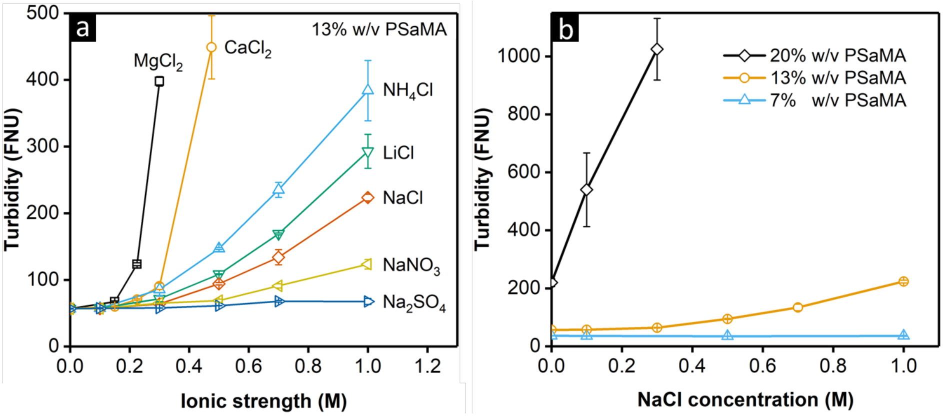


Figure 4.1. Turbidity in formazin nephelometric units (FNU) of (a) 13% w/v PSaMA solutions depending on the ionic strength of different salts, and (b) different PSaMA concentrations depending on the ionic strengths of NaCl. Note the differences in scale on the y-axis. Error bars are the sample standard deviation of two measurements.

Figure 4.1a clearly shows that dramatic ion specific effects are present with PSaMA in solution. This indicates that the precipitation behaviour of PSaMA will be influenced by different types and concentrations of salt. Figure 4.1b shows, as expected, that besides salt concentration the polymer concentration also significantly affects solution turbidity. At 7% w/v PSaMA it is observed that the turbidity is independent of NaCl concentration, while at 20% w/v the dependency is increased significantly. This is as expected as at higher polymer concentrations there are more interactions between the polymer chains. For 20% w/v polymer, it is also observed that even at 0 M salt the solution is already quite turbid, indicating that even without any additives PSaMA undergoes partial phase separation. In the coming sections, it will be shown that by tuning the salt type and concentration it is possible to control the phase separation process and prepare different type of membrane structures.

4.3.2 Ion specific effects on membrane formation

To investigate ion specific effects on membrane formation, membranes were prepared using a 20% w/v PSaMA solution with 40% v/v acetic acid precipitated in a coagulation bath containing 2 M acetic acid, 0.1 M NaCl and 0.04 M HCl. These conditions were optimized in Chapter 3 to prepare microfiltration membranes with a good separation performance.[11] Herein, to investigate the influence of salt type the NaCl in the coagulation bath is substituted by 0.1 M ionic strength of Na_2SO_4, $NaNO_3$, LiCl, NH_4Cl, $MgCl_2$ or $CaCl_2$. As with the turbidity experiment in Figure 4.1a, equal ionic strengths were used instead of equimolar concentrations to allow comparison between the divalent and the monovalent ions. In Figure 4.2, significantly different membrane structures are observed when different ions are present in the coagulation bath. Overall, three distinct types of membrane structures are observed. Firstly, Na_2SO_4 and LiCl lead to the formation of a very open symmetric structures without distinct top layers. With $MgCl_2$, $NaNO_3$, NH_4Cl, and NaCl, the structures are also open, but now distinct porous top layers are observed. When $CaCl_2$ is used in the coagulation bath, the resultant structure is asymmetric with macrovoids in the support structure and the film has a dense top layer with a significant amount of pin hole defects.

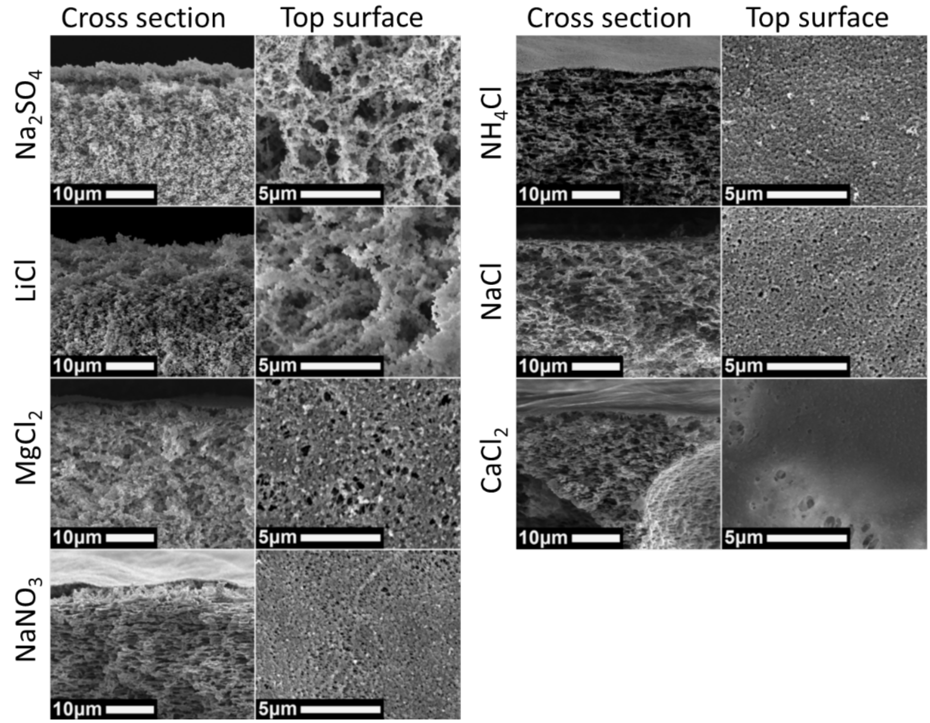


Figure 4.2. SEM images of cross sections and top surfaces of membranes prepared in a coagulation bath with 2 M acetic acid, 0.04 M HCl and 0.1 M ionic strength of Na_2SO_4, LiCl, $MgCl_2$, $NaNO_3$, NH_4Cl, NaCl, and $CaCl_2$ using a 20% w/v PSaMA, 40% v/v acetic acid polymer casting solution.

A more open structure results from slower precipitation kinetics and can be linked to how the ions in the coagulation bath interact with PSaMA. Conversely, faster precipitation results in more dense structures. The ions that lead to longer precipitation times (i.e. slower precipitation kinetics) can be considered as having a salting-in effect (or a minimal salting-out effect) on the anionic polyelectrolyte. While, ions that lead to more rapid precipitation of the polyelectrolyte can be thought of as having a salting-out effect. Based on the SEM images, when the ions are ordered from those that have the strongest salting-out effect to the least, the following series are obtained for cations: $Ca^{2+} > Mg^{2+} \sim NH_4^+ \sim Na^+ > Li^+$, and anions: $Cl^- \sim NO_3^- > SO_4^{2-}$. It is difficult to directly link these series to the lyotropic/Hofmeister series since it follows neither the direct nor indirect series, indicating that there is likely a complex interplay of a number of factors. Differences in the charge density, polarizability, hydration strength and 'hydrophobicity' of the ions all likely play a role in how they interact with PSaMA and how PSaMA interacts with water.[31]

Since PSaMA is a copolymer with both anionic and neutral monomers it is expected that ions will interact differently with both monomers. For the hydrophobic styrene monomers, larger and more weakly hydrated ions (e.g. NH_4^+) are expected to have a stronger interaction than smaller more strongly hydrated ions (e.g. Li^+).[36-37] While for the ionisable maleic acid monomer one might expect very different ion–polymer interactions. For example, Schwierz et al. demonstrated that Li^+ has a high affinity for carboxylate groups and thus Li^+ may be able stabilise the PSaMA in solution, which may explain why Li^+ gives more open membrane structures.[25] Mg^{2+} and Ca^{2+} result in vastly different membrane structure, but this is not predicted when considering the Hofmeister series. This is likely due to the high polymer concentrations used in this Chapter, which allows for the formation of substantial interpolymer ionic crosslinking. Ca^{2+} leads to more denser structures than Mg^{2+} indicating that Ca^{2+} has a much stronger salting-out effect than Mg^{2+}, probably caused by a stronger affinity of Ca^{2+} to carboxylate groups of PSaMA than Mg^{2+}. In support of this hypothesis, it is known that Ca^{2+} promotes gelation of alginate through ionic crosslinking of carboxylate groups, while Mg^{2+} does not.[38-39] One should also take into account that ion specific effects are pH dependent[24-25] and therefore will change during the phase separation process.

When comparing the membrane structures observed with SEM (Figure 4.2) to the turbidity data (Figure 4.1) the trends are very similar except for Li^+ and Mg^{2+}, with these differences discussed in detail above. One very important difference between the two experiments is that during membrane formation, the salt is present in the coagulation bath and not the polymer solution like in the turbidity measurements. Therefore, the salt must diffuse into the precipitating polymer film to be able to interact with the polyelectrolyte (PSaMA); thus the diffusion coefficients of the ions becomes an important parameter to consider during membrane preparation while it is not as significant for the turbidity experiment. In Table 4.1, the diffusion coefficients[40] are listed for the ions and salts used in this Chapter. The relatively low diffusion of LiCl in comparison to NaCl and NH_4Cl can be a possible explanation as to why a more open structure is formed when LiCl is used. Even though $MgCl_2$ has a strong effect on the phase separation as seen in Figure 4.1a, $MgCl_2$ also has a low mobility in the coagulation bath, which may explain why the resultant membrane has an open structure. However, this diffusion argument does not explain the structure obtained when $CaCl_2$ is used. Based on the relatively low diffusion coefficient of $CaCl_2$ an open structure would be expected, yet an asymmetric structure with a dense top layer is observed. Most likely the strong affinity of Ca^{2+} to carboxylate groups and its ability to ionically crosslink PSaMA means that for Ca^{2+} a dense top layer is rapidly formed when the film of PSaMA is exposed to the coagulation bath that in turn hinders the diffusion of acetic and hydrochloric acid into and out of the precipitating film, resulting in the formation of macrovoid defects. This shows that the phase separation is a complex process in which ion specific effects and mobilities clearly play an important role in determining the structure of the membrane even at concentrations as low as 0.1 M ionic strength.

Table 4.1. Diffusion coefficients in water at 25 °C of the ions and salts used in this Chapter.[40]

Ion	D (10^{-5} cm^2 s^{-1})	Salt	D (10^{-5} cm^2 s^{-1})
H^+	9.31	HCl	3.34
NH_4^+	1.96	NH_4Cl	1.99
Na^+	1.33	NaCl	1.61
Li^+	1.03	$NaNO_3$	1.57
Ca^{2+}	0.79	LiCl	1.37
Mg^{2+}	0.71	$CaCl_2$	1.34
Cl^-	2.03	$MgCl_2$	1.25
NO_3^-	1.90	Na_2SO_4	1.23
CH_3COO^-	1.09		
SO_4^{2-}	1.07		

In the turbidity experiment of Figure 4.1, it is observed that at higher ionic strengths the ion specific effects become more pronounced. To study this concentration effect on membrane formation, membranes were prepared at 0.3 M and 0.9 M ionic strength for each of the salts. In Figure 4.3, already at 0.3 M ionic strength, the structures of the precipitated films are drastically different from the 0.1 M films. For all conditions at 0.3 M, membranes with a denser top layers are formed compared to the mostly open structures observed in Figure 4.2. Such behaviour can be attributed to the increased charge screening which results in a reduction of the electrostatic repulsion between the carboxylate groups of PSaMA. This in turn leads to the more rapid onset of phase inversion, which favours the formation of membranes with denser top layers. The structures prepared with 0.3 M ionic strength of Na_2SO_4 and LiCl now have dense top layers, but they have multiple pinhole defects. The membrane prepared with LiCl has less pinhole defects but the top layer delaminates from the support structure. For all other salts, asymmetric structures are observed with thin dense top layers and macrovoids in the support structures. From the SEM images, the membrane prepared with 0.3 M ionic strength $CaCl_2$ appears to be the only membrane without defects in the top layer. For the other salts the macrovoids are situated very close to the top layer resulting in many pinhole defects.

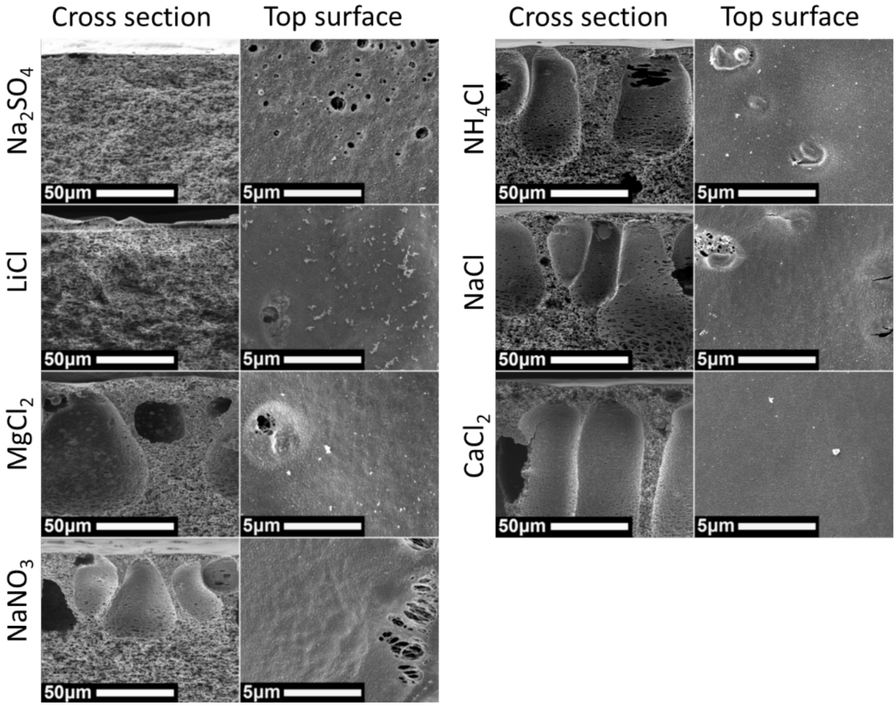


Figure 4.3. SEM images of cross sections and top surfaces of membranes prepared in a coagulation bath with 2 M acetic acid, 0.04 M HCl and 0.3 M ionic strength of Na_2SO_4, LiCl, $MgCl_2$, $NaNO_3$, NH_4Cl, NaCl, and $CaCl_2$ using a 20% w/v PSaMA, 40% v/v acetic acid polymer casting solution.

Further increases in the ionic strength of salt in the coagulation bath to 0.9 M ionic strength results in further densification of the top layer as observed in Figure 4.4. All structures are now asymmetric with macrovoids including the ones prepared with Na_2SO_4 and LiCl, although they still have multiple defects in the top layer. The membranes prepared with $MgCl_2$ and $NaNO_3$ also have a significant number of defects in the top layer. When 0.9 M ionic strength of NH_4Cl, NaCl, and $CaCl_2$ are used in the coagulation bath, no defects are observed in the top layer. Indicating that these films may have interesting membrane properties. When comparing the SEM images in Figure 4.2, 4.3, and 4.4, a very clear trend is observed; where increases in salt concentration lead to denser top layers and more asymmetric structures. In addition, significant ion specific effects are observed at each concentration, salts like LiCl and Na_2SO_4 are very suitable to prepare open structures, while $CaCl_2$ can be used even at low concentrations to prepare membranes with dense separation layers. From the results discussed above, it appears that the affinity of ions to the polymer as well as the mobility of the ions in the coagulation bath both play very important roles. For instance, Ca^{2+} ions that can likely form strong ionic crosslinks with the polymer, give rise to denser membrane structures, while Li^+ may be able to better stabilise the polymer in solution resulting in more open membrane structures. Overall, this data shows that salt type and concentration provide two additional control parameters that can be used to fine tune the structure of membranes made using the Aqueous Phase Separation process.

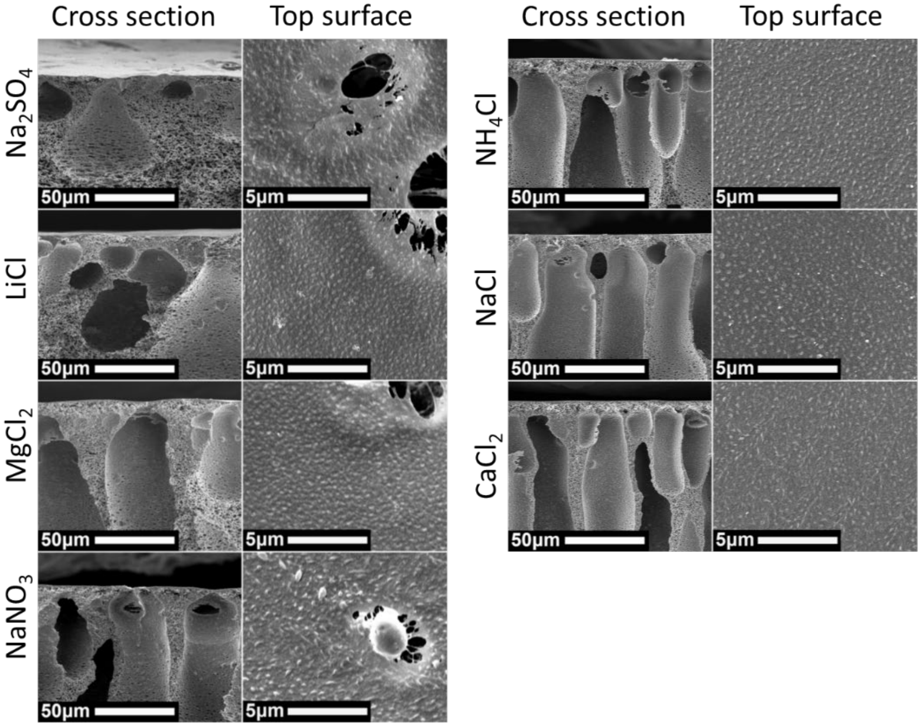


Figure 4.4. SEM images of cross sections and top surfaces of membranes prepared in a coagulation bath with 2 M acetic acid, 0.04 M HCl and 0.9 M ionic strength of Na_2SO_4, LiCl, $MgCl_2$, $NaNO_3$, NH_4Cl, NaCl, and $CaCl_2$ using a 20% w/v PSaMA, 40% v/v acetic acid polymer casting solution.

4.3.3 Membrane performance

To investigate the performance of the membranes produced using the different salts, pure water permeability and retention measurements were performed. In Figure 4.5, the pure water permeability and oil droplet retention is displayed of the membranes prepared with 0.1 M ionic strength of the different salts. The oil droplets are part of an oil-in-water emulsion stabilized by SDS with an average droplet size of 3–5 micron.[41] The membranes show a pure water permeability varying from 1000 to 6000 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$ which is in the microfiltration regime. It is interesting that the membranes prepared with Na_2SO_4 and LiCl show the lowest permeability while having the most open structure. A possible explanation is that since the support structure appears to have a smaller pore size compared to the other membranes it has a higher resistance. For the membrane prepared with Na_2SO_4 it is also observed that the top structure partially collapses under applied water pressure and this structural compaction reduced the water permeability as seen in Figure S4.1. The membranes prepared with $MgCl_2$, $NaNO_3$, NH_4Cl, and NaCl have similar water permeabilities, but the NH_4Cl membranes showed quite some deviation in the measured permeability, shown by the large error bar. The large deviations in permeability between the measured samples (at least 6) indicates that some of the membranes prepared with NH_4Cl have defects in the selective layer which can greatly enhance the flux, but always in a irreproducible way. This was confirmed by the SEM images, as some of the membranes had multiple defects resulting in a locally increased pore size and porosity of the selective layer. Surprisingly, even though the top layer of the 0.1 M $CaCl_2$ membrane is mostly dense (by SEM), it has much the same water permeability as the other 0.1 M membranes. Here, for the 0.1 M $CaCl_2$ membrane, it is expected that the water permeability is completely dominated by the many defects present in the selective layer which would also explain the large standard deviation for this system. For the oil droplet retention, all membranes besides the one prepared with $CaCl_2$ have >99% retention which is as expected since all pores observed with SEM imaging are significantly smaller than the size of the oil droplets. The much lower retention for the membrane prepared with $CaCl_2$ is likely because of the defects in the top layer of which some are larger than the size of the oil droplets. This shows that all other membranes have no major defects which would otherwise affect their microfiltration performance.

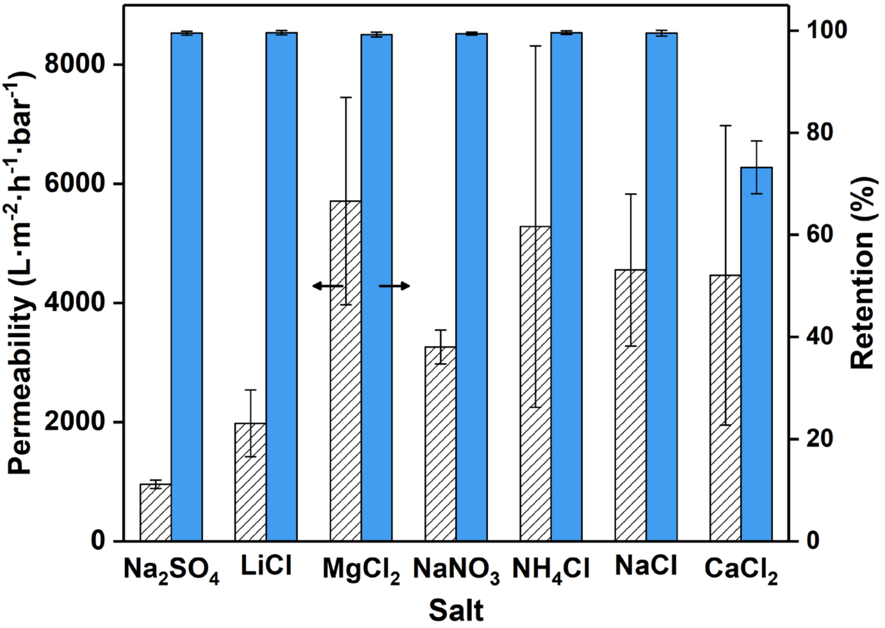


Figure 4.5. Pure water permeability and oil droplet retention of membranes prepared in a coagulation bath with 2 M acetic acid, 0.04 M HCl and 0.1M ionic strength of different salts using a 20% w/v PSaMA, 40% v/v acetic acid polymer casting solution. Pure water permeability is measured at 1 bar of applied pressure, oil droplets retention is measured using an oil-in-water emulsion stabilized by SDS, average droplet size 3–5 micron at 0.5 bar of applied pressure. The data shown is the average of at least 6 different membranes with the error bars showing the sample standard deviation.

Of the membranes prepared with higher salts concentration in the coagulation bath those prepared with 0.3 M (Figure 4.3) and 0.9 M (Figure 4.4) ionic strength of $CaCl_2$ were investigated further with water permeability and salt retention measurements. As seen in Figure 4.6 the water permeability is low for both membranes, which is not unexpected as these membranes have a dense top layers. Moreover, similar membranes in Chapter 3 also had a low water permeabilities.[11] The $MgSO_4$ retention of the membrane prepared with 0.3 M ionic strength of $CaCl_2$ was found to be quite low. This indicates that the membrane most likely has some very small defects in the top surface, which is why this membrane was not investigated further. The membrane prepared with 0.9 M ionic strength $CaCl_2$ displayed a slightly lower water permeability, but an excellent $MgSO_4$ retention that is on par with nanofiltration membranes produced by conventional phase inversion methods.[42-

[43] The retention of other salts was measured to acquire an understanding of the predominant separation mechanism. When comparing the retention of Na_2SO_4 and $MgCl_2$ it is observed that Na_2SO_4 is retained more and this is most likely due to the negative charge of PSaMA membranes. Ion size and valency also plays an important role as the small and monovalent NaCl is retained the least. To estimate the ability of the membrane to retain organic molecules, molecular weight cut-off measurements where performed using small polyethylene glycol (PEG) molecules. As seen in Figure S4.2, a molecular weight cut-off of 230 ± 30 g·mol^{-1} was measured, which confirms that this membrane is a nanofiltration type membrane. This shows that with salt type and concentration the aqueous phase separation can be controlled to produce both open and dense membranes in a way that is simply not possible in conventional NIPS.

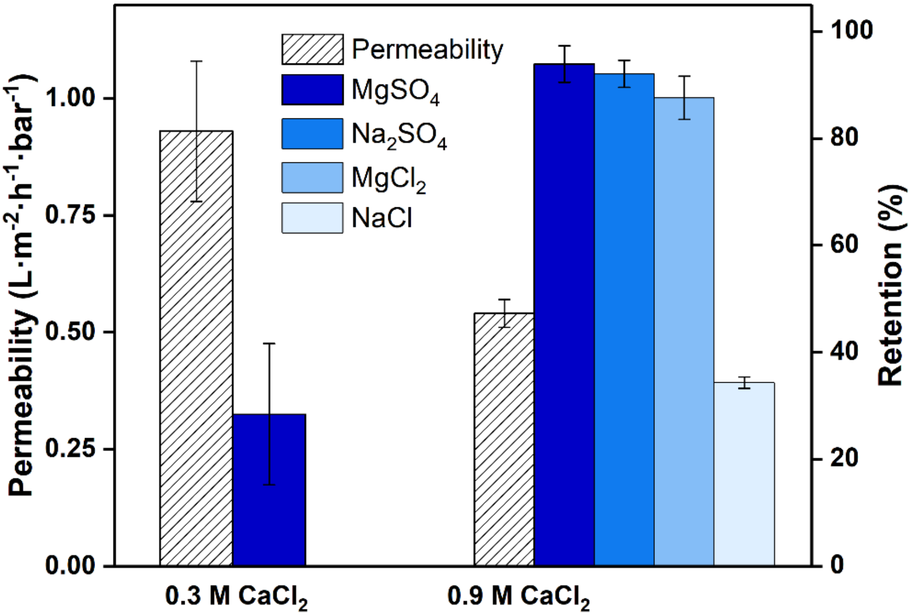


Figure 4.6. Pure water permeability and salt retentions of membranes prepared in coagulation baths with 2 M acetic acid, 0.04 M HCl and 0.3 M or 0.9 M ionic strength $CaCl_2$, using a 20% w/v PSaMA, 40% v/v acetic acid polymer casting solution. Pure water permeability and salt retentions is measured at 4 bar applied pressure. Salt retention was measured using a 5 mM salt solution ($MgSO_4$, $MgCl_2$, Na_2SO_4, or NaCl).The data shown is the average of at least 3 different membranes with the error bars showing the sample standard deviation.

4.4 Conclusions

Chapter 2 and 3 highlight the promise of aqueous phase separation as a more sustainable approach to preparing polymeric membranes.[11-12] In this Chapter, it is shown that the precipitation of a weak polyelectrolyte into different porous membrane materials is strongly dependent on salt identity and salt concentration. Initial polymer stability studies indicated that substantial specific ion and concentration effects would be present during membrane formation by phase inversion. Divalent cations strongly promoted the precipitation of the responsive copolymer PSaMA, which was likely due to ionic crosslinking effects. The impact of the different salts on aqueous phase separation and resultant membrane structure was systematically investigated and it was found that at equal ionic strengths, Na_2SO_4 and LiCl gave more open structures compared to $MgCl_2$, NH_4Cl, $NaNO_3$, and NaCl. $CaCl_2$ on the other hand led to denser membrane structures. At higher salt concentrations, the influence of salt identity followed the same order as at lower concentrations, but all the membranes were denser. Overall, ion mobility and the affinity of the ions to polymer are both expected play an important role in how ions affect the phase inversion and thus resultant membrane morphology. Divalent cations are of particular interest as they densify the membrane structure most likely due to ionic crosslinking interactions during the precipitation.

The open microfiltration membranes exhibited high oil droplet retentions with water permeability dependent on the type of salt used in the coagulation bath during phase inversion. The dense top layer nanofiltration membranes prepared with 0.9 M ionic strength $CaCl_2$ exhibited excellent retentions towards divalent ions, good retention towards NaCl, and a low MWCO value. The performance of these membranes is the same as those prepared in Chapter 3,[11] and in addition their ion retentions and MWCO is on par with commercial membranes prepared using conventional NIPS methods albeit with lower water permeability.[44-45] One needs to keep in mind that the state-of-the-art NIPS process has now been researched for approximately 60 years. The significant advantage of this alternative APS process is that it offers a more sustainable route to membrane preparation. Overall, this Chapter demonstrates for the first time that the salt identity and concentration are additional control parameters that can be used in the APS approach to control membrane morphology and performance in a way that is often not possible in conventional NIPS. Additional optimization remains possible through changes in both the polymer casting solution and coagulation conditions, which we expect will lead to membranes with higher water permeability and further improved ion and molecule retentions.

4.5 Acknowledgements

The authors acknowledge funding support from the "Vemieuwingsimpuls" programme through project VIDI 723.015.003 (financed by the Netherlands Organization for Scientific Research, NWO), and from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (ERC StG 714744 SAMBA).

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4.7 Supporting information

4.7.1 SEM

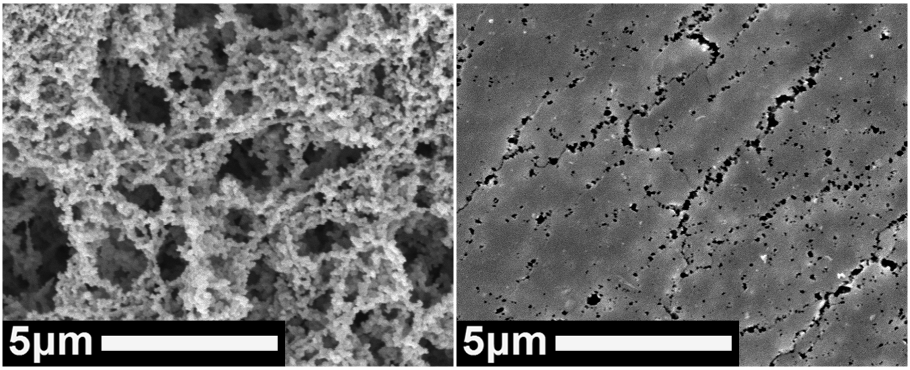


Figure S4.1. SEM images of the top surfaces of a membrane prepared in a coagulation bath with 2 M acetic acid, 0.04 M HCl and 0.033 M Na_2SO_4 (0.1 M ionic strength), using a 20% w/v PSaMA, 40% v/v acetic acid polymer casting solution. On the left: taken from a piece before the pure water permeation test, on the right: taken from a piece after the pure water permeation test.

4.7.2 Molecular weight cut-off

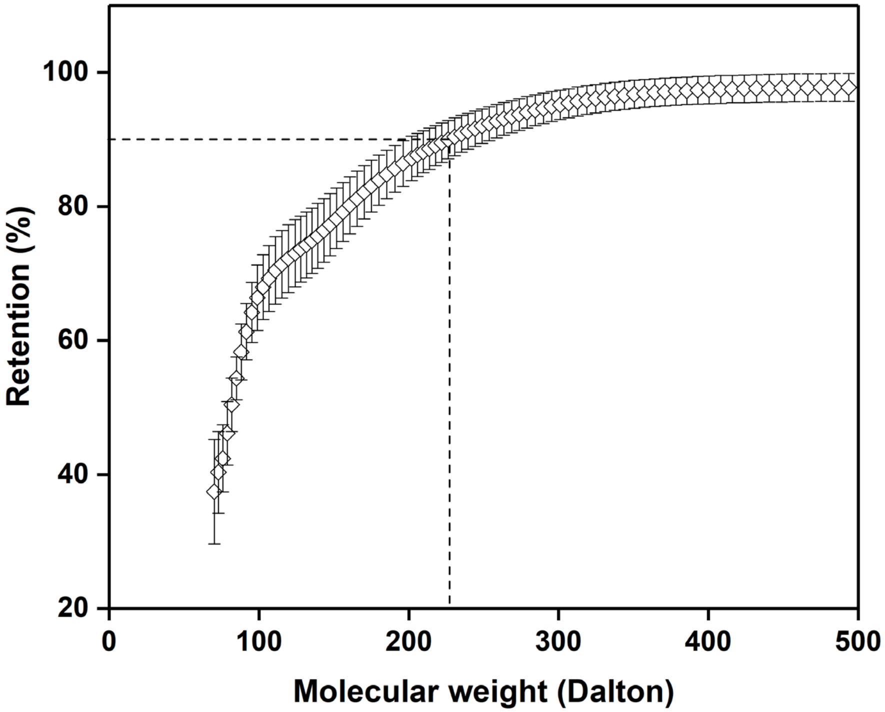
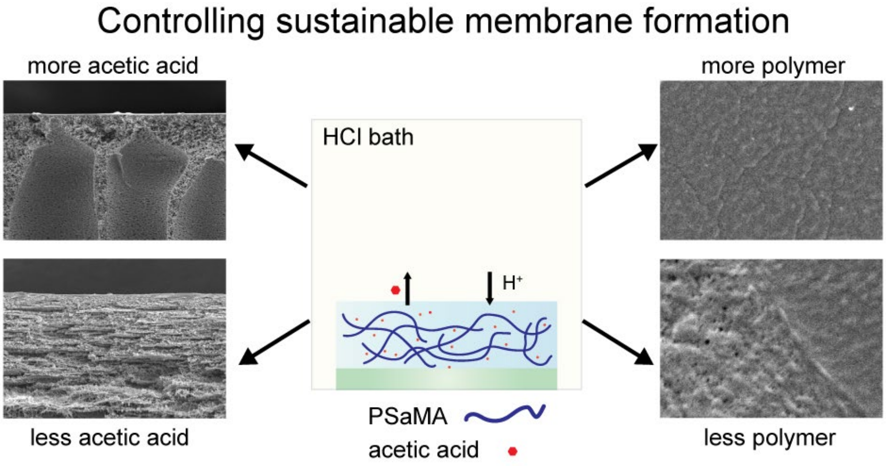


Figure S4.2. Retention of PEG chains based on their molecular weight of membranes prepared with a 20% w/v PSaMA solution with 40% v/v acetic acid in a coagulation bath with 2 M acetic acid, 0.3 M $CaCl_2$ (0.9 M ionic strength), and 0.04 M HCl. The molecular weight cut-off is determined at which molecular weight ≥90% of the PEG is retained, as indicated by the dashed line. The data shown is the average of at least 3 different membranes with the error bars showing the sample standard deviation.

Chapter 5

Effect of solution viscosity on the precipitation of PSaMA in Aqueous Phase Separation-based membrane formation.



This chapter has been published as:

Effect of Solution Viscosity on the Precipitation of PSaMA in Aqueous Phase Separation-Based Membrane Formation. Nielen, W. M.; Willott, J. D.; Galicia, J. A. R.; de Vos, W. M. Polymers 2021, 13 (11), 1775.

Abstract

Aqueous phase separation (APS) is a recently developed sustainable alternative to the conventional organic solvent based non-solvent induced phase separation (NIPS) method to prepare polymeric membranes. In APS, polyelectrolytes are precipitated from aqueous solutions through pH or salinity switches. Although APS differs from NIPS in the polymer and solvents, there exist many shared tuning parameters. In this Chapter, we investigate the APS-based preparation of membranes from poly(styrene-alt-maleic acid) (PSaMA) with a focus on acid concentration in the coagulation bath, and polymer and additive concentration in the casting solution. Nanofiltration membranes are prepared using significantly lower concentrations of acid, 0.3 M HCl compared to the 2 M of either acetic or phosphoric acid used in Chapter 3 and 4. It is shown that higher polymer concentrations can be used to prevent defect formation in the top layer. In addition acetic acid concentration also strongly affects casting solution viscosity and thus can be used to control membrane structure, where lower acetic acid concentrations can prevent the formation of macrovoids in the support structure. The prepared nanofiltration membranes exhibit a very low molecular weight cut-off (210 ± 40 Dalton), making the these sustainable membranes very relevant for the removal of contaminants of emerging concern. Understanding how the parameters described here affect membrane preparation and performance is essential to optimizing membranes prepared with APS towards this important application.

5.1 Introduction

The preparation of polymeric membranes through non-solvent induced phase separation (NIPS) has been extensively investigated since its invention in the 1960s.[1-4] With NIPS it is possible to prepare defect-free membranes in a simple and scalable way for wide range of applications.[3, 5] In addition there are many system variables that can be used to control membrane structure. Typical tuning parameters for the phase separation include: choice of solvent and polymer[6], polymer concentration[5, 7-8], additives in the polymer solution[9-11], composition of non-solvent[12-14], and temperature.[15-16] Through precise tuning of these parameters the flux and retention of the resultant membranes can be optimized towards a specific application. In recent years there has been quite some research into preparing membranes using different variants of NIPS in an effort to find more sustainable alternatives.[17-18] Most of this research has focused on using non-toxic or green solvents instead of the commonly used N-methyl pyrrolidone (NMP) or dimethylformamide (DMF) which are reprotoxic and used in large quantities resulting in large amounts of contaminated waste water.[18-19] This includes the use of solvents like dimethyl sulfoxide (DMSO)[20], supercritical CO_2[21], ionic liquids[22], and new synthetic solvents.[23-24]

An especially promising alternative to NIPS is APS, where water acts as both the solvent and the non-solvent during membrane fabrication.[25-30] To facilitate this polyelectrolytes are used as the polymer/membrane material, which are highly charged polymers. Polyelectrolytes are divided into two categories, strong or weak, depending on the nature of the charged group. Weak polyelectrolytes such as poly(acrylic acid) and poly(ethylene imine) are highly sensitive to pH and can be either charged or uncharged based on their environment. Strong polyelectrolytes such as poly(styrene sulfonate) or poly(diallyldimethylammonium) are typically always charged and are generally insensitive to pH but are still sensitive to the salt concentration. APS uses a switch in pH or salinity to precipitate polyelectrolytes from solution to form membranes.[25-30] Although very different polymers and solvents are used most tuning parameters used in NIPS can also apply to APS systems. For example, the polymer concentration is an important parameter commonly used in NIPS which can also be applied to the APS approach. Where an increased polymer concentration leads to an increased solution viscosity through increased polymer entanglement and vice versa. In NIPS a low polymer concentration is used to prepare more open structures while an increased concentration is used for denser structures with smaller pore sizes.[2, 7] In the recent work of Baig et al.,[29] where a pH shift is used to induce a polyelectrolyte complexation induced precipitation, it was observed that polymer concentration has a strong effect on the pore size and permeability following the exact same trend as in regular NIPS. Additives to the polymer casting solution are another commonly used tuning parameter in NIPS which has parallels in APS. In NIPS the addition of non-solvent molecules or polymers can be used to suppress macrovoid formation, tune the solution viscosity, improve pore formation and interconnectivity.[4] In Chapters 3 and 4 similar results were observed where the addition of acetic acid to the polymer casting solution strongly affected the solution viscosity and membrane structure.[26, 28] Finally, non-solvent composition is another strong tuning parameter in NIPS for which similar effects can be found in APS. In regular NIPS the addition of solvent to the non-solvent is commonly employed to lower the driving force of precipitation and prevent instant demixing which can be used either to prepare denser membranes,[6, 31] or open membranes in combination with other parameters.[32] In the work of Durmaz et al.[27] it was observed that while using a salinity driven APS method, in which salt can be seen as the solvent, the addition of salt to the nonsolvent coagulation bath resulted in membranes with lower permeabilities and higher retentions. While in APS methods that use a pH switch it has been observed that a lower pH difference between polymer solution and non-solvent results in more open structures.[26, 33] While the previously mentioned parameters appear to be quite similar for both NIPS and APS there are also a new set of tuning parameters.

Due to the highly charged nature of polyelectrolytes the system is sensitive to new parameters. We know from other works that salt type and concentration play an important role in the behavior of polyelectrolytes[34] and can strongly affect the formation and resulting properties of membranes.[27, 29-30, 35] It was found that when preparing membranes with Poly(stryrene-alt-maleic acid) (PSaMA) the addition of LiCl to the coagulation bath lead to more open structures while $CaCl_2$ densified the membrane.[35] In systems were two oppositely charged polyelectrolytes undergo complexation to form membranes it has been found that the mixing ratio of the two polyelectrolytes is an additional parameter to control the phase separation.[30, 33, 36] This shows while there are a lot of similarities there are also intrinsic differences in the APS method compared to NIPS which need to be thoroughly investigated to fully comprehend the system.

In this Chapter the focus lies on further investigating the APS system where membranes are prepared using PSaMA. This method uses HCl and acetic acid instead reprotoxic solvents to prepare membranes. In Chapter 3 and 4, it was found that membranes were most easily prepared using 2 M of either acetic (12.0% w/w) or phosphoric acid (19.6% w/w) in the coagulation baths.[26, 35] While the sustainability of acetic acid is not a problem as it can be biosourced,[37] waste streams with large amounts of acid are problematic and therefore using less acid is better. Here we aim to further improve the sustainability of this

APS method by using much lower acid concentrations to precipitate PSaMA. In conjunction with this the effect of viscosity of the polymer casting solution is investigated to determine how this can be used to improve membrane structure and performance. This is done either through an increased polymer concentration, which increases polymer entanglements, or a reduction of acetic acid in the casting solution, which increases inter-/intrapolymer hydrogen bonding. Through tuning of these parameters, the porosity of the top layer as well as the overall membrane structure is controlled. The nanofiltration membranes prepared in this work have a low molecular weight cut-off which allows them to effectively remove micropollutants. With these membranes it is possible to in a sustainable way remove these pollutants that are currently appearing with increasing concentrations in waste waters, surface waters, and even drinking waters.[38-40]

5.2 Experimental section

5.2.1 Materials

Poly(styrene-alt-maleic acid) sodium salt solution 13% (M_w 350,000 g·mol^{-1}, PSaMA), polyethylene glycol (M_w 200 g·mol^{-1}, PEG 200; M_w 400 g·mol^{-1}, PEG 400; M_w 600 g·mol^{-1}, PEG 600; M_w 1500 g·mol^{-1}, PEG 1500; M_w 2000 g·mol^{-1}, PEG 2000), Dextran from Leuconostoc spp./mesenteroides (Mw 60,000-76,000 Mw 100,000-200,000, Mw 450,000-650,000), (polyethyleneimine, branched (M_n 600 g·mol^{-1}, PEI 600), N-(3-Dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC), N-Hydroxysuccinimide (NHS), magnesium sulfate, magnesium chloride, sodium sulfate, glacial acetic acid, and hydrochloric acid 37% were purchased from Sigma Aldrich. Ethanol 100% technical grade, was bought from Boom B.V. N-hexane 99+% was purchased from Acros organics. Sodium chloride (Sanal® P) was received from AkzoNobel. Deionized water (DI, 1.0 µS·cm^{-1}) was used for the preparation of coagulation baths, Milli-Q water (Millipore, 0.6 µS·cm^{-1}) was used to prepare solutions. Apart from PSaMA which was dried at 100 ^{o}C for 16 hours all chemicals were used as received.

5.2.2 Membrane preparation

Table 5.1. Overview of the conditions used to prepare membranes

Polymer solution composition		**Coagulation bath conditions [HCl]**
PSaMA% w/v	**Acetic acid% v/v**	
20	40	0.05, 0.1, 0.2, 0.3, 0.4, 0.5
20	30	0.1, 0.2, 0.1
20	25	0.1, 0.2, 0.1
22.5	40	0.1, 0.2, 0.1
24	40	0.1, 0.2, 0.1

Membranes were prepared using the methods described in Chapter 3 and 4 with the vital details reported below, where Table 5.1 gives an overview of all conditions used to prepared membranes in this study.[26, 35] Polymer casting solutions were prepared by dissolving PSaMA in water mixed with acetic acid. After homogenous solutions were obtained through agitation on a roller bank they were filtered through a Bekaert 25 µm Bekipor ST25 AL 3 steel filter. Solutions were typically allowed to rest for 24 hours to degas. Membranes prepared in coagulation baths containing 0.1 M HCl or less were cast onto a nonwoven fabric (polyphenylene sulfide) for additional mechanical support while membranes prepared at higher concentrations of HCl were cast onto a glass substrate. It is unlikely that the type of support has a significant effect on the selective layer of the membrane. Regardless of the substrate a steel casting knife with a 0.3 mm gap height was used. After casting the membranes were immediately submerged into the coagulation bath (± 20L per m^2 of membrane), typically for 5 minutes although some membranes prepared in 0.1 M HCl coagulation bath were left for up to 15 minutes to ensure complete precipitation. After precipitation, the membranes were rinsed twice using 0.2 M HCl baths (± 20L per m^2 of membrane). To improve chemical stability and prevent PSaMA from dissolving at a neutral pH an aqueous carbodiimide based crosslinking mechanism with low molecular weight PEI as the crosslinker was used.[41] Crosslinking concentrations were based on the amount of carboxylic acid groups using Equation 5.1:

$$C = \frac{h \cdot A \cdot w \cdot a}{M_w} \tag{5.1}$$

where C is the number of carboxylic acid groups, h the gap height of casting knife, A the surface area of the membrane, w the fraction of polymer in the casting solution, a the amount of acid group per polymer chain, and M_w the molecular weight of the polymer. Typically a 1 : 1 : 0.4 : 0.33 ratio of carboxylic acid groups : EDC : NHS : PEI was used. Using HCl the pH of the crosslinking bath was set to approximately 5. After crosslinking membranes were washed twice for 30 minutes using DI water.

5.2.3 Membrane performance tests

To assess membrane performance, stirred dead-end filtration cells with a pressurized feed vessel were used in a similar fashion as in Chapter 3 and 4.[26, 35] Free standing membranes with 380 mm^2 permeable surface area supported by nonwoven fabric were studied for pure water permeability and their ability to retain salts, PEG or dextran at 4 bars of applied pressure. 5 mM salt solutions of the various salts were used and the conductivity of the feed, retentate, and permeate was used to calculate the retention with Equation 5.2:

$$R = \left(1 - \frac{C_p}{\frac{C_f + C_r}{2}}\right) \cdot 100\% \tag{5.2}$$

where R is the retention and C_p, C_f, and C_r is the conductivity in the permeate, feed and retentate. The molecular weight cut-off measurements were performed using 1 g·L^{-1} of the various PEG or dextran molecules, in case of dextran 0.1 g·L^{-1} ethylene glycol was used as an internal standard. Samples were analyzed via gel permeation chromatography (Agilent 1200/1260 Infinity GPC/SEC series, Polymer Standards Service data center and column compartment). For PEG measurements Milli-Q eluent containing 50 mg·L^{-1} NaN_3, at 1 mL·min^{-1}, two Polymer Standards Service Suprema 8x300 mm columns in series: 1000 Å, 10 µm followed by 30 Å, 10 µm were used. For dextran measurements Milli-Q eluent containing 50 mg·L^{-1} NaN_3 and 0.1 M $NaNO_3$, at 1 mL·min^{-1}, four Polymer Standards Service Suprema 8x300 mm columns in series: Guard 5 µm, 1000 Å, 5 µm, 1000 Å, 5 µm, and 30 Å, 5 µm were used. Concentrations were calculated via refractive index detection and with Equation 2, the retention for the different molecules was calculated, where R is the retention and C_p, C_f, and C_r is the concentration in the permeate, feed and retentate.

5.2.4 Scanning electron microscopy (SEM)

SEM samples were prepared with using the same method as in Chapter 3 and 4. A solvent exchange with ethanol (twice for 30 minutes) followed by hexane (twice for 30 minutes) was used to remove water and prevent pore collapse during drying. Using liquid nitrogen the samples were, fractured, and mounted on sample holders. After at least 4 hours in a vacuum oven at 30 °C the samples were coated with 5 nm platinum-palladium using a Quorum Q150T ES and imaged using a Jeol JSM-6010LA scanning electron microscope.

5.2.5 Dynamic viscosity measurements

The dynamic viscosity of the polymer solutions were measured using a HAAKE Viscotester 550 Rotational Viscometer with a SV-DIN rotor and cup, with shear rates 2.6–258 s^{-1} and temperature 20–60 °C.

5.3 Results and discussion

This Chapter investigates how acid concentration in the coagulation bath and polymer casting solution viscosity affect the preparation of membranes using PSaMA in an aqueous phase separation system. To further improve the sustainability of the method a significantly reduced acid concentration in the coagulation bath is used compared to Chapter 3 and 4.[26, 35] The effect of polymer casting solution viscosity is investigated by systematically changing the polymer and acetic acid concentrations in the casting solution.

5.3.1 Reduced acid concentration

In Chapter 3 and 4 membranes prepared with PSaMA were typically precipitated in coagulation baths consisting of either 2 M acetic or phosphoric acid. [25, 34] Such large amounts of weak acid were used as it was shown that hydrogen bonding between the polymer weak acid played a significant role during precipitation. In this Chapter, to further improve the sustainability of this APS method, the use of lower acid concentrations using HCl instead of acetic acid was investigated. As HCl is a strong acid lower concentrations are required to reach the pH at which PSaMA precipitates in addition it lacks the buffer capacity weak acids have which can potentially lead to different membrane morphologies. Using the same polymer casting solution as before (20% w/v PSaMA with 40% v/v acetic acid) membranes were prepared in coagulation baths containing 0.05–0.3 M HCl of which the SEM images can be seen in Figure 5.1. A general trend is observed where an increasing acid concentration results in membranes with denser top layers, which is as expected as the acid concentration is the main driving force for precipitation of PSaMA.[26] Membranes prepared in 0.05 M HCl have a very open top layer and the entire film has poor mechanical properties. It has been observed in Chapter 4 that membranes with structures like this have a very low water permeability as the top layer collapses on itself due to the membrane's poor mechanical stability.[35] The resulting dense support structure is expected to have a high resistance to water. This behavior was confirmed in that the pure water permeability of the membrane was only 23 ± 1 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$, 2 orders of magnitude lower than comparable porous membranes prepared in Chapter 3 and 4.[26, 35] The low permeability combined with the open selective layer as seen in the SEM images makes it unlikely that these membranes have any relevant selective properties and thus were not further investigated. The pure water permeability of the other membranes shown in Figure 5.1 is discussed later in the section on the effect of polymer concentration.

With 0.1 M HCl in the coagulation bath, a porous sponge-like structure is observed with a similar support structure to the one prepared with 0.05 M, but here the top layer appears to have a lower surface roughness. The structures prepared with 0.2 M and 0.3 M HCl in the coagulation bath are similar to each other with macrovoids in the support structure and visible defects in the top layers. While most of the top surface is dense, at somewhat regular intervals there are patches where pores are visible. It is hypothesized that these porous patches are formed due to shrinkage of the top layer. In some extreme cases, as seen in Figure S5.1, extensive patterning is observed, which is similar to patterns created when layers shrink as they dry.[43-44] It is possible that the patterns are formed during the sample preparation, however as SEM samples were prepared with the same method as in Chapter 3 and 4 where this effect was not observed, this scenario is unlikely. The porous nature of these surface patches is further confirmed by dextran separation experiments performed on membranes that were never dried. In Figure S5.2, the results of a molecular weight cut-off measurements are shown for the membranes prepared in 0.2 M HCl. Figure S5.2 shows that the retention of dextran is almost completely independent of dextran size indicating these membranes contain a significant amount of so-called pinhole defects. Therefore it can be assumed that the deformations of the top layer are not simply the result of drying. It is expected that at some point in the phase inversion or the crosslinking step, the top layer shrinks causing the formation of the defects.

When comparing the coagulation bath conditions used to prepare the membranes in Figure 5.1 to those used in Chapter 3 and 4 we observe that while pH is an important driving force for precipitation it is only one part of a complex system.[26] For instance, membranes prepared in 2 M formic acid which is approximately pH 1.7 were asymmetric with a dense top layer,[25] while Figure 5.1 shows membranes prepared in pH 1 are symmetric and porous. An important difference between these two systems is the strong buffering capacity that weak acid have especially at concentrations like 2 M. Calculations based on Equation 1 for required crosslinking concentrations show that a typical membrane with a 100 cm^2 surface area has approximately 5.5 mmol acid carboxylic acid groups. At 0.1 M HCl there is only approximately 10 mmol HCl within 1 cm from the interface, although HCl has a high diffusion rate the HCl concentration at the precipitation interface can be expected drop as PSaMA is protonated. With a high concentration of a weak acid in the coagulation bath the pH might be higher and the initial H^+ concentration near the interface lower but due to the buffer capacity it remains more constant. Further increases in acid concentration of the coagulation bath did not yield better results as seen in Figure S5.3 where similar structures as with 0.2 M and 0.3 M HCl are observed. It therefore appears that the defect formation in the selective layer is intrinsic to the conditions in which these membranes are prepared and further investigations focused on changing the polymer casting solution instead tuning the HCl concentration.

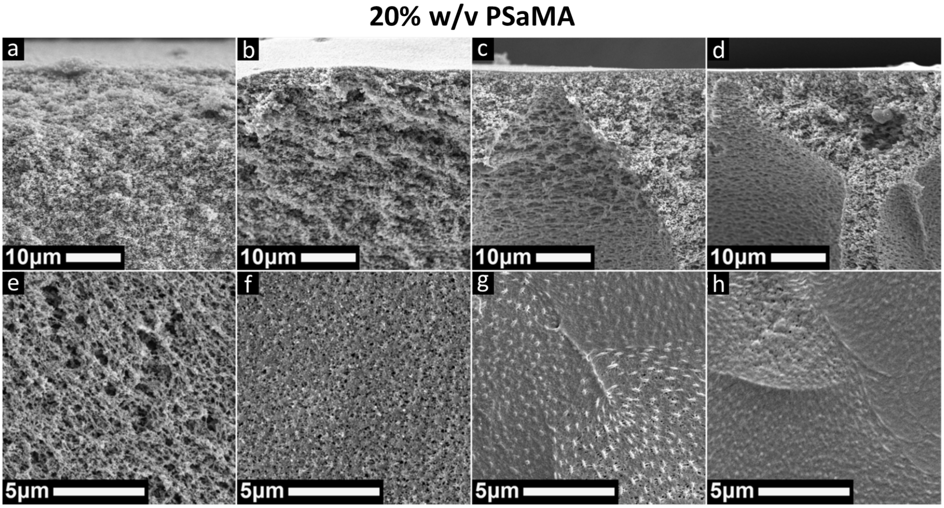


Figure 5.1. SEM images of cross sections and top surfaces of membranes prepared in a coagulation bath with 0.05 M HCl (a, e), 0.1 M HCl (b, f), 0.2 M HCl (c, g), 0.3 M HCl (d, h), using a 20% w/v PSaMA, 40% v/v acetic acid polymer casting solution.

5.3.2 Polymer concentration

It is well established that polymer concentration has a strong effect on the membrane formation where increased polymer concentrations typically lead to denser structures and can suppress macrovoids.[7] An increased polymer concentration leads to more entanglements between polymers and therefore is expected to strengthen the top layer of the membranes and prevent it from shrinking as was observed in Figure 5.1. Solutions were prepared at different concentrations of PSaMA while keeping the acetic acid concentration constant at 40% v/v. The dynamic viscosity measurements in Figure 5.2 show that as expected the viscosity increases significantly at higher polymer concentrations indicating increased entanglement of the polymers.

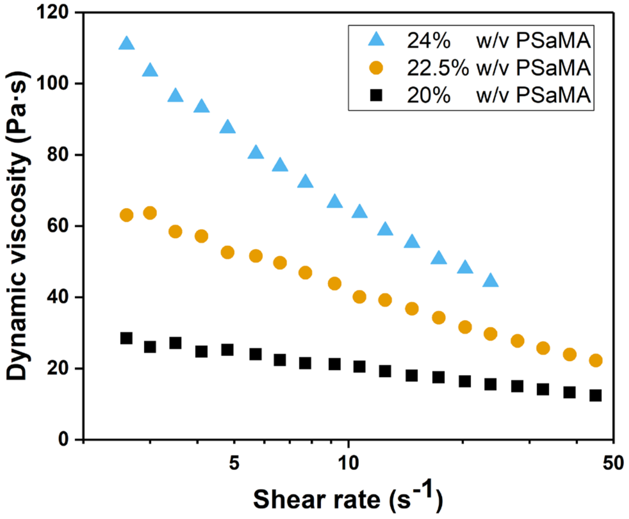
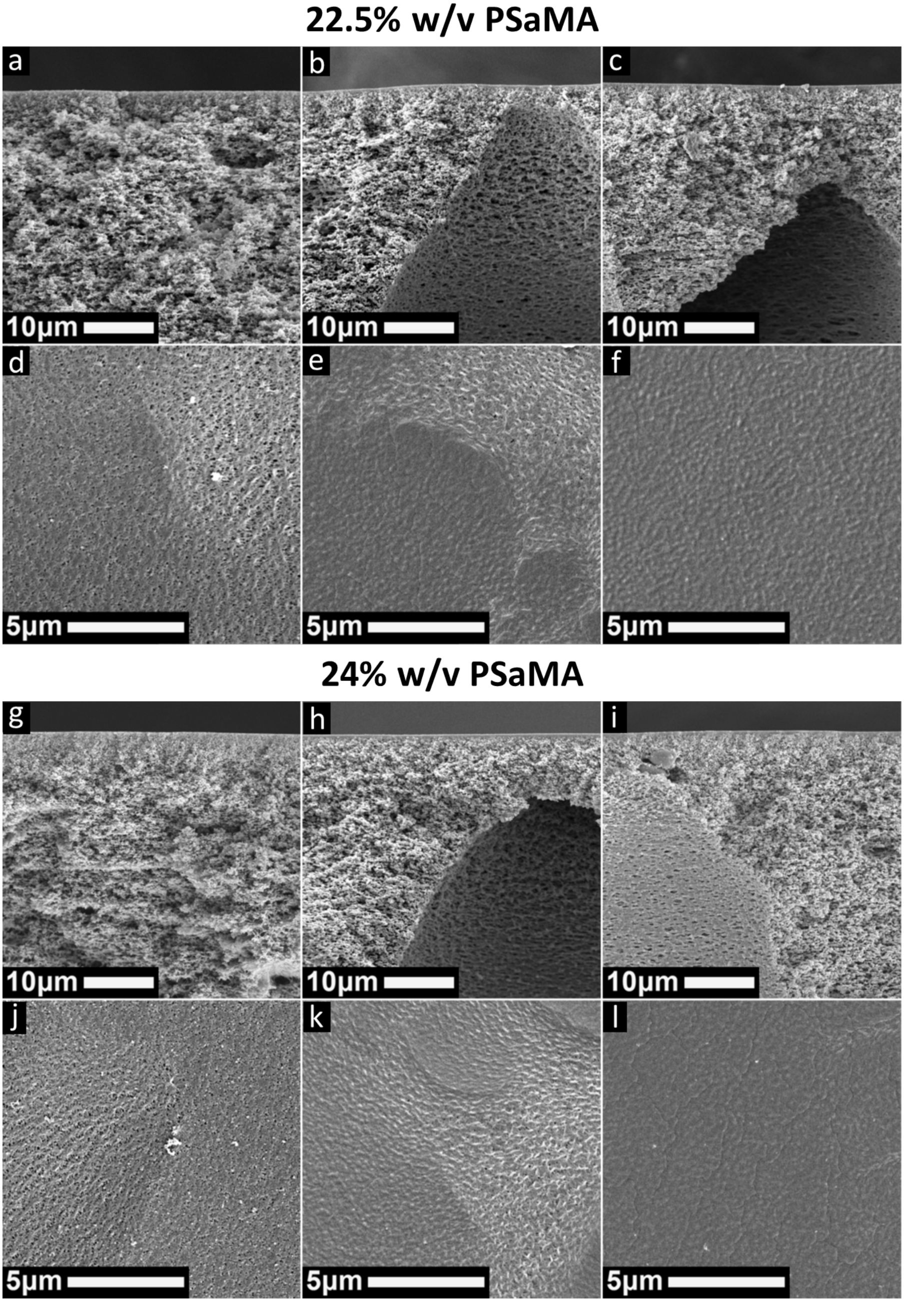


Figure 5.2. Dynamic viscosity for PSaMA solutions with 40% v/v acetic acid at different polymer concentrations, for different shear rates at 20 °C. The dynamic viscosity of the solution prepared with 24% w/v PSaMA reached the measurement limit of the viscometer at shear rates higher than 25 s^{-1}. Data is from a single measurement.

As with the 20% w/v PSaMA casting solutions discussed earlier, membranes were prepared with casting solutions with higher (22.5% and 24%) polymer concentration. As seen in Figure 5.3, when 22.5% w/v PSaMA is used a similar trend in the morphology of the cross-section is observed as when a 20% w/v PSaMA solution was used (Figure 5.1). At 0.1 M HCl, a symmetrical sponge-like structure is observed, while at higher acid concentrations (0.2, 0.3 M) an asymmetric structure with macrovoids is seen. When looking at the top surfaces, as before similar patches with an increased porosity are observed. However, when 0.3 M HCl is used these patches are not observed, indicating that the top layer of the membrane could now be defect-free as desired. The structures of membranes prepared with 24% w/v PSaMA in the solution look very similar to those prepared with 22.5% w/v PSaMA. This indicates that the increased polymer concentration can indeed help prevent the shrinkage observed earlier in Figure 5.1, yet that a certain amount of driving force, in this case at least 0.3 M HCl is required.



22.5% w/v PSaMA

24% w/v PSaMA

Figure 5.3. SEM images of cross sections and top surfaces of membranes prepared either with a 22.5% w/v PSaMA, 40% v/v acetic acid solution (top) or a 24% w/v PSaMA, 40% v/v acetic acid solution (bottom). Coagulation bath conditions are 0.1 M HCl (a, d, g, j), 0.2 M HCl (b, e, h, k), 0.3 M HCl (c, f, i, l).

To investigate the properties of the membranes prepared with the different polymer concentrations their pure water permeabilities were measured, see Figure 5.4. As expected based on the SEM images (Figure 5.1 and 5.3) the acid concentration in the coagulation bath has the largest effect on permeability. A higher acid concentration leads to a denser top layer and thus a lower water permeability. For membranes prepared in the 0.1 M HCl coagulation bath, the influence of polymer concentration in the casting solution on resultant membrane water permeability is relatively small. This is supported by their SEM images as all structures look quite similar.

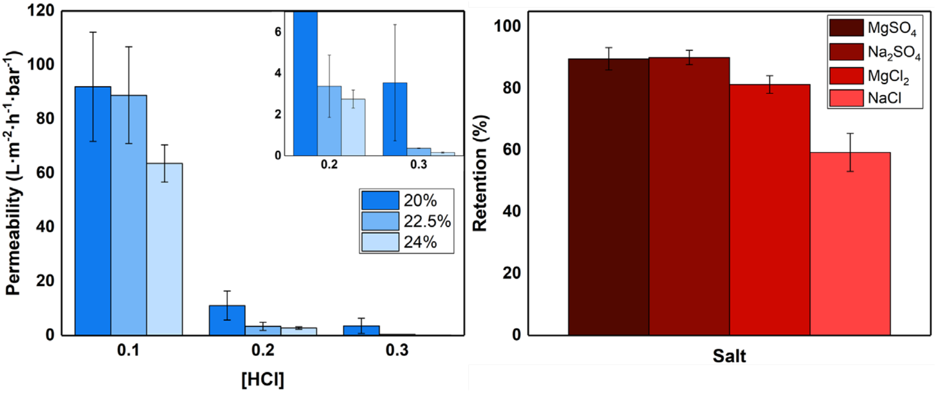


Figure 5.4. Left: pure water permeability of membranes prepared in a coagulation bath containing 0.1–0.3 M HCl using casting solutions containing either 20, 22.5, or 24% w/v PSaMA and 40% v/v acetic acid. The inset zooms in on the permeability of the membranes prepared in 0.2 M, and 0.3 M HCl. Right: retention of various salts by membranes prepared with a 24% w/v PSaMA 40% v/v acetic acid solution in a coagulation bath with 0.3 M HCl. The error bars represent the sample standard deviation of at least three separate membranes.

The membranes prepared in 0.2 M HCl have low water permeabilities, but as seen in the SEM images of Figure 5.1 and 5.3, these membranes all have mostly dense top layers albeit with a significant number of defects. From this it is expected that most of the permeate flows through the defects making them unsuitable for all membrane applications. To confirm this, filtration experiments were performed using dextran macromolecules of varying sizes. These dextran retention experiments showed, Figure S5.2, 5.4, 5.5, that retention is independent of molecular weight/size proving that defects play a significant role during filtration.

When 0.3 M HCl is used in the coagulation bath the lowest water permeabilities are measured especially for the membranes prepared from the 22.5% and 24% w/v PSaMA casting solutions. The low water permeability of these membranes is in agreement with the SEM images observed in Figure 5.3, indicating that the top layers are most likely defect free. The membrane prepared in 0.3 M HCl with the 24% w/v PSaMA solution was further investigated. The retention of various salts is shown in the right plot of Figure 5.4 and shows a relatively high overall retention with higher retentions for divalent salts compared to monovalent salts similar to what was observed in Chapter 3 and 4. This falls within expectations as divalent ions such as Mg^{2+} and SO_4^{2-} have a large hydrodynamic radii and are therefore retained more than small monovalent ions such as Na^+ and Cl^-. The difference between Na_2SO_4 and $MgCl_2$ can be explained by electrostatic interaction with the large amount of the negatively charged carboxylate groups in the membrane, which makes it easier for large positively charged ions to permeate. To investigate the retention of uncharged molecules molecular wight cut-off measurements were performed using PEG as seen in Figure 5.5 on the left. The low molecular weight cut-off of 210 ± 40 Da further demonstrates these membranes are dense nanofiltration membranes. Further performance analysis of these membranes was done using a mixture of multiple small organic micropollutants (216–361 Dalton) with various charged states. The membranes show a very high retention for all these micropollutants (97 ± 1.9%) demonstrating their relevance to remove emerging contaminates in waste waters, surface waters, and drinking waters even though the water permeability of these membranes is low.[38-40] This shows that polymer concentration, like in classical NIPS, is a very important parameter that can be used to tune the APS process, enabling the formation of defect-free dense NF membranes with very high retentions at bath acid concentrations as low as 0.3 M HCl. The performance of these membranes is very similar to those prepared in Chapter 3 and 4[26, 35] with 2 M acetic (12.0% w/w) or phosphoric acid (19.6% w/w) demonstration such acid concentrations are not required to obtain NF membranes with high retentions.

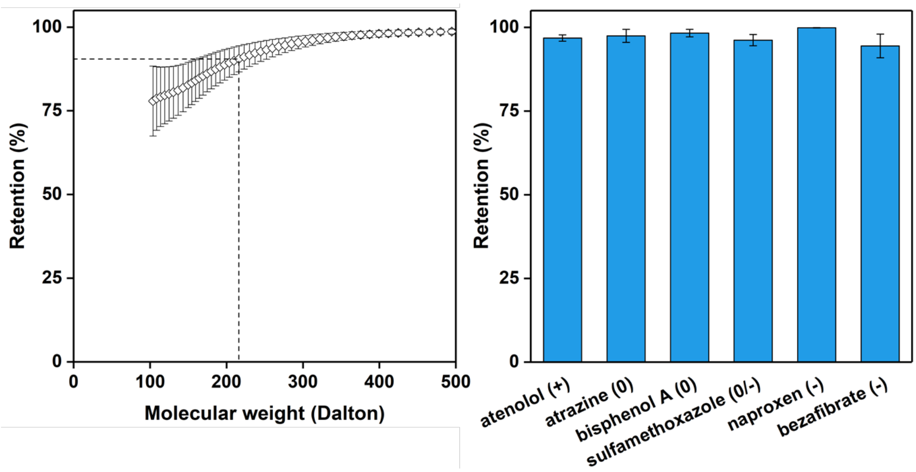


Figure 5.5. Left: Molecular weight cut-off, right: retention of various micropollutants, of membranes prepared with a 24% PSaMA solution with 40% acetic acid in a coagulation bath with 0.3M HCl. The 90% molecular weight cut-off is at 210 ± 40. The error bars represent the sample standard deviation of at least three separate membranes.

5.3.3 Acetic acid concentration

As shown in this Chapter and in literature, polymer concentration has a strong effect on the phase separation behavior.[7-8] Polymer concentration directly affects solution viscosity, which in turn influences the diffusion of different species during the phase separation process. Besides polymer concentration, additives can also be used to control solution viscosity. In this APS system, as in Chapter 3 and 4, acetic acid is one such additive whose concentration strongly affects the viscosity of the polymer casting solution. Figure 5.6 shows the dynamic viscosity of solutions prepared with different concentrations of acetic acid. Here, an increase in the acetic acid concentration results in a decreased viscosity until a certain minimum is reached, which in this case appears to be around 40% v/v.[26] Lowering the acetic acid concentration results in a higher viscosity and with less than 25% v/v acetic acid it becomes increasingly difficult to obtain a solution.

The behavior of acetic acid in this system is complex as acetic acid both affects the kinetics of the phase inversion, by its effect on the viscosity, and also the thermodynamics, as it is a non-solvent for PSaMA but its strength as a non-solvent strongly depends on the concentration. At low concentrations it results in the precipitation of PSaMA but at higher concentrations as seen in Figure 5.6 the solution viscosity is inversely depended on the acetic acid concentration. The reason acetic acid affects the solution viscosity like this is that it lowers the solution pH and therefore changes the polymer by partially protonating the acid groups. The protonated carboxylic acid groups of PSaMA can form hydrogen bonding pairs with other carboxylic acid groups which causes an increase in inter-/intrapolymer interaction resulting in an increased viscosity. However, since acetic acid is a weak acid, at the concentrations used here ± 99% of it is in the protonated form in which it can also form hydrogen bonding pairs with PSaMA. Therefore, at a high concentration e.g. 40% v/v, acetic acid behaves like a solvent, significantly reducing the inter-/intrapolymer hydrogen bonding interactions of PSaMA and thus lowering the solution viscosity. At lower concentrations such as 25% v/v acetic acid the effect is less pronounced and an increase in inter-/intrapolymer interactions resulting in an increased viscosity is observed thus acetic acid act similar to a non-solvent. When comparing the viscosity data in Figure 5.6 to the viscosity data from Chapter 3 it is observed that the viscosity of the solutions used in this work is lower than of those used in the previous work, most likely this is due to differences in the batch of polymer used. It is also observed that the viscosity of solutions with low acetic acid concentrations is strongly temperature dependent due to the dynamic nature of hydrogen bonds. The viscosity of the 20% w/v PSaMA 25% v/v acetic acid solution and the 24% w/v PSaMA 40% v/v acetic acid solution are quite at room temperature, but as seen in Figure S5.6, at elevated temperatures the viscosity of the 20% w/v PSaMA 25% v/v acetic acid solution is significantly lower than that of the 24% w/v PSaMA 40% v/v acetic acid solution. While this is an interesting phenomenon, due to the impracticality of preparing flat sheet membranes at elevated temperatures this was not further investigated.

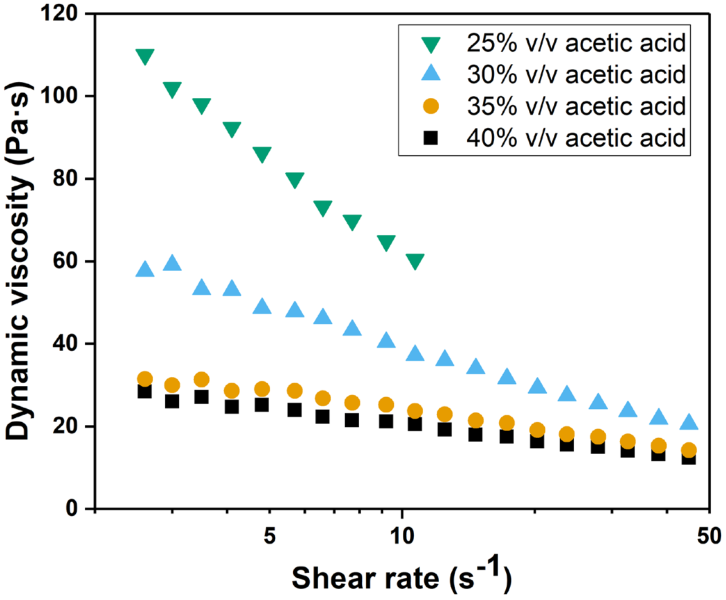


Figure 5.6. Dynamic viscosity for 20% w/v PSaMA solutions with different concentrations of acetic acid for different shear rates at 20 °C. The dynamic viscosity of the solution prepared with 20% w/v PSaMA 25% v/v acetic acid reached the measurement limit of the viscometer at shear rates higher than 10 s^{-1}. Data is from a single measurement.

In Figure 5.7, SEM images of membranes prepared with casting solutions of 20% w/v PSaMA and 30% v/v acetic acid and 20% w/v PSaMA and 25% v/v are shown. The most striking difference is that regardless of the acid concentration used in the coagulation bath, no macrovoids are observed in the cross-section images. Secondly, the top layers of the membranes prepared in 0.1 M HCl are quite irregular, and at higher acid concentrations in the coagulation bath they are similar to before, with a mostly dense top layer with occasional defects. The large differences in the support structure of the membranes prepared with 0.2 M and 0.3 M HCl are unlikely to be solely caused by the effect of viscosity as then it would also have been observed earlier when an increased polymer concentration was used. Most likely the differences in support structure are caused by how the reduced acetic acid concentration changes the behavior of the polymer casting solution.

Initial expectations were that a high concentration of acetic acid present in the film during precipitation acts as solvent and delays the precipitation. Due to the dense layer that quickly forms on contact with the coagulation bath, the diffusion of acetic acid out of the film is impeded, and this prolonged high concentration of acetic acid in the support structure slows precipitation allowing macrovoids to form. Following that logic, it would be safe to assume that by starting with a lower acetic acid concentration in the polymer casting solution, the precipitation of the support is more rapid and this suppresses the formation of macrovoids. This behavior appears to be confirmed by the SEM images in Figure 5.7 where no macrovoids are observed.

Yet when the speed of precipitation of all membranes prepared in this study was analyzed, as seen in Figure S5.7–8, it was observed that a lower acetic acid concentration in the polymer casting solution significantly slows down the total speed of precipitation. The SEM images show that the top layers are quite comparable regardless of which polymer casting solution is used. This indicates the morphology of the top layer is mostly determined by the acid concentration in the coagulation bath and that acetic acid concentration in the polymer casting solution has the biggest effect on the supporting structure. It is expected that these differences are largely cause by inter-/intra hydrogen bonding of PSaMA and its interactions with PSaMA.

While the difference in dynamic viscosity of the 24% w/v PSaMA 40% v/v acetic acid and 20% w/v PSaMA 25% v/v acetic acid polymer casting solutions is small, the origin of their viscosity is significantly different. The high viscosity of the solution with 24% w/v is caused by an increased amount of polymer entanglement compared to a 20% w/v solution. For the solution with only 25% v/v acetic acid the increased viscosity is caused by a strong increase in inter-/intrapolymer hydrogen bonding which are significantly more dynamic than polymer entanglements. This is observed by the increased response to temperature, as seen in Figure S5.6, and also a slight elastic behavior of the solution. This elasticity is most likely caused by the inter-/intrapolymer hydrogen bonding as this allows the formation of large dynamic supramolecular structures which can be broken under shear stress, which can be compared to a shear thinning hydrogen bond based hydrogels.[45] Further indications of this can be found in the cross-section SEM images that show a somewhat laminar structure in which occasional fiber like structures are observed, see Figure S5.10. It is hypothesized that these structures are formed by the shear stress caused by the casting of the film where the hydrogen bonded supramolecular formations are stretched and broken apart. With the high viscosity and the formation of new hydrogen bonds these structures do not have time to relax before precipitation occurs and can therefore be observed. Due to the immobile nature of these large supramolecular complexes, the kinetics of the phase separation are significantly slowed down and macrovoids cannot form resulting in the spongy structure observed in the SEM images even though the precipitation kinetics are extremely slow. Therefore, our hypothesis is that the difference in precipitation speed of the solutions with lower acetic acid concentrations (25-30% v/v) compared to those prepared with 40% v/v acetic acid is also caused by these large supramolecular complexes which create a gel like phase which strongly slows down the kinetics during the phase separation process severely hindering the exchange of acid and solvents. Further research will be needed to confirm this and unfortunately as seen in the SEM images and the relatively high permeability (Figure S5.11), the selective layers of these membrane still have multiple defects. Nonetheless this research provides interesting and relevant information for further optimizing this APS system as it demonstrates a method to prepare macrovoid free membranes, which is of interest when membranes with high mechanical stability are desired.

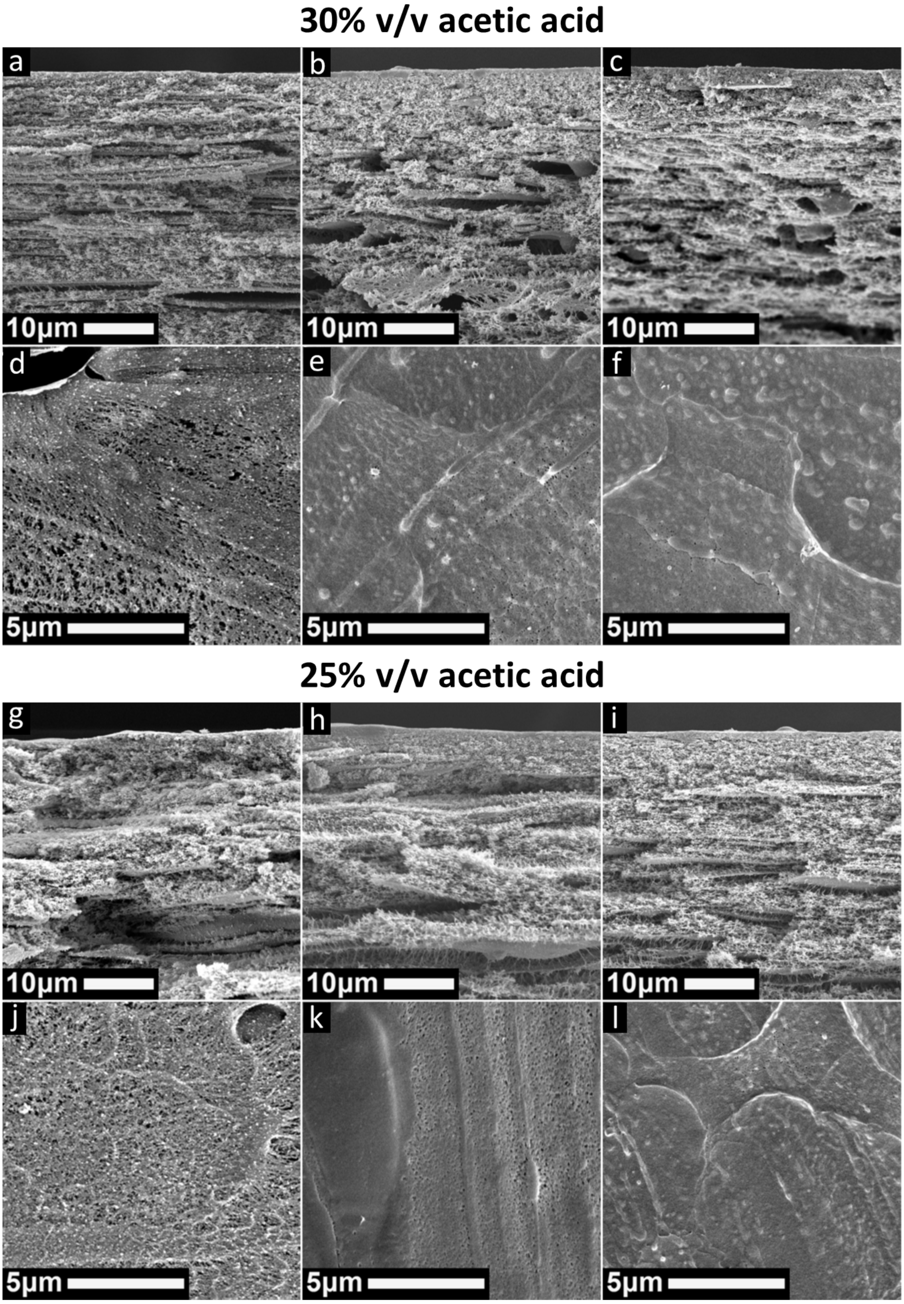


Figure 5.7. SEM images of cross sections and top surfaces of membranes prepared either with a 20% w/v PSaMA, 30% v/v acetic acid solution (top) or a 20% w/v PSaMA, 25% v/v acetic acid solution (bottom). Coagulation bath conditions are 0.1 M HCl (a, d, g, j), 0.2 M HCl (b, e, h, k), 0.3 M HCl (c, f, i, l).

5.4 Conclusions

Using the APS approach membranes were prepared with PSaMA at reduced acid concentrations to further improve the sustainability of the method. Using 0.1 M HCl in the coagulation bath open, porous membranes could be prepared albeit with a low water permeability. At higher acid concentrations, dense membranes were prepared but these contained multiple defects in the top layer making them unsuitable for separation purposes. The problem of defects formation was overcome by increasing the polymer concentration in the casting solution (24% w/v instead of 20% w/v PSaMA), with which defect free dense membranes were prepared in acid concentrations as low as 0.3 M HCl. These membranes showed high salt retentions as well as a low molecular weight cut-off (210 ± 40 Da) well within the nanofiltration regime. Furthermore, very high retentions (on average 97 ± 1.9%) for various small organic micropollutants (216–361 Da) were obtained which demonstrates the relevance of these membranes for the removal emerging contaminants. A recurring issue however, is that the water permeability of NF membranes prepared with PSaMA is, as in Chapter 3 and 4, quite low. However, Chapter 3 and 4 also show that it is possible to prepare open membranes with a high water permeability which makes it interesting to focus future investigations on using PSaMA membranes as a support for composite membranes.

Besides polymer concentration, the acetic acid concentration (an additive) in the polymer casting solution has also shown to be an important control parameter in the phase separation process. Acetic acid regulates the extent of inter-/intrapolymer hydrogen bonding between PSaMA in the casting solution, where the acetic acid concentration is inversely correlated to the solution viscosity. It is observed that at 25–30% v/v acetic acid the kinetics of the phase separation is significantly slower compared to solutions with a higher acetic acid concentration. The slowed kinetics are most likely caused by the formation of large supramolecular complexed formed by hydrogen bonding and can be used to suppress the formation of macrovoids in dense asymmetric membranes. Increasing the polymer concentration and lowering the acetic acid concentration both result in an increased viscosity. But interestingly the polymer concentration mostly seems to affect the structure of the selective layer while the acetic acid concentration mostly affects the morphology of the support structure. Although no defect-free membranes were prepared using a reduced acetic acid concentration, a greater understanding of the precipitation behavior of PSaMA and its interaction with acetic acid were gained. As the effects of a low acetic acid concentration on viscosity of the polymer casting solution are strongly temperature dependent it is expected that temperature is also a very interesting parameter when membranes are prepared with PSaMA.

5.5 Acknowledgements

The authors acknowledge funding support from the “Vemieuwingsimpuls” programme through project VIDI 723.015.003 (financed by the Netherlands Organization for Scientific Research, NWO), and from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (ERC StG 714744 SAMBA). Iske Achterhuis is acknowledged for her help with the micropollutant retention experiments.

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5.7 Supporting Information

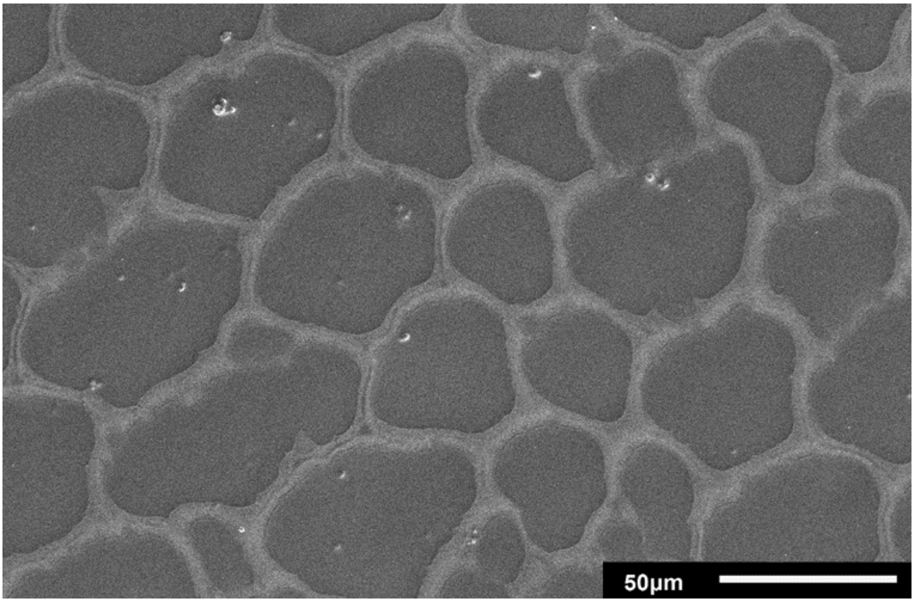

Figure S5.1. SEM image of the top surface of a membrane prepared with a PSaMA 20% w/v acetic acid 40% v/v solution in a coagulation bath with 0.2 M HCl.

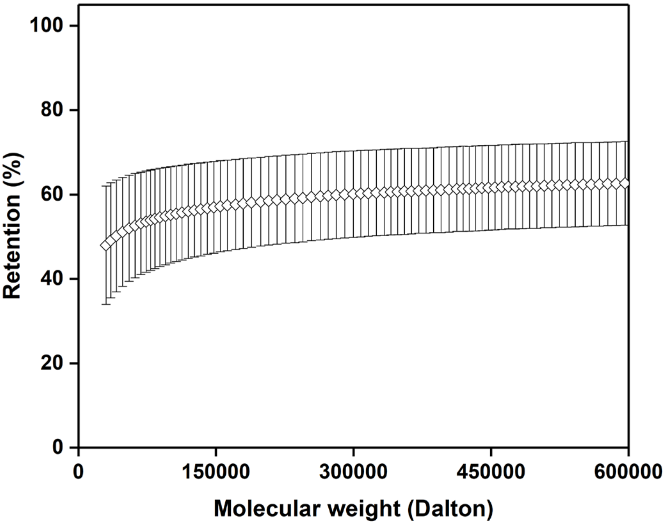

Figure S5.2. Molecular weight cut-off graph of membranes prepared with a 20% PSaMA solution with 40% acetic acid in a coagulation bath with 0.2M HCl.

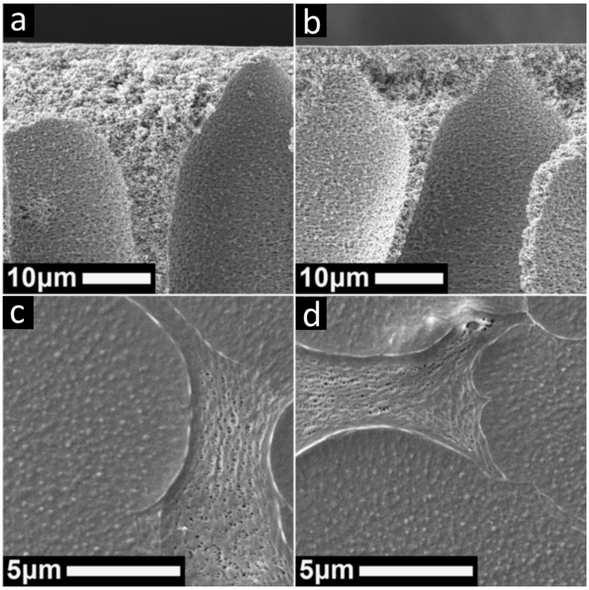

Figure S5.3. SEM images of cross sections and top surfaces of membranes prepared in a coagulation bath with 0.4 M HCl (a, c), 0.5 M HCl (b, d), using a 20% w/v PSaMA, 40% v/v acetic acid polymer casting solution.

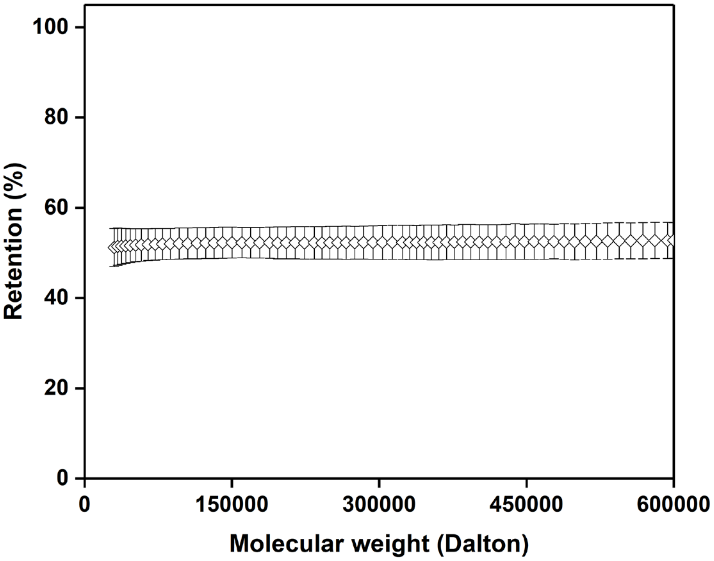

Figure S5.4. Molecular weight cut-off graph of membranes prepared with a 22.5% PSaMA solution with 40% acetic acid in a coagulation bath with 0.2M HCl.

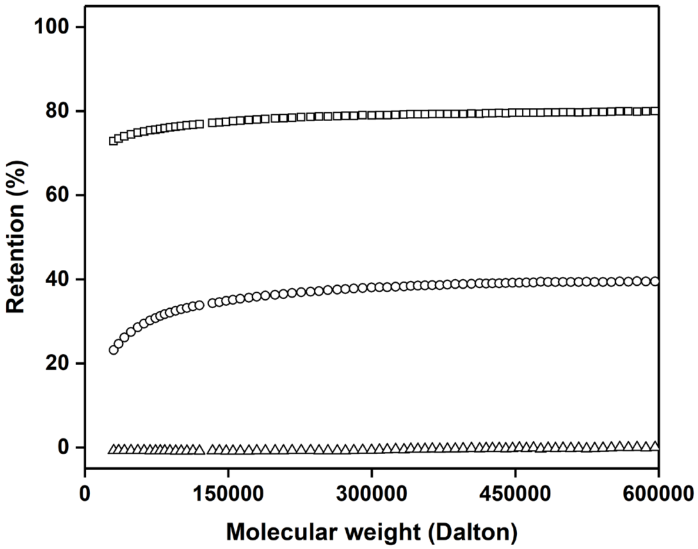

Figure S5.5. Molecular weight-cut off graph of membranes prepared with a 24% PSaMA solution with 40% acetic acid in a coagulation bath with 0.2M HCl.

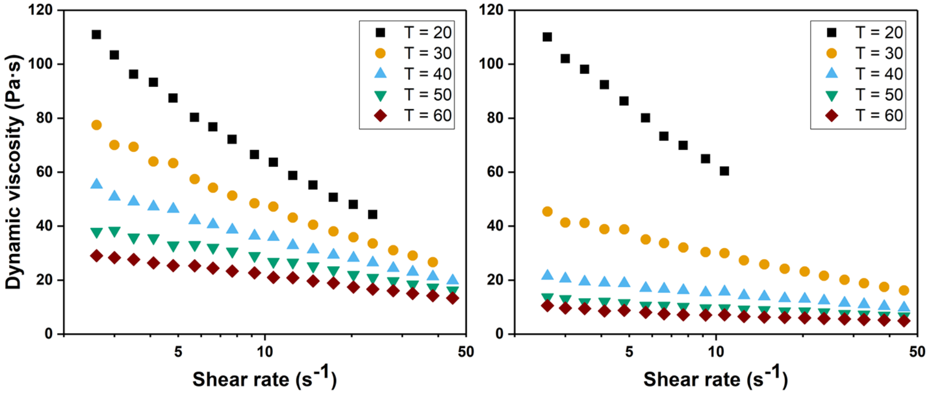

Figure S5.6. Dynamic viscosity measurements of a 24% w/v PSaMA 40% v/v acetic acid solution (left) and a 20% w/v PSaMA 25% v/v acetic acid solution for different shear rates at different temperatures (°C). The dynamic viscosity of the solutions at 20 °C reached the measurement limit of the viscometer. Data was taken from a single measurement.

Figure S5.7. Frames taken at different times from movies of the precipitation of different polymer solutions (where P20 AA25 means 20% w/v PSaMA 25% v/v acetic acid) in a 0.1 M HCl coagulation bath.

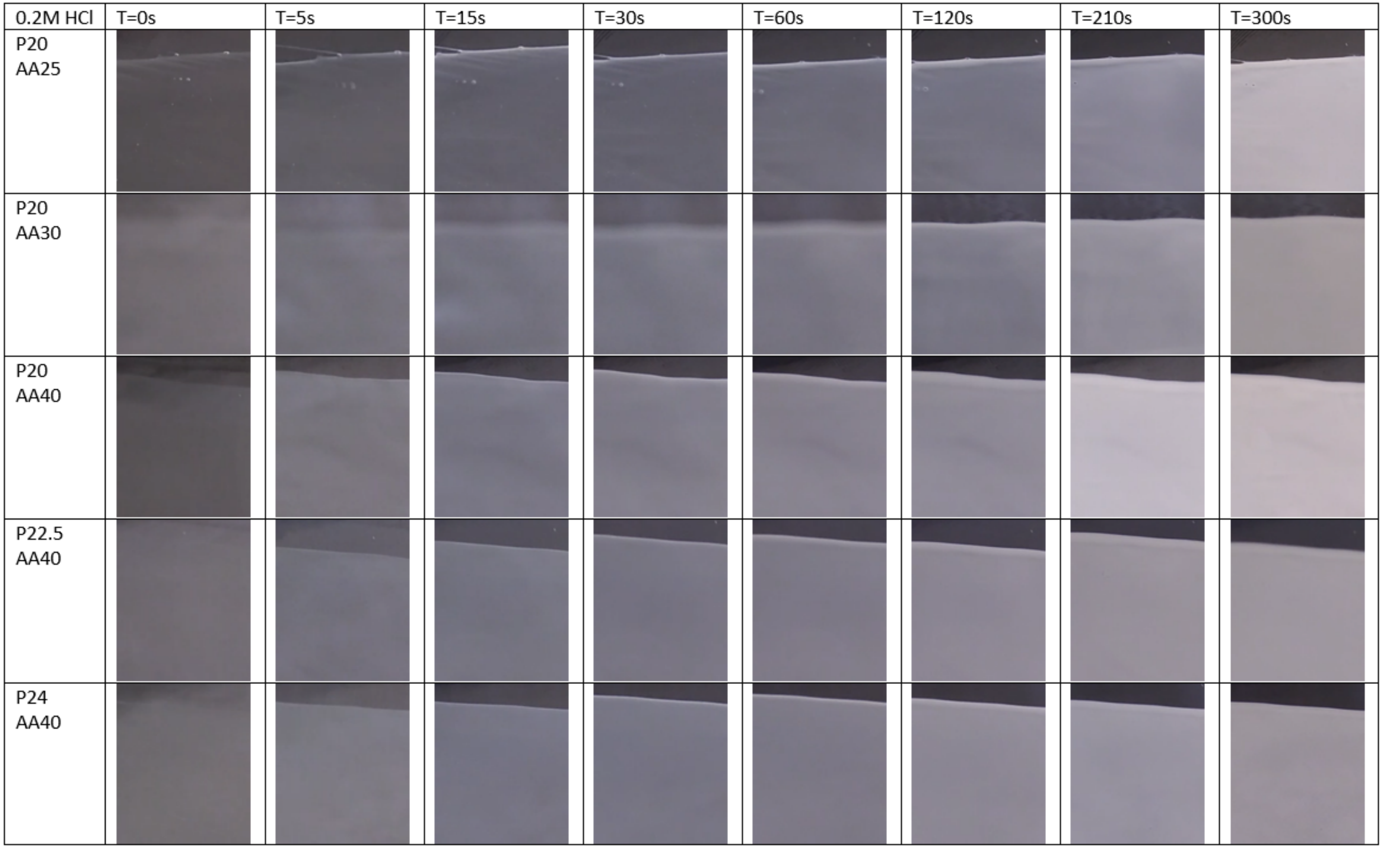

Figure S5.8. Frames taken at different times from movies of the precipitation of different polymer solutions (where P20 AA25 means 20% w/v PSaMA 25% v/v acetic acid) in a 0.2 M HCl coagulation bath.

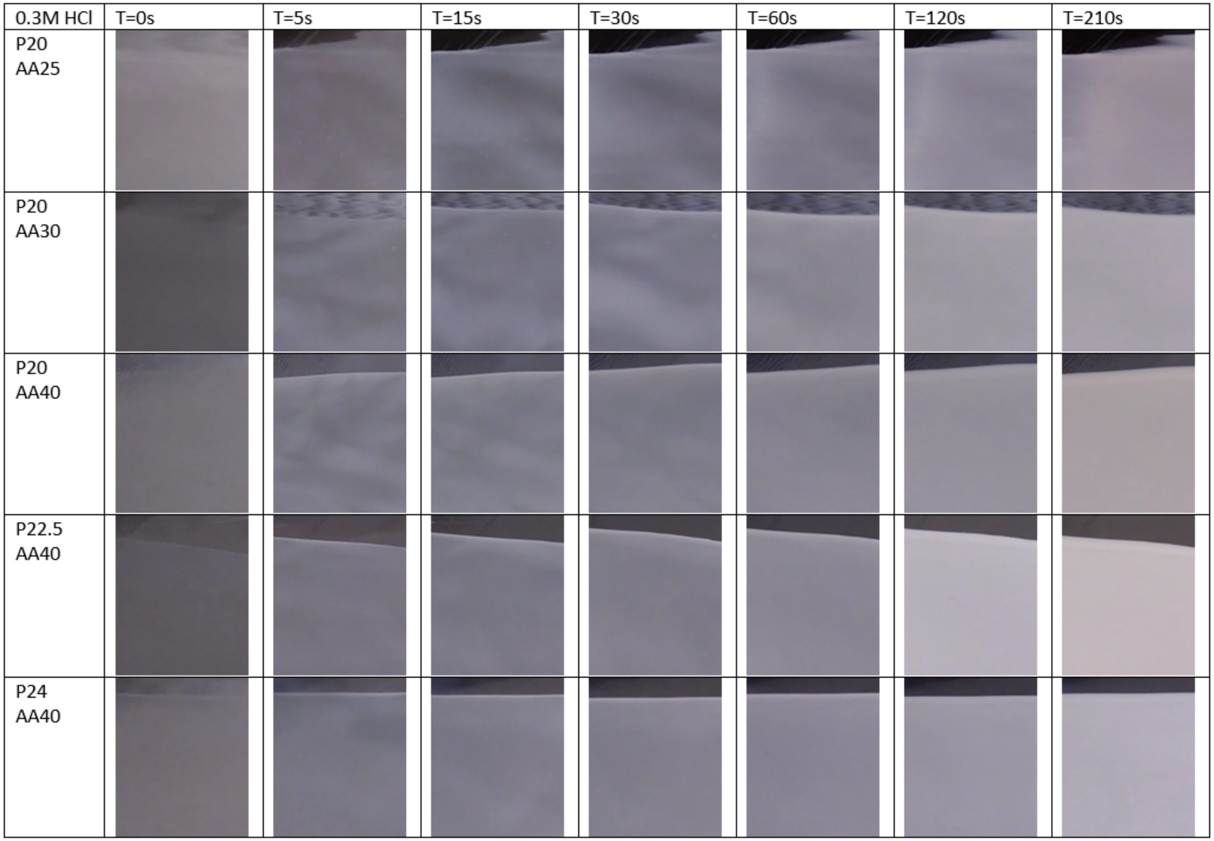

Figure S5.9. Frames taken at different times from movies of the precipitation of different polymer solutions (where P20 AA25 means 20% w/v PSaMA 25% v/v acetic acid) in a 0.3 M HCl coagulation bath.

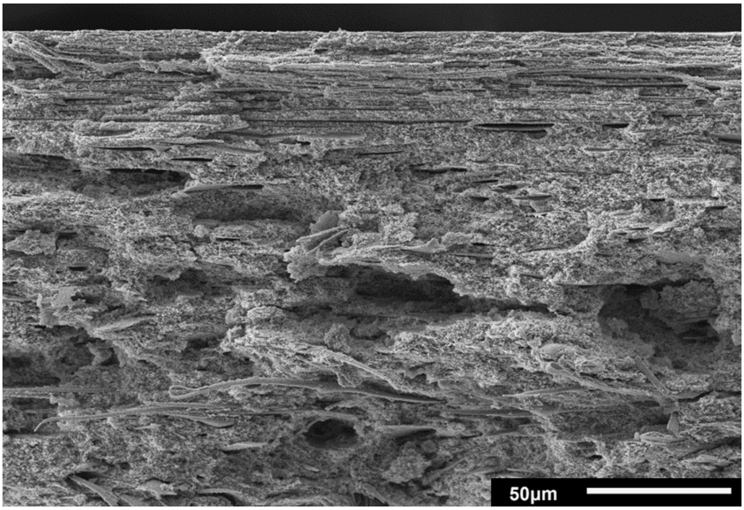

Figure S5.10. SEM image of the cross section of a membrane prepared with a PSaMA 20% w/v acetic acid 30% v/v solution in a coagulation bath with 0.1 M HCl.

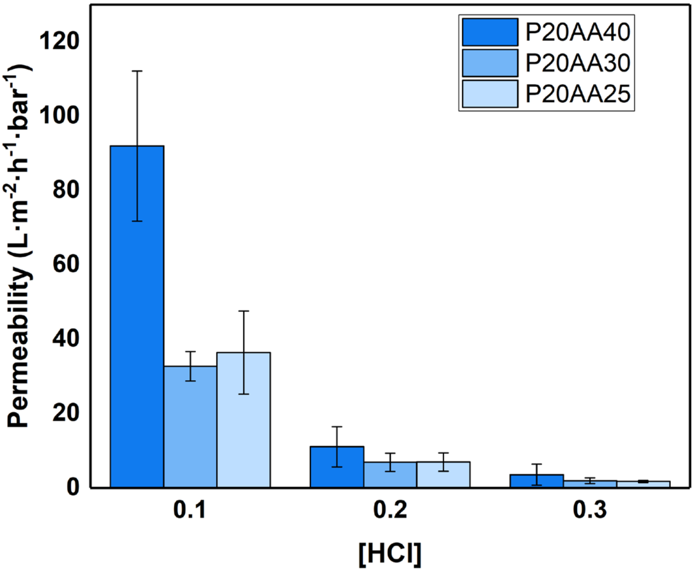

Figure S5.11. Pure water permeability of membranes prepared in a coagulation bath containing 0.1–0.3 M HCl using casting solutions containing 20% w/v PSaMA and either 40%, 30% or 25% v/v acetic acid. The error bars represent the sample standard deviation of at least three separate membranes.

Chapter 6

Solvent and pH stability of poly(styrene-alt-maleic acid) (PSaMA) membranes prepared by aqueous phase separation (APS)

This chapter will be submitted as:

Solvent and pH stability of poly(styrene-alt-maleic acid) (PSaMA) membranes prepared by aqueous phase separation (APS). Nielen, W. M.; Willott, J. D.; de Vos, W. M.

Abstract

In the single-polyelectrolyte aqueous phase separation (APS) approach membranes are prepared by precipitating a weak polyelectrolyte from a concentrated aqueous solution using a pH switch. This has proven to be a versatile and more sustainable method compared to conventional approaches as it significantly reduces the use of organic solvents. Poly(styrene-alt-maleic acid) (PSaMA) is a polymer that has been extensively investigated for APS and has been the basis for both open as well as dense membranes with good performances. These membranes are chemically crosslinked and in this Chapter we further investigate ultrafiltration (UF) and nanofiltration (NF) membranes prepared with PSaMA for their stability in various organic solvents and at different pH conditions. It is shown these membranes have stable performances in both isopropanol (IPA) and toluene, and a slightly reduced performance in *N*-methyl-2-pyrollidone (NMP). However, PSaMA does not perform well as a selective layer in these solvents. Therefore, we think that the real opportunity would be to use the UF type PSaMA membranes as solvent stable support for composite NF membranes. Additionally, the membranes proved to be stable in an acidic to neutral pH regime (pH 2–7) and due to the pH responsive nature of PSaMA, for the NF membranes a pH dependent retention of Mg^{2+} and SO_4^{2-} ions was observed and for the UF membranes a strong responsive behavior was observed, where the pH can be used to control the membrane permeability. However, long term exposure to elevated pH conditions (pH 8–10), resulted in severe swelling of the NF membranes resulting in defect formation, and compaction of the UF membranes. For the UF membranes this compaction did prove to be reversible for some but not all of the membrane samples measured. These results show that in aqueous systems membranes prepared with PSaMA have interesting responsive behavior, but perform best at neutral and acidic pH values. Moreover the membranes exhibited excellent stability in the organic solvents IPA and toluene.

6.1 Introduction

Membrane technology plays an increasingly large role in optimizing and improving industrial processes, making them more efficient as well as offering new opportunities for advanced separations. [1-4] Besides improved chemical separations membrane technology also offers solutions for environmental problems such as water scarcity[5] and increased contamination of surface waters.[6-8] Yet for all the advantages membrane technology offers it also has several disadvantages. During membrane preparation large quantities of organic solvents are used and massive amounts of contaminated waste water is produced.[9] Commonly used solvents are *N*-methyl pyrrolidone (NMP), dimethylformamide (DMF), and dimethylacetamide (DMAc) which are unsustainable and reprotoxic.[9-10] Therefore it is important to not only investigate how membranes can be used to improve global sustainability or how more selective membranes can be made, but also how membranes themselves can be produced in a more sustainable way.

As of yet, a significant amount of research has already been done towards using alternative safer and more sustainable solvents for membrane preparation.[11-13] This research partially focusses on using less toxic solvents, for instance dimethyl sulfoxide[14] and ionic liquids[15-16] but also on more sustainable solvents such as methyl lactate[17], and newly designed synthetic solvents.[18-19] While good membranes can be prepared using these alternative methods, they still rely on the use of organic solvents.

Aqueous phase separation (APS), a recently developed alternative method aims to improve the sustainability of membrane preparation by avoiding the use of organic solvents.[20-21] One of the main differences with the conventional and the previously mentioned alternative approaches to prepare membranes is that APS uses polyelectrolytes instead of conventional polymers. Polyelectrolytes are highly charged polymers which are typically responsive to salt concentration and, depending on the charged group of the polyelectrolyte, also to pH.[22] Typically polyelectrolytes are highly soluble in water due to their charged nature, but through clever use of their responsiveness membranes can be prepared by precipitating them from aqueous solutions. There are multiple ways that this can be done which are briefly discussed here. The single-polyelectrolyte APS approach uses a weak polyelectrolyte, whose charged state is pH dependent, which is dissolved at a pH where it is charged and water soluble and then precipitated using a pH switch to a regime where the polyelectrolyte is uncharged and insoluble in water.[20, 23-24] Through parameters such as the pH difference between the polymer solution and the coagulation bath,[20] polymer concentration, salt identity and concentration,[24] and type of acid used,[23] the precipitation can be controlled to prepare different types of membranes. Other APS approaches use a combination of two oppositely charged polyelectrolytes to prepared membranes. There are two distinct way this two-polyelectrolyte approach; the first method uses one weak polyelectrolyte and one strong polyelectrolyte, whose charged state is independent on pH, which are mixed at a pH in which the weak polyelectrolyte is uncharged. With a pH switch the weak polyelectrolyte can become charged which then induces complexation between the oppositely charged polyelectrolytes which becomes insoluble and can be precipitated into a membrane.[21, 25-27] Another way membranes can be prepared with the two-polyelectrolyte approach is by mixing two oppositely charged strong polyelectrolytes which typically complex, but this complexation can be redissolved by using extreme salt concentrations. Then by using a switch in salinity the polyelectrolytes form again a complex and can be precipitated into a membrane.[25, 28-32]

This Chapter further investigates membranes prepared with poly(styrene-alt-maleic acid) (PSaMA) using the single-polyelectrolyte APS approach. In Chapter 3–5, various open and dense membranes were prepared and investigated which displayed high retentions and good mechanical stability, demonstrating the versatility of this APS approach.[23-24] However, as of yet the solvent stability of the membranes prepared with PSaMA has not been investigated. PSaMA membranes are typically chemically crosslinked with short chain poly(ethyleneimine) PEI using a carbodiimide based crosslinking method[33] to improve the pH stability of these membranes at neutral and basic conditions where PSaMA is typically charged and water soluble. Thus, as these membranes are crosslinked and crosslinked membranes are of interest for applications where solvent stability is required,[34] it is important to investigate whether the crosslinking method for PSaMA membranes also provides solvent stability to the membranes. If PSaMA membranes are stable in various organic solvents it would be possible to use these membranes for challenging separations under harsh conditions in industrial processes.[35-36] Additionally as PSaMA is a weak polyelectrolyte and crosslinked with PEI, another weak polyelectrolyte, it is of interest to investigate the pH responsiveness and stability of these membranes. Herein we demonstrate that crosslinked membranes prepared with PSaMA using the single-polyelectrolyte APS approach have good solvent stability in various organic solvents, are pH responsive and stable in neutral and acidic conditions (pH 2–7), but problems are encountered in basic pH regimes (pH 8–10).

6.2 Experimental section

6.2.1 Materials

Poly(styrene-alt-maleic acid) sodium salt solution 13% (M_w 350,000 g·mol^{-1}, PSaMA), polyethylene glycol (M_w 200 g·mol^{-1}, PEG 200; M_w 400 g·mol^{-1}, PEG 400; M_w 600 g·mol^{-1}, PEG 600; M_w 1500 g·mol^{-1}, PEG 1500; M_w 2000 g·mol^{-1}, PEG 2000), (polyethyleneimine, branched (M_n 600 g·mol^{-1}, PEI 600), N-(3-Dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC), N-Hydroxysuccinimide (NHS), magnesium sulfate, Sudan Black B, citric acid, trisodium citrate, sodium bicarbonate, glacial acetic acid, phosphoric acid 85%, and hydrochloric acid 37% were purchased from Sigma Aldrich. Ethanol 100% technical grade and isopropyl alcohol (IPA) technical grade was bought from Boom B.V. *N*-Methyl-2-pyrrolidinone(NMP) 99%, *n*-hexane 99+% was purchased from Acros organics. Sodium chloride (Sanal® P) was received from AkzoNobel. Toluene 99.8% anhydrous was purchased from ABCR. All chemicals were used as received except PSaMA which was dried at 100 °C for up to 10 hours. Coagulation baths were prepared using deionized water (DI, 1.0 µS·cm^{-1}) whereas all other solutions were prepared with Milli-Q water (Millipore, 0.6 µS·cm^{-1})

6.2.2 Membrane preparation

The membranes were prepared and cross-linked using the same methods described in Chapter 3–5 and for the reader's convenience the vital details are reported here.[23] PSaMA was dissolved in water with acetic acid and mixed on a roller bank. After the PSaMA was fully dissolved Bekaert 25 µm Bekipor ST25 AL 3 steel filters were used to remove any particulate matter and the solution was allowed to rest for at least 24 hours to degas. The nanofiltration (NF) membranes were cast onto a glass substrate and prepared in 2.5 M H_3PO_4 while the ultrafiltration (UF) membranes were cast on a nonwoven fabric (polyphenylene sulfide) and prepared in 0.1M HCl. Casting was performed using a steel casting knife with a 0.3 mm gap height and the membranes were subsequently immediately submerged into the coagulation bath. 15 minutes after being submerged in the coagulation bath, the membranes were removed and submerged twice for 30 minutes in a 0.2 M HCl bath. The membranes were crosslinked with an aqueous carbodiimide based mechanism using low molecular weight PEI as the crosslinker.[33] Crosslinking reactions were performed using approximately 1.04g EDC (5.45 mmol), 0.25g NHS (2.18 mmol), 1.09g PEI (1.82 mmol) per 100 cm^2 of membrane surface area at pH 5 (set with HCl). After crosslinking membranes were washed twice for 30 minutes using DI water.

6.2.3 Membrane performance tests

The organic solvent stability tests were performed using dead-end filtration cells with a pressurized feed vessel. Membranes with 1290 mm^2 permeable surface area supported by nonwoven fabric (polyphenylene sulfide, resistant to all solvents used) were studied using pure water as well as various solvents at 1 bar of applied pressure. The pH stability measurements were performed with four crossflow cells (3650 mm^2 permeable surface area) with Naltex™ Alternating Strand Design feed spacers operated in parallel at 0.2 m·s^{-1} crossflow velocity for measurements with NF membranes, due to limitations of the setup 1 m·s^{-1} was used for measurements with UF membranes. During the measurement both retentate and permeate were recycled directly into the feed except when permeate samples were taken. The pH dependent permeability for the UF membranes was measured using 0.02 M buffer solution using phosphate (pH 2, 7, and 8), citrate (pH 4 and 6) and carbonate (pH 9 and 10) buffers. The retention for different ions was measured with a 5mM NaCl, 5mM $MgSO_4$ salt solution set to the desired pH using HCl and NaOH and with a ion chromatograph (Metrohm ECO IC) concentrations in the feed and permeate samples were measured. To determine the concentrations of Cl^- and SO_4^{2-} a Metrosep A Supp 17 - 150/4.0 anion column with 5 mM Na_2CO_3 and 0.2 mM $NaHCO_3$ as eluent at 0.9 mL·min^{-1} was used, and for Na^+ and Mg^{2+} a Metrosep C 6 - 150/4.0 cation column with 4 mM HNO_3 as eluent at 0.6 mL·min^{-1}. The retention was determined by comparing the concentration of the permeate to that of the feed. Molecular weight cut-off measurements were performed using 1 g·L^{-1} of the various PEG molecules and analyzed with gel permeation chromatography (Agilent 1200/1260 Infinity GPC/SEC series, Polymer Standards Service data center and column compartment). Two Polymer Standards Service Suprema 8x300 mm columns in series: 1000 Å, 10 µm followed by 30 Å, 10 µm were used with 50 mg·L^{-1} NaN_3 as eluent at 1 mL·min^{-1}. Concentrations were determined via refractive index detection of the feed and permeate.

6.2.4 Scanning electron microscopy (SEM)

SEM samples were prepared after a solvent exchange with ethanol (twice for 30 minutes) followed by hexane (twice for 30 minutes). The samples were fractured using liquid nitrogen. After at least 4 hours in a vacuum oven at 30 °C the samples were coated with 5 nm platinum-palladium (80-20) using a Quorum Q150T ES and imaged with a Jeol JSM-6010LA scanning electron microscope.

6.2.5 Zeta potential

The zeta potential measurements were performed with an Anton Paar SurPASS electrokinetic analyzer. 5 mM KCl was used as electrolyte and the streaming potential was measured at different pH values (sweeping from low to high) in an adjustable gap height cell using a 110 μM gap height. The Fairbrother and Mastin (FM) method was used for the calculation of the zeta potential.[37]

6.3 Results and discussion

Herein we investigate the organic solvent and pH stability of PSaMA membranes prepared with a single-polyelectrolyte APS approach. Both open ultrafiltration (UF) membranes as well as dense nanofiltration (NF) membranes were prepared using a casting solution containing 20% w/v PSaMA with 40% v/v acetic acid in water and cross-linked with short chain PEI. Based on the results of Chapter 3–5 we chose to prepare open UF membranes with a mild coagulation bath of 0.1M HCl as this gives highly porous membranes, see Figure 6.1a, b. Image analysis reveals that in its dried state the UF membrane has an average pore size 32±17 nm although a small portion of the pores are as large as 100 nm, see Figure S6.1 for the pore size distribution. The dense NF membrane was prepared using the same casting solution and 2.5M H_3PO_4 in the coagulation bath as this gives membranes with a thin (approximately 300 nm), dense selective layer with few macro voids in the substructure, see Figure 6.1c,d.[23]

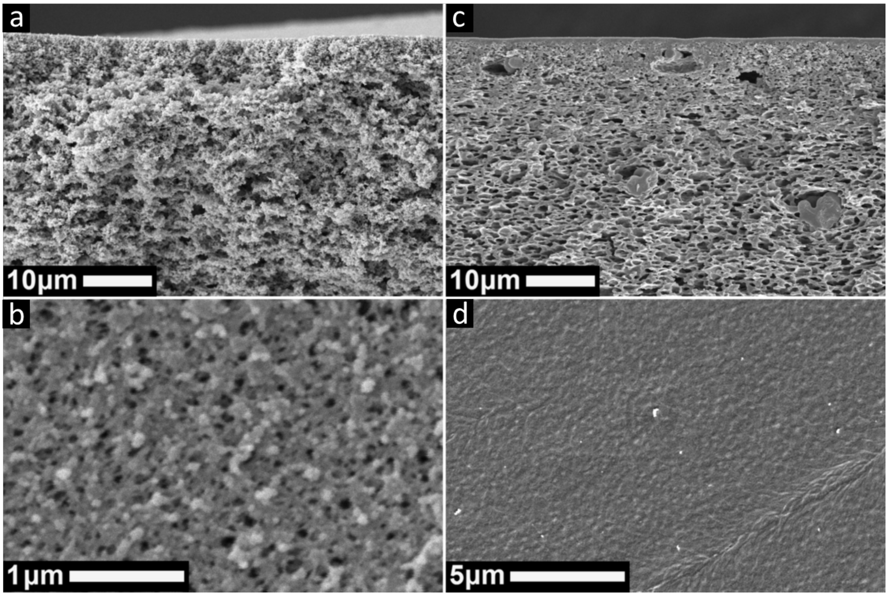

Figure 6.1. SEM cross section and top surface images of membranes prepared in a coagulation bath with 0.1 M HCl (a, b) or 2.5 M H_3PO_4 (c,d) using a 20% w/v PSaMA, 40% v/v acetic acid polymer casting solution.

6.3.1 Organic solvent stability

The organic solvent stability of the membranes was investigated using the NF and UF membranes of Figure 6.1a, b. As crosslinking is a common method to improve the solvent stability of membranes[34] it is thus expected that these membranes are to a certain extent resistant to exposure to organic solvents. In Figure 6.2a the permeability of toluene and IPA through the NF membranes is shown which is observed to be stable after initial compaction, but very low. As the toluene permeability is significantly higher than that of IPA a retention experiment in toluene was performed using a small dye molecule (Sudan Black B, 456.5 Dalton). It was found that there was no retention of the dye at all, which is surprising as measurements in water have shown that these membranes have a molecular weight cut-off of 220 ± 20 Dalton (Figure S6.3a). Therefore, it is highly likely that the measured higher permeability for toluene is predominantly caused by defects in the selective layer. As the membrane shrinks ± 5% during the solvent exchange to toluene it is expected that due to the stress of shrinking defects in the selective layer are formed. Regardless of the low permeability and defects, the membranes have a relatively stable performance in both IPA and toluene at high applied pressures. This shows that PSaMA is simply not a material that is useful as the selective layer for the filtration of these solvent, but that it does have good mechanical stability in these solvents.

To further investigate the solvent stability of cross-linked PSaMA membranes the UF membranes were tested. As seen in Figure 6.2bc, significant differences in permeability are observed depending on the solvent. However, as permeability is inversely related to viscosity (η) it is important to take the difference in viscosity of the solvents into account.[38] When normalized for viscosity differences, Figure 6.2d. the IPA and toluene permeability are the same as the water permeability demonstrating that these membranes are completely stable in those solvents over a measured period of 2 hours. For NMP this is not completely the case as even when the viscosity is taken into account the permeability is somewhat lower than that of the other solvents. However, while the permeability is lower it does remain stable during the measurement, indicating a small degree of compaction instead of instability of the membrane. To test whether this is an effect of swelling or shrinking of the membrane the water permeability was measured again after the NMP filtration which resulted in a stable but similarly reduced permeability. This indicates the membranes were irreversibly compacted during the NMP filtration experiment. When the SEM images from after the solvent filtration were compared to those from before no significant changes were observed, Figure S6.2a–d. This indicates that the membranes are mostly stable in NMP and it is expected that it is possible to achieve full stability in NMP by for instance increasing the crosslink density.

The stability of these membranes in the various organic solvents demonstrates it is possible to use these membranes for demanding applications involving harsh organic solvents. These membranes can be used as they are but can also be an interesting substrate for interfacial polymerization or (polyelectrolyte) dip coating to prepare high performance thin film composite membranes for organic solvent nanofiltration applications.

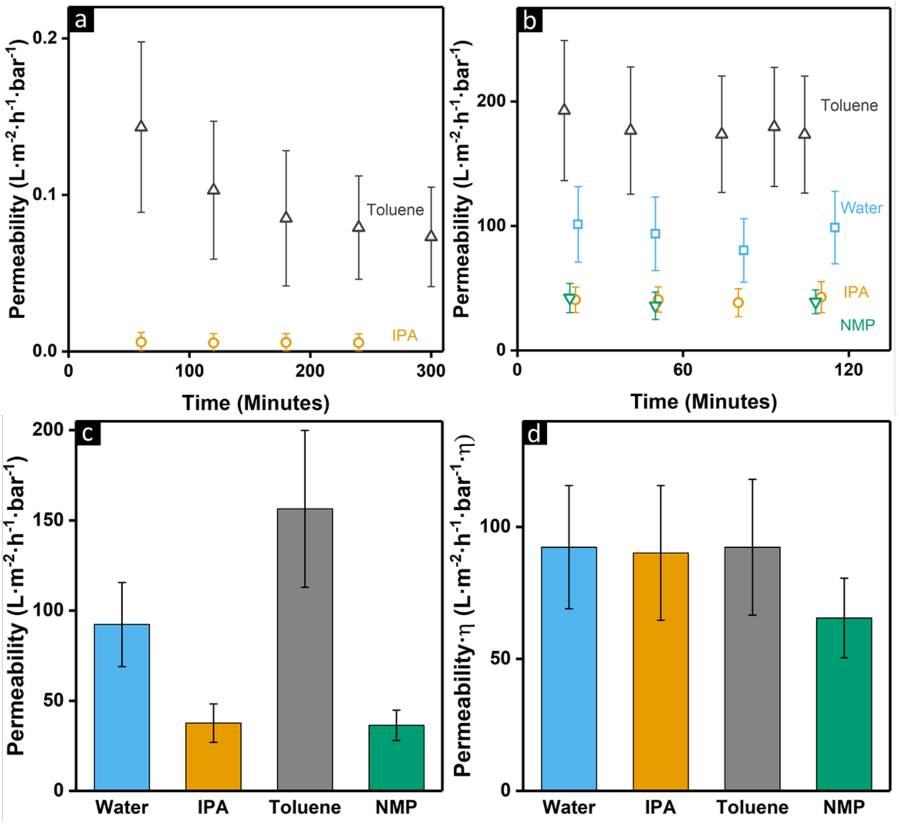

Figure 6.2. (a) Permeability of toluene and IPA (20 bar applied pressure), through NF membranes prepared with a 20% w/v PSaMA with 40% v/v acetic acid polymer casting solution prepared in a 2.5 M H_3PO_4 coagulation bath and crosslinked with PEI. (b) Permeability of various solvents through UF membranes at 1 bar applied pressure, prepared with a 20% w/v PSaMA with 40% v/v acetic acid polymer casting solution prepared in a 0.1 M HCl coagulation bath and crosslinked with PEI. (c) The average permeability of various solvents through UF membranes at 1 bar applied pressure. (d) The average permeability of the solvents though the UF membranes at 1 bar applied pressure multiplied by the viscosity (η) of the solvent. The error bars indicate the standard deviation of at least 3 different membrane samples.

6.3.2 pH responsiveness and stability

As PSaMA is a pH responsive polymer and the membranes are crosslinked with short chain poly(ethyleneimine) (PEI), another pH responsive polymer, it is natural to assume that the resultant membrane has some sort of a pH responsive behavior. To measure the extent of this pH responsiveness, zeta potential measurements were performed using the PSaMA

NF membranes. As seen in Figure 6.3, at a low pH the surface is positively charged which is logical as the carboxylic acid groups are protonated and uncharged, while the amine groups of the PEI are also protonated and therefore positively charged. As the pH is increased the measured zeta potential becomes lower until it becomes negative at pH 8.5. This matches with the pK_a values of PSaMA which are approximately 4.5 and 9[39], but is somewhat surprising as one would expect that at pH 6 already a large amount of the PSaMA is negatively charged and thus the membrane as well. That the zeta potential only becomes negative around pH 8.5, which is close to the pK_a values of PEI (8.18–9.94)[40], indicates that PEI has a strong effect on the isoelectric point of the membrane. This is not surprising as during the crosslinking charges PSaMA are neutralized and replaced with amine groups of PEI, additionally there is also a large possibility that PEI is grafted onto the top layer of the membrane and therefore has a large influence on the surface properties of the membrane. At a pH above 8.5 the zeta potential becomes increasingly more negative indicating more groups are deprotonated meaning PEI becomes uncharged and the negative charges of PSaMA start to dominate the membranes net charge. At a pH above 10 a problem is encountered as the membranes start to swell significantly which results in unreliable data. This swelling irreversibly damages the membrane and is most likely caused by a combination of the negative charges of the carboxylate groups of PSaMA repelling one another and hydrolysis of the crosslinks. It is expected that this results in a very high local concentration of negative charges (potentially up to 5 M if PSaMA is fully charged) after which the electrostatic repulsion and osmotic pressure forces a polymer rearrangement which results in swelling and a loss of structural integrity of the membrane.

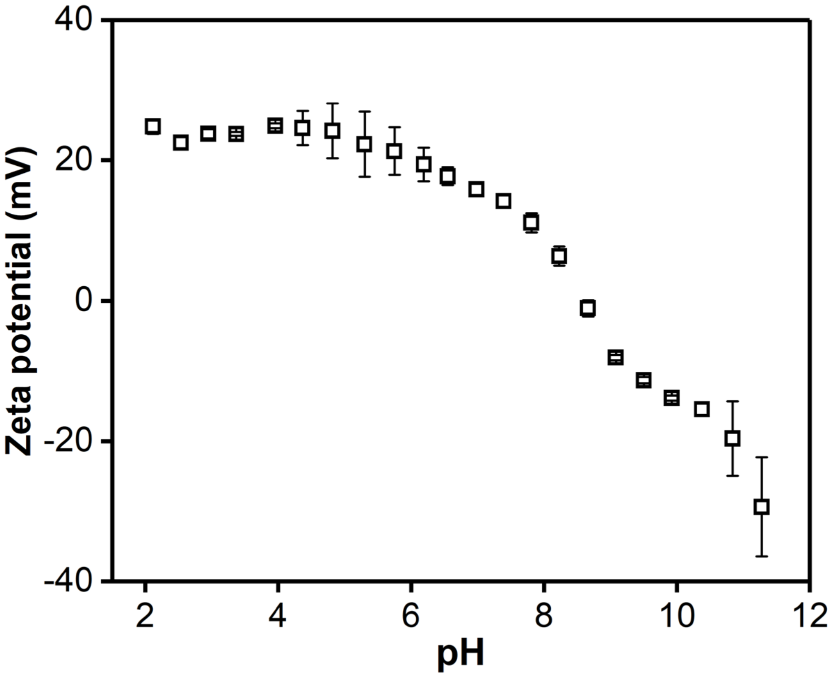

Figure 6.3. Zeta potential of the PSaMA NF membranes at different pH values calculated using the Fairbrother and Mastin (FM) method measured from low to high pH values. The error bars indicate the standard deviation of 4 measurements on a single membrane sample.

To further investigate the pH stability and responsiveness of the PSaMA NF membranes, the permeability and ion retention was measured at different pH values, ranging from pH 2.5–10, see Figure 6.4ab. In the low pH range (2.5–3.3) a high retention for the Mg^{2+} is observed and a low retention for SO_4^{2-}, which is as expected as the zeta potential measurements show the membrane has a positive charge in that range and thus based on Donnan exclusion species with the same charge as the membrane are retained more than oppositely charged ones.[41] However, since the retention of $SO_4^{2-}$is still relatively high it is highly likely that besides Donnan exclusion, dielectric exclusion plays a large part in the ion retention.[42] Very interesting is that, especially at a feed pH of 2.5, the retention for both Mg^{2+} and Na^+ is much higher than that of the anions. This means that, since charge neutrality must be maintained, a significant amount of H^+ has to permeate through the membrane indicating these membranes are selective for H^+ over Na^+. It is not unexpected that H^+ can permeate more easily through the membrane than Na^+ as the Na^+ ions have to physically permeate through the entire membrane while the H^+ ions can easily hop between water molecules and functional groups.[43] The increased H^+ permeation was confirmed by pH measurements which showed that while the feed pH was stable at 2.5 and the pH of the permeate samples was reduced to 2.4 (~ 26% increase in H^+ concentration). At higher feed pH values the retention of Mg^{2+} decreases while the retention of SO_4^{2-} increases which fits with the pH responsive behavior of PSaMA which becomes more negatively charged. What is interesting is that in the zeta potential measurements the largest differences were observed when the pH was higher than 6 while in the ion retention experiment the largest differences are seen below pH 6. An explanation is that the zeta potential only measures the surface charge of the membrane which is strongly influenced by the presence of grafted PEI chains. For the ion retention the charge inside the selective layer is more important which is determined by PSaMA, the membrane material itself, as due to the low molecular weight cut-off of the membrane it is unlikely that there is a large amount of PEI (M_n 600) inside the selective layer. It is expected that PEI is predominantly present in the porous support structure and the top surface of the membrane. Therefore, the charge inside the selective layer is much more dependent on PSaMA instead of PEI.

With a feed pH value higher than 6.5 difficulties were encountered as unbuffered salt solutions were used for the retention measurements as the presence of buffer would affect the salt retention therefore the buffer capacity of the membranes themselves and CO_2 absorption from the atmosphere reduced the pH values during the measurement. Before these measurements the membranes were equilibrated to the desired pH by operating them for 16 hours while recycling the permeate into the feed, after which a fresh feed with the desired pH was used for the measurement. For pH values of pH 6.5 and lower this provided a stable pH and performance throughout the entire measurement, however at higher pH values significant discrepancies were observed. When a feed pH of 8 was used the pH quickly dropped to 6.5 due to the membranes buffer capacity and dissolved CO_2. When a feed solution at pH 10 was used it was observed that while the pH of the feed solution was slowly decreasing the ion retention followed the same trend as before where the SO_4^{2-} retention was slightly increased and the Mg^{2+} slightly decreased measured when the feed pH was at 9.1. Interestingly the pH of the permeate samples was still at 6.5 during this measurement, indicating the membrane itself was buffering the pH of the permeate. After another 24 hours of permeating this feed solution a significant change was observed as the permeability was strongly increased and the ion retentions severely decreased. When molecular weight cut-off measurements from after the high pH exposure were compared to those before strong differences were observed, see Figure S6.3. That after high pH exposure a maximum of only 75% retention was achieved regardless of the molecular weight, indicates the presence of newly formed defects, Figure S6.3b.

Further investigation into the pH stability of PSaMA membranes was done by measuring the permeability of the UF membranes in 0.02 M buffer solutions at different pH values, see Figure 6.4c. After initial compaction, steady permeability values were measured over several hours at each of the different pH values measured from low to high pH. At pH 8 a 66 hour experiment was performed which revealed that the permeability significantly decreases over time, which can either be due to instability of the membrane at these pH values leading to additional compaction or due to fouling. After the permeability at pH 9 and 10 were measured the permeability was again measured at pH 4 which was significantly lower than before, indicating an irreversible reduction of flux. It is however important to note that, as seen by the increased error bars, the variation between the different membrane sample is large and that one of the four measured sample actually recovered approximately 96% of its original flux at pH 4. This means that while most membranes were irreversibly compacted during the long term exposure to pH 8 and higher, it is possible for these membranes to be stable in these pH conditions. A possible explanation for the variation in stability between the different membranes is that while the same conditions were used the crosslinking density is different and with insufficient crosslinking the membrane structure has more mobility and compacts more. However, when SEM images were taken of the different membranes after the permeation experiments apart from a small amount of biofouling no significant structural differences were observed, see Figure S6.2.

Comparing the NF and UF membranes performances it is observed that both have an optimum in permeability at pH 4 and that at pH7 and higher the permeability is significantly lower. It demonstrates that membranes prepared from the responsive PSaMA indeed retain their relevant responsive behavior allowing control over permeability and separation properties. At pH 8–10 it is observed that while the NF membranes show severe performance issues and defects are formed, the UF membranes only have a reduction of flux, which for some of the membranes is reversible. It is expected that it is caused by swelling of PSaMA which becomes more charged under these pH conditions, which for the NF membranes results in defect formation in the dense selective layer, but as with the UF membranes as there is no dense layer, the effect is less severe and only leads to some compaction of the membrane.

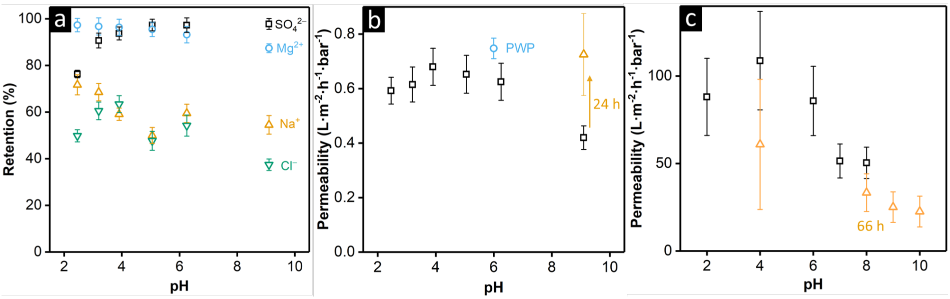

Figure 6.4. (a) Retention of various ions at different feed solution (5mM $MgSO_4$ plus 5mM NaCl) pH values by the PSaMA NF membranes. (b) Permeability of the PSaMA NF membranes at the different pH conditions from (a), and the pure water permeability (PWP) measured with deionized water. At pH 9.1 the permeability had significantly changed after 24 hours, shown by the second data point at pH 9.1 (Δ). (c) The water permeability of the PSaMA UF membranes of 0.02 M buffer solutions at different pH values measured over several hours from low to high pH after which the permeability at pH 4 was measured again. At pH 8 a long term experiment (66 hours) was performed after which reduced permeability values were observed (Δ). The error bars indicate the standard deviation of measurements from 4 different membrane samples.

6.4 Conclusions

UF and NF membranes have been prepared with PSaMA using the single-polyelectrolyte APS approach. While the performances of these membranes in aqueous systems at a neutral pH have been extensively investigated in Chapter 3–5,[23-24] their stability in organic solvents (IPA, toluene, NMP) and different pH values (acidic and alkaline) have not been reported. In IPA and toluene, the membranes show excellent stability even at high pressures, while in NMP a slight reduction in the viscosity normalized permeability is observed compared to the other solvents. It shows that PSaMA does not perform well as a selective layer in these solvents, indicating that the real opportunity would be to use the UF type PSaMA membranes as solvent stable support membranes. Investigations into the pH stability and responsiveness of PSaMA membranes show that the NF membranes have a fully stable performance between pH 2.5 and 6.5 and that the retention of divalent ions is pH dependent. At pH 2.5 the higher Mg^{2+} retention was measured (97 ± 3%), while the SO_4^{2-} retention (76 ± 2%) was at its lowest. At pH 6.5, a lower Mg^{2+} retention (93 ± 4%) and a significantly higher SO_4^{2-} retention (97 ± 3%) was measured. At higher pH values severe swelling issues are encountered which result in defect formation in the dense selective layer and therefore a loss of performance for the NF membranes. The UF membranes show very relevant responsive behavior, where the pH can be used to control the membrane permeability, with the highest permeability at pH 4 (109 ± 28 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$) and lowest at pH 10 (23 ± 9 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$). Additionally, it was observed that long term exposure to pH conditions of 8 or higher lead to compaction of the membranes which was reversible for one of the measured membrane samples but irreversible for others. This demonstrates that cross-linked membranes prepared with PSaMA using the single-polyelectrolyte APS approach are stable in various organic solvents, and show relevant pH responsive behavior in aqueous conditions. The membranes do lose some of their stability at higher pH conditions and in NMP however it is expected that with increased crosslink densities it is possible to achieve full stability in all these conditions.

6.5 Acknowledgements

The authors acknowledge funding support from the “Vemieuwingsimpuls” programme through project VIDI 723.015.003 (financed by the Netherlands Organization for Scientific Research, NWO), and from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (ERC StG 714744 SAMBA).

6.6 References

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6.7 Supporting Information

6.7.1 Pore size distribution

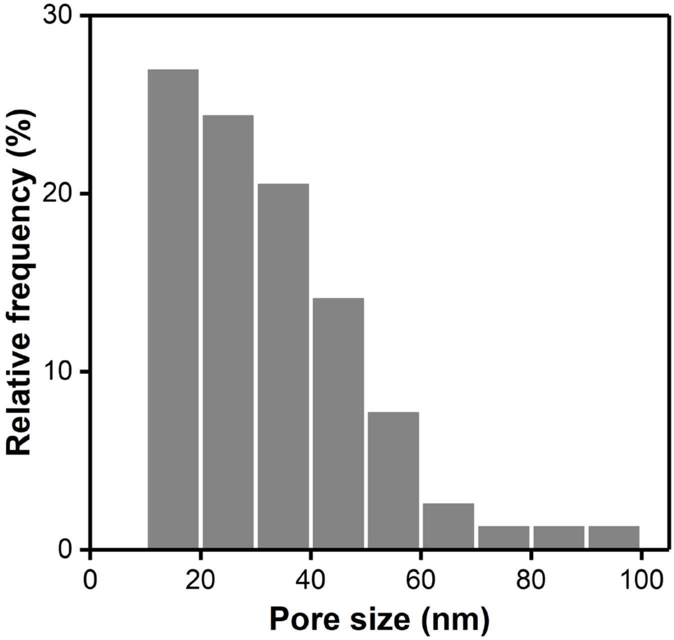

Figure S6.1. Pore size distribution of the UF membranes prepared in a coagulation bath with 0.1 M HCl using a 20% w/v PSaMA, 40% v/v acetic acid polymer casting solution. Pore sizes were analyzed using ImageJ software.

6.7.2 SEM images

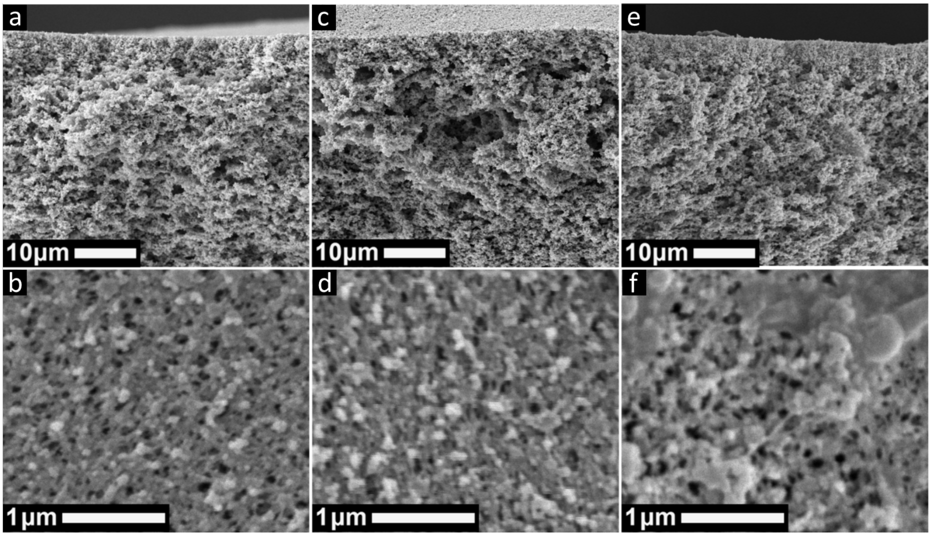

Figure S6.2. SEM cross section and top surface images of membranes prepared in a coagulation bath with 0.1 M HCl using a 20% w/v PSaMA, 40% v/v acetic acid polymer casting solution before (a, b), after (c, d) solvent filtration with IPA, toluene, and NMP, and after (e, f) filtration at different pH conditions for 7 days.

6.7.3 Molecular weight cut-off

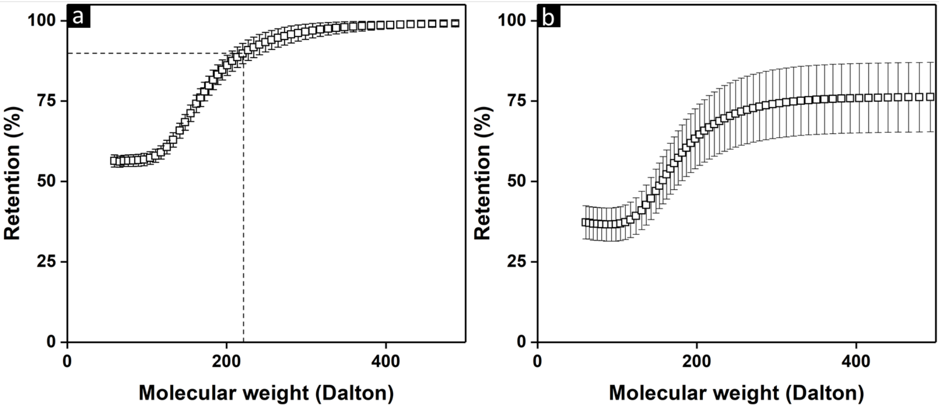

Figure S6.3. Molecular weight cut-off of the NF membranes prepared in a coagulation bath with 2.5 M H_3PO_4 using a 20% w/v PSaMA, 40% v/v acetic acid polymer casting solution before exposure to a pH 10 feed solution for 48 hours (a) and after (b).

Chapter 7

Outlook

In this thesis, the preparation of a new class of polymeric membranes made via a single-polyelectrolyte aqueous phase separation (APS) approach has been extensively investigated. As discussed in Chapter 1 the overall goal of this work is to showcase an alternative and more sustainable approach to prepare polymeric membranes that avoids the use of toxic organic solvents. This thesis highlights the viability of this APS approach as both open microfiltration (MF) and ultrafiltration (UF) membranes as well as dense nanofiltration (NF) membranes have been prepared through tuning of several different system parameters. These parameters include polymer concentration and the pH difference between the membrane casting solution and the coagulation bath (analogous to the solvent-to-nonsolvent ratio) which are very similar to tuning parameters used in traditional nonsolvent induced phase separation (NIPS) processes. The effect of other tuning parameters however, such as salt identity and concentration, and acid type and concentration are quite unique to the APS process. This thesis shows that with poly(styrene-alt-maleic acid) (PSaMA) membranes can be prepared with excellent retention performances in aqueous environment and have mechanical stability at high applied pressure and chemical stability in various solvents, demonstrating the potential of the APS approach. There is however always room for improvement. For the membranes prepared with PSaMA in Chapter 3, 4, and 6, significant amounts of acetic acid and/or phosphoric were used in both the solution and the coagulation bath which works against the goal of sustainability. However, Chapter 5 has demonstrated it is also possible to significantly reduce the amount of acid in the coagulation bath and still prepare good membranes. Another recurring issue has been with the relatively low permeability the NF membranes, while they show excellent retention properties, the water permeability is typically an order of magnitude lower than those that are commercially available. In this Chapter several suggestions and preliminary findings are presented which can provide a basis for further investigations into the single polyelectrolyte APS approach.

7.1 Choice of polymer

In Chapter 2, membranes were prepared with poly(4-vinylpyridine) (P4VP) and they possessed decent retention and water permeability, but their mechanical stability at higher pressures was lacking. Crosslinking P4VP quarternizes the amine groups of the polyelectrolyte, introducing permanent positive charges to the membranes which leads to swelling of the polymer matrix and ultimately introduced instability in the membrane over time. A way to overcome these problems was explored in Chapter 3 by using a different polyelectrolyte, PSaMA, which by combining responsive monomers with hydrophobic monomers resulted in membranes with an improved mechanical stability. In addition, the carboxylic acid groups of PSaMA could be cross-linked without introducing permanent charges. Using these advantages, better membranes could be prepared. However, large quantities of acetic acid were needed in the casting solution for the formation of porous membrane structures. Attempts to prepare membranes with PSaMA without acetic acid in casting solution have not been successful as only dense films with a very low porosity and no water permeability could be prepared. Another issue of using PSaMA is that casting solutions thereof always have a high turbidity as seen in Chapter 4. This high turbidity means that PSaMA solutions are past the cloud point and are actually a seemingly stable suspension of small PSaMA particles in solution. This indicates there are strong polymer-polymer interactions which are expected to be caused by hydrophobic interactions of the styrene functionality. While Chapter 3-6 demonstrate that it is still possible to prepare good membranes with these PSaMA solutions, the expectation is that better membranes can be obtained when using a polymer that is not already partially precipitated before it is made into a membrane.

7.1.1 Tailoring of the copolymer's hydrophobic group

A simple approach for trying out alternative polymers is to substitute the styrene groups of PSaMA with other hydrophobic monomers. In Figure 7.1, the chemical structure of PSaMA as well as several potential alternative polymers are shown. In Chapter 2, it is discussed that an alternating copolymer is preferred over a random copolymer as the homogenous distribution of hydrophilic and hydrophobic parts most likely aids in the homogenous precipitation of the polymer. However, the ability to obtain alternating copolymers with radical polymerization depends on the reactivity ratios of the two monomers.[1] Apart from PSaMA the polymers depicted in Figure 7.1 will most likely be random copolymers when polymerized, but as long as the distribution is more or less homogeneous no serious problems are expected. In work performed, but not discussed in this thesis, it was found that when poly(1-hexene-co-maleic acid) (PHaMA) and poly(1-octene-alt-maleic acid) (POaMA) were synthesized these polymers, unlike PSaMA, formed transparent solutions with a low turbidity (< 1 FNU). Unfortunately, the molecular weights of the synthesized polymers were quite low (M_w <50,000 g/mol) which resulted in structures with poor mechanical properties. It widely known that mechanical properties of polymeric material are strongly dependent on the molecular weight of the polymer, where a higher molecular weight gives better mechanical properties due to an increased amount of polymer entanglement.[2] In membrane preparation besides the mechanical properties, also the overall membrane properties are affected as the solution viscosity and precipitation of the polymer are also affected by the molecular weight of the polymer.[3-4] Based on the chemical similarity of HSaMA, POaMA, and PSaMA the expectation is that with a higher molecular weight membranes can be prepared with HSaMA and POaMA using the APS approach. As the solutions prepared with these polymers are not already past the cloud point a greater control over membrane structure is expected which can lead to membranes with improved properties. Within this thesis there was unfortunately not enough time fully investigate and optimize the polymerization process.

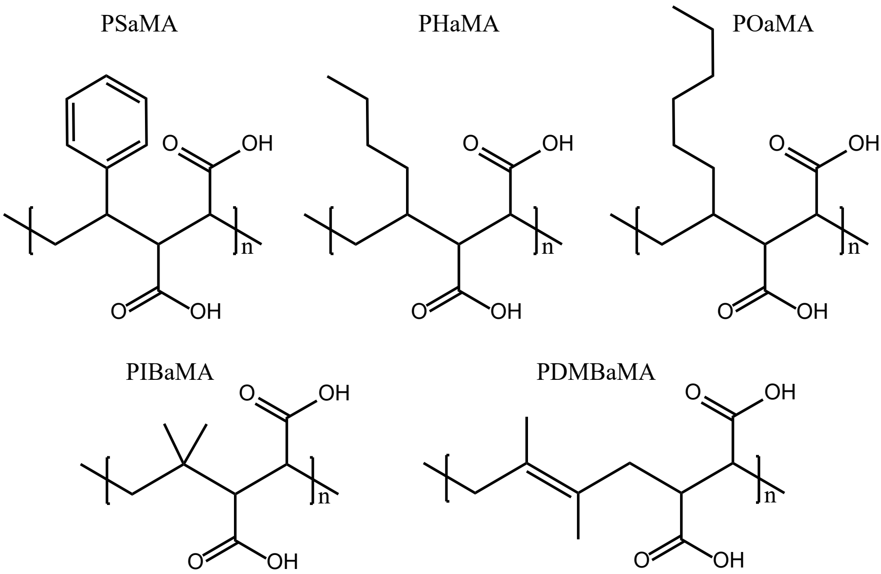

Figure 7.1: Chemical structures of polystyrene-alt-maleic acid (PSaMA), poly-1-hexene-alt-maleic acid (PHaMA), poly-1-octene-alt-maleic acid (POaMA), polyisobutylene-alt-maleic acid (PIBaMA), poly-2,3-dimethyl-1,3-butadiene-alt-maleic acid (PDMBaMA).

Poly(isobutylene-alt-maleic acid) (PIBaMA) is a polymer with a rubber functionality as the hydrophobic group, which is expected to improve the mechanical stability of the membranes by reducing brittleness. Initial testing with PIBaMA, obtained after hydrolysis of poly(isobutylene-alt-maleic anhydride) (ISOBAM™-18 polymer received from Kuraray), revealed that PIBaMA is more hydrophilic than the other polymers of Figure 7.1 as the isobutylene group is relatively small. As a result, it was necessary to use extreme pH conditions to precipitate PIBaMA. To allow for precipitation in milder condition the hydrophobicity of the polymer was increased by modifying the ISOBAM™-18 with 2-

methoxyethylene amine (MEA) instead of hydrolysing it, resulting in a more hydrophobic responsive polymer as depicted in Figure 7.2a. Using this modified PIBaMA membrane structures were be prepared as seen in Figure 7.2b, c. These membranes displayed strong elastic properties as the film could be extended laterally over 100% of their original dimensions without causing permanent visible deformation. Unfortunately, the crosslinking method used for PSaMA membranes was ineffective as most likely the amic acid groups are significantly less reactive than the maleic acid groups. This shows that using a rubbery monomer as the hydrophobic group has potential but does require further investigation. As the low hydrophobicity of isobutylene is an issue, an interesting alternative would be to use larger and therefore more hydrophobic rubber groups such as 2,3-dimethyl-1,3-butadiene as used in poly(2,3-dimethyl-1,3-butadiene-alt-maleic acid) (PDMBaMA), Figure 7.1.

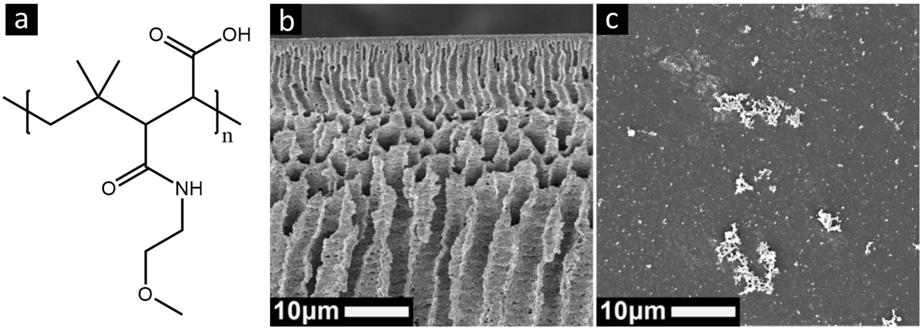

Figure 7.2: (a) MEA modified PIBaMA. (b, c) SEM images of the cross section and top surface of a membrane prepared with MEA modified PIBaMA.

7.1.2 Tailoring of the copolymer’s responsive group

Besides changing the hydrophobic monomer of the copolymer it is also possible to replace the maleic acid group with a different hydrophilic, responsive monomer. At the beginning of the project polymethacrylic acid was investigated but was found to be too hydrophilic to precipitate without using extreme pH conditions (pH ≤0). Increasing the hydrophobicity of the polymer by copolymerizing methacrylic acid with a small hydrophobic monomer such as isobutylene, propylene, or ethylene might provide interesting materials for the APS system. Stepping away from carboxylic acid groups is also an interesting possibility as carboxylic acid groups are always charged at a neutral pH which makes it necessary to perform a crosslinking step after membrane formation. Aromatic alcohol groups are an interesting alternative as they can typically be de-protonated to have a negative charge at pH>10 which would make it possible to have a stable membrane at neutral and acidic pH conditions without the need for crosslinking. Poly(4-hydroxystyrene) (P4HS) is such a polymer but unfortunately the molecular weight of commercially available polymers is too low (M_w <30,000) and would need to be synthesized at a higher molecular weight to be used for membrane preparation which is possible using anionic polymerisation.[5] Instead of using acidic responsive monomers, basic responsive monomers (like those of P4VP) are also of interest, although these are more limited. Most basic polymers are based on amine functionalities and typically are water-soluble even when uncharged. A polybase polymer like P4VP which is hydrophobic enough to be insoluble in water when uncharged is definitely of interest for APS, as long as it does not rely on tertiary amine group such as P4VP does as that complicates any crosslinking due to the introduction of generally unwanted permanent charges.

7.1.3 Use of step growth polymers

In Chapter 2 it is mentioned that when combining hydrophobic and responsive hydrophilic monomers into an APS polymer it is important to have a homogenous distribution of hydrophilic and it to undergo a homogenous precipitation. As mentioned before. with chain-growth copolymerization this is always difficult to achieve as while it can be steered with the reactivity ratios, each monomer is randomly added to the growing polymer chain.[6] Step-growth polymerization is an interesting alternative as, depending on the monomer selection the polymers are intrinsically alternating. This way, by combining a responsive monomer with an unresponsive one, perfectly alternating copolymers for APS can be prepared. The disadvantage of step-growth polymers is that most polymers made this way, such as polyesters, polyamides, and polyurethanes are vulnerable to oxidation and degradation during common membrane cleaning procedures involving strong pH environments and oxidizing agents like sodium hypochlorite.[7] A solution could be to look at chemically stable high performance polymers such as polyether sulfone (PES) and polyether ether ketone (PEEK). These polymers are commonly used in conventional membrane processes and have very good chemical and mechanical properties.[8] If polymers like these can be made to be pH responsive they would be very interesting to use in APS. In fact, one such a polymer has already been reported in literature. In 1998 Trotta et al. reported a highly sulfonated variation of PEEK: sulfonated poly(oxa-*p*-phenylene-3,3-phthalido-*p*-phenylene-oxa-*p*-phenylene-oxy-phenylene) (SPEEK-WC) which is water-soluble under most conditions and becomes water-insoluble at pH values <1.[9] Figure 7.3 shows the chemical structure of SPEEK-WC. Designing specialty polymers like SPEEK-WC for APS would be an interesting step towards the preparation of high performance APS membranes.

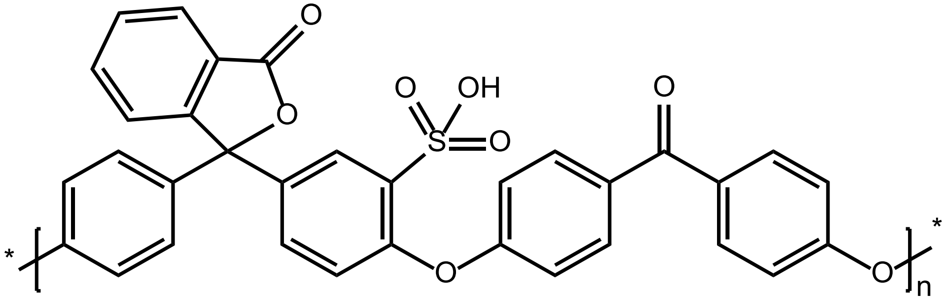

Figure 7.3. Chemical structure of sulfonated poly(oxa-*p*-phenylene-3,3-phthalido-*p*-phenylene-oxa-*p*-phenylene-oxy-phenylene) (SPEEK-WC).

7.2 Polymer quality and its molecular weight distribution

To prepare reproducible polymeric membranes of high quality it is important to have a consistent polymer quality with preferably a polydispersity (PDI) ≤ 3. During this thesis several issues with reproducibility were encountered which after thorough experimentation were found to be caused by changes in the quality of the PSaMA. While nuclear magnetic resonance (NMR) analyses showed no significant differences in the chemical composition of different batches of the polymer, gel permeation chromatography (GPC) analysis of the different polymer samples revealed that all had a bimodal chain lengths distribution; one part was the desired high molecular weight polymer chains and the other part a very low molecular weight polymer, Figure 7.4. This shows that there is a massive amount of short chains, which are no larger than a couple of monomers, in each polymer sample. The amount of this low molecular weight fraction varies widely depending on the polymer sample, causing an extremely high PDI values ranging from 15 to almost 70. While typically for polymers prepared with free radical polymerization a PDI of 2–3 can be expected.[6] Such large changes in the dispersity, and thus the quality of polymer, were not expected as all the polymer was bought from the same supplier and no changes in the product specification were noticed. For all the received polymer, the pre-use treatment i.e., evaporation of water at 100 ^{O}C, and the listed average mass average molar mass (M_w) was the same. However, as M_w is mostly determined by the high molecular weight fraction it is actually relatively similar (within 10% error) for all polymer samples. This indicates that a full analysis of received material can be essential to obtain reproducible results.

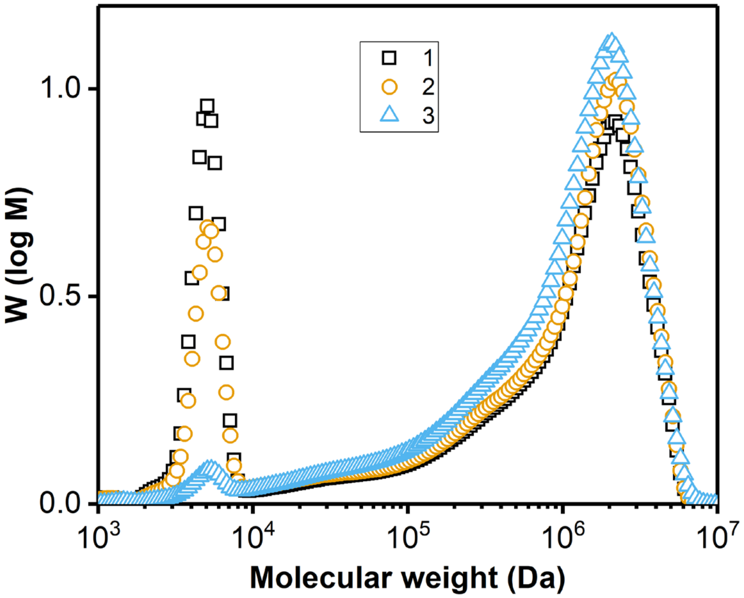

Figure 7.4. Weight distribution of three different PSaMA samples. The GPC is calibrated to dextran standards which means that the actual molecular weight of the PSaMA sample can be different than indicated.

The presence of a low molecular weight fraction can significantly lower the mechanical properties of any material.[2] It is suspected that the large amounts of defects observed in the membranes prepared in Chapter 5 are a direct result of the large dispersity of the PSaMA that was used in those experiments. To confirm this, two 20% w/v PSaMA, 40% v/v acetic acid polymer solutions were prepared using polymer sample 1 and 3 from Figure 7.4. With these solutions membranes were prepared in a similar fashion as in Chapter 5 which revealed that defect formation in the top layer of the membranes is indeed strongly affected by the polydispersity of the PSaMA, Figure 7.5. While the top layers of both membranes show some sort of patterning, the pattern of the membrane prepared with polymer sample 1, with a high polydispersity, is more distinct and that membrane has a large amount of defects in the top layer similar to those of the membranes prepared in Chapter 5. Defects like those observed here are completely detrimental for membrane performance and make them unsuitable for any application. For the membrane prepared with polymer sample 3, while some patterning is observed, no such defects were found. As discussed in Chapter 5 these patterns appear to be formed due to a shrinking of the top layer, which most likely is caused by the presence of the low molecular weight fraction of the PSaMA. As the molecular weight is so low for that fraction it is most likely not crosslinked and is potentially washed out of the membrane during the crosslinking step. It is expected that the voids left by the removal of this low molecular weight material causes stress in the top layer of the membrane which results in the formation the observed patterning and defects. It is expected that with a PSaMA sample with a dispersity ≤ 3 the membrane would be entirely defect-free and no patterning would be observed.

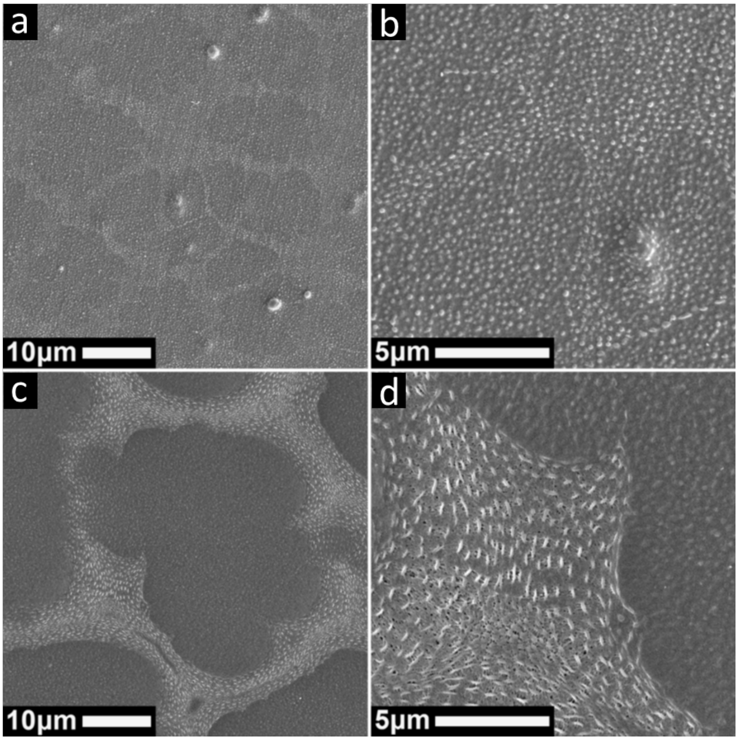

Figure 7.5. SEM images of the top surface of membrane prepared in 0.2M HCl using a 20% w/v PSaMA, 40% v/v acetic acid polymer solution. The membrane in a, b is prepared with polymer sample 3 which has a polydispersity of 15.5 while the membrane in c, d is prepared with polymer sample 1 which has a polydispersity of 67.

7.3 Making the transition to a hollow fiber geometry

All the previous chapters in this thesis have solely discussed the preparation of flat sheet membranes as with flat sheet membranes it is easy to study a wide variety of system parameters which is highly preferable when developing a new process. However, from an application point of view hollow fiber membranes are often a much more desired geometry. Hollow fibers offer high packing densities with a large surface area, while also requiring less pre-treatment and are less prone to fouling than spiral wound modules commonly used with flat sheet membranes.[8, 10] It is therefore relevant to investigate the possibilities of preparing hollow fiber membranes with the APS approach. Preliminary investigations performed recently show that it is indeed possible, although there are still several major issues to overcome. Figure 7.6 shows a hollow fiber membrane that was prepared using the single-polyelectrolyte APS approach, but it has severe delamination of the inner and outer structures. It is expected that this is caused by the relatively slow precipitation speed of PSaMA as it required approximately two minutes to fully precipitate instead of in the order of seconds which is common for conventional NIPS systems. Shrinking of the membrane during the precipitation is also a factor as it has been observed previously that flat sheet PSaMA membranes, when prepared in phosphoric acid, typically have a thickness of only 30% of the original casting height. To overcome these issues different acid types, such as formic and malonic acid which do not induce shrinking of the membrane thickness can be used and the polymer solution can be tuned using different polymer and additive concentrations, or a different polymer can be used. Another solution for the slow precipitation speed would be to use slow spinning speeds in combination with a deeper coagulation bath giving the fiber more time to precipitate and solidify. Similar to flat sheets prepared in low pH conditions the shell (outer) side of the membrane has a dense layer, however a very porous layer is observed on the bore side even though a dense layer was expected there as a low pH was used in the bore. Apparently when spinning hollow fibers, the precipitation kinetics of PSaMA on the bore side are significantly different compared to the flat sheet membranes where 2.5M H_3PO_4 causes a dense layer to form. Most likely the difference is caused by the significant difference in volume of the bore liquid compared to a coagulation bath. In Chapter 2 it is described how the addition of acetic acid to the coagulation bath can be used to control the rate at which PSaMA precipitates and how that can be used to create open porous structures. The hypothesis is that something similar is happening in the bore of the hollow fiber. Solvent exchange of acetic acid from the polymer solution with the bore liquid is causing a significant increase in acetic acid concentration in the bore liquid which then changes the precipitation behavior of PSaMA. Therefore, to prepare hollow fibers with a dense layer on the inside it can be beneficial to reduce the acetic acid concentration in the polymer solution as discussed in Chapter 5. However, it is important to take into account that a reduction in acetic acid concentration also significantly slows down the precipitation of PSaMA.

From this initial spinning experiment it can be concluded that preparation of hollow fibers is definitely possible with the single-polyelectrolyte APS approach and that as expected some parameter behave similarly as with flat sheets and some definitely do not. The development of hollow fibers prepared via the APS approach is an important step towards a wider application of the APS technique and highlights a way to increase the sustainability of the membrane industry.

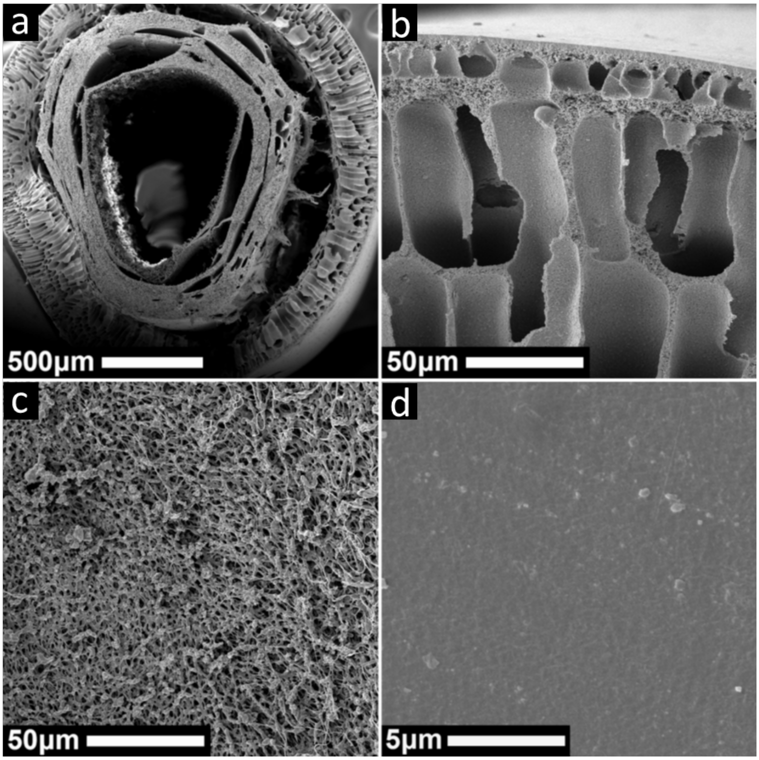

Figure 7.6. SEM images of a hollow fiber prepared with PSaMA, showing the cross section (a, b), bore side surface (c), and shell side surface (d). The hollow fiber was prepared using 2.5M H_3PO_4 in the bore and 0.25 M H_3PO_4 with 0.5M HCl in the coagulation bath using a 20% w/v PSaMA, 40% v/v acetic acid polymer solution.

7.4 Summary

This thesis has thoroughly investigated the preparation of membranes using single-polyelectrolyte APS approach with the P4VP and PSaMA polymers. It has demonstrated the versatility of the approach by highlighting how a wide range of system parameters, some of which are similar to those in conventional NIPS while others are unique to the APS system, can be employed to prepare various open MF and UF membranes, and dense NF membranes. Extensive investigation into the performance of these membranes has revealed they can have excellent retention properties, mechanical stability, chemical stability in various solvents neutral to acidic conditions and, apart from the NF membranes, permeability. In essence, the single-polyelectrolyte APS is a promising sustainable alternative to conventional membrane preparation methods which is currently in its early years of development with room for improvement.

7.5 References

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Summary

This thesis investigates and demonstrates how polymeric membranes can be prepared using the new and more sustainable aqueous phase separation (APS) approach. Polymeric membranes are used on huge scales for kidney dialysis, wastewater treatment, drinking water production, and as a less energy intensive alternative to conventional industrial separation processes. However, the vast majority of polymeric membranes are produced via an unsustainable and environmentally unfriendly process which uses large amounts of reprotoxic chemicals like N-methyl-2-pyrrolidinone (NMP) and dimethylformamide (DMF). Unlike the conventional methods the APS approach is a water based system using a pH or salinity switch instead of reprotoxic organic solvents to prepare membranes. This allows for a more sustainable membrane production process without the use of reprotoxic solvents. In the past few years three different APS approaches have been established; the first is the single-polyelectrolyte approach, where a responsive polyelectrolyte solution is precipitated by a pH switch. The second and third approach, on the other hand, use a two polyelectrolyte APS system where the complexation of oppositely charged polyelectrolytes forms the membrane either through a pH or a salinity switch. This thesis focusses on the single polyelectrolyte approach and investigates two different polyelectrolytes that can be used in this approach as well as various parameters that can be used to control and tune the membrane preparation.

In Chapter 1 an introduction to membrane technology and applications is provided along with an overview of parameters used in conventional polymeric membrane preparation, the non-solvent induced phase separation (NIPS) approach. Several alternative methods to prepare polymeric membranes, which use different and less toxic solvents than the conventional NIPS method, are discussed. These methods aim to improve the sustainability of polymeric membrane production but ultimately still rely on organic solvents which the APS approach tries to avoid.

The preparation of membranes using the pH-responsive polymer poly(4-vinyl pyridine) (P4VP) is discussed in Chapter 2. P4VP is a polybase and is dissolved at low pH where the polymer is charged and water-soluble, and subsequently casting the solution as a thin film. Switching to a high pH where the polymer becomes uncharged and insoluble results in controlled phase separation and solidification of the polymer into porous membrane structures. By tuning the pH of the coagulation bath and the polymer and acid concentration in the polymer casting solution a large control over the membrane structure

is achieved. It was found that by using acetic acid instead of hydrochloric acid in the polymer casting solution the highest control over structure and reproducibility was achieved, most likely due to the weak acid acting as a buffer. By using these tuning parameters both symmetric porous microfiltration membranes and asymmetric dense nanofiltration membranes were prepared. In addition, the pH-responsive nature of P4VP automatically leads to a pH-responsive membrane where the degree of responsive behaviour can be tuned by the degree of crosslinking. This responsive behaviour makes it possible to easily clean the membrane, without using harsh chemicals.

While good permeability and retentions were achieved with the P4VP membranes, the mechanical stability was found to be suboptimal, as failure of the membranes was observed at an applied pressure of more than 4 bar. To prepare membranes with high mechanical stability using the APS approach the copolymer polystyrene-alt-maleic acid (PSaMA) was used in Chapter 3. PSaMA combines the responsive monomer maleic acid, required for APS, with the unresponsive hydrophobic styrene which enhances the mechanical stability of the resultant membranes. The precipitation of PSaMA can be precisely controlled which allows the preparation of a wide range of membranes, from microfiltration membranes capable of treating oily waste water, to dense nanofiltration-type membrane with excellent micropollutant retentions. As with the P4VP system weak acids again are a key parameter in controlling the precipitation behavior of the polyelectrolyte. Acetic acid is used in the polymer casting solution, where it brings the polymer close to the point of precipitation, as well as in the coagulation bath where it controls the precipitation rate of PSaMA. By tuning the final pH of the coagulation bath MF and UF membranes are prepared and by using phosphoric acid instead of acetic acid in the coagulation bath dense NF membranes. The mechanical stability of the PSaMA membranes is significantly better than the P4VP membrane prepared in Chapter 2 as the membranes presented in this chapter demonstrate stable operation up to 20 bar of applied pressure.

The phase behavior of polyelectrolytes can be determined by the pH and salinity, but also by the exact nature of the used counter-ions. In Chapter 4 it is investigated how salt type can affect, and thus be used to control, the phase separation of PSaMA. At equal ionic strengths, it is found that Na_2SO_4 and LiCl lead to the formation of more open structures compared to NaCl, $NaNO_3$, NH_4Cl, and $MgCl_2$, while $CaCl_2$ leads to densification of the top layer. These ion-specific effects appear to be caused by a combination of ion mobility and the interaction potential between the ion and the polymer. With increasing salt concentration similar effects are observed for all salt types, the formation of asymmetric membranes with denser top layers. Overall, it is shown that salt identity and concentration are key parameters in the APS process, and can be used to prepare both open microfiltration as well as dense nanofiltration membranes.

While in Chapter 3 and 4 good membranes have been prepared, large amounts of acetic or phosphoric acid were used in the coagulation baths. To further improve the sustainability of the APS approach it is important to reduce the amounts of acid used and prepare membranes in milder conditions. In Chapter 5 it is demonstrated that it is possible to prepare membranes with PSaMA while only using low concentrations (0.1–0.3 M) of hydrochloric acid in the coagulation bath. Additionally, it is shown that polymer and acetic acid concentration in the polymer casting solution have significant effects on the membrane formation. Polymer concentration in APS behaves the same as in regular NIPS, where an increased concentration leads to denser structures and vice versa. In Chapter 5 this is employed to prevent defect formation in the selective layer of the nanofiltration membranes. Differences in the acetic acid concentration in the polymer casting solution appear to mostly affect the support structure of the membrane where a reduced concentration significantly reduces the formation of macrovoids. Understanding of how these parameters affect membrane preparation and performance is essential to optimizing membranes prepared with APS.

The membranes prepared with PSaMA are typically chemically cross-linked to prevent the polymer from redissolving at neutral pH conditions. As crosslinking is a common method to make membrane resistant to organic solvents it is of interest to investigate if the standard crosslinking of PSaMA membranes also makes them solvent resistant. In Chapter 6, it is demonstrated that PSaMA membranes have stable performance in both isopropanol (IPA) and toluene, and a slightly reduced performance in *N*-methyl-2-pyrollidone (NMP). However, PSaMA does not perform well as a selective layer in these solvents, indicating that the real opportunity would be to use the UF type PSaMA membranes as solvent stable support membranes. Additionally, in Chapter 6 the pH stability and responsiveness of PSaMA membranes is also investigated. The membranes are shown to be stable in neutral and acid pH regimes (2–7) and the NF membranes demonstrate a pH dependent retention of Mg^{2+} and SO_4^{2-} ions while the UF type membranes show a strong pH responsive behavior in regards to permeability. However, long term exposure to elevated pH conditions (pH 8–10), result in severe swelling of the NF membranes resulting in defect formation, and compaction of the UF membranes. For the UF membranes this compaction was found to be reversible for some but not all of the membrane samples measured. These results show that in aqueous systems membranes prepared with PSaMA have interesting responsive behavior, but perform best at neutral and acidic pH values. Moreover, the membranes exhibited excellent stability in the organic solvents IPA and toluene.

While the single-polyelectrolyte APS approach is extensively investigated in Chapter 2–6 research is never finished and there is plenty of work left to be done. In Chapter 7 an overview of different avenues to continue the investigation into the single-polyelectrolyte APS approach is provided. This includes a selection of interesting polymers specifically designed for the APS approach which can lead to new and improved membranes. Another important step in development of APS is the preparation of hollow fiber membranes, which offers some distinct advantages over flat sheet membranes, such as reduced fouling and higher packing densities. Initial results are shown which demonstrate that it is possible to prepare hollow fibers using the single-polyelectrolyte APS approach. Additionally, some issues that were encountered concerning the polymer quality are discussed which can have a severe impact on the formation on (defect free) membranes.

Overall, this thesis showcases the single-polyelectrolyte APS approach, a highly novel sustainable approach to prepare polymeric membranes. The approach offers distinct advantages over conventional membrane preparation methods as it does not rely on reprotoxic solvent. Moreover, it matches the versatility of the conventional methods as it allows for the preparation of both open and dense membranes. The prepared membranes can match commercial available membranes with retention in aqueous environments, have high mechanical stability and are resistant to various organic solvents. However, the permeability of the dense membranes still requires improvement. With these results this thesis makes the beginning of the new APS method which has the potential to significantly improve the sustainability of the membrane industry.

Samenvatting

Dit proefschrift onderzoekt hoe polymeermembranen gemaakt kunnen worden met de nieuwe en duurzame waterige fase scheidingsmethode (APS). Polymeermembranen worden hedendaags op grote schaal gebruikt voor onder andere: nierdialyse, afvalwater zuivering, drinkwater productie, en als energiezuinig alternatief voor veel traditionele industriële scheidingsprocessen. De meeste polymeermembranen worden echter gemaakt met een niet duurzame, milieuonvriendelijke methodes die grote hoeveelheden reprotoxische chemicaliën zoals N-methyl-2-pyrrolidinone (NMP) en dimethylformamide (DMF) verbruiken. In plaats daarvan gebruikt de APS methode een systeem gebaseerd op water, waar een wisseling in pH waarde of het zoutgehalte wordt gebruikt om het membraan te maken. Dit zorgt voor een duurzamer productieproces zonder reprotoxische oplosmiddelen. In de afgelopen jaren zijn er drie verschillende varianten van de APS methode ontwikkeld; als eerste de enkele-polyelektrolyt variant waar een polyelektrolyt wordt neergeslagen uit oplossing door een pH wisseling. In de tweede en derde variant worden twee verschillende soorten polyelektrolyten gebruikt waarbij de complexatie van de verschillende polyelektrolyten als gevolg van een wisseling in de pH of het zoutgehalte het membraan vormt. In dit proefschrift ligt de nadruk op de eerste enkele-polyelektrolyt variant en wordt onderzocht hoe membranen hiermee gemaakt kunnen worden en hoe verschillende parameters gebruikt kunnen worden om de eigenschappen van het membraan te sturen.

In Hoofdstuk 1 wordt een introductie gegeven over membraan technologie en toepassingen van membranen. Verder is er een overzicht van verschillende parameters die gebruikt worden in de traditionele membraan productieprocessen met de niet-oplosmiddel geïnduceerde fase scheidingsmethode (NIPS). Ook worden verschillende alternatieve methodes om polymeermembranen te maken met minder toxische oplosmiddelen besproken. Hoewel deze alternatieve methodes de duurzaamheid van het productie proces kunnen verbeteren, zijn ze nog steeds afhankelijk van organische oplosmiddelen voor de fasescheiding waar de APS methode water met zuur en base voor gebruikt.

Het bereiden van membranen met de pH-responsieve polymeer poly(4 vinyl pyridine) (P4VP) wordt besproken in Hoofdstuk 2. P4VP is een polybase en kan opgelost worden in water met een lage pH waarde waarin de polymeer een positieve lading krijgt en dus water oplosbaar wordt. De oplossing wordt als een dunne laag uitgestreken en door het in een waterbad met een hoge pH waarde te stoppen verliest de polymeer zijn lading waardoor die gecontroleerd neerslaat en een poreuze membraan structuur vormt. Door de pH van het coagulatiebad en de hoeveelheid zuur in de polymeer oplossing te veranderen kunnen verschillende soorten membranen gemaakt worden. Het is ondervonden dat door azijnzuur in plaats van zoutzuur te gebruiken in de polymeer oplossing, de beste controle over de membraan structuur en de hoogste reproduceerbaarheid kan worden bereikt. Waarschijnlijk komt dit door de buffercapaciteit van azijnzuur. Met behulp van deze parameters zijn zowel symmetrische en asymmetrische membranen gemaakt. Door de pH responsieve eigenschappen van P4VP zijn de membranen ook pH responsief, wat gestuurd kan worden door de hoeveelheid verknopingen. Met deze responsieve eigenschappen is het mogelijk om het membraan makkelijk schoon te maken met een pH wisseling in plaats van agressieve chemicaliën.

Hoewel een goede permeabiliteit en retentie behaald werd met de P4VP membranen was de mechanische stabiliteit niet zo goed aangezien ze vaak kapot gingen bij een druk hoger dan 4 bar. Om membranen te maken met een goede mechanische stabiliteit is de copolymeer polystyreen-alt-maleïnezuur (PSaMA) gebruikt in Hoofdstuk 3. PSaMA combineert het pH responsieve monomeer maleïnezuur, wat nodig is voor APS, met het niet responsieve hydrofobe styreen wat zorgt voor een betere mechanische stabiliteit. De precipitatie van PSaMA kan goed gestuurd worden wat het mogelijk maakt om veel verschillende membranen te maken. Van microfiltratie (MF) membranen, geschikt voor het behandelen van oliehoudend afvalwater, tot nanofiltratie (NF) membranen met zeer goede retentie voor microverontreinigingen. Net als met P4VP zijn zwakke zuren erg belangrijk voor het sturen van de fasescheiding van PSaMA. Azijnzuur wordt in de polymeeroplossing gebruikt om de polyelektrolyt dicht bij het punt te brengen waarop deze zal neerslaan. Azijnzuur wordt ook in het coagulatiebad gebruikt waar het de snelheid stuurt waarmee PSaMA precipiteert. Door het afstellen van de pH in het coagulatie bad kunnen MF en ultrafiltratie (UF) membranen gemaakt worden en als fosforzuur gebruikt wordt in plaats van azijnzuur kunnen NF membranen gemaakt worden. De mechanische stabiliteit van deze membranen is significant beter dan die van de P4VP membranen in Hoofdstuk 2 aangezien deze membranen stabiel blijven tot zeker 20 bar aan toegepaste druk.

De fasescheiding van polyelektrolyten kan beïnvloed worden door de pH en het zoutgehalte maar is ook afhankelijk van het soort ion. In Hoofdstuk 4 is het onderzocht hoe het zout type gebruikt kan worden om de fasescheiding van PSaMA en dus de membraanstructuur te sturen. Bij gelijke ionische kracht zorgen Na_2SO_4 en LiCl voor een meer open structuur dan NaCl, $NaNO_3$, NH_4Cl, en $MgCl_2$, terwijl $CaCl_2$ zorgt voor een dichtere toplaag. Deze ionspecifieke effecten zijn waarschijnlijk het gevolg van zowel de mobiliteit en het interactiepotentiaal tussen ionen en de polymeer. Als een hogere zoutconcentratie wordt gebruikt worden er vergelijkbare effecten gezien voor alle zouten, namelijk dat asymmetrische structuren met een dichte toplaag gevormd worden. Dit laat zien dat zout concentratie en type belangrijke parameters zijn in de APS methode en dat ze gebruikt kunnen worden om zowel open MF als dichte NF membranen te maken.

Hoewel in Hoofdstuk 3 en 4 goede membranen zijn gemaakt is er relatief veel azijn en fosforzuur gebruikt. Om de duurzaamheid van de APS methode te verbeteren is het belangrijk om zo min mogelijk zuur te gebruiken. In Hoofdstuk 5 wordt aangetoond dat het mogelijk is om membranen te maken van PSaMA met relatief lage concentraties HCl (0.1–0.3 M ten opzichte van 2 M). Daarnaast wordt ook aangetoond dat de concentratie van polymeer en azijnzuur in de polymeeroplossing zelf een sterk effect heeft op de vorming van de membraan structuur. Het effect van polymeerconcentratie in APS is vergelijkbaar als in NIPS, waar een hogere concentratie leid tot dichtere structuren en vice versa. In Hoofdstuk 5 wordt dit gebruikt om de formatie van defecten in de selectieve laag van de NF membranen tegen te gaan. Verschillen in de azijnzuurconcentratie in de polymeeroplossing hebben voornamelijk een effect op de ondersteunende structuur van de membranen en door een lagere concentratie te gebruiken wordt de hoeveelheid macroleegtes in het membraan sterk verminderd. Het goed begrijpen van de effecten van deze parameters is essentieel voor het optimaliseren van de APS methode.

De membranen gemaakt met PSaMA worden standaard chemisch verknoopt om te voorkomen dat de polymeer oplost bij een neutrale of basische pH. Het verknopen van membranen is een gebruikelijke methode in membraantechnologie om een membraan stabiliteit te geven in organische oplosmiddelen. Het is daarom interessant om te onderzoeken wat de stabiliteit van verknoopte PSaMA membranen in verschillende oplosmiddelen is. In Hoofdstuk 6 wordt aangetoond dat verknoopte PSaMA membranen stabiel zijn in zowel isopropanol (IPA) en tolueen, en een licht verminderde prestatie hebben in NMP. PSaMA functioneert echter niet goed als een dichte selectieve laag in deze oplosmiddelen, wat aangeeft dat het waarschijnlijk interessanter is om PSaMA UF membranen als steun membraan te gebruiken voor een selectieve laag van een ander materiaal. Daarnaast is in Hoofdstuk 6 de pH responsiviteit van PSaMA membranen onderzocht. De membranen zijn zoals verwacht stabiel in zure en neutrale omstandigheden (pH 2–7) en de NF membranen hebben pH afhankelijke retentie van

Mg^{2+} en SO_4^{2-} terwijl permeabiliteit van de UF membranen duidelijk pH afhankelijk is. Echter bij blootstelling aan een hoge pH voor een langere tijd zwellen de NF membranen en krijgen ze defecten en dat de UF membranen compacteren. De compactie van de UF membranen is grotendeels reversibel maar niet voor alle membranen die gemeten zijn. Dit laat zien dat PSaMA membranen een interessant responsief gedrag hebben in water en het beste functioneren in zure en neutrale omstandigheden. Daarbij hebben de membranen een goede stabiliteit in IPA en tolueen.

Hoewel de enkele-polyelektrolyt APS methode uitgebreid onderzocht is in Hoofdstuk 2–6 is het onderzoek nooit klaar. In Hoofdstuk 7 worden verschillende interessante onderwerpen voor een vervolgonderzoek gegeven. Onder andere een selectie van interessante polymeren die specifiek voor de APS methode ontwikkeld zijn wordt gegeven waar waarschijnlijk nieuwe en betere membranen mee gemaakt kunnen worden. Een andere belangrijke stap in de ontwikkeling van de APS methode is het maken van holle vezel membranen aangezien die verschillende voordelen bieden ten opzichte van vlakke vel membranen, zoals minder vervuiling en een hogere verpakkingsdichtheid in membraanmodules. De eerste resultaten laten zien dat dit mogelijk is met de APS methode. Verder worden een aantal problemen besproken die tijdens het onderzoek voor dit proefschrift zijn ondervonden.

Al met al laat dit proefschrift zien hoe met de nieuwe duurzame enkele-polyelektrolyt APS methode polymeermembranen gemaakt kunnen worden. Deze methode heeft duidelijke voordelen ten opzichte van conventionele methodes omdat er geen reprotoxische oplosmiddelen gebruikt worden. Net als de conventionele methode heeft de APS methode een goede flexibiliteit aangezien het mogelijk is om verschillende soorten membranen te maken met zowel een open als een dichte structuur. Verder hebben deze membranen en goede retentie in water, een goede mechanische stabiliteit, en zijn ze resistent tegen verschillende oplosmiddelen. Echter voor de permeabiliteit van de dichte membranen is er nog verbetering nodig. Met deze resultaten maakt dit proefschrift een belangrijk begin voor de ontwikkeling van de nieuwe APS methode die de potentie heeft om de membraan industrie significant duurzamer te maken.

Acknowledgements

“The Acknowledgements section is the most important part of the thesis since it is the most read”

Matthijs Oosterbeek 2021

Acknowledgements

This is the part where I would like to thank everyone who helped me, supported me and made the 4.167 years of my PhD a very pleasant and educative experience.

Wiebe I would like to thank you for offering me this opportunity. I remember that it went rather fast, just a few days after our first interview you already offered me the position. To me it felt as that you were very confident I was a good person for the job. During the project that feeling has never left me. You gave me the freedom to do things my way and helped me focus when I was enthusiastically experimenting away, varying multiple parameters at once. Whenever my experiments weren't going as planned and I didn't know how to proceed you were always available for a quick talk and helped me see things weren't as bad as I thought and a way to proceed. I think your way of supervision is inspiring and I greatly appreciate everything you have done for me.

A lot of people have been involved in my project and Josh you have been there with me from start to finish, helping me with excellent and critical feedback, thank you. Micah and Julia, it was a very educative experience for me to supervise you and both of you were amazing students and I will not forget your enthusiasm. Elif and Irshad it was very pleasant to work and share an office with you and I'm looking forward to reading your theses on the polyelectrolyte complexation APS system. Lily thanks a lot for your help with the graphical abstracts, it was very nice to work with you. Ameya thanks for your interest in sometimes unconventional taste of music, it was always nice to work on the lab with you around. I have always enjoyed being part of MSuS, so thanks to everyone who was a part of it!

Dennis, we have been sitting together in the office since the beginning and we have had a lot of fun times as well as some good scientific discussions. It was a lot of fun to be your paranymph when you graduated last year and now our roles are reversed and you are supporting me, thanks a lot! Reinier, you are my brother, very good friend, and now also paranymph. One of the reasons why I did not hesitate to move all the way out to Enschede for my PhD was that were already living here and I looked forward to seeing you on a weekly basis again. I really appreciate the support you and also Anna have given me. Even though most of what I have done is not your area of expertise, discussing problems I encountered with you was always fruitful and helped me to achieve a greater understanding of them as well as potential ways to solve them.

Harmen, thanks for always being available for questions about anything related to membranes and helping me build my own set-up. Iske, it was very nice working with you and thanks for all the help. Bob, you were my favorite technician called Bob in the MST cluster. Ineke I really appreciate your readiness to help me with whatever I needed when I was finishing my PhD. Frank, you were always helpful, especially when I needed to borrow something from the IM group. Almohanad, thanks for the help with the IC. Esra, thanks for the excellent fume hood decoration.

Coffee and thee breaks as well as the Friday afternoon borrels were always nicely relaxing and entertaining and I have had many interesting conversations over the years. Alberto, Anne, Antoine, Burak, Dennis, Denys, Esra, Hans David, Harmen, Iske, Jan, Janieke, Jurjen, Mariël, Matthijs, Moritz, Nicole, Nikos, Oguz, Patrick, Wendy, Youri, and others I forgot to mention, thanks for all the fun times.

I’m a big fan of board games and luckily I wasn’t the only one in the MST cluster. Burak, Elif, Esra, Hans David, Harmen, Iske, Jeff, Jéré, Jurjen, Lily, Moritz, Nicole, Renaud, Timon, Wendy, Tao, and Youri, thanks for all the fun playing board games with you, around the table as well as online.

I also want to thank my friends from the various Dungeons and Dragons groups I have played with the during my PhD. Anna, Carolien, Erik, George, Jelle, Matthijs, Marijn, Martin, Reinier, Stan, Tim, Wendy, Wouter. The magnificent adventures we have had with our various groups including “The Phandalin Protectorate”, “de fantastische fijf”, and “de GOATs” have been an amazing way to relax after work.

Erik, Matthijs, and Milan thanks for all the good times. Playing board/card/computer games with you in the weekends and complaining about PhD life to you was very nice.

I also want to thank everyone of the BHV team. It was very nice to be a part of the team knowing that whatever happens together we will all work together to help as best as we can.

Carolien, thanks for designing the cover, it looks amazing.

Pap en Mam, thanks for everything, without you I would have never gotten this far.

Then there are many more people, colleagues, friends, and family I haven’t mentioned but who have all supported me in some way or another. Thanks a lot.

List of publications

Per July 2021

Willott, J. D.; Nielen, W. M.; de Vos, W. M. Stimuli-Responsive Membranes through Sustainable Aqueous Phase Separation. *ACS Applied Polymer Materials* **2020,** *2* (2), 659-667.

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Nielen, W. M.; Willott, J. D.; Galicia, J. A. R.; de Vos, W. M. Effect of Solution Viscosity on the Precipitation of PSaMA in Aqueous Phase Separation-Based Membrane Formation. *Polymers* **2021,** *13* (11), 1775.

To be published:

Nielen, W. M.; Willott, J. D.; de Vos, W. M. Solvent and pH stability of poly(styrene-alt-maleic acid) (PSaMA) membranes prepared by aqueous phase separation (APS).

About the author

Wouter Martinus Nielen was born the 14th of April in 1993 in Best, the Netherlands. In 2011 he obtained his VWO diploma at the Pleincollege Bischop Bekkers in Eindhoven after which he started his bachelor studies in Molecular Life Sciences at the Wageningen University. In 2014 he graduated and continued with a master Molecular Life Sciences. During his master studies Wouter did an internship at the University of Auckland in New Zealand investigating advanced conducting polymer. After the internship Wouter finished his master with a thesis on smart self-healing polymer networks at the Laboratory of Organic Chemistry in Wageningen and graduated in 2016. In 2017 he started his PhD at University of Twente which resulted in the work presented in this Thesis. During his PhD Wouter was also part of the emergency response team of the university trained with self-contained breathing apparatus. As of April 15th Wouter has joined the European Membrane Institute as researcher.