New Polymeric Membranes for Organic Solvent Nanofiltration

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ABSTRACT

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The focus of this dissertation was the development, synthesis and modification of polymers for the preparation of membranes for organic solvent nanofiltration. High chemical stability in a wide range of solvents was a key requirement. Membranes prepared from synthesized polymers as well as from commercial polymers were designed and chemically modified to reach OSN requirements.

A solvent stable thin-film composite (TFC) membrane is reported, which is fabricated on crosslinked polythiosemicarbazide (PTSC) as substrate. The membranes exhibited high fluxes towards solvents like THF, DMF and DMSO ranging around 20 L/m² h at 5 bar with a MWCO of around 1000 g/mol.

Ultrafiltration PTSC membranes were prepared by non-solvent induced phase separation and crosslinked with GPTMS. The crosslinking reaction was responsible for the formation of an inorganic-type-network that tuned the membrane pore size. The crosslinked membranes acquired high solvent stability in DMSO, DMF and THF with a MWCO above 1300 g/mol.
Reaction Induced Phase Separation (RIPS) was introduced as a new method for the preparation of skinned asymmetric membranes. These membranes have two distinctive layers with different morphologies both from the same polymer. The top dense layer is composed of chemically crosslinked polymer chains while the bottom layer is a porous structure formed by non-crosslinked polymer chains. Such membranes were tested for vitamin B12 in solvents after either crosslinking the support or dissolving the support and fixing the freestanding membrane on alumina.

Pebax® 1657 was utilized for the preparation of composite membranes by simple coating. Porous PAN membranes were coated with Pebax® 1657 which was then crosslinked using TDI. Crosslinked Pebax® membranes show high stability towards ethanol, propanol and acetone. The membranes were also stable in DMF once crosslinked PAN supports were used.

Sodium alginate polymer was investigated for the preparation of thin film composite membranes. Composite membranes were prepared using PAN and crosslinked PAN supports; these membranes were tested for methanol and DMF. Freestanding nanofilms fixed on alumina were also tested for methanol and DMF as well as many other harsh solvents. The alginate composite membranes showed excellent solvent stability and good permeances and a MWCO of around 1300 g/mol.
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CHAPTER 1: Research motivation and objectives

1.1 Research motivation

Organic solvent nanofiltration is an emerging frontier in molecular separation. The potential of OSN is very large because it can replace thermal separation techniques such as distillation. It can easily be shown that for many separations the pressure driven OSN has a 10 times better energy efficiency than distillation. There are numerous potential applications for OSN such as: separation of medium MW species in solvents, molecular fractionation, organometallic catalyst recovery and reuse, bio-oil processing, chiral separation in organic media, room temperature solvent exchange, selective rejection and purification of pharmaceutical intermediates and many others. In spite of the huge potential of OSN the current market is still relatively small. The current choice of membranes is quite limited hindering a wider application of OSN.

The project aimed to investigate the potential of polymers, which have not been used as membrane material for OSN. The first one is lab-synthesized polythiosemicarbazide (PTSC) as a new material for OSN membranes. This polymer has been studied thoroughly as a polymer for metal complexation processes, but never as a nanofiltration membrane material. Thin film composites as well as integral asymmetric membranes were prepared from PTSC polymer and tested for harsh solvent filtrations. The second choice is a commercial polyether amide (Pebax) as a possible material for solvent filtration. Pebax has been described as membrane material before, but not for OSN. The
third choice is a “green alternative”. Biodegradable environmental friendly sodium alginate (NaAlg.) is crosslinked and tested for OSN applications.

1.2 Objectives

- Objective 1: characterization of PTSC and PTU polymers and membranes. (Chapter 3)
- Objective 2: Improvement of the chemical stability of PTSC membranes in organic solvents, specifically in polar aprotic solvents, which degrade the membrane integrity and performance (Chapter 4).
- Objective 3: Study thin film composite membranes prepared via interfacial polymerization on top of crosslinked PTSC membranes. (Chapter 4).
- Objective 4: preparing NF membranes, which are integrally skinned asymmetric through facile crosslinking reaction. (Chapter 5).
- Objective 5: preparing thin film composite membranes homogenous in material heterogeneous in structure through modified phase inversion technique. (Chapter 6).

1.3 Thesis structure

- Chapter 2
A literature review of membranes and membrane processes is presented in this chapter.
Research reported previously regarding OSN membranes is included. The general experimental and theoretical background on membrane formation and function is summarized.

- Chapter 3
This chapter discusses the preparation of PTSC polymer as well as the characterization methods used. Afterwards the characterization of membranes prepared.

- Chapter 4
The chemical resistance of PTSC membranes in organic solvents, such as polar aprotic solvents was discussed. The stability of the polymer in the chosen organic solution plays a key role in the performance of the membrane. In order to obtain a membrane stable towards harsh organic solvents, the main post-formation treatment used is chemical modification of the polymer by crosslinking the chains with each other or by functionalizing the groups present. For this purpose, crosslinking agent –dibromoxyylene (DBX) – was studied and the membranes were tested in harsh conditions. The membranes were characterized based on the structural and performance parameters. The MWCO value of these membranes was brought down to the nanofiltration range through the interfacial polymerization thin film preparation.

- Chapter 5
Integrally skinned asymmetric PTSC membranes were subjected to a facile crosslinking reaction. This reaction resulted in the formation of mixed matrix membranes that are
stable in harsh solvents as well as able to reject solute in the nanofiltration range without the addition of a selective layer. The crosslinking reaction was proved by NMR analysis and the time of reaction was optimized based on the TGA analysis.

• Chapter 6
A new method was presented called reaction induced phase separation (RIPS). This method is discussed in details for the preparation of composite like structure, however ISA membranes PTSC solvent resistant membranes. The isolation of dense selective layer was possible as well as post treatment of the membrane via further crosslinking to insure solvent resistivity towards harsh solvents.

• Chapter 7
The synthesis of Polythiourea polymer was discussed in chapter 3 however chemically modified PTU membranes served as OSN membranes are being discussed in this chapter.

• Chapter 8
Commercialized polymers are attractive for the use in research as well as industry due to their availability and in some cases being relatively cheap. OSN membranes prepared form commercialized polymers often require chemical modification to achieve high chemical stability in harsh solvents. In this chapter, the well-known Pebax polymer is used for the preparation of thin film composite membranes via coating. Pebax was subjected to chemical crosslinking to resist solvents such as ethanol (good solvent for Pebax) and DMF. The incorporation of GO nanosheets in the Pebax polymer matrix will
be discussed for enhancement of permeance.

- Chapter 9

The use of environmentally friendly biodegradable materials for membranes is highly recommended especially in the OSN membranes. This will lead to a greener process. Sodium alginate (NaAlg.) polymer was utilized to prepare membranes that are solvent stable and can serve as non-aqueous NF membranes.

- Chapter 10

Conclusions and future remarks are granted.
2.1 Membranes: General definition and classification.

A membrane is a semi-permeable barrier between two phases, which allows the selective transport of species (liquid or gas) under the influence of a driving force. The driving force can be concentration, pressure, temperature, or an electrical potential gradient. The barrier divides a feed stream into a permeate and a retentate (Fig. 2.1). Membranes can be classified in several ways. (1) Membranes can be synthetic or biological by nature. Biological membranes, which can be subdivided into living and non-living examples, are found in cells, kidneys, and other organs. (2) Synthetic membranes can be classified in terms of their constituent materials and can be divided into organic (polymeric or liquid), inorganic (ceramic or metal), or hybrid organic/inorganic (also called mixed-matrix) membranes. (3) Membranes also may be classified in terms of separation mechanism. Size exclusion occurs when the rejected species is larger and the permeable species is smaller than the size of the pores. Surface charge and hydrophilicity also play a role in membrane separation. Solution diffusion is a mechanism that involves adsorption of a species at the surface, absorption into the polymer matrix, diffusion across the barrier, and desorption upon exiting the membrane. (4) The driving force, which may be passive or active, is another means of membrane classification. (5) Membrane charge, which may be positive, negative, or neutral is a further example of classification. (6) Membrane morphology is an informative classification, because it illustrates the separation mechanism and potential applications of the membrane. As depicted in Fig. 2.2,
membrane morphology may be either symmetric or asymmetric, and symmetric membranes may be either porous or non-porous. Symmetric membranes that have a uniform pore size across the entire thickness are called porous symmetric. Non-porous or dense membranes are considered symmetric, because their density is uniform. Asymmetric membranes have a pore size that decreases gradually from bottom to top and typically contain a skin or a dense layer overlaying the porous layer. Composite membranes are considered asymmetric membranes that consist of a thin layer deposited on a porous support, each part of which can be optimized independently. The two layers may be the same or different materials.

![Fig. 2.1: Schematic representation of a membrane separation process. A feed stream containing species 1 and 2 subjected to a driving force (pressure, concentration, temperature or electrical potential) is divided into a retentate stream concentrated with species 1 and a permeate stream consisting of mainly species 2.](image-url)
Because membranes are fabricated for separation purposes, categorization based on filtration processes is only partially informative. Here, separation occurs between two phases, and membrane terminology is assigned accordingly. If the separation occurs between two liquid phases (L/L), microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), or reverse osmosis (RO) is used to describe the process. All share the same driving force (pressure gradient). Electrodialysis (ED), membrane contactors (MC), and membrane distillation (MD) processes are driven by electric potential, concentration, and temperature and pressure gradients, respectively. Separation processes between two gas phases (G/G) include pressure-driven gas permeation and vapor permeation. Finally, pressure-driven pervaporation is a separation process involving two different (L/G) phases. Membrane performance in a filtration process is related jointly to the morphology and average pore size of the membrane. Dense, non-porous membranes are
commonly used in gas separation, vapor permeation and reverse osmosis, whereas porous membranes are employed in MF, UF, and NF.

2.2 Liquid separation membrane processes:

Membrane filtration was not considered a technologically important separation process until 35 years ago. Today, membranes have gained an important place in chemical technology and are used in a broad range of applications due to their multidisciplinary characteristics. Pressure-driven liquid-phase separation processes utilizing membranes are well established, and the market is served by a number of experienced companies. The processes include MF, UF, NF, and RO.

A. Microfiltration

Microfiltration terminology is determined by the range of pore sizes. Suspended particle sizes of 0.1–10 µm can be separated by porous membranes. MF typically operates at low transmembrane pressures of approximately 0.1–2.0 bar to minimize build-up of suspended solids at the membrane surface. MF has the largest pore size compared to other liquid separation methods and can retain bacteria, starches, molds, and emulsified oils. Some principal applications of MF are sterilization (food and pharmaceuticals), clarification (beverages), wastewater treatment, bacterial removal in the milk industry, fat removal from whey, and separation of oil-water emulsions.¹³
B. Ultrafiltration

Ultrafiltration bridges the gap between microfiltration and nanofiltration. The pressure-driven separation process is primarily size-exclusion dependent. The pore size of UF membranes ranges from 5-50 nm. UF membranes typically are integrally skinned asymmetric membranes. The skin layer is responsible for the separation and provides a molecular weight cut-off (MWCO) of 1000–100,000 g/mol with the open support providing mechanical stability. The MWCO loosely defines the molecular weight of species that are 90% rejected by the membrane. The suitable operating pressure with UF membranes is 2–10 bar.²,⁴

C. Nanofiltration

NF membranes were first recognized in the late 1980’s and are defined as loose reverse osmosis membranes, because they have a relatively low sodium chloride rejection (20–80%), but much greater water permeability. The MWCO of these membranes is 200–1000 g/mol. NF membranes are used when low molecular weight solutes (e.g., salt, glucose, lactose, or micropollutants) must be rejected at an operating pressure of 10–25 bar. Most NF membranes are composite membranes consisting of a thin, dense layer of <2 nm pore size coated or interfacially polymerized on an open support. NF applications include desalination of brackish water, removal of micropollutants, water softening, wastewater treatment, and retention of dyes in the textile industry.¹ Over the past 8 years,
the significant growth of papers published on NF membranes in many different areas highlights the importance of this process.\textsuperscript{5}

D. Reverse osmosis

RO membranes find their widest application in the desalination of seawater, where the operating pressure of 30–100 bar has to overcome the osmotic pressure. Most RO membranes are regarded as pore-free membranes. The choice of membrane material in RO directly influences the separation efficiency. The membrane must have a high affinity for the solvent (typically water) and a low affinity for the solute.\textsuperscript{1,6-7} Polymeric materials such as cellulose and polyamide are widely used in the production of commercial RO membranes.

2.3 Organic Solvent Nanofiltration (OSN)

2.3.1 From aqueous to non-aqueous nanofiltration

Nanofiltration became widely recognized around the end of the 20\textsuperscript{th} century. A timeline of the most significant events contributing to the development of the field is shown in Fig. 2.3. The term “nanofiltration” was proposed during a FilmTec meeting in 1984, at which time the RO process was well established. The definition refers to a “loose” reverse osmosis process that allow ionic solutes in water to pass through a membrane.\textsuperscript{8} Loeb and Sourirajan were pioneers in the introduction of asymmetric membranes to aqueous applications in 1960’s.\textsuperscript{9} They observed that the preparation and immersion of a
cellulose acetate/solvent film in water results in the formation of a layer with asymmetry from top to bottom. The side of the membrane on the casting surface must be in contact with the brine solution during use.\textsuperscript{10} Application of these membranes to filtration in non-aqueous systems first occurred in 1964 for the separation of hydrocarbon solvents.\textsuperscript{11} The growing number of patents acquired by oil companies in a search for new materials applicable in organic solvents drew attention to solvent resistant nanofiltration membranes.\textsuperscript{12-16}

Fig. 2.3: Milestone of the development of aqueous and non-aqueous nanofiltration membranes.

Thin film composite membranes were first prepared in 1964 by float-casting cellulose acetate on water.\textsuperscript{17} This technique provided an improved means of preparing asymmetric membranes by separately fabricating the skin and porous layers and joining them later as
laminates. The approach maximized performance. In 1981, Cadotte introduced thin film composite polyamide membranes made by interfacial polymerisation. Because OSN membranes occupy only a small niche of the industrial membrane market, the relatively few commercially available examples do not meet the needs of all OSN separations. Often, membranes must be developed from lab-scale to industrial-scale production for a targeted application. OSN membranes developed between 1990–2000 include polymeric membranes such as those of Koch, Grace Davison, GMT, and SolSep. Later, Starmem, DuraMem, and PuraMem membranes emerged based on a stable polyimide polymer. The greatest industrial scale success was the MAXDEWAX process, which was installed at the Exxon Mobil Beaumont refinery. The process was used for the recovery of dewaxing solvents from lubrication oil filtrates. Increasing interest in OSN is evident from the graph in Fig. 2.4, which indicates the number of publications per year in the field. The research of the last 15 years has been cataloged in the Web of Knowledge using “organic solvent nanofiltration”, “solvent resistant nanofiltration”, or “organophilic nanofiltration” as a keyword.
Fig. 2.4: Number of publication per year for the period of 2000-2015. The search was carried out in web of knowledge using “organic solvent nanofiltration”, “solvent resistant nanofiltration” and “organophilic nanofiltration” as keywords.

OSN technology has enlarged the range of nanofiltration applications to filtration in harsh solvents. It is a membrane process that separates a liquid into a permeate, which passes through, and a concentrate, which is retained, under the influence of a pressure difference. OSN can separate solutes with molecular weights of 200 to 2000 g/mol from organic solvents. Membrane separation is among the best available technologies (BATs) in wastewater and gas treatment systems. OSN has the potential to become a BAT in organic media. This conclusion is based on the following advantages offered by OSN in the energy and environment sectors: (i) low energy requirement, (ii) low solid waste generation, (iii) moderate temperature and pressure operating conditions, (iv) straightforward scale-up possibilities, (v) chemical resistivity in harsh environments allowing flexibility of choice of pH, temperature, and solvent, and (vi) application to high and low boiling point solvents.
2.3.2 Commercially available OSN membranes

OSN membranes occupy a narrow niche in the industry market. Because there are few commercially available OSN membranes, many potential applications are not covered by available products. The first company to enter the OSN market was Koch Membrane Systems, U.S.A. in the late 1990s. Koch Membrane Systems offers a comprehensive line of chemically resistant NF membranes called SelRO for acidic, basic, and organic solvent streams. These membranes are used in many applications in food, pharmaceutical, and chemical industries. The MPF-50 and MPF-60 membranes, which have been withdrawn from the market, are chemically stable flat-sheet hydrophobic composites produced by the same company. The top layer consists of polydimethylsiloxane (PDMS) coated on a crosslinked polyacrylonitrile (PAN) support. These membranes are proposed to be stable in solvents such as methanol, ethanol, isopropanol, butanol, acetone, n-hexane, cyclohexane, methyl ethyl ketone (MEK), dichloroethane, pentane, trichloroethane, formaldehyde, tetrahydrofuran (THF), diethyl ether, ethyl acetate, acetonitrile (ACN), xylene, dioxane, and toluene and to have limited stability in N,N-dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), and N,N-dimethylacetamide (DMAc) containing mixtures. Applications requiring these membranes include isolation of triglycerides from n-hexane, recovery of organometallic complexes from dichloromethane (DCM), THF, and ethyl acetate, recovery of phase transfer catalysts from toluene, and solvent exchange in pharmaceutical manufacturing. Machado et al. tested the membranes for solvent nanofiltration. They reported minimal swelling (<3% in ethanol, methanol, n-propanol, and acetone) of MPF-50 and
MPF-60. However, more severe tests carried out by Van der Bruggen et al.\textsuperscript{30} revealed the membranes to be only partially stable with visible damage apparent after ten days exposure to methylene chloride, acetone, hexane, ethanol, and ethyl acetate.

The STARMEM\textsuperscript{TM} series was distributed by W.R. Grace & Co.\textsuperscript{31} for membrane extraction technology. The membranes are integrally skinned asymmetric hydrophobic OSN membranes manufactured from polyimides.\textsuperscript{32} STARMEM\textsuperscript{TM} is stable in a wide range of solvents including ethanol, isopropanol, butanol, \textit{n}-hexane, \textit{n}-heptane, MEK, and butyl acetate. Although no longer on the market, STARMEM\textsuperscript{TM} membranes were used extensively in research owing to their good resistance to organic solvents.\textsuperscript{33-36} STARMEM\textsuperscript{TM} membranes were the first OSN membranes with large scale use in the refining industry and have been used for solvent recovery from lubricating oil dewaxing since 1998 (MAX-DEWAX).\textsuperscript{22}

The Dutch company, SolSep BV,\textsuperscript{37} develops and manufactures membrane and modules (elements) for ultra- and nanofiltration in organic solvents. SolSep\textsuperscript{TM} membranes are stable in methanol, ethanol, propanol, acetone, ethyl acetate, hexane, toluene, and chlorobenzene. SolSep BV UF and NF membranes are designed specifically for organic solvent applications such as acetone recovery in oleochemistry, hexane and ethanol recovery from extraction operations, solvent recovery from paints and polymer synthesis, and recovery of homogeneous catalysts. SolSep membranes are TFC membranes with a PDMS or silicone coating.\textsuperscript{38} SolSep NF030306, which is a silicone-based polymer membrane with a MWCO \(\geq 500\) g/mol, exhibited superior performance in the recovery of solvents from edible oil-solvent mixtures.\textsuperscript{39} SolSep NF010206 with a MWCO \(\geq 300\) g/mol was tested for the removal of genotoxic impurities (GTI) formed during the
synthesis of active pharmaceutical ingredients (APIs). The membranes showed excellent performance in solvents such as THF and MEK.\textsuperscript{40} SolSep nanofiltration membranes also were used to study a transport model for solvent permeation.\textsuperscript{41}

DuraMem\textsuperscript{TM} Membranes are a series of integrally skinned asymmetric crosslinked polyimide membranes\textsuperscript{42} commercialized by Evonik-MET, Ltd.\textsuperscript{43} DuraMem offers long term stability in aggressive media such as polar aprotic solvents (e.g., acetone, THF, and DMF)\textsuperscript{44} and rejection of the smallest molecules in the MWCO = 150–900 g/mol nanofiltration range. They are limited to a maximum temperature of 50 °C, because reimidization and loss of crosslinking occurs at elevated temperatures. Filtration with these membranes is not recommended in the presence of chlorinated solvents or strong amines. Pharmaceutical applications of DuraMem membranes include separation of impurities (pyridine, acetic anhydride, and bromine) from APIs and diafiltration.\textsuperscript{45}

Evonik-MET, Ltd. also provides a new series called PuraMem\textsuperscript{TM} membranes.\textsuperscript{43} In contrast to DuraMem, PuraMem membranes are integrally skinned asymmetric membranes based on non-crosslinked polyimide. The membranes have a MWCO range of 280–600 g/mol and possess excellent chemical stability in apolar hydrocarbon-based solvents including toluene, heptane, hexane, methyl ethyl ketone, methyl isobutyl ketone, and ethyl acetate. However, use is not recommended in chlorinated environments and most polar aprotic solvents, because the membranes are not crosslinked. PuraMem S600 membranes are non-crosslinked, polyimide rubber-coated thin-film composite membranes. They are stable in ethanol, isopropanol, butanol, \textit{n}-hexane, \textit{n}-heptane, toluene, MEK, and ethyl acetate with a MWCO of 600 g/mol.\textsuperscript{46}
GMT membranes, which are distributed by GMT-GmbH, Germany, are silicone selective-layer TFC membranes that are coated on a support and crosslinked by a patented irradiation method. GMT offers the membranes in two forms — a spiral wound version for treatment of aqueous/organic liquids and an envelope-type module for organophilic nanofiltration. The membranes are chemically and mechanically stable in solvents such as alkanes, alcohols, ketones, aromatics, ethers, and esters and provide outstanding performance with regard to permeability and selectivity. Applications of GMT membranes include recovery of homogeneous catalysts from reaction mixtures, conditioning of liquid hydrocarbons, purification of organic solvents, and product refining in the flavor industry.

PoroGen membranes utilize a melt-extruded porous polyether ether ketone (PEEK) polymer in hollow-fiber and flat-sheet configurations. PEEK-SEP has a tailored pore size and surface chemistry to meet specific separation requirements. It can perform at temperatures as high as 200 °C in aggressive solvents. PEEK-SEP™ membranes are used for purification of natural gas, volatile organic carbon (VOC) abatement, and filtration of aggressive solvents. PoroGen claims that their patented PEEK membranes have the highest particle retention efficiency with sizes on the order of nanometers and offer stable performance at high flow rates.

Chemically and thermally stable NanoPro (180–1000 g/mol MWCO) and UltraPro (2500–10,000 g/mol MWCO) membranes are produced by AMS technologies. Theses ultra- and nanofiltration membranes are acid-resistant, alkali-resistant, solvent-stable and operate at high fluxes at temperatures up to 70 °C. AMS membranes are employed in mineral extraction (mining) and in situations with harsh operating environments such as
the chemical, pharmaceutical, pulp, rayon, and dairy industries. PolyAn is a nanotechnology company specializing in surface modification and surface imprinting. The company combines specifically designed separating layers with chemically robust membrane materials. PolyAn produces composite membranes for organophilic nanofiltration and pervaporation with long-term chemical stability in organic media such as hexane, toluene, ethanol, THF, acetone, and ethyl acetate.

2.3.3 Literature review of polymeric OSN nanofiltration membranes

Although OSN membranes can be prepared from inorganic or mixed-matrix materials; the following literature review deals only with polymeric organic solvent nanofiltration membranes. The first part discusses integrally skinned asymmetric (ISA) membranes. The second part treats TFC membranes prepared by interfacial polymerization, coating, and plasma polymerization.

2.3.3.1 Research on integrally skinned asymmetric (ISA) OSN membranes

ISA membranes consist of a skin layer on top of a porous support. The two layers are fabricated with the same material and are formed at the same time. The skin layer is responsible for membrane selectivity and permeance. The necessary morphology is obtained by the Loeb-Sourirajan phase inversion process. The process consists of immersing a thin casting solution film in a non-solvent bath (usually water), where precipitation occurs. The film quickly precipitates from the top surface down as a result of water-solvent exchange. The initial single homogenous phase from the casting solution is converted into two phases — a polymer-rich, solid phase that forms the membrane
matrix and a polymer-poor, lean phase that forms the membrane pores. Upon exposure to water, the top surface of the cast film solidifies rapidly forming a dense selective layer. This layer acts as a barrier between the water bath and the rest of cast solution film. Thus, entry of water into the underlying polymer solution slows down resulting in a more porous substrate.

The preparation of ISA membranes begins by dissolving the polymer of interest at 10–30% in a good solvent to form a homogenous solution. The polymer solution is then spread homogenously across a non-woven support. This is done using an adjustable blade casting knife to control the film thickness, which is commonly 50–300 µm. This is followed by immersion in a non-solvent where precipitation takes place as illustrated in Fig. 2.5.

The ternary phase diagram in Fig. 2.6 describes the thermodynamic behavior of the polymer solution during phase inversion. The diagram is an equilateral triangle with each corner corresponding to one pure component (polymer, solvent, or non-solvent). Two regions are crucial to membrane formation. One region is enclosed within the binodal curve, which is a two-phase region where phase separation occurs. The area outside the binodal curve is a one-phase region where all components are miscible. The area between binodal and spinodal curves is a metastable region, and the area within the spinodal curve is an unstable or demixing gap.
Fig. 2.5: Schematic representation of immersion precipitation phase inversion using continuous casting machine.

Fig. 2.6: The three-component (solvent, non-solvent and polymer) ternary phase diagram used to describe the membrane formation during immersion phase inversion.
Several approaches have been developed to understand membrane formation by phase inversion. Most involve the three-component ternary phase diagrams popularized by Michaels, Strathmann, and Smolders. The blue line in Fig. 2.6 describes the membrane formation path. The solution at the initial point (A) consists of a small percentage of polymer and a large percentage of solvent. The composition changes during phase inversion by liquid-liquid demixing to reach the final membrane composition (D), where non-solvent is introduced to the system. The location of point D on the polymer/non-solvent axis, where phases S and L are in equilibrium, establishes the overall porosity of the membrane. S stands for the solid or polymer-rich phase, whose composition defines the matrix of the membrane. L stands for the liquid or polymer-poor phase, which fills the membrane pores by precipitation at the indicated composition.

Point B, where the formation path enters the demixing gap by intersection with the binodal, defines the concentration at which the polymer initially precipitates. If the intersection falls within the metastable region, nucleation and growth (NG) occur. However, if the intersection enters the unstable region through the critical point (E), spinodal decomposition (SD) takes place. The viscosity increases due to solvent loss as precipitation proceeds, until a point is reached where the precipitated polymer is regarded as a solid (C). Factors affecting the size and location of the demixing gap include the molar volumes of the components, polymer/solvent interactions, polymer/non-solvent interactions, and solvent/non-solvent interactions. Altena et al. and Yilmaz et al. have discussed the influence of these variables on the phase diagrams. In terms of kinetic characteristics, two types of demixing — instantaneous and delayed — prevail.

If the solution composition lies in the thermodynamically unstable region shortly after
immersion in the non-solvent bath, instantaneous demixing is expected. This leads to rapid precipitation, and a porous structure is obtained. However, if the polymer solution remains in the thermodynamically stable region after immersion, delayed demixing occurs, the red path in Fig. 2.6 is favored, and a denser structure is formed. Parameters influencing the phase inversion process and morphology of the membrane product include the polymer concentration, solvent/co-solvent ratio (if pertinent), evaporation step before immersion, and coagulation bath composition. Denser skin layer membranes are obtained at higher polymer concentrations, leading to greater selectivity at the expense of lower permeability. The presence of volatile solvents in the dope solution facilitates an evaporation step prior immersion in the non-solvent bath. This improves performance in terms of selectivity and results in defect-free membranes.

Polyimides (PI) such as Matrimid and P84 have been investigated extensively for their performance in OSN ISA membranes. The reported MWCOs are in the range of 200−1200 g/mol, and permeance values range from 0.5−7 L/m²·hr·bar in DMF. Polysulfone (PSF) polymer also has been explored for its possible use as a membrane for mild organic solvent filtrations. Holda et al. reported that an increased concentration of PSF enhanced membrane performance by increasing the rejection of Rose Bengal dye (1017 g/mol) from 37 to 92%, although the permeance decreased significantly from 9.7 to 0.07 L/m²·hr-bar. A similar enhancement of Rose Bengal rejection from 47 to 76% was observed when the evaporation time of the volatile co-solvent THF was increased. Polyphenylsulfone (PPSF) also has been mentioned as a material for mild organic solvent filtration. In a study of polymer concentration using solvent systems such as DMAc, NMP, or a mixture of DMF and NMP, the final membranes exhibited 88% Rose Bengal
rejection in methanol. Hollow fiber membranes prepared from PPSF exhibited 98.6 and 73.5% rejection of Rose Bengal and Bromothymol blue, respectively, with 0.02 L/m²·hr·bar isopropanol permeance.  

Polyether ether ketone (PEEK) also is a promising material for OSN. It is solvent stable, exhibits a high glass transition temperature, has mechanical strength, and is hydrophobic. ISA membranes have been produced using phenolphthalein-based PEEKWC. Greater than 90% rejection of Rose Bengal has been achieved in isopropanol and methanol with permeances of 0.9 and 1.7 L/m²·hr·bar, respectively. Hendrix et al. reported the formation of crosslinked PEEK membranes from lab synthesized polymer via the phase inversion method. They modified the PEEK polymer backbone with carboxylic acid groups, which subsequently can be crosslinked using diamines. Membranes crosslinked with 1,6-hexanediamine (HDA) were tested for Rose Bengal rejection in isopropanol and acetone and produced 90% rejection for both, although the permeances were low. Da Silva recently investigated non-modified, non-sulfonated PEEK membranes for OSN under harsh conditions including polar aprotic solvents (DMF and THF), high temperatures, and acidic and basic environments. Membranes with a MWCO of 400 g/mol and a permeance of 0.22 L/m²·hr·bar in THF were obtained.

Chemical stability and separation quality can be improved by post treatment of membranes. Post treatment methods include crosslinking, annealing, solvent exchange drying, and conditioning. Crosslinking of polymer chains by heat treatment, chemical reaction, or radiation is crucial for OSN and has a large effect on the physical, chemical, mechanical, and thermal properties of membranes. P84 PI ISA membranes have been crosslinked in DMF. Crosslinked p-xylenediamine Matrimid PI membranes show
excellent resistivity in DMAc, dimethylsulfoxide (DMSO), NMP, THF, and DMF. In some cases, crosslinking of polymer chains can be combined with phase inversion in one step by addition of the crosslinker to the non-solvent bath. In the \( p \)-xylenediamine crosslinking of PI polymer,\(^8^3 \) this leads to a more inexpensive and environmentally friendly process. Membranes prepared by crosslinking commercial polyamide imide with diisocyanate have been reported; the crosslinking reaction requires 13 days. The resulting membranes exhibit good mechanical stability and have a MWCO of 260 g/mol for polystyrene in acetone. Membranes soaked for 6 months in NMP were tested for cholesterol (380 g/mol)/NMP rejection and exhibited good chemical stability with 85% rejection.\(^8^4 \) Crosslinking of polyaniline (PANI)\(^8^5-^8^6 \) membranes allows these materials to serve as supports for OSN. Their stability in THF, DMF, and acetone has been reported. Polybenzimidazole (PBI), which has superior chemical resistivity, has supplanted PI in some cases. Dibromoxylene (DBX)-crosslinked PBI membranes have been developed by Valtcheva et al.\(^8^7 \) and show good tolerance to extreme pH conditions. PBI also has been chemically crosslinked with two different reagents—glutaraldehyde (GA) in water and 1,2,7,8-diepoxyoctane (DEO) in \( n \)-heptane. The GA crosslinker enhances stability in ethanol (3.7 L/m\(^2\)-hr-bar permeance) and ethyl acetate (5.2 L/m\(^2\)-hr-bar), but no resistivity in DMSO was noticed. DEO-crosslinked membranes exhibited good stability in DMSO and lower permeances in ethanol.\(^8^8 \)

2.3.3.2 Research on thin film composite (TFC) OSN membranes

TFC membranes consist of an ultrathin selective layer on top of a chemically distinct porous support. Independent preparation of both layers enables independent optimization
of both layers and maximization of overall membrane performance. The size of the porous support is usually in the UF range and must provide mechanical and chemical stability and the ability to promote formation of a defect-free top layer. Methods used to engineer a TFC-layered structure include (i) lamination of an ultrathin film formed separately by casting onto a support, (ii) interfacial polymerization on the surface of a support, (iii) dip-coating/spin-coating/solvent casting of a polymer solution onto a support, (iv) post-curing heat treatment or irradiation of a support that was previously dip-coated with a solution of reactive monomer or prepolymer, and (v) deposition of a barrier film directly from a gaseous phase monomer plasma.

- Thin film composite membranes by interfacial polymerization.

The upper layer is formed by an in situ polymerization reaction on the surface of the porous support. The reaction takes place at the interface between two immiscible phases, each of which contains a reactive monomer. The procedure is initiated typically by impregnating a porous support with an aqueous solution containing a diamine monomer for specific time. After removal of excess water, the saturated support is exposed to an organic phase containing acyl halide. The reaction between monomers commences immediately upon exposure and leads to the formation of a thin, continuous, selective polyamide (PA) layer. The choice of diamine was examined in the formation of polyamide NF membranes for aqueous applications. Diamines including piperazine (PIP), N,N'-diaminopiperazine (DAP), 1,4-bis(3-aminopropyl)piperazine (DAPP), and N-(2-aminoethyl)piperazine (EAP) were reacted with trimesoylchloride (TMC). Membrane
morphology, surface charge, and membrane performance were significantly influenced by the identity of the diamine. Polyamide thin films prepared from PIP/m-phenylenediamine (MPD) and TMC on a polyacrylonitrile (PAN) support were investigated using mild solvent. Good performance was observed in methanol, acetone, and ethanol, but the membranes cannot be used in apolar solvents. Poly(ethyleneimine) (PEI) also can be used as a reactant in interfacial polymerizations. PEI was reacted with diisocyanate on a solvent resistant nylon-6,6 support to separate lubrication oil from solvents. Poly(amide imide) (PAI) is considered to be a thermally and chemically stable alternative to PA in preparing TFC membranes. In addition to the PAN support mentioned above, polypropylene has been used to support TFC OSN membranes. PAN polymer has been post-treated by crosslinking to improve its solvent stability. The resulting material is an excellent support for TFC OSN membranes. Diamine-crosslinked PIs are very attractive supports for TFC OSN, and high-flux interfacially polymerized TFC membranes have been prepared on this material. Because the support is a major component of TFC membranes, Jimenez-Solomon et al. studied the impact of the support on thin film formation via interfacial polymerization. Surface hydrophilicity plays a major role. Polymer nanofilms with enhanced microporosity have been prepared by a novel modification of conventional interfacial polymerization. Use of contorted monomers as building blocks leads to formation of ultrathin crosslinked polyacrylate nanofilm membranes with enhanced microporosity. These materials offer outstanding performance in organic solvents.
Thin film composite membranes via coating.

Dip coating, spin coating, and solvent casting are among the techniques used to coat a porous support with a polymer solution. Parameters essential to successful preparation of coated TFC membranes are the coating polymer solubility in different solvents, its mechanical and chemical stability, its ability to form films, and its ability to crosslink. Coating polymers include polydimethylsiloxane (PDMS), poly (vinyl alcohol) (PVA), chitosan, cellulose derivatives, poly(ether block amide) (Pebax), poly(acrylic acid) (PAA), and poly[1-(trimethylsilyl)-1-propyne] (PTMSP). Composite membranes made with PDMS coated on a crosslinked PI support have been advocated for filtration in isopropanol. Although good performance was achieved, excessive swelling was observed in THF and toluene. Hydrophobic glassy PTMSP coatings can form highly permeable TFC membranes for OSN applications. These membranes exhibit an exceptional ethanol permeance of 4.8 L/m²·hr·bar with 90% rejection of Remazole Brilliant Blue dye (626 g/mol). With free-standing PTMSP membranes, the retention of Sudan Blue 35 was highly influenced by the solvent used. Membranes introduced by Fontananova et al. consisting of a crosslinked P84 PI support and 5% P84 PI coating are homogenous in composition, but composite in structure. The advantage of this approach over ISA is the independent optimization of each layer. Use of the same polymer material for coating and support guarantees a high affinity between the two layers. In situ polymerization is an additional technique for applying a thin top layer on a support. In one example, a pyrrole monomer/ethanol mixture was coated on supports such as PI, PSF, and SPEEK and polymerized to form a polypyrrole (PPy) upper layer.
The membranes displayed stable permeabilities and retention over a 30-hour exposure to DMF. A high THF permeance of 67 L/m²·hr·bar was observed with 98% rejection of Rose Bengal dye. Lower methanol, ethanol, and isopropanol permeances of 1.46, 1.3, and 0.79 L/m²·hr·bar, respectively, resulted when PPy composite membranes on hydrolyzed PAN were examined. Polymers with intrinsic microporosity (PIMs) are a recent addition to the evolution of membranes that is intended to counteract compaction and aging. The microporosity of these ultrahigh free volume polymers arises directly from the shape and rigidity of the macromolecular chains. A large free volume enables high permeance without compromising rejection. Most applications of PIM membranes occur in gas separation and pervaporation. However, TFC membranes using PIM-1 for OSN have appeared lately and exhibit 30-times greater permeance than commercial Starmem 240 without compaction at high pressure after a 300-h exposure. PIM-1 also was prepared as a free standing 35-nm film by spin coating and used to construct a composite membrane by floating and transferring the spin-coated film onto a polymeric or ceramic support. The maximum permeance of \( n \)-heptane was 18 L/m²·hr·bar. Peinemann et al. pioneered phase inversion asymmetric self-assembly block copolymer membranes with a nanostructured morphology. Use of nanostructured TFC membranes for OSN was recently reported by Li et al. The upper layer, which was deposited on an organic or inorganic support, used a blend of poly(ethylene oxide)/polystyrene-b diblock copolymer and poly(acrylic acid) as a template.
2.3.4 Current challenges

A. Concentration polarization

The term fouling describes the process whereby the deposition of suspended or dissolved substances takes place on the membrane surface near the pore openings or within pores, which leads to the loss of membrane performance.\textsuperscript{116} Fouling is caused by complex physical and chemical interactions between the interfering species or between these species and the membrane surface and is provoked by factors that include surface morphology, hydrophobicity, and charge.\textsuperscript{117,118} Concentration polarization can be regarded as a reversible flux depending on fouling mechanism whereby the feed mixture components permeate at different rates and create a concentration gradient on both sides of the membrane. In most cases, the permeate side composition depends only on the ratio of components permeating, especially when the bulk flow through the membrane is continuous. Thus, concentration polarization is considered only on the feed side.\textsuperscript{2} The boundary layer on the feed side adjacent to the membrane demonstrated in Fig. 2.7 becomes depleted in the permeating component (j) and enriched in the retained one (i). The decrease in the permeate concentration lowers the driving force across the membrane (smaller concentration difference) and reduces the flux and selectivity. At the same time, the osmotic pressure in the retentate increases ($\Delta \pi$) due to component accumulation, which decreases the pressure based contribution to the driving force ($\Delta P - \Delta \pi$). Van’t Hoff’s equation is used to describe the osmotic pressure difference across pressure-driven water separation membranes.\textsuperscript{119} However, further research is needed to determine its
relevancy in solvent filtration.\textsuperscript{120} Although it has been reported that sunflower oil behaves ideally in toluene\textsuperscript{121} and that the osmotic pressure can be interpreted by the van’t Hoff model, permeation of tetraoctylammonium bromide (TOABr)/toluene mixtures through a PAN/PDMS membrane exhibits non-ideality and no osmotic phenomena. The clustering of TOABr ion-pairs in toluene is responsible for the non-ideality. The consequences of concentration polarization can be reduced by decreasing the thickness of the boundary layer. This can be accomplished by establishing hydrodynamic conditions on the feed side of the membrane using feed spacers or turbulence promoters. Modification of the membrane surface also will increase fouling resistance.\textsuperscript{122}

![Concentration profile in pressure driven membrane processes such as MF, UF, NF and RO.](image)
B. Compaction

Chains of polymeric molecules within a membrane tend to reorganize and deform when subjected to pressure for long periods of time. Volume porosity is lowered, and the structural densification increases membrane resistance and decreases permeance.\textsuperscript{123} In the presence of organic solvent, rearrangement of partially solvated polymer chains occurs.\textsuperscript{27,124} Deformation often is irreversible and is destructive in the sense that the flux generally does not return to its original value after relaxation. The time required for the membrane flux to reach equilibrium can be as long as several days depending on the pre- or post-treatment of the membrane.\textsuperscript{125} Several approaches can prevent compaction. One is the incorporation of fillers in the membrane matrix to form a mixed-matrix membrane (MMM).\textsuperscript{126-127}

C. Chemical stability

Chemical stability is a crucial component of membrane performance. The polymer and non-woven materials must be readily soluble in a common organic solvent to accomplish membrane film formation, but it must be resistant to other solvents during filtration. Solvent stability can be improved by functional group modification of the polymer. OSN membranes require additional stability to tolerate conditions of extreme pH, solvent exchange, and high temperatures that increase membrane solvation.
D. Swelling

Swelling of nanofiltration membranes in organic solvents is important, because the “channels” created in the dense selective layer of the membrane can increase permeability and change rejection. Introduction of a swelling solvent expands the polymer chains and reduces the void volume of a membrane. The flux through a swollen membrane will be reduced, although the swelling may improve selectivity (Fig. 2.8).

Hildebrand solubility parameters can indicate the ability of solvents to swell polymeric membranes. Many methods have been used to determine the extent of swelling. Sirkar’s method involves determining the difference in weight between dry and solvent-wet polymer samples. Other methods simultaneously evaluate the solubility, diffusion coefficient, and swelling of a solvent/polymer combination such as acetonitrile/polyetherurethane using a quartz spring microbalance. The extent of
polymer swelling also is influenced by the degree of polymer crosslinking and the affinity between the polymer and the solvent. However, crosslinked membrane performance in terms of solvent flux and solute rejection cannot be correlated with the results of swelling experiments.\textsuperscript{132,133}

E. Mechanical properties

The polymer chosen for OSN and other membrane materials must be able to form defect-free, flexible films and to withstand high operational pressures and temperatures. Optimization of the polymer concentration can promote polymer solubility and film formation. However, flexibility is an important issue in large scale applications, where some polymers suffer from brittleness and membrane handling leads to breakage.

2.3.5 Applications of OSN membranes

Organic solvent nanofiltration is widely applied in the refining industry, the fine chemical industry, solvent recovery processes, organic synthesis, and pharmaceutical purifications.\textsuperscript{27} Conventional methods of reaction, separation, and recycling may be costly and environmentally harmful. OSN has the potential to convert conventional practices in chemical industries to greener ones. Hybrid processes in which OSN is paired with other purification technologies can lead to greener operation and improved yields and purities.\textsuperscript{24} OSN applications can be divided into three categories (Fig. 2.9). The goal of purification is the separation of a desired substance from impurities. Purification is
achieved by passing one component through a membrane based on size while retaining another on the other side. Concentration involves increasing the population of a desired component in the feed stream by permeating solvent through the membrane and increasing the concentration of the component in the retentate. In solvent exchange, a second solvent is pumped into a sample solution to replace the initial solvent.

![Membrane separation process](image)

Fig. 2.9: Membrane separation process for liquid applications, concentration (top), purification (middle) and solvent exchange (bottom). (Adopted from Reference 139).
A. Concentration

Concentration is a process whereby a solution is enriched in content for the purpose of recovering a high-value solute from a dilute solution or by removal of the solvent (solvent recovery) from an impurity dissolved in it. The traditional concentration technique is distillation, which is energy intensive and can degrade solutes at elevated temperatures. OSN membranes operate at lower temperatures hence no phase change is experienced therefore are a superb substitute for distillation. Typical OSN membrane applications in pharmaceutical industries involve the isolation and concentration of antibiotics, pharmaceutical intermediates, or peptides from organic solvents or aqueous/organic solvents mixtures. High rejection (90–95%) accompanied by low product loss has been achieved in the recovery of 6-aminopenicillanic acid (6-Apa, MW = 216 g/mol) from its bioconversion solution. Cao et al.\textsuperscript{134} used an OSN membrane (MPS-44) from Koch for this recovery. OSN membranes also are used in the extraction and concentration of minerals, antioxidants, and natural components of aromatic herbs and seeds. A DuraMem 200 membrane has been used to concentrate antioxidant extracts of rosemary herb in ethanol. Peshev et al.\textsuperscript{135} achieved complete extraction of rosmarinic acid with good permeant fluxes.

Industrial processes often consume and discharge large volumes of organic solvents, which upon handling can cause a number of unwanted outcomes such as increased risks of cancer, mental diseases, air pollution, and contamination of soil and groundwater. The recovery of such solvents can be carried out with OSN membranes. Solvent lubrication oil dewaxing (MAX-DEWAX) is one of the largest successful industrial scale
applications of OSN membranes.\textsuperscript{21,22} It is used in refineries worldwide. In this process, a waxy oil stream is mixed with an organic solvent like toluene, and the waxy component is collected by precipitation and filtration upon cooling. This procedure avoids the need to recover the dewaxed solvent mixture by conventional multistage flash and distillation operations. The OSN membrane alternative reduces energy consumption and increases the purity of the product.

B. Solvent exchange

Solvent exchange is a process involving a system of two solvents and one solute, in which a second solvent (A) is pumped into a solution of the solute in the first solvent (B) as the solute is retained in the membrane. The solution changes from being rich in B to rich in A over time. Replacement of a high-boiling with a low-boiling solvent is one advantage of OSN membranes.\textsuperscript{136} MPF-50 and MPF-60 nanofiltration membranes have been employed to exchange ethyl acetate for methanol in the pharmaceutical preparation of erythromycin.\textsuperscript{137}

C. Purification

The goal in purification is to separate a valued solute, which may be the main product of a reaction, from impurities. Membrane based purifications are favored,\textsuperscript{139} because they involve low energy,\textsuperscript{138} continuous mode operation, and straightforward scale-up. Separation and purification of xanthophyll, a naturally occurring oxygenated yellow-
orange pigment in corn that is co-extracted with an ethanol-soluble protein, has been accomplished using solvent resistant UF membranes. The pigment is subsequently separated from the solvent with an OSN membrane.\textsuperscript{140}

### 2.4 Membrane characterization techniques

Characterization of membrane structure, morphology, and properties provides insight to better understanding and prediction of performance. Characterization tools can be divided into groups dealing with performance and structural parameters.

#### 2.4.1 Characterization of performance parameters

Permeance ($J$) is defined as the volume ($V$) of liquid flowing through a membrane per unit area ($A$), time ($t$), and applied pressure ($P$). It is expressed in units of $\text{L/m}^2 \cdot \text{h-bar}$ by equation (2.1):

$$J = \frac{V}{t \cdot A \cdot P}$$

(2.1)

Rejection ($R\%$) describes the selectivity of a membrane. It is calculated as a function of the solute concentration in the permeate ($C_P$) and feed ($C_F$) streams by equation (2.2):

$$R \% = \left(1 - \frac{C_P}{C_F}\right) \times 100\%$$

(2.2)
The separation performance of any membrane also can be described by the molecular weight cutoff value (MWCO). The MWCO represents the molecular weight (MW) of a reference compound that typically is 90% retained by the membrane. The value is determined from a MWCO plot, which is constructed by plotting measured rejection percentages versus the MW of reference compounds. OSN membranes typically show MWCOs of 200–2000 g/mol. Membrane selectivity should ideally provide a sharp separation between target and undesired compounds. For example, if it is desired to separate compound X with a MW of 450 g/mol from impurity Y with a MW of 200 g/mol, an ideal OSN membrane should reject X 100% while passing Y with 0% rejection (red line in Fig. 2.10). However, in a typical case (black line) X will be 97% rejected and Y will be 20% rejected. In large scale industrial applications, such behavior results in expensive product loss and incomplete purification. One way to address this challenge is to improve membrane performance by tuning pore size.

![MWCO Curve](image)

**Fig. 2.10:** MWCO Curves describing the performance of ideal and typical OSN membrane.
The process of optimization is directed towards achieving high membrane permeability coupled with high rejection and a small range of MWCO values. Although several authors have studied the filtration data and MWCO values of OSN membranes, different experiments cannot be reliably compared. The reason is that markers of different structure, size, charge, and concentration have been used for characterization. The most common markers the field are listed in Table 2.1. The properties of the solvents used and the experimental filtration conditions of applied pressure and temperature differ in most studies, which makes comparison difficult. Styrene oligomers\textsuperscript{141} have been suggested as a first step to developing a consistent and universal method for characterizing the performance of OSN membranes.

Table 2.1: Markers used to identify the MWCO of OSN membranes.

<table>
<thead>
<tr>
<th>Marker</th>
<th>References</th>
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</thead>
<tbody>
<tr>
<td>Linear and branched n-alkanes</td>
<td>White et al.\textsuperscript{142}</td>
</tr>
<tr>
<td>Dyes</td>
<td>Bhanushali et al.\textsuperscript{143-144}</td>
</tr>
<tr>
<td>Hexaphenyl benzene (HPB)</td>
<td>Bhanushali et al.\textsuperscript{143} and Fritsch et al.\textsuperscript{112}</td>
</tr>
<tr>
<td>Polyethylene glycol (PEG)</td>
<td>Kwiatkowski et al.\textsuperscript{147}</td>
</tr>
<tr>
<td>Polyisobutylene</td>
<td>Stafie et al.\textsuperscript{150} and Van der Bruggen et al.\textsuperscript{151}</td>
</tr>
<tr>
<td>Oligostyrenes (PS)</td>
<td>See Toh et al.\textsuperscript{141} and Dutczak et al.\textsuperscript{152}</td>
</tr>
</tbody>
</table>

2.4.2 Characterization of physicochemical and structural parameters

Physicochemical parameters include pore size and shape distribution, surface hydrophilicity, surface charge, surface chemistry, and chemical composition. Structural parameters include surface roughness and membrane thickness. Better understanding of
these parameters will allow better prediction of membrane performance and enable further improvements in membrane design.

Surface hydrophilicity or hydrophobicity can be determined by contact angle measurement. This method measures the wettability of a solid surface by a specific liquid by placing a drop of liquid on the surface and reading the angle (θ) formed between the surface and the drop. As a rule of thumb, a small contact angle (θ < 90°) forms when the surface is hydrophilic and favorably wetted by the chosen liquid. When the contact angle is large (θ > 90°), the surface is considered hydrophobic and has low wettability (Fig. 2.11).

Fig. 2.11: Schematic representation of contact angle formed between hydrophobic/hydrophilic surface and a liquid drop.

Yong’s equation (2.3) describes the relationship between the contact angle and the surface tensions (γ) at liquid-gas (LG), solid-liquid (SL), and solid-gas (SG) interfaces.

\[ \gamma_{LG} \cos \theta = \gamma_{SG} - \gamma_{SL} \]  

(2.3)
Fourier transform-infrared spectroscopy (FTIR) involves passing infrared radiation through a sample to determine its chemical composition. Certain wavelengths are absorbed while others are transmitted. The FTIR spectrum of every material is unique, because each functional group absorbs light of a particular wavelength. FTIR is very useful for membrane characterization and is used to investigate polymer chemistry including the presence of newly formed bonds during crosslinking or modification\textsuperscript{155} and the presence or absence of additives in the membrane matrix.

Microscopic imaging techniques such as scanning electron microscopy (SEM) facilitate membrane characterization by enabling the study of structure at the nanoscale.\textsuperscript{156-157} The sample is bombarded under vacuum with high-energy electrons, which are absorbed or scattered by the membrane. The secondary electrons are collected by a detector to create an image. A drawback of SEM imaging is that polymeric membranes are not conductive and must be coated with a conductive material such as gold particles. The features in the SEM images are therefore those of the coated surface. Another problem arises from the applied voltage, which must be increased to provide better resolution. However, the sensitivity of polymeric materials to higher voltages can damage the membrane surface. A common voltage is 10 kV, which allows structures of about 5 nanometers to be observed. The selective layer pores of OSN membranes are believed to be between 0.5 and 2 nm and are not commonly visible in SEM images. SEM images also can provide information about the thickness of the separation layer and the structure of the support layer, if macrovoids or sponge-like voids exist.
2.5 Transport Models

The driving force for membrane transport is the chemical potential gradient of the solute across the membrane. The chemical potential gradient derives from differences in pressure, temperature, concentration, or electrical potential. Mathematical models have been established to understand membrane transport. In organic solvent nanofiltration, it is important to have a fundamental understanding of the separation mechanism to improve and tune materials to meet the growing needs and applications. Knowledge of transport mechanisms is key to describing and predicting the fluxes and rejections of solutes and solvents through porous and non-porous membranes. However, aqueous media transport mechanisms cannot be extended straightforwardly to non-aqueous systems due to significant differences in the structures and properties of the solvents.\textsuperscript{158-159} Two mathematical models describing the transport of a compound through a membrane as a function of its structure and physicochemical properties and the properties of the membrane are the solution-diffusion (SD)\textsuperscript{160} and pore-flow (PF)\textsuperscript{161,162} models.

2.5.1 Pore flow model

The pore-flow model assumes that the transport of a compound through a membrane takes place within the permeation channels or pores. These pores are larger in diameter than the solute and solvent. The PF model also considers that the concentrations of solute and solvent are constant across the membrane and that the chemical potential gradient derives from a pressure difference that leads to convective flow through the pores\textsuperscript{27} (Fig. 2.12).
In the absence of a concentration difference, Darcy’s Law describes solute transport through a porous membrane in terms of the flux produced by a difference in pressure according to equation (2.4):

\[ J_l = k \left( \frac{P_o - P_l}{l} \right) \]

(2.4)

In equation (4), \( l \) is the membrane thickness, \( k \) is the permeability coefficient, which is a function of membrane structural features including pore size, porosity, and tortuosity, and \( P_o \) and \( P_l \) are the high low pressures, respectively. The flux of pure solvent (\( J_{solvent} \)) is governed by the Hagen–Poiseuille equation. This model describes the flow through uniform and cylindrical pores due to a pressure difference in terms of equation (2.5):

Fig. 2.12: Profiles of chemical potential, pressure and solvent activity of pressure-driven filtration of one component solution through porous membrane according to pore-flow transport model.
where $\eta$ is the viscosity, $\tau$ is the tortuosity, $l$ is the membrane thickness, $\varepsilon$ is the porosity, and $r_p$ is the pore radius.

2.5.2 Solution-diffusion model

The solution-diffusion model was developed by Lonsdale et al.,\textsuperscript{163} revisited by Wijmans and Baker,\textsuperscript{160} and adopted by White\textsuperscript{142} and Peeva et al.\textsuperscript{33} This model describes transport through a membrane under the influence of a concentration difference between the feed and permeate (Fig. 2.13). The chemical potential within the membrane is determined by the concentration gradient, while the pressure is fixed uniformly at the greater value throughout the membrane. This popular model commonly is used to interpret transport in RO and gas separation. The solution-diffusion model assumes that the fluxes of solute and solvent are independent of one another.

The solution-diffusion model is applicable to dense membranes and differs from the pore-flow model of porous membranes, where transport occurs through pores that are fixed in time and space. The motion of permeants occurs on the same time scale as the statistical fluctuations of free-volume elements in dense membranes. According to this model, permeants dissolve in the membrane matrix and diffuse across a concentration gradient.
The solute and solvent fluxes in the solution-diffusion model obey Fick’s Law (equation (2.6)):  

$$ J_i = -D_i \frac{dc_i}{dx} $$  

(2.6)

where $D_i$ is the diffusion coefficient. The solution-diffusion model uses equation (2.7) to describe the flux across the membrane in terms of pressure and concentration differences:

$$ J_i = \frac{D_i K_i}{l} \left\{ c_{i,o} - c_{i,l} \exp \left[ -\frac{\nu_i (P_o - P_l)}{RT} \right] \right\} $$  

(2.7)

where $K_i$ is the sorption coefficient, $\nu_i$ is the molar volume, $c_i$ is the concentration, $T$ is the temperature, and $R$ is the ideal gas constant. Equation (2.7) is valid for both solute and
solvent. After certain assumptions, it can be simplified to describe solvent flux \((i)\) as equation (2.8):

\[
J_i = \frac{D_i K_i v_i c_i a}{lRT} (\Delta P - \Delta \pi)
\]

(2.8)

Where \(\pi\) is the osmotic pressure. The solute flux \((j)\) is given by equation (2.9):

\[
J_j = \frac{D_j K_j}{l} (c_{jo} - c_{ji})
\]

(2.9)

Paul\(^{164}\) critically discussed the limitations of the solution-diffusion model for OSN. He indicated that solution-diffusion theory fails to describe separation in various organic systems, because it does not account for coupling between the solute and solvent.\(^{165}\) Bhanushali et al.\(^{143}\) highlighted the difference between aqueous and non-aqueous systems by considering membrane swelling and various interaction parameters for non-aqueous systems. Silva et al.\(^{166}\) reported solvent mixture fluxes using Starmem\(^{TM}\) 122 membranes. A good correlation was found between experimental data and the solution-diffusion model. See-Toh et al.\(^{65}\) used both models to describe PI P84 membrane performance with changing polymer concentration. The change in performance due to membrane morphology was adequately explained by both the solution-diffusion and pore-flow models.
2.6 References


*Desalination* 1977, 21 (3), 241-255.


101. Jimenez-Solomon, M. F.; Gorgojo, P.; Munoz-Ibanez, M.; Livingston, A. G., Beneath the surface: Influence of supports on thin film composite membranes by


CHAPTER 3: Synthesis of polythiosemicarbazide (PTSC) and polythiourea (PTU) polymers and membrane preparation.

3.1 Introduction

Campell first introduced polythiosemicarbazide (PTSC) in the 1960’s as a polymer for chelating purposes \(^1\) due to the presence of the stable-chelate forming thiosemicarbazide group \(^5\). Other forms of PTSC polymers were synthesized for the same purpose and reported \(^6\). PTSC pendant polymers were also designed to form biologically active polymers \(^7\). Later on, membranes were prepared from PTSC for (i) gold recovery from dilute solutions via chelation formation \(^8\) and (ii) for catalytic application through in situ growth of gold nanoparticles \(^9\)\(^-\)\(^10\). Campell reported the synthesis of PTSC polymer in detail; the PTSC was formed by condensation polymerization between diamine and di-isothiocyanate monomers. Although the reported PTSC polymer was initially targeting metal complexation applications, it is the difficulty in finding a good solvent for this polymer that made it attractive for organic solvent nanofiltration applications. PTSC has two interesting functional groups that allow further modifications to establish better chemical resistivity to harsh solvents; one functional group is the thiosemicarbazide group and the other is the piperazine group.

In this chapter synthesis of the PTSC polymer is presented followed by polymer characterization techniques.
3.2 Diamine monomer synthesis

PTSC polymer synthesis requires the (N,N’-diaminopiperazine) monomer. This monomer however is not available commercially hence lab synthesis is needed. The synthesis of this monomer started by using piperazine to prepare N, N’-dinitrosopiperazine as intermediate product, followed by the reduction of N,N’-dinitrosopiperazine step, according to the following reaction, Fig. 3.1:

I- The first step of this reaction is to prepare dinitrosopiperazine, the procedure is as follows;

- 15 g piperazine was placed in 250 ml round bottom flask with magnetic stirrer.
- 180 ml distilled water and 28.8 ml of (37%) hydrochloric acid was added.
- The solution was stirred vigorously and maintained at 80 C° by heating in oil bath.
• A dropping funnel was supplied to the round flask containing a mixture of 48 g sodium nitrate and 135 ml distilled water; this mixture was added over a period of an hour.

• Stirring and heating were continued for two hours, after all the sodium nitrite solution was consumed.

• Filtration of the yellow precipitant, yellow crystals of dinitrosopiperazine were obtained.

• Drying in oven at 70 C° overnight.

To evaluate the success of this reaction, the yield was calculated by measuring the final dry weight of dinitrosopiperazine and comparison with the initial piperazine mass. The yield obtained was around (86%).

II- The second step is to reduce dinitrosopiperazine to obtain diaminopiperazine:

• Using 1 L round bottomed flask, provided with a magnetic stirrer, dropping funnel.

• To the previous apparatus, 15 g dinitrosopiperazine, 175.44 ml distilled water and 50 g of 100% zinc dust were added.

• Mixture was stirred and the round bottom flask was fixed in an ice bath while 77 ml acetic acid is dripping from the dropping funnel over a period of two hours.

• After the acetic acid was all consumed, the reaction mixture was heated for an hour at 65 C° using oil bath.

• Allowing the mixture to cool of away from the heat.

• The excess zinc dust was filtered and washed with distilled water.
• The filtrate (aqueous liquor) has a pH of 5, it was transferred to a 1 L flask and the pH was adjusted to 10 using sodium hydroxide solution. The mixture became white and cloudy.
• Placing the mixture in the rotary evaporator to reduce water content.
• The partially dried powder (diaminopiperazine) is placed in distillation unit at 110 C° with aluminum foil raped on the neck of the flask to keep the temperature of the water vapor until it reaches the condenser and condense.
• The dried solid was transferred to a sublimation unit, in this unit the powder is heated to 110 C° under vacuum in which the diaminopiperazine powder turns into vapor and get condensed into a solid again on the inner surface of the cold finger. This process usually provides 4 g product.

To achieve higher product purity, diaminopiperazine is purified by re-crystallization. Diaminopiperazine was dissolved in the smallest amount of hot chlorobenzene solvent thus making a saturated solution. The solution is then allowed to cool. As the solution cools the diaminopiperazine crystallizes and the purified diaminopiperazine is obtained via filtration.

3.3 PTSC polymer synthesis

The polythiosemicarbazide (PTSC) was synthesized following a procedure described in the literature with slight modification ¹, the reaction scheme is presented in Fig. 3.2. Equimolar quantities of the two monomers in DMSO were heated at 50 °C for two days. The homogenous solution is then precipitated in hot stirred water and then dried after
filtration under vacuum at 60 °C for another two days. The monomers are 4,4'-methylenebis(phenyl isothiocyanate) and 1,4-diaminopiperazine.

![Diagram of monomers and polymer](image)

Fig. 3.2: Synthesis reaction of polythiosemicarbazide (PTSC) polymer.

### 3.4 Polymer characterization

#### 3.4.1 Proton Nuclear Magnetic Resonance (1H NMR) analysis

1H NMR spectra of the PTSC polymer was evaluated on a Bruker AVANCE III 700 MHz liquid NMR instrument equipped with a TCI Cryoprobe. DMSO-d$_6$ was used as a solvent at 298 K.

Fig. 3.3 present the $^1$H NMR spectra of PTSC. It is evident from the spectrum that chemical shifts at 2.90-2.97 (A) are attributed to the hydrogen atoms in the piperazine
group whereas the 3.91-ppm (B) chemical shift is attributed to the hydrogen in the CH$_2$ group of the PTSC chain. The appearance of chemical shift at 7.18 ppm (D) is due to the hydrogen on the aromatic group that is under the effect of the NH; the 7.46-ppm (C) chemical shift is representing the same aromatic ring but the hydrogen atoms are under the effect of CH$_2$. The hydrogen in the NH group is responsible for the chemical shift at 9.28 ppm (F) where this shift is under the influence of the piperazine group. The hydrogen in the NH group near the aromatic group however is located at the chemical shift of 9.52 ppm (E).

Fig. 3.3: NMR spectra of PTSC polymer.
3.4.2 Gel Permeation Chromatography (GPC)

The average molecular weight and polydispersity of PTSC polymer was determined using an Agilent GPC with Wyatt modules for Triple Detection (Optilab T-rEX, DAWN HELEOS II and Viscostar II).

The molar mass of the PTSC is an important parameter for membrane forming properties. Generally, for the formation of functional membranes, the polymers should have molar mass above 15000 g/mol. It is essential to characterize the polymer molar mass as well as the molar mass distribution. Table 3.1 shows the molar mass of the PTSC polymer determined by GPC, in which $M_n$ represents the number average molar mass; $M_w$ represents the weight average molar mass, and PDI for polydispersity index. The polydispersity index is used as a measure of the broadness of a molecular weight distribution of a polymer. The larger the polydispersity index, the broader the molecular weight. The PTSC polymerization reaction is condensation step reaction type; step polymerization reactions typically yield values of PDI of around 2.0 \(^1\)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$ (kg/mol)</th>
<th>$M_w$ (kg/mol)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTSC</td>
<td>21.37</td>
<td>50.85</td>
<td>2.38</td>
</tr>
</tbody>
</table>
3.4.3 Thermogravimetric analysis (TGA)

The thermal stability was evaluated using Thermogravimetric analysis (TGA). The measurements were conducted on a TGA Q5000 with a heating rate of 3 °C min\(^{-1}\) under airflow, from 30 to 700 °C.

The thermal stability of the PTSC polymer prepared was evaluated by recording the TGA curves of the pristine PTSC polymer Fig. 3.4.

The pristine PTSC exhibit two degradation stages; one is in the range of 190-300 °C and the other is in the range of 550-600 °C. The TGA results show that PTSC polymer undergoes a major thermal degradation first at an initial temperature of 196.4 °C with a significant weight loss of 37.8 % and a second 3.82 % weight loss degradation at 552.9 °C.

![TGA analysis of PTSC polymer](image)

Fig. 3.4: TGA analysis of PTSC polymer.
3.4.4 Differential Scanning Calorimetry (DSC)

DSC thermogram of the synthesized PTSC and PTU polymers were recorded on a DSC Q 2000 instrument in the temperature range of 0–300 °C at a heating rate of 10 °C/min in nitrogen atmosphere.

DSC analysis was carried for PTSC polymer to determine its glass transition temperature, Fig. 3.5 demonstrates the DSC curve with a Tg peak around 158.6 °C. Further decomposition of PTSC polymer was observed above 200 °C.

Fig. 3.5: DSC analysis of PTSC polymer.

3.4.5 Polymer chemical stability

Polymer samples were dried at 50 °C in oven under vacuum for two days to assure complete dryness. Next, these samples were immersed in several solvents for different
time intervals. The shape and color changes of the polymer samples were carefully observed.

The solubility parameter $\delta$ is a tool for predicting the interaction forces between the molecules in a given molecular structure \(^{12}\). This parameter can be helpful in many areas including membranes, where expressing the interaction force between the polymer molecules themselves as well as between the polymer molecule and the solvent or non-solvent molecule. The use of this parameter benefits the understanding of the three-system (polymer, solvent and non-solvent) membrane fabrication in many ways: (i) through the understanding of polymer/solvent solubility parameter ($\Delta \delta_{PS}$), a prediction of the ability of a solvent to swell a polymer is obtained. This parameter is also related to the polymer/solvent affinity hence low value represents a thermodynamically suitable solvent in where the polymer is in a "relaxed" state and the contact between solvent and polymer is favored. However high value, signify that the solvent is poor and polymer chain aggregation occurs. (ii) Solvent/non-solvent solubility parameter ($\Delta \delta_{SNS}$) depicts the solvent/non-solvent exchange rate during the immersion of the polymer film in the coagulation bath and authorizes the assumptions about the structures formed in a membrane during phase inversion. Low affinity between the solvent and the non-solvent, which is expressed by the high value of that parameter, indicate slower diffusion of the non-solvent into the polymer film and tight membranes are produced. (iii) Polymer/non-solvent solubility parameter ($\Delta \delta_{PNS}$) also impacts the morphology of the final fabricated membrane, high affinity between polymer and non-solvent favors delayed phase separation hence denser morphology \(^{13}\).
The Hansen solubility parameter is one among other parameters used to calculate the solubility properties of a material. The total Hansen solubility parameter $\delta_{t,i} (\text{MPa}^{1/2})$ is a three component system developed in 1966 $^{14-16}$ and it accounts for the dispersion forces $\delta_{d,i}$, the polar forces $\delta_{p,i}$ and the hydrogen bonding $\delta_{h,i}$ (equation 3.1).

\[
\delta_{t,i}^2 = \delta_{d,i}^2 + \delta_{p,i}^2 + \delta_{h,i}^2
\] 

(3.1)

The difference between the solubility parameters $\Delta \delta_{ij}$ of two of the components i and j can be used as a measure of their thermodynamic affinity.

PTSC was tested in several solvents to identify its chemical stability. Table 3.2. Good stability was visually recorded in the solvents acetone, ethanol, methanol, acetonitrile, heptane, DCM and ethyl acetate. Chemical stability also was noticed for other solvents where no dissolution occurred however slight color changes were noticed; these solvents include isopropanol, dioxane and toluene. Mild solvation occurred when PTSC polymer was immersed in THF solvent for time interval longer than 10 days. Severe dissolution or solvation was recorded for harsh solvents such as DMF, NMP and DMAc where the polymer disintegrates into small fragments. A complete dissolution was only recorded in DMSO solvent, which is considered as a good solvent for this polymer.
Table 3.2: Chemical stability of PTSC polymer upon exposure to solvents for different periods of time.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Hansen Solubility Parameter (MPa$^{1/2}$)</th>
<th>Stability after 5 days</th>
<th>Stability after 10 days</th>
<th>Stability after 15 days</th>
<th>Stability after 20 days</th>
<th>Stability after 25 days</th>
<th>Stability after 30 days</th>
<th>Stability after 1 year</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>20</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>polymer turns brownish</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>24.5</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>polymer turns yellow</td>
</tr>
<tr>
<td>Ethanol</td>
<td>26.5</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>29.6</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td></td>
</tr>
<tr>
<td>Isopropanol</td>
<td>23.5</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>18.2</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td></td>
</tr>
<tr>
<td>Heptane</td>
<td>15.3</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td></td>
</tr>
<tr>
<td>Hexane</td>
<td>14.9</td>
<td>Not stable</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMF</td>
<td>24.8</td>
<td>Not stable</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DCM</td>
<td>20.3</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td></td>
</tr>
<tr>
<td>DMAc</td>
<td>22.8</td>
<td>Not stable</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMSO</td>
<td>26.7</td>
<td>Not stable</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMP</td>
<td>22.9</td>
<td>Stable</td>
<td>Not stable</td>
<td>Not stable</td>
<td>Not stable</td>
<td>Not stable</td>
<td>Not stable</td>
<td>Not stable</td>
<td></td>
</tr>
<tr>
<td>THF</td>
<td>19.4</td>
<td>Stable</td>
<td>Not stable</td>
<td>Not stable</td>
<td>Not stable</td>
<td>Not stable</td>
<td>Not stable</td>
<td>Not stable</td>
<td></td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>18.2</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td></td>
</tr>
<tr>
<td>Dioxane</td>
<td>20.5</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td></td>
</tr>
</tbody>
</table>

To calculate the solubility parameter for PTSC, the group contribution method was followed based on the contribution of the structural groups to the cohesion energy $E_{coh}$ (J/mol) and the molar volume $V$ (cm$^3$/mol)\(^{18}\). The following equation 3.2 was used to determine $\delta$ (MPa$^{1/2}$):

$$\delta = \sqrt{\frac{\Sigma E_{coh}}{V}}$$

(3.2)

The values of $E_{coh}$ for the functional groups in PTSC polymer repeat unit are presented in Table 3.3.
Table 3.3: Cohesion energy values for functional groups present in PTSC polymer.

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Number of functional group per repeat unit</th>
<th>Ecoh (J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>31,940</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4,940</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8,370</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25,120</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16,740</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,050</td>
</tr>
</tbody>
</table>

The density of the PTSC ($\rho_{PTSC}$) polymer was calculated using the following equation based on Archimedes principle in equation 3.3:

$$\rho_{PTSC} = \frac{A}{A - B} (\rho_o - \rho_L) + \rho_L$$

(3.3)

Where A is the weight of the polymer in air (dry), B is the weight of the polymer in the auxiliary liquid (iso-octane), $\rho_o$ is the density of the auxiliary liquid ($\rho_{Iso-octane} = 0.688 \text{ g/cm}^3$ at 25 °C) and $\rho_L$ is the density of air (0.0012 g/cm³).

Dense film of 2% PTSC polymer was prepared via casting and evaporation of solvent. The weight of the dense film was recorded in air and in iso-octane solvent. The density of PTSC is 1.253 g/cm³.
The total $E_{coh}$ calculated is 170,330 J/mol. The molar volume (cm$^3$/mol) of PTSC is calculated based on the density and the molecular weight (398.55 g/mol). Hence the solubility parameter for PTSC is 23.14 MPa$^{1/2}$.

### 3.5 Effect of diamine monomer

Polymerization reaction of PTSC involves the use of diaminopiperazine monomer. We used another diamine monomer to obtain a different polymer. 4,4'-oxydianiline (ODA) monomer was used and the effect of different diamine monomer was tested.

Polythiourea (PTU) polymer was synthesized following a similar procedure as the PTSC synthesis however, diaminopiperazine was replaced by 4,4'-oxydianiline (ODA) monomer, reaction scheme is shown in Fig. 3.6. Equimolar quantities of the monomers in DMSO were heated at 50 °C for two days. This was followed by precipitation in hot water and a drying step after filtration under vacuum at 60 °C for another two days.

![Synthesis reaction of polythiourea (PTU) polymer.](image)

Fig. 3.6: Synthesis reaction of polythiourea (PTU) polymer.
3.5.1 PTU polymer characterization results

3.5.1.1 $^1$H NMR analysis

Fig. 3.7 present the $^1$H NMR spectra of PTU polymer. It can be observed from the spectrum that the chemical shift at 0.5 (a) is attributed to the CH$_2$ group whereas the 7.07 (b) and 7.3 (c) ppm chemical shifts are attributed to the hydrogen in the aromatic group of the polymer chain that neighbors the CH$_2$. The aromatic ring hydrogen atoms that neighbor the oxygen are represented by the chemical shifts at 7.2 (e) and 6.8 (f). The appearance of the chemical shift at 9.5 ppm (d) is due to the hydrogen-nitrogen bond.

Fig. 3.7: NMR spectra of PTU polymer.
3.5.1.2 Gel Permeation Chromatography (GPC)

Table 3.4 shows the molar mass of the PTU polymer determined by GPC, in which $M_n$ means number average molar mass; $M_w$ represents weight average molar mass, and PDI for polydispersity index. The PDI is used as a measure of the broadness of a molecular weight distribution of a polymer. The larger the polydispersity index, the broader the molecular weight. The PTU polymerization reaction is a condensation step reaction type; step polymerization reactions typically yield values of PDI of around 2.0 \(^{11}\).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$ (Kg/mol)</th>
<th>$M_w$ (Kg/mol)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTU</td>
<td>25.6</td>
<td>53.76</td>
<td>2.1</td>
</tr>
</tbody>
</table>

3.5.1.3 Thermogravimetric analysis (TGA)

The thermal stability of the PTU polymer prepared was evaluated by recording the TGA curves Fig. 3.8. The pristine PTU exhibit two degradation stages; one is in the range of 180-478 °C and the other is in the range of 478-625 °C. The TGA results show that PTU undergoes a major thermal degradation first at an initial temperature of 180.3 °C with a significant weight loss of 57.2 % and a second of 10.44 % weight loss degradation at 478.5 °C.
3.5.1.4 Differential Scanning Calorimetry (DSC)

DSC analysis was carried for PTU to determine its glass transition temperature, Fig. 3.9

Demonstrate the DSC curve with a $T_g$ peak around 155.4 °C.
3.5.1.5 PTU polymer chemical stability

PTU was tested with several solvents to identify its chemical stability; the results are similar to the PTSC polymer. Color and shape changes are summarized in Table 3.5. Good stability was visually confirmed in the solvents such as acetone, ethanol, methanol, acetonitrile, heptane, DCM and ethyl acetate. Chemical stability was also noticed for other solvents where no dissolution occurred however slight color change were noticed; these solvents include isopropanol, dioxane and toluene. Mild solvation occurred when PTU polymer was immersed in THF solvent for a time interval longer than 10 days. Severe dissolution or solvation was recorded for harsh solvents such as DMF, NMP and DMAc where the polymer disintegrates into small fragments. A complete dissolution was only recorded in DMSO solvent, which is considered as a good solvent for this polymer.

Table 3.5: Chemical stability of PTU polymer upon exposure to solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Hansen Solubility Parameter (MPa^{1/2})</th>
<th>Stability after 5 days</th>
<th>Stability after 10 days</th>
<th>Stability after 15 days</th>
<th>Stability after 20 days</th>
<th>Stability after 25 days</th>
<th>Stability after 30 days</th>
<th>Stability after 1 year</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>20</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Brownish, Light yellow</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>24.5</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Strong dissolution</td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
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<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
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</tr>
<tr>
<td>Methanol</td>
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<td>Stable</td>
<td>Stable</td>
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<tr>
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<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
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<tr>
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<td>Stable</td>
<td>Stable</td>
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<td></td>
</tr>
<tr>
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<td>Not stable</td>
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<td>Not stable</td>
<td>Not stable</td>
<td>Not stable</td>
<td>Not stable</td>
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<td>Not stable</td>
<td>Severe dissolution</td>
</tr>
<tr>
<td>Ethyl acetate</td>
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<td>Not stable</td>
<td>Stable</td>
<td>Not stable</td>
<td>Stable</td>
<td>Not stable</td>
<td>Yellow</td>
<td></td>
</tr>
<tr>
<td>Dioxane</td>
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<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Yellow</td>
<td></td>
</tr>
</tbody>
</table>
To calculate the solubility parameter for PTU, the group contribution method was followed based on the contribution of the structural groups to the cohesion energy $E_{coh}$ (J/mol) and the molar volume $V$ (cm$^3$/mol)\textsuperscript{18}. Equation 3.2 was used. Table 3.6 present the values of $E_{coh}$ for the functional groups existing in the PTU repeat unit.

Table 3.6: Cohesion energy values for functional groups present in PTU polymer.

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Number of functional group per repeat unit</th>
<th>$E_{coh}$ (J/mol)\textsuperscript{18}</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Structural group 1]</td>
<td>4</td>
<td>31,940</td>
</tr>
<tr>
<td>![Structural group 2]</td>
<td>1</td>
<td>4,940</td>
</tr>
<tr>
<td>![Structural group 3]</td>
<td>4</td>
<td>8,370</td>
</tr>
<tr>
<td>![Structural group 4]</td>
<td>2</td>
<td>25,120</td>
</tr>
<tr>
<td>![Structural group 5]</td>
<td>1</td>
<td>3,350</td>
</tr>
</tbody>
</table>

The density of the PTU polymer was calculated using the previous equation, 2% PTU solution was prepared to obtain dense film and the weight of this film in air and in iso-octane was recorded. The density of PTU is 1.278 g/ cm$^3$.

The total $E_{coh}$ calculated is 219,770 J/mol. The molar volume (cm$^3$/mol) of PTU is calculated based on the density and the molecular weight (482.62 g/mol). Hence the solubility parameter for PTU is 24.12 MPa\textsuperscript{1/2}.
3.6 Membrane preparation

Microporous support membranes were fabricated from PTSC and PTU polymers via the phase inversion method. A dope solution of 15% (w/w) of polymer was prepared in DMSO at 65 °C under stirring for 7 h until a homogeneous solution was obtained. Then the solution was left for an hour to allow air bubbles to escape prior to casting. Membranes were cast on a polyester fabric support with the prepared dope solutions using a casting knife with a casting thickness of 100 µm. The membranes were immediately immersed in a water bath at room temperature where the precipitation occurs by nonsolvent induced phase separation (NIPS). The wet membranes were transferred to room temperature DI water bath for at least 12 h to remove any excess solvents and to maintain its wetness to avoid any pore collapse.

3.7 PTSC and PTU membrane performance

PTSC and PTU filtration experiments were carried out using integrally skinned asymmetric (ISA) membranes of these two polymers. The water flux was measured at 4 bar using a stirred dead-end filtration cell with an effective membrane area of 4 cm², permeate samples for flux and rejection measurements were collected after obtaining a steady state condition. The rejection studies were carried out using a feed solution of 0.1% polyethylene glycol (PEG) (3K, 6K, 10K and 35K) in water. Analysis of the PEG was done on an Agilent GPC system with tungsten lamp RID detector, which emits in the visible range set at a wavelength higher than 380 nm. Another solute marker was 0.0005% (w/w) Brilliant blue (BB) dye (825.97 g/mol) in water and the analysis was
done via UV–Vis spectroscopy. The size of the BB molecule in water was analyzed using Zetasizer Nano Zs particle size zeta potential. Solvent flux \( (J) \) was determined by measuring permeate volume \( (V) \) per unit area \( (A) \) per unit time \( (t) \) using the following equation 3.4:

\[
J = \frac{V}{t \cdot A}
\]

(3.4)

PTSC membranes had a permeance of 650 L/m².h.bar, SEM image in Fig. 3.10 e shows that these membranes have pore sizes in the 30-50 nm ranges. Testing these membranes for BB dye rejection shows excellent membrane performance with 100% rejection. Fig. 3.10 c. shows UV analysis for feed, permeate and retentate samples and Fig. 3.10 b. presents a digital photo of the three samples. The increase of the retentate concentration proves that the dye is rejected and not adsorbed on the membrane. This indicates that the MWCO of these membranes is around 825 g/mol. However referring to the zeta size analysis in Fig. 3.10 a, the BB molecules experience severe agglomeration in water solution showing a diameter of around 94 nm which means that the molecules are bigger than the actual size hence the rejection is complete.
Fig. 3.10: PTSC performance a) structure and size analysis of Brilliant Blue dye in water, b) digital images of Brilliant Blue/water mixture of feed, permeate and retentate samples after filtered by PTSC membrane, c) UV-Vis analysis of PTSC membrane filtration of Brilliant Blue/water, d) permeance values of PTSC membrane with changing the percentage of DAP monomer, e) SEM images of surface of PTSC membrane.

Analysis of the rejection performance of PTSC membranes using a mixture of PEG with different molecular weights was performed to identify the MWCO of these membranes. The GPC analysis of feed, permeate and retentate of PEG/water samples affirms that the MWCO of these membranes is higher than 35,000 g/mol. PTU membranes although exploit complete BB dye rejection in water, the permeance is about 60% lower than the PTSC membranes. The reason might be higher hydrophilicity nature of the DAP
monomer. It was reported that the DAP monomer has an octanol-water partition coefficient value higher than other diamine monomers which lead to higher water permeabilities \(^{19}\). Fig. 3.10 d. assigns water permeances to percentages of DAP monomer used in the synthesis where 100% DAP relates to the PTSC and the 0% DAP relates to the PTU polymer. Different percentages of both monomers were also explored to prepare polymers with altering diamine monomer moieties. Obviously the higher the percentage of the ODA monomer the lower the water permeances.

### 3.8 Composition of the Coagulation bath

The affinity between the solvent in the casting solution and the non-solvent in the coagulation bath can play a major role on the membrane morphology and the membrane performance. The provoked phase separation is highly dependent on the solvent / non-solvent miscibility. The presence of a solvent with low affinity to the non-solvent will decrease the diffusional driving force which as a result will slow down water in-diffusion into the polymer film \(^{20-21}\). This diffusion is crucial for the skin layer formation and has significant impact on the morphology of the membrane \(^{22-23}\). Porous open or dense tight structures are governed by the ratio of the diffusion rate of solvent to non-solvent; increasing the diffusion rate will lead to a formation of dense skin layer. Water is a preferred non-solvent because it is cheap and miscible with wide range of common polymer solvents like DMF, NMP, DMSO and DMAc. However other organic liquids can serve as precipitation medium depending on the polymer used.

Dual bath precipitation technique was introduced to achieve a dense layer on top of a
porous support depending on the solvent/non-solvent affinity properties \(^{24-25}\). This technique involves a first bath of a non-solvent for the polymer with low affinity towards the polymer solvent used, and a second bath that consists of water. A PTSC/DMSO cast film precipitated in water directly results in an ultrafiltration membranes is formed. To study the effect of the coagulation bath iso-propanol (IPA) solvent was used as a non-solvent in addition to water. First, the effect of the composition of non-solvent bath was investigated by adding IPA to the water bath. Fig. 3.11 present the flux of water tested for membranes precipitated in mixtures of IPA and water using different concentrations and immersion times.

![Graph showing flux values for PTSC membranes precipitated using dual bath precipitation.](image)

Fig. 3.11: Flux values for PTSC membranes precipitated using dual bath precipitation.

The blue points refer to the immersion in the IPA/water bath mixture for 2 sec while the red points refer to the immersion time of 1 minute. Membranes immersed in pure water showed high flux value of 2700 L/m\(^2\).h at 2 bar. However mixing 60% IPA in the coagulation bath resulted in a 70% flux decline to reach 800 L/m\(^2\).h at 2 bar. This is
expected since the demixing is delayed leading to a tighter skin layer. A 100% IPA coagulation bath led to a very low flux of 0.527 L/m².h at 2 bar. An increase in the IPA content is accompanied by a decrease in the flux value was also witnessed for immersion time of 1 min. However the values are lower when compared to the same IPA content for 2 sec immersion due to the longer exposure time. Fig. 3.12 show SEM cross-section images of PTSC membranes immersed in 90: 10 % IPA: water for 1 min. The detachment of the top layer from the support reveal the porous support openness as well as the dense skin layer which has a thickness of around 400 nm.

Fig. 3.12: SEM images of PTSC membrane immersed in 90:10 % IPA: water for 1 min.

The effect of utilizing a dual bath precipitation for the creation of dense skin layer on top of a porous support was investigated. The first bath contained 100% pure IPA while the second bath was water; immersion time varied from 2 to 10 sec in the first bath. Fig. 3.13 describe the flux and the thickness of the dense top layer change with immersion time.
Fig. 3.13: Thickness of skin layer and flux change with percentage of IPA used in the first bath of dual bath precipitation

As the IPA exposure time increases the thickness of the skin dense layer increase hence a significant decrease of water flux. Fig. 3.14 exhibits SEM cross-section images of PTSC membranes precipitated in 100% IPA in the first coagulation bath for different time intervals (2, 4, 6, 8 and 10 sec). Fig. 3.15 show a close up of the dense 600 nm skin layer resulted from 10 sec exposure to IPA.
Fig. 3.14: SEM images of PTSC membranes immersed in 100% IPA first bath for a) 2 sec, b) 4 sec, c) 6 sec, d) 8 sec and e) 10 sec.

Fig. 3.15: SEM cross-section image of PTSC membrane immersed for 10 sec in 100% IPA first bath.
3.9 References


4 CHAPTER 4: Thin film composite crosslinked polythiosemicarbazide membranes for organic solvent nanofiltration

4.1 Abstract

A new solvent stable thin-film composite (TFC) membrane is reported. The membrane is based on a porous crosslinked polythiosemicarbazide (PTSC) as substrate that exhibits superior stability compared with other solvent stable polymeric membranes reported up to now. Asymmetric PTSC membranes were prepared by the phase inversion process and crosslinked with an aromatic bifunctional crosslinker to improve the solvent stability. TFC membranes were obtained via interfacial polymerization using trimesoyl chloride (TMC) and diaminopiperazine (DAP) monomers. The membranes were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and contact angle measurement.

The membranes exhibited high fluxes toward harsh solvents like tetrahydrofuran (THF), dimethylformamide (DMF) and dimethylsulfoxide (DMSO) ranging around 20 L/m\(^2\) h at 5 bar with a molecular weight cut off (MWCO) of around 1000 g/mol. The PTSC-based thin-film composite membranes are very stable toward polar aprotic solvents and they may find applications in the petrochemical and pharmaceutical industry.

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### 4.2 Introduction

Various techniques like distillation, adsorption, and chromatography are widely being used for the separation of solutes from organic solvents. These processes often have high energy and operation costs\(^1\)-\(^2\). An alternate approach of using polymeric membranes for such separation processes can in many cases reduce these costs effectively\(^3\)-\(^7\).

Organic solvent nanofiltration (OSN) is an emerging membrane based separation process which separates mixtures on a molecular level\(^6\) very efficiently compared with other traditional industrial processes. OSN is a pressure driven separation process without phase transfer and uses membranes with pore size diameters between 0.2 and 0.5 nm that are capable of separating solutes with molecular weights (MWCOs) of 200–1000 g/mol\(^6\),\(^8\)-\(^9\) in organic solvents.

One of the mostly studied polymers for OSN is polyimide (PI). Crosslinked PI membranes are chemically stable toward organic solvents\(^10\)-\(^14\) and are used for separations widely. However these membranes usually suffer from compaction and flux decline and they require additives like PEG before drying to prevent pore collapse\(^15\).

Research in this area is always heading toward finding new polymeric membranes that are stable in a wide range of organic solvents and which can compete with existing membranes in terms of fluxes and rejections. One attractive polymer is polythiosemicarbazide (PTSC), which was first introduced in early 60’s for its ability to form stable chelates with wide range of metals\(^16\)-\(^17\). PTSC was only recently utilized as membrane material\(^18\). The PTSC was complexed with gold nanoparticles and the gold loaded membranes were used as a catalytically active membrane in water. Relying on
PTSC membranes ability to complex with metal ions, gold ions recovery from dilute solutions was achieved. PTSC dissolves very well in dimethylsulfoxide (DMSO) and partially in other polar aprotic solvents. In this work a dope solution of PTSC dissolved in DMSO was used to cast membranes. Chemical crosslinking is a well-known technique that promotes additional resistance of polymers to chemical dissolution. It additionally reduces the mobility of the polymer chains, which leads to higher selectivity and stability while maintaining permeability. Crosslinking with an aromatic bifunctional crosslinker can enhance the stability of polymers toward organic solvents. In this work α, α-dibromo-p-xylene (DBX) crosslinker was used as a crosslinking agent for PTSC support membranes.

Preparation of thin-film composite (TFC) membranes via interfacial polymerization (IP) is a promising approach to manufacture membranes for nanofiltration and organic solvent nanofiltration. From literature studies, it is believed that TFC – OSN membranes have the potential to achieve higher fluxes compared with integrally skinned asymmetric OSN membranes without compromising high rejection. First successful TFC membranes were developed by Cadotte and they are largely used for reverse osmosis (RO) and nanofiltration processes. It is a simple and easy method to obtain a highly crosslinked ultra-thin polyamide selective layer on a porous membrane substrate by interfacially polymerizing an aqueous phase containing m-phenylenediamine (MPD) monomer and an organic phase containing trimesoyl chloride (TMC). The thickness of the polyamide can be controlled by factors like reaction time, concentration of the monomers, and pore size of the substrate. The current work used diaminopiperazine (DAP) in water and trimesoyl chloride (TMC) in cyclohexane as
monomers to prepare TFC membranes. Membranes prepared using DAP–TMC monomers had a smooth and flat surface, which is preferred for low fouling properties \(^{30}\). The interfacially polymerized layer made from DAP and TMC has not been described before as selective layer for nanofiltration in organic solvents, but the main innovation described here is the solvent resistant crosslinked PTSC support membranes. The membranes were characterized using FTIR, contact angle measurement and SEM.

### 4.3 Materials

Dimethylsulfoxide (DMSO), N, N-dimethylformamide (DMF), tetrahydrofuran (THF), \(\alpha\), \(\alpha\)-dibromo-p-xylene (DBX), acetone, Rose Bengal dye, (2-hydroxypropyl)-b cyclodextrin, trimesoyl chloride, Protoporphyrin IX dimethyl ester, Protoporphyrin IX disodium salt, Safranin O were purchased from Sigma Aldrich Co., \(\alpha\)-cyclodextrin and hexakis-(6-deoxy-6-iodo)-\(\alpha\)-cyclodextrin were received from Arachem Co. Diaminopiperazine was synthesized in our lab following a procedure described by Campbell and Tomic \(^{16}\). Cyclohexane and Brilliant Blue dye were purchased from Fisher Scientific. Polyester support was purchased from Sojitz Europe, Germany. Polythiosemicarbazide (PTSC) was synthesized according to literature by the reaction of N, N-diaminopiperazine and methylenebis (4-phenylisothiocyanate) in DMSO \(^{16}\).
4.4 Crosslinked PTSC support membranes preparation

Microporous support membranes were fabricated from PTSC polymer via the phase inversion method. A dope solution of 15% (w/w) PTSC was prepared in DMSO at 65 °C under stirring for 7 h until a homogeneous solution was obtained. Then the solution was left for an hour to allow air bubbles to escape prior to casting. Membranes were cast on a polyester fabric support with the prepared PTSC dope solution on a continuously operating casting machine with a casting thickness of 100 µm at a casting speed of 2 m/min. The membranes were immediately immersed in a water bath at room temperature where the precipitation occurs by nonsolvent induced phase separation. After the casting process, the wet membranes were immersed in DI water bath at room temperature for at least 12 h to remove any excess solvents and to maintain its wetness to avoid any pore collapse.

Wet PTSC membranes were chemically crosslinked with 0.5 wt% dibromo-p-xylene (DBX) dissolved in acetone for 2 hours Fig. 4.1 demonstrate the chemical reaction. After crosslinking, the membranes were washed thoroughly with acetone and then stored in DI water.
4.5 Crosslinked PTSC support membranes characterization

4.5.1 FTIR:

Fourier transform infrared spectra were recorded on a Nicolet iS10 FTIR spectrometer in the range of 4000–500 cm$^{-1}$ at room temperature. The samples were fixed on a zinc/selenium diamond plate with the separating layer facing the beam. Prior to FTIR measurements the membranes were dried. Spectra of PTSC membrane and the crosslinked PTSC membranes were compared. Fig. 4.2 show the FTIR spectrum of pure PTSC and dibromoxylene PTSC membranes crosslinked for 2 h and 30 h. The pure PTSC shows a strong absorption band at 1511 cm$^{-1}$ (C=S) and (3271 cm$^{-1}$, 1612 cm$^{-1}$, 815 cm$^{-1}$) for aromatic C–H stretching, bending and aromatic C=C present in the polymer backbone. Absorption bands at 1018 cm$^{-1}$ and 2839 cm$^{-1}$ represents the aliphatic C–N stretch and C–H alkyl group present in the piperazine moiety. PTSC crosslinked for 2 h and 30 h shows slight shift in the C–N absorption band from 1018 cm$^{-1}$ to 1117 cm$^{-1}$,
which reveals the quaternization of piperazine moiety by the dibromoxylene. A new peak at 1612 cm\(^{-1}\) corresponds to the aromatic group present in the crosslinker and the aromatic C–H stretch at 3271 cm\(^{-1}\) was shifted and broadened for the crosslinked membranes. All the above data suggests the occurrence of crosslinking reaction between the dibromo-p-xylene and piperazine moiety of the PTSC membranes.

![Fig. 4.2: FTIR analysis of pristine and crosslinked PTSC membranes.](image_url)
4.5.2 Contact angle measurement:

Contact angle measurements were performed with an Easy-Drop Instrument (manufactured by Kruss) at room temperature using the drop method, in which a drop of water was deposited on the surface of a piece of membrane using a micropipette. The contact angle was measured automatically by a video camera in the instrument using drop shape analysis software. Three measurements on different membrane pieces were performed. All membranes were dried prior to measuring their contact angle. The contact angle of crosslinked PTSC membranes was measured and compared with non-crosslinked PTSC samples. The contact angle of the pristine PTSC membrane was 70 ± 1°, the contact angle after crosslinking 59 ± 2°. The membranes became more hydrophilic after crosslinking. This is probably caused by the formation of positive charges due to the formation of quaternary nitrogen atoms. The positive charge on the surface orients surrounding water molecules by Coulombic attraction with the negative dipoles of water.

4.6 Thin film composite crosslinked PTSC membranes preparation

Thin-film composite (TFC) membranes were prepared by interfacial polymerization with diaminopipеразине (DAP) and trimesoyl chloride (TMC) as monomers in deionized water and cyclohexane respectively. The wet crosslinked PTSC membranes were immersed in 2% (w/v) aqueous solution of DAP for about 2 min and the excess solution was wiped gently from the surface by a rubber roller. Subsequently, the impregnated membrane was then laid on a sponge (with the PTSC surface facing down), which was soaked with the
solution of TMC in cyclohexane (0.2 wt.%). The membrane was then gently pressed from the backside with a rubber roll for 1 min; after that the resulting membranes were lifted from the sponge and left to dry for 5 min. The same procedure was repeated again to achieve a double layer interfacial polymerization and after 5 min reaction the membranes were rinsed with water. Finally, the membranes were stored in water at room temperature. The chemical structures of the monomers used for the interfacial polymerization reaction are shown in Fig. 4.3.

![Chemical Structures](image)

Fig. 4.3: Interfacial polymerization reaction on top of PTSC porous support.

4.7 **Thin film composite crosslinked PTSC membranes Characterization**

4.7.1 Scanning electron microscopy (SEM)

The surface and cross-section of different TFC crosslinked PTSC membranes were characterized by scanning electron microscopy. For the analysis of a membrane’s surface, samples were prepared by cutting small squares of membranes and mounting these on to
SEM stubs. The cross-section images were obtained by fracturing the membrane samples in liquid nitrogen. The samples were then sputtered with Iridium under an argon atmosphere to achieve the necessary conductivity. The microscopic analyses were performed at 2 kV using a high-resolution scanning electron microscope (Magellan).

Scanning electron microscopy was carried out for PTSC membranes precipitated in water and the cross-section image in Fig. 4.4 shows that the membrane has a skin layer supported by sponge-like sub-layer followed by finger-like macro voids support. Fig. 4.5 presents the surface images of PTSC membrane and PTSC with the interfacial polymerization layer on top. PTSC membranes precipitated in water have pores of approximately 30-40 nm in diameter. The thin-film composite PTSC does not show any pores at the same magnification, which proves the formation of a thin dense layer on top. Fig. 4.6 show cross-section SEM images of PTSC support (left) and TFC PTSC membranes (right) with a close up on the thin top layer that has a thickness of 100 nm.

Fig. 4.4: SEM cross-section images of left) PTSC porous support and right) close up on the skin layer of PTSC support.
Fig. 4.5: SEM surface images of left) porous PTSC membranes and right) thin film interfacial polymerization PTSC membrane.

Fig. 4.6: SEM cross-section images of right) PTSC membrane support, left) thin film composite PTSC membranes and far left) a close up on the dense top layer with 100 nm thickness.

4.7.2 Zeta potential

The zeta potential was measured using a SurPass Electro- Kinetic Analyzer. The pH of 0.1 M NaCl solutions was varied between 3.0 and 8.8 by adding aqueous solutions of 0.1
M NaOH or 0.1 M HCl.

Fig. 4.7 demonstrates how the zeta potential of PTSC membranes changes with pH. Three curves represent PTSC, crosslinked PTSC and the interfacially polymerized thin top film. For the pristine PTSC membranes the zeta potential is more negative with the increasing pH. The piperazine group is mainly governing the zeta potential of these membranes. After the crosslinking reaction a positive charge is introduced to the membrane and it can be seen that the zeta potential for crosslinked membranes shift its isoelectric point to higher pH value.

The polyamide top layer on the other hand has similar isoelectric point compared with PTSC membranes.

![Zeta potential analysis of PTSC, crosslinked PTSC and thin film composite PTSC membranes.](image)
4.7.3 Performance of TFC-X-PTSC membranes:

All non-aqueous filtration experiments were carried out at 5 bar using a stirred dead-end filtration cell shown in Fig. 4.8.

The effective membrane area was 12 cm², permeate samples for flux and rejection measurements were collected after obtaining steady state condition. Filtrations with aqueous solutions were done at 2 bar. The MWCO was determined by interpolating the rejection curve against molecular weight of marker compounds. Rejection studies were carried out using a feed solution of 1 g/L cyclodextrines in DMF and DMSO. Analysis of the cyclodextrines was done on an Agilent GPC system with tungsten lamp RID detector, which emits in the visible range set at a wavelength higher than 380 nm. Another solute marker was 0.001% (w/w) Rose Bengal dye to study the membranes performance with the solvents THF, DMF and DMSO and the analysis was done via UV–Vis spectroscopy. Solvent flux (J) was determined by measuring permeate volume (V) per unit area (A) per
unit time (t) according to equation 4.1.

\[ J = \frac{V}{A \times t} \]  

(4.1)

The rejection \( R_i \) of markers was calculated from equation 4.2. Where \( CF_i \) and \( CP_i \) correspond to the marker concentration in the feed and permeate, respectively.

\[ R_i = \left( 1 - \frac{CP_i}{CF_i} \right) \times 100\% \]  

(4.2)

Each filtration experiment with the different solvents was at least repeated twice with two membrane coupons. Repetition with more membrane samples was not possible at this stage, because we synthesized the PTSC in relatively small batches (10 g scale).

The main purpose of this work is the development of solvent resistant NF-membranes. However, the membrane might also find applications in aqueous solutions. Therefore the performance in water is of interest. Flux and rejection performance of TFC membranes were studied with various dyes (Safranin O, Protoporphyrin IX (water soluble) (PPHiX), Brilliant Blue and Rose Bengal) at a concentration of 0.001% (w/w) in DI water, Fig. 4.9. The properties of these dyes are summarized in Table 4.1. Membranes showed a flux of 17 L/m² h at 2 bar and a MWCO of about 400 g/mol. The positively charged Safranin with a molecular weight of 350 g/mol was rejected to 92%, the higher molecular weight dyes Protoporphyrin (MW 590), Brilliant Blue (negatively charged, MW 825) and Rose Bengal (negatively charged, MW 1017) were rejected to 100%. The water flux of the crosslinked PTSC membrane without a coating layer was much higher (around 750 L/m²
h at 2 bar), rejection for the dyes was negligible; this confirms the formation of selective layer.

Fig. 4.9: MWCO curve for different dye mixtures in water filtered using TFC PTSC membranes
Table 4.1: Chemical structures and molecular weights of dyes used for MWCO determination.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Molecular weight (g/mol)</th>
<th>Chemical structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Safranin O</td>
<td>350</td>
<td><img src="image" alt="Safranin O structure" /></td>
</tr>
<tr>
<td>PPiX</td>
<td>590</td>
<td><img src="image" alt="PPiX structure" /></td>
</tr>
<tr>
<td>Brilliant blue</td>
<td>825</td>
<td><img src="image" alt="Brilliant blue structure" /></td>
</tr>
<tr>
<td>Rose Bengal</td>
<td>1017</td>
<td><img src="image" alt="Rose Bengal structure" /></td>
</tr>
</tbody>
</table>
Pure solvent fluxes were measured and compared in Fig. 4.10. All solvents showed a flux of more than 20 L/m² h at 5 bar pressure except toluene. The low flux of toluene was due to the membranes hydrophilic nature, which is in agreement with the contact angle measurement. The fluxes of solvent compared to the flux of water were lower by almost 50%; this is an indication of a possible swelling of the polymer chains in solvents leading to a reduced flux. Longer filtration period was performed continuously over 6 hours for DMF, DMSO and THF solvents, reduction due to swelling and compaction of around 3.8% was noticed Fig. 4.11.

![Solvent flux values measured with TFC PTSC membranes at 5 bar.](image1)

**Fig. 4.10:** Solvent flux values measured with TFC PTSC membranes at 5 bar.

![Flux measurements for DMSO, DMF and THF using TFC PTSC membranes versus time](image2)

**Fig. 4.11:** Flux measurements for DMSO, DMF and THF using TFC PTSC membranes versus time.
Rose Bengal dye was used as one of the markers for characterizing OSN membrane; TFC/crosslinked PTSC membranes exhibit very good rejections of this dye in the three solvents DMSO, DMF and THF.

Fig. 4.12 show the UV–Vis spectra of feed and permeate samples. Flux and rejections studies of TFC are illustrated in Table 4.2. Apart from Rose Bengal dye various other solutes were also used to characterize the TFC membranes performance in the same solvents.

Fig. 4.12 shows the chemical structure of cyclodextrines. TFC membranes showed excellent stability toward all the solvents with high flux and remarkable rejection.

Fig. 4.12: MWCO curve of TFC PTSC membranes and UV-Vis analysis of Rose Bengal in DMSO, DMF and THF.
Flux and rejection values measured at 5 bar of the markers used to determine the MWCO of TFC PTSC membranes are summarized in Table 4.2. TFC PTSC membranes were able to reject all markers in all solvents tested with a rejection above 90%, this indicates that the MWCO of these membranes is in the range of 1000 g/mol.

Table 4.2: Flux and rejection values of different markers for TFC PTSC membranes.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Rose Bengal</th>
<th>α-cyclodextrin Mw= 973 g/mol</th>
<th>(2-hydroxypropyl)-β-cyclodextrin Mw= 1350 g/mol</th>
<th>Hexakis-(6-deoxy-6-iodo)-α-cyclodextrin Mw= 1623 g/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Flux (L/m².h)</td>
<td>Rejection (%)</td>
<td>Flux (L/m².h)</td>
<td>Rejection (%)</td>
</tr>
<tr>
<td>DMSO</td>
<td>23</td>
<td>91</td>
<td>26</td>
<td>95</td>
</tr>
<tr>
<td>DMF</td>
<td>26</td>
<td>99</td>
<td>24</td>
<td>98</td>
</tr>
<tr>
<td>THF</td>
<td>23</td>
<td>100</td>
<td>NM</td>
<td>NM</td>
</tr>
</tbody>
</table>

* NM – Not Measured

The effect of the DAP and the TMC monomer concentrations and reaction time was tested and summarized in Table 4.3. Increasing the concentration of TMC from 0.1 to 0.2% effectively increased the rejection from 80 to 91%. Decreasing impregnating and reaction time resulted in lower rejections.
Table 4.3: Effect of monomer concentration, time of impregnating and time of reaction on the performance of TFC PTSC membranes.

<table>
<thead>
<tr>
<th>(0.001%) Rose Bengal/DMSO</th>
<th>Flux at 5 bar (L/m².h)</th>
<th>Rejection of Rose Bengal Dye</th>
</tr>
</thead>
<tbody>
<tr>
<td>IP 1: 2% DAP/water 2 min 0.1% TMC/cyclohexane 1 min</td>
<td>27</td>
<td>80%</td>
</tr>
<tr>
<td>IP 2: 3% DAP/water 1 min 0.2% TMC/cyclohexane 30 sec</td>
<td>30</td>
<td>88%</td>
</tr>
<tr>
<td>IP 3: 2% DAP/water 2 min 0.2% TMC/cyclohexane 1 min</td>
<td>23</td>
<td>91%</td>
</tr>
</tbody>
</table>

One can get deeper insight in the solvent stability of NF membranes when alternate filtrations are performed in water and in an organic solvent. A protocol was proposed by Yang et al. 31, that consists of a number of steps including measuring fluxes and rejections using the same membrane and comparing the results before and after the exposure to the solvents. We selected DMSO as a solvent and followed this protocol. A membrane was placed in the filtration cell and flux of pure water as well as rejection of cyclodextrines in water was measured; these values were compared with those done after exposure to DMSO. The membrane exhibited complete rejection of cyclodextrines in water, but we observed a remarkable drop in water flux, when we switched from pure water to a cyclodextrin solution. Pore blockage/concentration polarization might be a
reason for this reversible flux decline. The cyclodextrin rejection in DMSO was 95%. The pure water flux was retained after the filtration of DMSO. This procedure allows a judgment whether the membrane is solvent-stable or not. Results are shown in Fig. 4.13.

![Chemical stability protocol for TFC PTSC membranes](image)

Experimental protocol:

1- Pure water permeation, flux = 86 L/m². hr
2- Rejection of α - cyclodextrin in water, flux = 30 L/m². hr , R = 100%
3- Rejection of α - cyclodextrin in DMSO, flux = 26 L/m². hr , R = 95%
4- Flush with water, flux = 86 L/m². hr
5- Rejection of β - cyclodextrin in water, flux = 27 L/m². hr , R = 100%
6- Rejection of β - cyclodextrin in DMSO, flux = 21 L/m². hr , R = 95%
7- Flush with water, flux = 86 L/m². hr

Fig. 4.13: Chemical stability protocol for TFC PTSC membranes
For comparison a plot of permeance versus molecular weight cut-off for polymeric TFC membranes made by interfacial polymerization on a support was constructed in Fig. 4.14. Solvent permeances of our TFC membranes were higher when compared with other crosslinked polyimide TFC membranes from the literature however their molecular weight cut off’s are lower than what we report.

![Polymeric TFC membranes via IP](image)

Fig. 4.14: MWCO versus permeance values for different TFC membranes prepared via interfacial polymerization.
4.8 Conclusion

Asymmetric polythiosemicarbazide (PTSC) membranes were prepared and crosslinked using dibromo-p-xylene (DBX). The crosslinked membranes were stable in various polar aprotic solvents and we found no weight loss after solvent exposure. A dense top layer was introduced over such crosslinked membranes using interfacial polymerization. The TFC membranes exhibited high flux and rejection with various solvents and solutes. Filtration experiments showed that crosslinked PTSC membranes could lead to a wider implementation of membrane technology in separation processes in harsh environments. PTSC based composite membranes are competitive with known OSN membranes. Hence, they have potential to be used as OSN membranes in various separation and purification processes. In conclusion, PTSC seems to be a promising membrane material for the application of OSN membranes. So far promising tests in solvents like DMSO have been performed for hours (filtration under pressure) and several days (storage), but long-term tests have to follow.
4.9 References:


5 CHAPTER 5: Silane crosslinked asymmetric polythiosemicarbazide membranes for filtrations of organic solvents

5.1 Abstract

Crosslinked polythiosemicarbazide (PTSC) membranes with positive charged surface were fabricated via a facile reaction with (3-glycidyloxypropyl)trimethoxysilane (GPTMS). Asymmetric ultrafiltration PTSC membranes can be easily prepared by non solvent induced phase inversion technique from PTSC which is completely soluble in dimethylsulfoxide (DMSO) and partially soluble in N,N'-dimethylformamide (DMF). After the proposed crosslinking of PTSC membranes with GPTMS, the membranes acquired high solvent stability in DMSO, DMF and THF and gained the ability to retain molecules of molecular weight above 1300 g/mol enabling these membranes to bridge the gap between ultrafiltration and nanofiltration regions. The influence of the crosslinking agent on the surface charge, membrane solvent resistance and membrane performance has been tested and discussed. One of our main observations was that crosslinked asymmetric PTSC membranes rejected 100% of Direct Red dye while pristine PTSC membrane do not show any rejection for this dye. This finding suggests that an inorganic-type-network was formed during the crosslinking reaction, which helped tuning the pore size of the prepared membranes. Weight loss measurements demonstrated that these membranes are completely stable in THF with 0% weight loss and

insignificant weight losses of 2\% and 1.1\% were detected for DMSO and DMF, respectively.

5.2 Introduction

Organic solvents are widely used in many industries, particularly in the chemical and pharmaceutical fields. Often there is a demand for separation, recycling or disposal of these solvents. Conventional separation processes such as evaporation, crystallization, chromatography and extraction that are frequently employed represent significant operation costs.\(^1\).

Membrane technology has been gradually utilized for industrial applications starting in late 1960’s thanks to their environmental, economic and safety benefits over conventional methods\(^{2-4}\). Organic solvent nanofiltration (OSN) membranes are a recent extension of nanofiltration membranes to the application in nonaqueous systems. The first application of membranes to nonaqueous systems was reported in 1964 by Sourirajan for the separation of hydrocarbon solvents using a cellulose acetate membrane\(^5\). Since then, researchers are focusing on finding new and better materials suitable for OSN membranes.

Polymeric membranes have the advantages of being inexpensive materials for fabrication and easy to scale up. There are numerous reports presenting the use of polymeric membranes as a separation barrier for OSN applications\(^{6-11}\). However, polymeric membranes often suffer from flux decline over time due to the polymer chains compaction or swelling of the polymer matrix upon the exposure to the organic solvents.
The chemical crosslinking of the polymer chains usually enhances the performance of the polymeric membranes for OSN applications and indeed most of the polymeric membranes used in OSN are post-treated through chemical crosslinking.

Inorganic membranes on the other hand offer stable flux performances since they do not endure compaction or swelling. Moreover, their high mechanical stability, high chemical tolerance at harsh conditions make them in general more resistant to organic solvents. However the main disadvantage of the inorganic membranes is their complex and expensive manufacturing on a large scale as well as the sealing and integration of these membranes in modules.

Combining organic/inorganic moieties in membranes in so-called mixed matrix membranes (MMM) is an attractive strategy to benefit from the simple production procedure of polymeric membranes and from the stability of inorganic materials. These two moieties could bond together via van der Waals forces, covalent or hydrogen bonds. MMM membranes can be prepared through either sol-gel method or through the in-situ polymerization where the inorganic fillers are dispersed in the polymer solution. However, in order to bond the inorganic filler covalently to the polymer matrix, the inorganic moiety should be functionalized with groups that react with the polymer chains. Hybrid polyfunctional compounds contain inorganic active site such as silane and organic active site, which could be amide (−NH−), amino (−NH2), thiol (−SH), hydroxyl (−OH) or carboxyl (−COOH). Using such hybrids as crosslinking agents for polymers where the organic active site reacts with polymer chains could lead to a successful incorporation of inorganic moiety into the polymeric matrix. Rzaev et al. reported the crosslinking of an anhydride containing copolymer with γ-aminopropyltrimethoxysilane (APTMS)
through anhydride unit - amine groups - ethoxysilyl groups intermolecular reactions. This resulted in the formation of hyperbranched network structure that contained amide and siloxane fragments. Nunes et al. 27 presented the preparation of hybrids of poly (ether imide) (PEI) and silica by *in-situ* growth of the inorganic network through the hydrolysis and condensation of tetraethoxysilane (TEOS). APTMS was added to generate an inorganic network that resulted in better flux performance under increased pressure. Siddique et al. 28 conducted the crosslinking of polyimide (PI) (P84) membrane with polyfunctional APTMS that also acts as organosilicone precursor to generate an inorganic organosiloxane (Si-O-Si) network. They demonstrated the preparation of compaction free OSN PI membranes with improved chemical, thermal and mechanical stability without the addition of a conditioning agent. Crosslinking with hybrid compounds was also reported by Chisca et al. 29, who prepared a copolyazole polymer crosslinked with (3-glycidyloxypropyl)-trimethoxysilane (GPTMS) to form inorganic networks within the polymer matrix. The resulting ultrafiltration membranes showed excellent stability towards solvents with antifouling property due to the presence of zwitterionic structures. Moreover they were able to tune the pores of the membranes and obtained a MWCO of 30,000 g/mol.

Fouling, which is considered to be one of the main challenges for membranes 30 is highly influenced by the membrane surface characteristics such as surface charge, roughness, wettability and the presence of surface functional groups 31. Positively charged structures are promising candidates, when it comes to fouling resistance for positively charged proteins due to the repulsion forces 31,32. The presence of positively charged moiety leads also to higher surface hydrophilicity and thus lower adhesion and adsorption 33-35.
Polythiosemicarbazide (PTSC) polymer was introduced in the 1960’s as a strong chelating polymer for metal ions. Our group lately reported the preparation of membranes from this polymer and it was shown that PTSC membranes could be potentially applied for gold recovery and as catalytic membranes when gold nanoparticles are chelated with the polymer chain. We have recently shown that PTSC membranes are promising for OSN due to the high chemical stability of the pristine PTSC in a wide range of solvents. Additionally the possibility of modifying this polymer via chemical crosslinking offers further enhancement of its resistivity towards even harsher solvents.

In our previous study we prepared a selective top layer by interfacial polymerization on PTSC crosslinked ultrafiltration support membranes using a bifunctional alkyl halide crosslinker. The obtained membranes showed high chemical resistivity towards aggressive solvents such as THF, DMF and DMSO.

Here we report the crosslinking of PTSC membranes with the polyfunctional (3-glycidyloxypropyl)- trimethoxysilane (GPTMS) agent. During the post treatment, the epoxy group of GPTMS reacted with the sulfur present in the backbone of the PTSC membrane while the trimethoxysilane end groups are expected to hydrolyse and develop a crosslinked inorganic network. This reaction tuned down the porosity of the membrane and increased the chemical resistivity towards harsh solvents. Additionally, positively charged crosslinked PTSC membranes showed a high fouling resistance in aqueous media based on repulsion forces.
5.3 Materials

Dimethylsulfoxide (DMSO), N, N-dimethylformamide (DMF), tetrahydrofuran (THF), (3-glycidyloxypropyl)-trimethoxysilane (GPTMS), ethanol and Direct Red 80 and Rose Bengal dyes were purchased from Sigma–Aldrich. Sojitz Europe, Germany supplied polyester nonwoven support. Polythiosemicarbazide (PTSC) was synthesized according to literature by the reaction of N, N-diaminopiperazine and methylenebis (4-phenylisothiocyanate) in DMSO $^{36}$. All chemicals were used directly without further purification.

5.4 Crosslinked membranes preparation

Microporous PTSC support membranes were fabricated via the phase inversion method. A dope solution of 15 wt. % PTSC in DMSO was prepared at 65 °C under stirring until a homogeneous solution was obtained (around 7 hours). Prior to casting the dope solution was left standing for an hour to remove air bubbles. Membranes were casted on polyester nonwoven using a casting knife with the height set to 150 μm. The casted membranes were immediately immersed in a water bath at room temperature. The membranes were then left in DI water bath at room temperature for at least 12 hours to remove any excess solvents. Wet PTSC membranes were chemically crosslinked with excess amount of GPTMS crosslinker (molar ratio 20:1 for GPTMS: PTSC) in ethanol-water (50:50 wt. %) at 85 °C, reaction is presented in Fig. 5.1. The effect of the duration (6, 12, 24 and 48 hours) of the crosslinking reaction to establish the organosiloxane network in the
membrane was tested. After crosslinking, the membranes were washed with ethanol and stored in DI water to avoid any pore collapse.

![Crosslinking reaction of PTSC membrane with GPTMS](image)

**Fig. 5.1**: Crosslinking reaction of PTSC membrane with GPTMS.

### 5.5 Crosslinked membrane characterization methods

Crosslinked and pristine PTSC polymers were characterized by $^{13}$C solid-state NMR spectroscopy. The success of the crosslinking reaction was confirmed by CP-MAS $^{13}$C solid state NMR spectroscopy. For comparative analysis we obtained the $^{13}$C NMR spectra for three samples under the same experimental and instrumental conditions. The solid state NMR experiments were carried out using a Bruker Avance III 900 MHz
spectrometer equipped with a triple-resonance 3.2 mm Bruker MAS probe. The $^{13}$C Cross Polarization Magic Angle Spinning (CP-MAS) NMR spectra were recorded at a resonance frequency of 226.38 MHz at different spinning rates (20 and 14 kHz) to differentiate the real NMR peaks from side band effect signals. To achieve a high signal to noise ratio, the $^{13}$C NMR spectra were recorded by collecting 12k scans with a recycle delay time of 5 s. The temperature for all experiments was kept at 298 K. The cross-polarization (CP) contact time was set to 3 ms, employing ramp100 for variable amplitude CP. Bruker Topspin 3.0 software was used for data collection and for spectral analysis.

The FTIR spectra were recorded on a Nicolet iS10 FTIR spectrometer with a Smart iTR Attenuated Total Reflectance (ATR) sampling accessory in the range of 500 – 3500 cm$^{-1}$ at room temperature. The samples were fixed between a diamond plate and pressure tower with the separating layer facing the beam. Membranes were dried prior to FTIR measurements. Spectra of different membranes prepared were compared.

The thermal stability was evaluated using Thermogravimetric analysis (TGA). The measurements were conducted on a TGA Q5000 with a heating rate of 3 °C min$^{-1}$ under airflow, from 30 to 700 °C.

The surface and cross-section of studied membranes were characterized by high-resolution scanning electron microscope (Magellan) at 2 kV. The samples for cross-section images were obtained by fracturing the membrane in liquid nitrogen. Prior to the SEM imaging the samples were sputtered with 3 nm thick Iridium coating using Quorum Q150T S sputter coater under an argon atmosphere to achieve the necessary conductivity. Contact angle measurements were performed with an Easy-Drop Instrument
(manufactured by Kruess, Germany) at room temperature using the drop method, in which a drop of water was deposited on the membrane’s surface with the micropipette. The contact angle was measured automatically by a video camera in the instrument using drop shape analysis software. A video was recorded and an image of the drop was snapped at the early seconds of formation on the surface. Three measurements on different membrane pieces were performed. All membranes were dried prior to the contact angle measurement.

Transmission Electron Microscopy (TEM) was used also to investigate the incorporation of Si within the membranes. The membrane was embedded in low viscosity epoxy resin and cured at 60 °C for 24 h. Ultrathin sections (80 nm) were prepared using an ultramicrotome (Leica EM UC6) and put on a 200 mesh TEM grid. Regular 2D projection images were obtained using a titan 80–300 cryo twin operating at 300 kV (FEI company). Images were recorded using a 4k × 4k CCD camera (Gatan Inc., Pleasanton, CA). The EELS signal from the silicon L edge (Si-L edge of 99 eV) was acquired in energy-filtered TEM (EFTEM) mode for the distribution of Si in the samples. Elemental maps were created using a 3-window method. Immersion tests were carried out with crosslinked and pristine PTSC polymer to determine the stability in THF, DMF, DMSO and NMP solvents over the period of 60 days at room temperature. Polymer pieces withdrawn after this period were carefully rinsed with water and dried at atmospheric condition. Their initial \((W_i)\) and final \((W_f)\) weights were recorded and the weight loss \((WL)\) percentage was calculated based on equation 5.1:

\[
WL = \frac{(W_i - W_f)}{W_i} \times 100 \%
\]  

(5.1)
The zeta potential was measured using a SurPass Electro-Kinetic Analyzer. The pH of 0.1 M NaCl solutions was varied between 3.0 and 8.8 by adding aqueous solutions of 0.1 M NaOH or 0.1 M HCl. Membrane performance was evaluated using Direct Red dye in different solvents. The solvent/dye mixture fluxes and rejections were measured at the feed pressure of 5 bar. The effective membrane area was 12 cm$^2$, permeate samples for determining flux and rejection values were collected after reaching the steady state. The MWCO was determined as a molecular weight value that the membrane rejects by 90% or more. Rejection studies were carried out using a feed solution of 0.0005 wt% Direct Red dye (1373 g/mol) in DMF, methanol and DMSO. Analysis of the dye’s concentration in feed and permeate was done by a UV–vis/near IR (Perkin Elmer Lambda 1050) spectrophotometer. Solvent flux $J$ (L/m$^2$.h) was determined by measuring permeate volume $V$ (L) per membrane’s area $A$ (m$^2$) per unit time $t$ (h) according to equation 5.2:

$$J = \frac{V}{A \times t}$$

(5.2)

The rejection $R_i$ of a component $i$ was calculated from equation 5.3, where $C_F$ and $C_P$ correspond to the component’s concentration in the feed and permeate, respectively.

$$R_i = \left(1 - \frac{C_P}{C_F}\right) \times 100\%$$

(5.3)

Each filtration experiment was at least repeated twice with two membrane coupons.
5.6 Crosslinked membranes characterization results and performance

In the first step we have studied the effect of the duration of the crosslinking reaction on the obtained crosslinking degree. The PTSC membranes reacted for 6 h, 12 h, 24 h and 48 h with GPTMS. The crosslinked samples were labeled as PTSC-X, where X refers to the reaction time. The chemical reaction between PTSC and GPTMS resulted in positively charged membranes. The reaction occurs between the epoxy ring of the GPTMS and the sulfur of thiosemicarbazide group by ring opening reaction. The Si-O-Si (siloxane) bond formation, which is responsible for the connection of two polymer chains, occurs after a hydrolysis reaction of methoxysilane under heat. Solid-state $^{13}$C NMR and FTIR spectroscopy was used to observe the chemical and structural modifications of the membranes during the crosslinking process. Fig. 5.2 shows the solid-state $^{13}$C NMR spectra of PTSC, PTSC-6 and PTSC-48 membranes. The chemical shift in the PTSC spectra located at 179 ppm corresponds to the thiosemicarbazide group while the chemical shift at 57 ppm corresponds to the piperazine group. Peaks at 127.5 and 138.9 ppm represent carbons of the aromatic ring. The –CH$_2$ group chemical shift occur at 41.6 ppm. The interaction of GPTMS with the PTSC backbone for 6-hour reaction is confirmed by the presence of the new peaks detected at 162 ppm which is the change expected on the thiosemicarbazide carbon after the reaction. The ring opening in the epoxy group involved in the crosslinking reaction caused a new chemical shift at around 15 ppm. The -CH$_2$ in the ester group presented in the crosslinking agent caused a new peak at 73 ppm chemical shift. PTSC-48 spectra was provided to determine the crosslinking degree in comparison with PTSC-6 through integration of peaks at 162 and
179 ppm and it was found roughly that almost 33 % crosslinking degree was established at the first 6 hour reaction while 50 % crosslinking degree was reached after 48 hours.

Fig. 5.2: NMR analysis of PTSC and GPTMS crosslinked PTSC.
Fig. 5.3 shows the FTIR spectra of pristine and crosslinked PTSC membranes. The embedding of the crosslinking agent in the polymer matrix is demonstrated by the presence of the new peak in the range of \( 2867-3000 \text{ cm}^{-1} \), which is attributed to aliphatic C–H stretching vibration from GPTMS. We observed the formation of C-S bond, confirmed by the band at \( 880 \text{ cm}^{-1} \), and the presence of a broad band in the range of \( 3375-3625 \text{ cm}^{-1} \), which indicates the formation of OH groups on the polymer chain after the crosslinking, also the intensity of characteristic absorption peak for ester group C-O-C (\( 1300 \text{ cm}^{-1} \)) spotted to be increasing with reaction time. The sharp peak at \( 1650 \text{ cm}^{-1} \) in the crosslinked PTSC reveals C-Si linkage. The presence of the Si-O-Si organic-inorganic intense bond was strongly represented in the absorption peak in the range of \( 1000-1200 \text{ cm}^{-1} \). This suggests that the condensation reaction occurred between two Si–OCH\(_3\) groups. As the reaction time increases the intensity of these peaks increases.
The thermal stability of the membranes was evaluated and compared by recording the TGA curves of the pristine PTSC and crosslinked PTSC membranes. Fig. 5.4 The pristine PTSC exhibits two degradation stages; one is in the range of 200-300 °C and the other is in the range of 550-600 °C. The TGA curves for crosslinked membranes show an additional third weight loss stage in the range of 250-350 °C. The thermal weight loss percentages are reported in Table 5.1. The TGA results show that PTSC polymer undergoes a thermal degradation first at 196.4 °C with a significant weight loss of 37.8 % and a second 3.82 % weight loss degradation at 552.9 °C. Crosslinked PTSC-24 and
PTSC-48 almost have identical curves with similar weight loss percentage; this is an indication that the crosslinking reaction takes place in the first 24 hours and after that no significant changes occur. This might be caused by the decrease in the number of active sites with increased reaction time. Additionally, the increasing rigidity of the crosslinked polymer matrix during the network formation diminishes the mobility of the polymer chains and subsequently the access of the crosslinker agent to the reactive polymer groups. Likewise, the steric hindrances and bulkiness factors are increasing with the incorporation of crosslinked segments, and the reactive groups, which would otherwise facilitate the reaction, are being disrupted. We conclude that the highest degree of crosslinking can be achieved at 24 hours of reaction. The first degradation step for crosslinked membranes, which occurs at 200–300 °C is slightly shifted to higher temperatures when the reaction time increases. This shift is coupled with reduced weight loss percentages since it corresponds to the degradation of the polymer backbone. The second degradation was observed only for the crosslinked membranes mainly because of the addition of Si-O-Si linkage during the crosslinker incorporation.
Table 5.1: Thermal weight loss percentages of PTSC and crosslinked PTSC membranes.

<table>
<thead>
<tr>
<th></th>
<th>First step of degradation</th>
<th>Second step of degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_i$ (°C)</td>
<td>$T_f$ (°C)</td>
</tr>
<tr>
<td>PTSC</td>
<td>196.4</td>
<td>352.2</td>
</tr>
<tr>
<td>PTSC-6</td>
<td>201.4</td>
<td>272.6</td>
</tr>
<tr>
<td>PTSC-12</td>
<td>205.3</td>
<td>279.2</td>
</tr>
<tr>
<td>PTSC-24</td>
<td>210</td>
<td>287.1</td>
</tr>
<tr>
<td>PTSC-48</td>
<td>215.6</td>
<td>290.8</td>
</tr>
</tbody>
</table>

5.6.1 Solvent resistance measurements and membrane properties

Solvent stability tests can provide valuable evidence that the crosslinking reaction took place. The stability of our crosslinked PTSC polymer was tested in the presence of four
aggressive organic solvents (THF, DMSO, DMF and NMP).

By measuring the chemical weight loss percentage we examined the polymer resistance to these solvents over a continuous 60 days exposure. The solvent resistance was estimated using Equation 5.1. Table 5.2 compares the solvent stability of the pristine PTSC and crosslinked PTSC polymer measured after immersion in each solvent. All crosslinked samples were insoluble in THF, DMF and DMSO and the weight loss percentages show that PTSC-24 and PTSC-48 polymers where completely stable in THF. Only 1.1 % and 2% weight losses were detected in DMF and DMSO, respectively. For comparison, the pristine PTSC is completely soluble in DMSO and partially soluble in DMF and THF. The crosslinked polymer showed stability for NMP solvent for 5 days while the pristine polymer disintegrate in NMP immediately after exposure. The excellent resistance to solubilization offered by the crosslinked polymers suggests that a high number of crosslinkable groups in the PTSC reacted with methoxy and epoxy groups of GPTMS under the chosen reaction conditions. This finding is in good agreement with the TGA results.

Table 5.2: Chemical weight loss percentages of PTSC and crosslinked PTSC membranes exposed to solvents for 60 days

<table>
<thead>
<tr>
<th>60 days exposure</th>
<th>THF</th>
<th>DMF</th>
<th>DMSO</th>
<th>NMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTSC</td>
<td>11%</td>
<td>33%</td>
<td>100%</td>
<td>Severe dissolution</td>
</tr>
<tr>
<td>PTSC-6</td>
<td>Color change 0%</td>
<td>Partial dissolution 9%</td>
<td>Complete dissolution 12%</td>
<td>Severe dissolution</td>
</tr>
<tr>
<td>PTSC-12</td>
<td>Color change 0%</td>
<td>3%</td>
<td>5%</td>
<td>Severe dissolution</td>
</tr>
<tr>
<td>PTSC-24</td>
<td>Color change 0%</td>
<td>1.1%</td>
<td>2%</td>
<td>Severe dissolution</td>
</tr>
<tr>
<td>PTSC-48</td>
<td>Color change 0%</td>
<td>1.1%</td>
<td>2%</td>
<td>Severe dissolution</td>
</tr>
</tbody>
</table>
The water–membrane contact angles measured for PTSC and crosslinked PTSC membranes are presented in Fig. 5.5. Changes in the surface hydrophilicity and/or hydrogen bond forming ability can be noted. The contact angle for pristine PTSC membrane was 69° whereas the crosslinked membranes PTSC-48 showed a decrease to 47.3° indicating more hydrophilic membranes. This decrease can be explained by the positive charge formed at the polymer backbone and by the formation of Si-O-Si bonds. As reported previously \cite{29, 42} this indicates that we can obtain a hydrophilic polymer by a facile reaction. The contact angles of the crosslinked membranes decrease from 61.3° to 47.3° as the reaction time increases.

![Fig. 5.5: Water contact angle measurements for PTSC and GPTMS crosslinked PTSC membranes.](image)

Thus, crosslinking of the PTSC polymer with GPTMS results in a more hydrophilic surface than the pristine PTSC. This feature is attractive for antifouling applications and we can expect that crosslinked PTSC will show a better fouling resistance when used in aqueous media.

TEM images confirm that the distribution is homogeneous and the GPTMS is well
incorporated and dispersed in the membrane matrix. Fig. 5.6 shows a bright field TEM image of a thin slice of the PTSC-24 membrane cut using an ultramicrotome. Fig. 5.7 shows an element-selective image in which brighter dots are richer in silicon. Fig. 5.7 explains the element selective image, where green represent silicone and red represents carbon. This figure shows a cross-section of the PTSC-24 membranes with green color dominating since the silicon network formation was within the pores of the membrane while the surface section where red color is dominant has less porosity hence carbon is the main element. The distribution is homogeneous and the GPTMS is well incorporated and dispersed in the membrane matrix.

Fig. 5.6: Bright field TEM image of PTSC-24 membrane.
Fig. 5.7: Elemental mapping for the Si L edge of PTSC-24 membrane (left). Right) color assigning where green represent Si rich region and red represent carbon rich region.

The PTSC membrane surface crosslinked with GPTMS was analyzed by EDX. Measurement points were averaged for the surface area selected to determine the silica contents Fig. 5.8. EDX analysis confirms the existence of the organosiloxane network throughout the membrane. The calculated theoretical amount of Si is 4.47 % (based on the expected chemical reaction in Fig. 5.1) for the final product ($C_{56}H_{84}N_{12}O_{9}S_{4}Si_2$) (1253.77 g/mol)). However, the silica content present in the membrane was increasing with increasing reaction time. Measurements demonstrate that after 6 hours of the crosslinking reaction the calculated amount of Si is less than the theoretical one indicating an incomplete reaction. Interestingly, after 12 hours and longer reaction the amount of Si is higher than the theoretical one, which may indicate that some of the GPTMS participated in the formation of the Si–O–Si network but did not interact with the PTSC matrix. Moreover, the increased silica content could be one of the reasons for
the membrane densification.

![EDX analysis of the surface of PTSC and GPTMS crosslinked PTSC membranes](image)

Fig. 5.8: EDX analysis of the surface of PTSC and GPTMS crosslinked PTSC membranes

5.6.2 Membrane performance

The flux and rejection of (0.0005 wt.%) Direct Red (1373 g/mol) dye in DMSO was tested for all crosslinked PTSC membranes and the obtained results are summarized in Table 5.3 and Fig. 5.9. A complete rejection (100 %) was detected for PTSC-24 and PTSC-48 membranes. The flux value for PTSC-12 is higher than the one for PTSC-6, which can be explained by the insufficient formation of Si-O-Si linkage that increased the chemical stability of PTSC-6 membranes. However this membrane still suffered from swelling and compaction. The significant flux decrease from PTSC-24 to PTSC-48 is due
to the more packed and dense polymer matrix that is formed with the crosslinking agent. When the crosslinked membranes are compared with the pristine ones, a shift from ultrafiltration to the nanofiltration range is achieved in terms of flux and rejection values. This is caused by the organic-inorganic network formation throughout the membrane matrix as well as the membrane pore wall (Fig. 5.10).

Table 5.3: Permeance values of PTSC and GPTMS crosslinked PTSC membranes for Direct Red dye in DMSO, DMF and methanol solvents.

<table>
<thead>
<tr>
<th>Filtration pressure</th>
<th>0.0005% DR/DMSO Flux (L/m².h)</th>
<th>0.0005% DR/DMF Flux (L/m².h)</th>
<th>0.0005% DR/MeOH Flux (L/m².h)</th>
<th>THF Flux (L/m².h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 bar</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PTSC</td>
<td>-</td>
<td>-</td>
<td>1910 ± 10</td>
<td>-</td>
</tr>
<tr>
<td>PTSC-6</td>
<td>8.9 ± 2</td>
<td>3.9 ± 1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PTSC-12</td>
<td>13.7 ± 3</td>
<td>4.8 ± 3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PTSC-24</td>
<td>11.0 ± 1</td>
<td>4.8 ± 2</td>
<td>8.9 ± 2</td>
<td>3.3 ± 2</td>
</tr>
<tr>
<td>PTSC-48</td>
<td>8.4 ± 2</td>
<td>3.5 ± 1</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Fig. 5.9: UV-Vis analysis of GPTMS crosslinked PTSC membranes for Direct Red dye in DMSO.

Fig. 5.10: Schematic representation of the silane network formation within the pores of crosslinked PTSC membranes.
In order to define if network formation of reduced the pore size, Direct Red dye in methanol mixture was filtered at 5 bar through pristine and crosslinked PTSC-24 membranes. The flux decreased drastically from 1910 L/m².h to 8.96 L/m².h and the rejection of the dye was utterly enhanced from 0 % to 100 %. Solutions of Rose Bengal (1017 g/mol) and Brilliant Blue (825.97 g/mol) dyes in DMSO were also tested for PTSC-24 membranes. We observed complete rejections due to their strong adsorption on the membrane’s surface (Fig. 5.11).

PTSC-24 membranes were further tested for the rejection of Direct Red dye in DMF and same results were obtained (Fig. 5.12). To confirm if crosslinking reduces swelling the PTSC-24 membrane was tested for DMSO flux then the same membrane was stored in DMSO for 10 days and tested again for DMSO flux. A flux decline of only 4% was encountered. This shows that crosslinking with organic-inorganic network reduces membrane swelling.
We reported previously the preparation of thin film composite membranes by interfacial
polymerization using bi-functional alkyl halide crosslinked PTSC as a support. A
MWCO of 1000 g/mol was achieved with a flux of 23 L/m².h for Rose Bengal in DMSO.
The crosslinked PTSC-24 described here shows higher MWCO of 1300 g/mol with lower
fluxes of 11 L/m².h for Direct Red dye in DMSO. But it is important to note, that the
GPTMS crosslinked PTSC membranes are easier to prepare since no additional coating
step is needed.

SEM cross-section images were captured for pristine and crosslinked membranes (Fig
5.13). The crosslinking has no significant effect on the morphology of the cross-sections
of the membranes. The finger-like structure is preserved with a thin skin layer around 30
nm.

Fig. 5.12: Membrane Photos after filtration with left) Rose Bengal dye in DMSO and
right) Direct Red dye in DMSO.
Fig 5.13: SEM cross-section images of a,f) PTSC and GPTMS crosslinked PTSC membranes for b,g) 6 hours, c,h) 12 hours, d,i) 24 hours and e,j) 48 hours.

Fig. 5.14 demonstrates how the zeta potential of the PTSC-24 membrane changes with pH compared to non-crosslinked PTSC membranes. For the pristine PTSC membranes the zeta potential is more negative with increasing pH. The piperazine group is mainly governing the zeta potential of these membranes. After the crosslinking reaction a positive charge is introduced to the membrane and it can be seen that the zeta potential for crosslinked membranes remains positive throughout the whole pH range.
Novel crosslinked polythiosemicarbazide (PTSC) membranes were prepared and tested for OSN applications. Asymmetric PTSC membranes were crosslinked with a silane agent (GPTMS). We have shown that we can tune the pores and obtain membranes with a MWCO of about 1300 g/mol with a facile reaction. With this MWCO these membranes are bridging the gap between ultra- and nanofiltration. The crosslinked PTSC membranes offered high stability in the common organic solvents THF, DMF and DMSO. The improved stability was attributed to the formation of the organic-inorganic network (–Si–O–Si–) within the membrane’s structure. Membranes crosslinked for 24 hours provided excellent chemical stability with high rejections and acceptable fluxes. The good performance of the crosslinked PTSC membranes in terms of flux and rejection makes them a promising candidate for different applications in harsh environments.
5.8 References


30. Van der Bruggen, B.; Mänttäri, M.; Nyström, M., Drawbacks of applying nanofiltration and how to avoid them: A review. *Separation and Purification Technology* **2008**, *63* (2), 251-263.


6 CHAPTER 6: Composite membrane formation by combination of reaction-induced and non-solvent induced phase separation

6.1 Abstract

We introduce a new method of preparing skinned asymmetric membranes. From now on we will refer to it as Reaction Induced Phase Separation (RIPS). These membranes have two distinctive layers with different morphologies but consisting of the same polymeric material. The top layer is composed of chemically crosslinked polymer chains that form a dense thin film while the bottom layer consists of a porous structure formed by non-crosslinked polymer chains. The top dense layer is formed by exposing a viscous polymer solution film to a good solvent for the polymer containing small amounts of a compound that can crosslink the polymer chains. Surprisingly, immediately after the contact a solid film forms at the surface of the viscous polymer solution film. This newly formed solid layer made of crosslinked polymer chains is insoluble due to the high crosslinking degree. The last step is immersion of the solid film on top of the viscous polymer solution in a non-solvent bath. In this step the common non-solvent induced phase inversion process will occur for the remaining viscous polymer solution beneath the solid dense layer forming the porous support (Fig. 6.1). The advantages of this method are:

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3 Aburabie, J; Villalobos, L; Peinemann, K-V. Composite membrane formation by combination of reaction-induced and non-solvent induced phase separation, *Macromol. Mater. Eng.* Accepted.
The thickness of the dense layer can be easily controlled. Changing the immersion time and the concentration of the crosslinker can lead to an increase or decrease in the thickness. The thickness of the dense layer can be controlled over several orders of magnitude, from less than 100 nm to a few micrometers.

The targeted functional groups present in the bi-functional crosslinkers can be incorporated in only the dense layer, avoiding their presence in the porous support.

![Fig. 6.1: Schematic representation of the RIPS method](image)

### 6.2 Introduction

The most common fabrication method for preparing membranes is non-solvent induced phase separation (NIPS). The simplicity and scalability of this process makes it the workhorse of the membrane manufacturing industry. When dealing with expensive membrane materials or with polymers that are not compatible with NIPS, the preparation of composite membranes is the method of choice. An inexpensive support prepared by
NIPS is used, and a thin dense selective layer is applied on top of it by coating or interfacial polymerization.

This letter describes a new way of composite membrane formation, applicable to crosslinkable polymers. We named this process reaction-induced phase separation (RIPS). It consists of a combination of reaction- and non-solvent induced phase separation made in two simple subsequent steps. A film of a concentrated polymer solution is immersed in a good solvent for the polymer containing crosslinker molecules. The crosslinking agent present in the solvent induces a surface precipitation, and the fact that a good solvent for the polymer is used ensures that the precipitation is due to the crosslinking reaction. The crosslinking reaction is then stopped by a subsequent immersion in a non-solvent bath without crosslinker. The resulting membrane is a composite-like asymmetric membrane that has a dense top layer consisting of chemically crosslinked polymer chains and a well-defined interface with a porous non-crosslinked support (Fig. 6.2). We described recently a similar process—complexation induced phase separation, or CIPS—that uses the intermolecular complexation of metal ions by polymer chains to form the dense top layer of membranes. In this case the surface precipitation was induced by metal complexation, leading to a top-layer highly loaded with metal ions. RIPS is not limited to metal complexing polymers, avoids the use of metal ions and facilitates the incorporation of desired organic functionalities in only the top dense layer of membranes.
Fig. 6.2: Cross-section of a polythiosemicarbazide (PTSC) membranes prepared by RIPS. a) Dense layer prepared with 2% DBX crosslinker for 20 sec (top-layer thickness: 370 nm). b) Dense layer prepared with 10% DBX crosslinker for 20 sec (top-layer thickness: 2000 nm). c) Dense layer prepared with 5% Tr-X crosslinker for 20 sec (top-layer thickness: 250 nm). Scale bars represent 10 µm in the main images and 1 µm in the inset.

The concept of phase separation, or phase inversion covers a range of different techniques in which a solidification process is initiated and eventually, the polymer precipitates. Precipitation can be achieved by shifting the homogenous polymer solution to a non homogenous state by processes such as decreasing the solvent concentration through solvent evaporation, changing the temperature of the solution, referred as thermally induced phase separation (TIPS), or the introduction of non-solvent to the polymer-solvent system, referred as NIPS. In the case of RIPS, the phase separation is induced by chemical crosslinking of the polymer chains via covalent bonds.
A high degree of crosslinking causes the polymer to precipitate out of the solvent (a good solvent for the polymer). A fast crosslinking reaction is essential. It should be faster than the dissolution reaction; otherwise the polymer chains will escape into the bulk of the solution before the crosslinker molecules are able to form a continuous 3-D network of them. Crosslinking of the polymer chains that form a membrane is a common practice to increase stability or add certain functionality to a membrane. Contrary to the RIPS process, the crosslinking approaches reported so far have been applied as a post treatment to already made polymeric membranes. Once made, membranes are immersed in a crosslinking bath for a specific time and at a certain temperature to ensure a crosslinking reaction. Recently, Hendrix et al. aimed to reduce the fabrication steps and use of materials by adding the crosslinker directly into the non-solvent bath. The crosslinking occurred in the entire membrane because the factor causing the precipitation was the non-solvent and not the crosslinking reaction. In the RIPS process the bath is made of a good solvent for the polymer directing the precipitation to the interface between the polymer solution film and the bath containing the crosslinker molecules. Making the dense layer and porous support in different steps allows more control in the final structure of the membrane and independent optimization of both. The thickness of the dense layer can be easily controlled. Changing the immersion time and the concentration of the crosslinker in the first bath can lead to an increase or decrease in the thickness.

The three general steps to prepare membranes using the RIPS process are: (i) casting of a thin film with the polymer solution; (ii) immersing the polymer film in a first bath of a good solvent for the polymer containing a certain concentration of crosslinker; (iii) placing the resulting film in a non-solvent bath. The second step is the key step, where
the polymer chains at the top layer of the casted film are chemically crosslinked creating a thin insoluble solid layer. The formation of this dense layer delays the diffusion of the crosslinker to the rest of the polymer film. The third step is responsible for the formation of a porous support by conventional non-solvent induced phase separation.

The most important parameters affecting the formation of the dense layer during the second step are the crosslinker concentration, the immersion time in the first bath, and the choice of crosslinker type. Longer immersion times and higher concentrations produced thicker layers. The thickness of the dense layer could be controlled over several orders of magnitude, from less than 100 nm to a few micrometers. Moreover, it was possible to add desired functional groups to the active layer of the membrane by choosing the appropriate crosslinker molecules. The size and chemical nature of these molecules had a strong influence on the performance of the final membrane.

The formation of the top layer of asymmetric membranes happens by a phenomenon called gelation. Gelation can be defined as the formation of a three-dimensional network that creates junctions between polymer chains either by chemical crosslinking or physical associations. Asymmetric membranes which relay on physical associations to form, experience two different types of phase separation: one is gelation induced by crystallization for the skin layer formation and the other is liquid-liquid demixing followed by gelation of the polymer rich phase to form the porous support. Gelation via chemical crosslinking, i.e., covalent binding of polymer chains by means of a chemical reaction, was reported to be unlikely to occur during formation of phase inversion membranes. This letter shows how by careful choice of the experimental parameters it is possible to precipitate the skin layer of a membrane using gelation via chemical
crosslinking. The RIPS method is the first method to use covalent bonds to form the dense top layer of asymmetric membranes prepared by phase inversion. Chemical crosslinking gelation offers options to optimize the morphology of the resulting skin layer independently from the porous support—an unlikely feat when physical associations are responsible to form the skin layer.

We developed the RIPS method with the polymer polythiosemicarbazide (PTSC) \(^{16}\), the structure is shown in Figure 2a, the synthesis procedure and characterization are presented below.

### 6.3 PTSC synthesis and characterization

The Polythiosemicarbazide (PTSC) polymer was synthesized following procedure described in literature with slight modification \(^1\). The reaction was of equimolar quantities of the polymer respective monomers in DMSO at 50 °C for two days. Followed by precipitation in hot water for two days and a drying step in the vacuum oven at 60 °C for another two days. The monomers are 4,4'-Methylenebis(phenyl isothiocyanate) (Sigma-Aldrich) and 1,4-diaminopiperazine (Ramidus AB). The average molecular weights and polydispersities of PTSC polymer were determined using an Agilent GPC with Wyatt modules for Triple Detection (Optilab T-rEX, DAWN HELEOS II and Viscostar II) and are presented in Table 6.1.
Table 6.1: Number average molecular weight ($M_n$), Weight average molecular weight ($M_w$), and Polydispersity index (PDI) of PTSC polymer.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$ (Kg/mol)</th>
<th>$M_w$ (Kg/mol)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTSC</td>
<td>15.9</td>
<td>53.1</td>
<td>3.3</td>
</tr>
</tbody>
</table>

Bruker AVANCE III 700 MHz liquid NMR instrument equipped with a TCI Cryoprobe was used to characterize the $^1$H NMR for PTSC polymer. Fig. 6.3

![PTSC chemical structure](image)

Fig. 6.3: PTSC chemical structure with assigned hydrogens for NMR analysis.

PTSC: $^1$H NMR (700 MHz, 298K, DMSO-d6, ppm) δ: 9.52 (s, 2H, e protons), 9.30 (s, 2H, d protons), 7.45 (d, 2H, b protons), 7.18 (d, 2H, c protons), 3.89 (s, 2H, a protons), 2.97-2.90 (m, 2H, f protons).

The crosslinkers used are $\alpha$, $\alpha$ dibromo-p-xylene (DBX) from Sigma-Aldrich and (2,3,6,7,14,15-Hexakis (bromomethyl)-9,10-dihydro-9, 10- [1’, 2’] benzenoanthracene) (Tr-X), which was synthesized in our lab following a procedure reported by Bonaccorsi
et al. Details of the Tr-X crosslinker synthesis procedure are presented below. Structures of both crosslinkers are shown in Fig. 6.4 b and c.

Fig. 6.4: Chemical structure of a) PTSC polymer, b) DBX crosslinker and c) Tr-X crosslinker.

### 6.4 Synthesis and characterization of Tr-X crosslinker

Synthesis of (2,3,6,7,14,15-Hexakis (bromomethyl)-9,10-dihydro-9,10-[1’, 2’]benzoanthracene) (Tr-X) was followed as reported. Reaction is illustrated in Fig. 6.5. Triptycene (0.90 g, 3.54 mmol) and paraformaldehyde (2.34 g, 77.92 mmol of monomer) were dissolved in HBr solution in AcOH (12.5 mL ≥ 33%, 71.38 mmol).
ZnBr$_2$ (2.63 g, 11.68 mmol) was slowly added to the solution, under stirring. The mixture was heated under reflux at 105 °C for 16 h and the reaction was monitored by TLC (hexane/DCM 60:40). The final mixture was dissolved in DCM (25 mL), washed with a saturated solution of NaHCO$_3$ ($2 \times 20$ mL), dried over Na$_2$SO$_4$, and the solvent was removed in vacuum.

The residue was purified by column chromatography (hexane with 10% DCM up to 70%)

Fig. 6.5: Bromine functionalized Triptycene reaction

$^{13}$C NMR: Fig. 6.6.

Tr-X: $^{13}$C NMR (700 MHz, 298K, DMSO-d6, ppm) $\delta$: 51.8 (sx, CH$_2$, a), 136 (sx, C, b), 122 (sx, CH, c), 60 (d, CH, d), 144 (sx, C, e).
Fig. 6.6: Bromine functionalized Triptycene $^{13}$C NMR assigning.

$^1$H NMR: Fig.6.7.

Tr-X: $^1$H NMR (700 MHz, 298K, DMSO-d6, ppm) δ: 4.4 (sx, 2H, a protons), 7.43 (sx, 1H, b protons), 5.6 (d, 1H, c protons).

Fig. 6.7: Bromine functionalized Triptycene $^1$H NMR assigning.
Recently, PTSC was introduced recently as a promising material for the preparation of organic solvent nanofiltration membranes through post crosslinking of the polymer chains with DBX crosslinker. Such membranes showed superior resistance to harsh solvents. Here we report a new approach for preparing asymmetric membranes that uses the same components but does the crosslinking before the membrane is completely formed to have more tunability of the final product and a more efficient fabrication process. The crosslinking reaction between PTSC and the type of crosslinkers used in this study is a nucleophile bimolecular $S_N2$ reaction called Menshutkin reaction where quarternization of the tertiary amine by alkyl halide takes place. This type of reaction is ideal to test the RIPS process because under the right conditions (i.e. nature of the nucleophile, nature of the leaving group, solvent used, and nature of the substituents bonded to the leaving group) the reaction kinetics can be very fast—faster than the dissolution kinetics of the polymer in the solvent used. Sufficient amount of crosslinks causes phase separation of the three dimensional network of polymer chains. The phase separation happens due to a chemical reaction; consequently the top layer thickness is dependent on variables that affect the reaction rate such as concentration and time. All the membranes presented were made by dissolving PTSC (15 wt%) in dimethyl sulfoxide (DMSO) under heat (65 °C) and stirring for at least 4 hours. Once a homogenous solution was obtained it was left aside to eliminate air bubbles. The polymer solution was then cast on a polyester nonwoven support or a glass plate using a casting knife with 250-µm air gap. The polymer film was then immersed in a bath of crosslinker (DBX or Tr-X) dissolved in DMSO for a certain time. Finally, the film was carefully removed from this bath and immersed in a water bath. The residence time in the
crosslinking solution had a strong influence on the thickness of the top layer; longer contact time resulted in thicker dense layers.

6.5 Membrane fabrication process (RIPS)

The three general steps of the process are: (i) casting of a thin film with the polymer solution (polymer + solvent A), (ii) immersing the polymer solution film in the same solvent A containing a specific concentration of polymer crosslinker, (iii) transfer it to a non-solvent bath. In this work all the membranes were casted with Gardco wet film applicators using a gap of 250 µm on a non-woven polyester support or a glass plate. The volume of the bath containing the crosslinker dissolved in DMSO was always enough to easily covering the polymer solution film casted in the first step. The whole process was done by hand and the non-solvent bath consisted of water. Figure S2 and S3 explains the procedure for both crosslinkers. The volume of non-solvent bath was always enough to easily cover the film obtained after the second step. The chemicals used in each step are the following.

Step (i): PTSC was synthesized following the procedure reported in section 1 of the supporting information. DMSO (Sigma-Aldrich) was used as the solvent to prepare polymeric solutions of both polymers. All the experiments were done using a 15wt% polymeric solution in DMSO. PTSC Solution was heated to 65 °C under constant stirring for PTSC to dissolve. After 4 hours of stirring at 65 °C, solution was taken out of the hot bath and allow to equilibrate its temperature with the environment prior casting the membranes. PTSC solution had to be used the same day it was prepared because after one
day a gel starts to form. The polymeric solution kept aside degassing before use to eliminate air bubbles. Step (ii): The solutions for the second bath were prepared by dissolving the corresponding crosslinker in DMSO with stirring at room temperature. Higher concentrations of crosslinker needed sonication for 1 hr in warm water to ensure total dissolution. The crosslinkers used were \( \alpha, \alpha \)-dibromo-\( p \)-xylene (DBX) from Sigma Aldrich and \( (2,3,6,7,14,15 \)-Hexakis (bromomethyl)-9,10-dihydro-9, 10- \[1', 2'\] benzenoanthracene) (Tr-X) synthesized in our lab. Step (iii): The non-solvent bath used was water treated by MilliQ system, steps of procedure are described in Fig. 6.8 and Fig. 6.9 for both crosslinkers.

![Polythiosemicarbazide PTSC and a,a-Dibromo-p-xylene](image)

Crosslinked PTSC

15% PTSC/DMSO

Casting Knife

Casting

Precipitation

x% DBX / DMSO

Conditions:
- Sonication 1 hr - warm water
- Left overnight
- Time: \( x \) sec

Water bath

Fig. 6.8: Preparation procedure for RIPS method using PTSC polymer and DBX crosslinker.
Fig. 6.9: Preparation procedure for RIPS method using PTSC polymer and Tr-X crosslinker.

Fig. 6.10 showcase a membranes prepared partially with RIPS method where 5% DBX/DMSO mixture was used as first bath for 20 sec, this part is showing shiny surface indicating the formation of dense layer while the other part (prepared by NIPS method) is showing normal white surface.
Fig. 6.10: Digital image of membrane prepared partially with RIPS method (5% DBX/DMSO 20 sec, the shiny section) and partially with NIPS method.

Fig. 6.11 illustrates the change in top layer thickness as a function of immersion time for two crosslinkers (DBX and Tr-X) and also highlights the thickness change with different concentrations of the DBX crosslinker.
Fig. 6.11: Effect of the crosslinker concentration and immersion time in the dense layer thickness for two different crosslinkers: DBX and Tr-X.

As soon as the film gets exposed to the crosslinker bath a dense film forms in less than one second. However, larger immersion times were needed to obtain stable (i.e. thicker) dense layers. The extra time after the appearance of the thin solid layer is the time needed for the crosslinker molecules to diffuse through the newly formed dense barrier and continue to crosslink polymer chains beneath it, growing the layer as a result. Fig. 6.12 shows a matrix of SEM images illustrating the effect of immersion time and DBX crosslinker concentration on the dense top layer thickness, which ranges between 100 nm and 2.5 µm. The top layer thickness can be tuned easily, within this range, by choosing suitable combination of crosslinker concentration and reaction time.
Fig. 6.12: SEM cross-section images of membranes prepared by the RIPS method from 15 wt% PTSC polymer, with different concentrations of DBX crosslinker in DMSO as first bath (values on the left side), the values on the top represent immersion time in crosslinker bath. Scale bars represent 10 µm.
6.5.1 SEM images for RIPS membranes with different crosslinkers

Effect of crosslinker type on the thickness of the top layer is presented in the following cross-section SEM images in Fig. 6.13. Both set of membranes for each crosslinker were prepared using same concentration 5%. With increasing time of immersion the tope layer becomes thicker, it was noticed that the thickness for the top layer for same concentration and time of immersion for different crosslinker varies. The growth of this crosslinked dense layer is different due to the steric hindrance effect, where bulker groups like Triptycene delay the possible reaction with the polymer chains.

![SEM images](image1)

**Fig. 6.13:** Cross-section SEM images of membranes prepared with RIPS method using 15% PTSC and 5% crosslinker concentration. a) Tr-X 1 sec (~ 150 nm), b) Tr-x 20 sec (~ 250 nm), c) Tr-x 45 sec (~ 450 nm), d) DBX 1 sec (~ 530 nm), e) DBX 20 sec (~ 950 nm) and f) DBX 45 sec (~ 1300 nm).

6.5.2 SEM micrographs of membranes prepared by RIPS (extreme cases studied)
Scanning electron microscope (SEM) images of the membranes cross-section were taken with a Quanta 600. Cross-section samples were prepared by fracturing the membranes right after having been exposed to liquid nitrogen for about 2 min. Cross-section samples were attached to an aluminum support with a conductive aluminum tape and coated with a thin film of Iridium to reduce charging during imaging. The following two SEM images correspond to the extreme cases in which a very thin or a very thick dense layer was obtained using the RIPS method, Fig. 6.14 and Fig. 6.15. Dibromo-p-xylene crosslinker was dissolved in DMSO with 1% as a concentration for the first bath and an immersion time of one second produced a very thin dense layer of around 100 nm. However such thin dense layers did not performed well in rejection experiments.

Fig. 6.14: SEM image of Cross-section of RIPS membranes with 1% DBX/DMSO for 1 sec as first bath.
Fig. 6.15: Cross-section SEM image of RIPS membranes prepared with 1% DBX for 1 sec. This image shows dense thin layer and immediate porous support.

On the other hand by using same crosslinker but with increased concentration of 10% and longer immersion times of 5 minutes it was possible to precipitate completely the polymeric solution in the first bath (crosslinker in DMSO) resulting in an entirely dense membrane, Fig. 6.16.
Fig. 6.16: SEM image of Cross-section of RIPS membranes with 10% DBX/DMSO for 5 min as first bath.

6.5.3 Surface images of RIPS and NIPS PTSC membranes

Fig. 6.17 presents the surface SEM images of PTSC membranes however the left image show PTSC membrane prepared via NIPS method where the polymer cast film precipitated in water only. The NIPS membrane shows pores of around 20 nm in diameter; on the other hand the RIPS membrane in the right image dose not show any pores at the same magnification. This membrane is prepared by immersing the polymer cast film in a first bath of 5% DBX/DMSO for 20 sec then in water.
6.5.4 FTIR analysis of top and bottom side of RIPS membranes with DBX crosslinker

Fig. 6.18 shows the ATR–FTIR spectrum of PTSC membrane prepared without non-woven using RIPS method with 5% DBX 20 sec. the IR spectra record the top and bottom side of the membrane. The idea of the test depends on the fact that the top layer will be crosslinked and the bottom one will not due to its formation via NIPS method. Both sides show a strong absorption band at 1511 cm$^{-1}$ corresponding to the C=S bond and characteristic absorption at 3271 cm$^{-1}$, 815 cm$^{-1}$ and 1612 cm$^{-1}$ for aromatic C-H stretching, bending and aromatic C=C present in the polymer backbone. Absorption bands at 1018 cm$^{-1}$ and 2839 cm$^{-1}$ represents the aliphatic C-N stretch and C-H alkyl group present in the piperazine moiety. The topside however shows slight shift in the C-N absorption band from 1018 cm$^{-1}$ to 1117 cm$^{-1}$, which reveals the quarternization of
piperazine moiety by the DBX crosslinker. Also the reaction of DBX with the polymer backbone on the surface added a new peak at 1633 cm\(^{-1}\), which corresponds to the aromatic group present in the crosslinker and the aromatic C-H stretch at 3271 cm\(^{-1}\) was shifted and broadened. All the above data suggests the occurrence of crosslinking reaction between the DBX and piperazine moiety on the topside of the RIPS PTSC membranes.

Fig. 6.18: FTIR analysis of top and bottom sides of RIPS membranes prepared without non-woven using 5% DBX/DMSO for 20 sec as first bath.
6.5.5 Filtration performance

The performance of PTSC membranes prepared with RIPS using different DBX concentrations and immersion times was evaluated by filtering 0.1% polyethylene glycol (PEG) aqueous solutions in a dead end pressurized stirred filtration cell and measuring the rejection. The results for different molecular weight PEGs is summarized in Fig. 6.19. 0.1% PEG in water mixture with molecular weight of 400, 3000, 10000 and 35000 g/mol was used to determine the rejection performance of RIPS membranes. GPC was used to analyze the samples.

![Graph](image)

**Fig. 6.19: Rejection performance for PEG/water solution for RIPS membrane**

The membranes showed increased rejection performance depending on the crosslinker concentration and immersion time in the crosslinker bath. For example using 1% DBX/DMSO as first bath for 20 sec showed no rejection for any of the PEGs. With
increasing concentration of the crosslinker to 2% and a short immersion time of one second, the membrane was able to reject only 10% of the 35K PEG. We observed no defects in the dense layer of these two membranes during the SEM analysis, however the low rejections suggest a significant presence of defects in the selective layer. We believe that these defects are cracks produced during transfer of the delicate support-free thin layers from one bath to the other. Defect-free layers could be obtained for fabrication conditions that produced thicker layers during the first step. Such membranes, prepared with 2% or 5% DBX/DMSO and 20 sec, showed more than 91% rejection of the smallest PEG tested (400 Da) and rejected completely (>99%) rose Bengal (RB, molecular weight 1017 g/mol, negative charge) in water.

6.5.5.1 OSN membranes via post-chemical crosslinking of RIPS membranes

To test their performance in harsh environments we submitted the membrane prepared using 5% DBX/DMSO and 20 sec to an extra step (immersion in 2% DBX/acetone for two hours) to crosslink the porous support and make it solvent-stable. The membrane was not able to reject successfully RB in DMSO and DMF, probably due to swelling of the selective layer in these solvents. Nevertheless, successful rejections were obtained for slightly larger molecules: > 99% rejection of direct red (DR, molecular weight 1373 g/mol, negative charge) in both solvents, and 93% and 91% rejections of vitamin B12 (molecular weight 1355 g/mol, neutral charge) in DMSO and DMF respectively. The UV-Vis analysis is presented in Fig. 6.20 and Fig. 6.21. Good rejection results were obtained with membranes prepared using the DBX crosslinker, however the permeances
were low. The membranes prepared using 2% DBX/DMSO (20 sec) and 5% DBX/DMSO (20 sec) presented a water permeance of 0.65, and 0.06 l/m² h bar respectively (Table 6.2 and Table 6.3). The MWCO of these membranes can be concluded as 1300 g/mol since the rejection of brilliant blue dye in DMSO was around 30%, Fig. 6.22. RIPS membranes on the other hand did not serve well in the presence of NMP solvent. Fig 6.20. We hypothesized that using a bulkier crosslinker would create more interconnected voids (i.e. channels) in the matrix of the top selective layer. True to our predictions, a membrane prepared using 5% of Tr-X—a bulky, rigid brominated triptycene— as the crosslinker showed a permeance increase of more than two orders of magnitude in comparison with a membrane made with the same conditions but using DBX—a linear and small crosslinker. The water permeance of the membrane prepared with Tr-X was 7.7-l/m² h bar and the rejection of RB was as high as its DBX counterpart (>99%). The increase in flux can be attributed partially to the thinner dense top layer formed when using Tr-X (250 nm) compared to the layer obtained with DBX for the same fabrication conditions (950 nm). However, the thickness is not the principal factor. Membranes prepared using DBX and fabrication conditions to obtain a layer of similar thickness (370 nm) still present a permeance more than an order of magnitude lower than the membrane prepared with Tr-X. For any fixed set of fabrication conditions, Tr-X produced thinner layers than DBX (Figure 3). It diffuses slower due to its larger size, resulting in a lower rate of crosslinking.
Table 6.2: Permeances for membranes prepared using different parameters for DR dye.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Permeance (L m$^{-2}$ h$^{-1}$ bar$^{-1}$)</th>
<th>Solvent</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIPS (immersed directly in water bath)</td>
<td>650</td>
<td>Water</td>
<td>Porous surface</td>
</tr>
<tr>
<td>RIPS, 1% DBX, 20 s</td>
<td>191</td>
<td>Water</td>
<td>Dense top layer with many defects</td>
</tr>
<tr>
<td>RIPS, 2% DBX, 1 s</td>
<td>10.5</td>
<td>Water</td>
<td>Dense top layer with few defects</td>
</tr>
<tr>
<td>RIPS, 5% DBX, 20 s</td>
<td>0.65</td>
<td>Water</td>
<td>Defect-free top layer</td>
</tr>
<tr>
<td>RIPS, 5% Tr-X, 20 s</td>
<td>7.7</td>
<td>Water</td>
<td>Defect-free top layer</td>
</tr>
<tr>
<td>RIPS, 5% DBX, 20 s + additional crosslinking step</td>
<td>0.48</td>
<td>DMSO</td>
<td>Defect-free top layer in crosslinked support</td>
</tr>
<tr>
<td>Isolated layer in alumina support (RIPS, 5% DBX, 20 s)</td>
<td>1.8</td>
<td>DMSO</td>
<td>Isolated defect-free top layer</td>
</tr>
<tr>
<td>Isolated layer in alumina support (RIPS, 5% DBX, 20 s)</td>
<td>4.5</td>
<td>DMF</td>
<td>Isolated defect-free top layer</td>
</tr>
</tbody>
</table>

Table 6.3: Permeances for RIPS membranes prepared using different parameters for DR and VB12 markers.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Solvent</th>
<th>Permeance 20 ppm VB12 (L m$^{-2}$ h$^{-1}$ bar$^{-1}$)</th>
<th>Permeance 5 ppm DR (L m$^{-2}$ h$^{-1}$ bar$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% DBX/DMSO 20 sec</td>
<td>MeOH</td>
<td>0.72</td>
<td>0.66</td>
</tr>
<tr>
<td>5% DBX/DMSO 20 sec, 2% DBX/acetone 2 hrs</td>
<td>DMSO</td>
<td>0.33</td>
<td>0.48</td>
</tr>
<tr>
<td>5% DBX/DMSO 20 sec, 2% DBX/acetone 2 hrs</td>
<td>DMF</td>
<td>0.51</td>
<td>0.52</td>
</tr>
<tr>
<td>5% DBX/DMSO 20 sec, 2% DBX/acetone 2 hrs</td>
<td>NMP</td>
<td>0.22</td>
<td>-</td>
</tr>
</tbody>
</table>
Fig. 6.20: UV-Vis analysis of 5% DBX 20 sec post crosslinked RIPS membranes using 20 ppm VB12 as a marker in DMSO, DMF, MeOH and NMP solvents.

Fig. 6.21: UV-Vis analysis of 5% DBX 20 sec post crosslinked RIPS membranes using 5 ppm DR dye as a marker in DMSO, DMF and MeOH.
6.5.5.2 Isolation of the dense top layer prepared via RIPS method.

The top dense layer of membranes prepared via RIPS should be very stable because it is made of crosslinked polymer chains. To test to which extent, a piece of a membrane prepared using a 5% DBX/DMSO solution and an immersion time of 20 sec was submerged in DMSO for 10 days. After some minutes, a transparent layer detached form the nonwoven support and floated on the surface, whereas the non-crosslinked support dissolved completely as for the rest of the time, the layer was maintained. Such thin, transparent layer was stable for the entire duration of the test. Overnight immersion of such membrane in DMSO was repeated and the isolated thin layer was transferred via a
glass slide to a water bath for better spreading and carefully placed on top of an inorganic porous alumina support (Anodisc 25, Whatman Ltd, 200 nm pore size). Water was permeated through it using different pressures up to 21 bars; the pressure limit of our setup. The membrane exhibited linear increase of flux with increasing pressure value. The flux increased linearly with the increase in pressure indicating that the layer did not suffer any compaction or rupture. Further verification of both, the mechanical integrity of the membrane and its stability in harsh solvents was done by permeating solutions of DR in DMSO and DMF and measuring its rejection. More than 99% rejection was obtained in DMSO and 93% rejection in DMF, UV analysis are in Fig. 6.23. The permeance of the isolated layer was much higher than the same layer on top of its original polymeric support (i.e. before isolation) for both solvents: 3.8 and 8.7 times higher for DMSO and DMF respectively.

Fig. 6.23: UV-Vis analysis of DR dye in DMSO and DMF for freestanding 5% DBX 20 sec RIPS membranes on alumina support.
SEM images of the nanofilm fixed on the alumina support are presented in Fig. 6.24 a and b. The image presented in c is the bottom side of the nanofilm where it clearly show the rough side that connect the dense to layer with the porous support formed once precipitated in water. Images in d and e are top and bottom sides of the nanofilm to compare the roughness of the surface as well as the porosity.

Fig. 6.24: SEM images of: a) and b) the isolated layer on top of alumina support, C) the bottom side of the nanofilm with 65° tilt and d) bottom side tilted with 45° of PTSC membranes prepared with RIPS, e) top side of the nanofilm prepared with RIPS.

Fig. 6.25 present AFM height mapping for a RIPS nanofilm layer prepared with 5% DBX/DMSO 20 sec condition and fixed upside down on alumina support. The thickness
of the nanofilm agrees with the reading of the SEM images around 1µm. The roughness of the bottom side of the nanofilm is presented as well.

Fig. 6.25: AFM analysis of RIPS nanofilm fixed upside down on alumina support a) the AFM images of the bottom side of the nanofilm, b) AFM height image and c) AFM height profile of a section of RIPS nanofilm.

Fig. 6.26 show the floating nanofilm prepared by RIPS method with 5% DBX/DMSO first bath exposed for 20 sec after being immersed in DMSO solvent to dissolve the porous NIPS support. Fig. 6.27 and Fig. 6.28 show the nanofilm after being fetched out form water on alumina support for further testing. Fig. 6.29 shows the nanofilm collected on circular metal wire.
Fig. 6.26: Floating freestanding nanofilm in water after dissolving the support in DMSO.
Fig. 6.27: Freestanding nanofilm on alumina support.

Fig. 6.28: Digital image of nanofilm on alumina support left) before color saturation and right) after color saturation.
6.5.6 Robustness of freestanding membranes.

The robustness of the freestanding crosslinked PTSC nanofilm (5% DBX 20 sec) on alumina support was confirmed by measuring the water flux through the nanofilm under applied pressure ranging from 3 – 21 bar (Fig. 6.30). A very good linear relationship indicates that the nanofilm provided a constant permeable area with sufficiently firm structure that it did not collapse under increasing applied pressure.
Fig. 6.30: Water permeance measurement through freestanding 5% DBX 20 sec RIPS membrane versus increasing applied pressure.

The freestanding nanofilm was sandwiched between two rubber rings with opening of 3 mm in diameter and fixed to an open ends tube with 10 mm in diameter (Fig. 6.31 demonstrate the setup). 20 ppm Rose Bengal dye in methanol was added slowly with a total of 4 ml (the capacity of the tube) while the tube is in vertical position to test the strength of the nanofilm. The nanofilm held 9 cm high column of methanol without rupturing. The weight of the liquid was around 600,000 times greater than the weight of the freestanding part of the nanofilm.
Fig. 6.31: Robustness determination of freestanding 5% DBX 20 sec RIPS membrane.

Up left: a column of 5 cm high of 20 ppm Rose Bengal dye in MeOH is supported by 3 mm diameter freestanding RIPS nanofilm. Up right: bottom view. Down left: 3 mm freestanding RIPS membrane is sandwiched between two 10 mm diameter rubber rings. Down right: the dissembled setup.
6.6 Conclusions

A new method called RIPS was successfully added to the family of phase inversion techniques to prepare composite-like asymmetric membranes. It relies on fast crosslinking reaction rates of polymer chains to form the skin dense layer of the membrane. The RIPS method was developed using the PTSC, a polymer which can be crosslinked with a sufficiently high reaction rate to favor the crosslinking reaction and no the dissolution reaction. Future studies will extend this method to other polymers. The two main advantages of RIPS are the tunability of the membrane structure and the possibility to incorporate specific functionalities in the top dense selective layer only. It was demonstrated how a bulky crosslinker can enhance dramatically the performance of the prepared membranes compared to a small one. Besides increasing the interchain spaces inside the dense layer by using a bulky crosslinker, we envision the use of RIPS to incorporate functionalities to help mitigate biofouling, enhance the transport of specific molecules, or capture selectively a compound.
6.7 References


CHAPTER 7: Crosslinked Polythiourea membranes for organic solvent nanofiltration applications

7.1 Introduction

Polymers containing thiosemicarbazide functional group may be prepared via condensation polymerization reaction between diamine and di-isothiocyanate monomers ¹, the different types of diamine and di-isothiocyanate used will produce different polymers. Polythiourea (PTU) is one example of such polymers, where the respective monomers are 4,4 oxydianiline and methylenebis (4-phenylisothiocynate). This polymer was never reported before until recently as a polymer capable of complexing with metal ions ². PTU polymer easily dissolve in DMSO to form stable homogenous solution in addition, it is chemically stability in wide range of solvents. Crosslinking of polymers is a well-established method in which rigid, chemically stable polymer matrix can be obtained, in this work; crosslinking of PTU polymer was investigated via two chemical reactions using two different crosslinking agents.

Room temperature ionic liquids (RTILs) showcase many attractive properties, such as negligible vapor pressure, no flammability as well as high thermal stability ³. Moreover, with the appropriate selection of anion and cation, their physicochemical properties can be tailored. Some encouraging results have been achieved regarding utilization of IL as a medium or solvent in a wide variety of applications such as separation of various compounds ⁴, extractions ⁵ and chemical reactions ⁶. Deep desulfurization of fuels has attracted lot of attention from growing number of
researchers due to more strict regulations imposed on sulfur content \(^7\). Furthermore, aromatic sulfur compounds are also inefficient to be removed in current technology. Ionic Liquids (ILs), as a class of green solvent, actually play important role as a promising alternative for desulfurization of fuels via extraction \(^8,9\). In spite of these attractive features, some limitations of IL such as the high price for synthesis and high-energy requirement for recycling, could affect the economic viabilities in some potential processes. To overcome these drawbacks the use of ionic liquid membrane (ILM) technology was proposed \(^10\), membrane-containing IL allow simultaneous extraction and stripping at the feed and permeate side of ILM. ILM are prepared via impregnating IL inside the pores of the support membrane. Although many advantageous can be achieved using ILM the problem of leaking or leaching of IL over time is still present. In this work we suggest the inclusion of anionic part of ionic liquid through the exchange with another present anion in membrane matrix \(^11\) to be used as extraction media of aromatic sulfur compounds from Dodecane solvent.

### 7.2 PTU asymmetric support membrane preparation

Microporous support membranes were fabricated from PTU polymer via the phase inversion method. A dope solution of 15\% (w/w) of polymer was prepared in DMSO at 65 °C under stirring for 7 hrs until a homogeneous solution was obtained. Then the solution was left for an hour to allow air bubbles to escape prior to casting. Membranes were cast on a polyester fabric support with the prepared PTU dope solution using casting knife with a casting thickness of 100 \(\mu\)m. The membranes were immediately immersed in a water bath at room temperature where the precipitation occurs by nonsolvent induced
phase separation (NIPS). NIPS wet membranes were transferred to DI water bath at room temperature for at least 12 h to remove any excess solvents and to maintain its wetness to avoid any pore collapse.

7.3 PTU TFC membranes via dual bath precipitation

A dope solution of 15% (w/w) of polymer was prepared in DMSO at 65 °C under stirring for 7 hours until a homogeneous solution was obtained. Then the solution was left for one hour to allow air bubbles to escape prior to casting. Membranes were cast on a polyester fabric support with the prepared PTU dope solution using casting knife with a casting thickness of 100 µm. The cast polymer solution then immersed in first coagulation bath consisted of Isopropanol/water (IPA/water) mixture for 1 min then transferred to a second water coagulation bath.

7.4 Crosslinked asymmetric PTU membranes preparation

PTU membranes were crosslinked via two methods using two different crosslinking agents.

7.4.1 Crosslinking with hydrogen peroxide

PTU supports were crosslinked using hydrogen peroxide/water solution dissolved in methanol with 1:4 volume ratio under acidic enviroment (pH <1) using acetic acid, the reaction was carried on at room temperature for 48 hours where oxidation of thiourea takes place Fig. 7.1.
7.4.2 Crosslinking with α,α Dibromo-p-xylene (DBX)

PTU supports were crosslinked using DBX crosslinker dissolved in ethanol under heat with temperature of 80 °C for 24 hours with 2:1 mole ratio of DBX to PTU polymer Fig. 7.2.
Fig. 7.2: Crosslinking reaction of PTU with DBX.

### 7.5 PTU crosslinked membranes exchanged with ionic liquid

The bulky anion of the ionic liquid bis (trifluoromethane) sulfonamide lithium salt Li [NTf₂] was used for the anion exchange with the bromide ion in the crosslinked PTU. It might be interesting to test, if the ionic liquid exchanged membranes can selectively transport sulfur components present in hydrocarbons. Li [NTf₂] was dissolved in both water and DMSO with concentration of 0.05 M and the exchange was carried under 40 °C for 24 hours Fig. 7.3.
Fig. 7.3: Crosslinked PTU membranes exchanged with ionic liquid.
7.6 Result and discussions

7.6.1 Crosslinking with hydrogen peroxide

The oxidation of thiourea was performed successfully and the membranes showed high stability in DMSO, NMP, DMAc and DMF Table 7.1; the membranes have changed visual color and unfortunately suffered from brittleness and poor mechanical stability after crosslinking reaction Fig. 7.4 Shows digital images of PTU membranes before (left) and after crosslinking (right).

<table>
<thead>
<tr>
<th>Solvents</th>
<th>PTU-pure</th>
<th>Crosslinked PTU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>Insoluble</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Ethanol</td>
<td>Insoluble</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Tetrahydrofuran (THF)</td>
<td>Partially soluble</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Dimethylformamide (DMF)</td>
<td>Soluble</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Dimethylsulfoxide (DMSO)</td>
<td>Soluble</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Dimethylacetamide (DMAc)</td>
<td>Soluble</td>
<td>Insoluble</td>
</tr>
<tr>
<td>N-methyl-pyrollidone (NMP)</td>
<td>Soluble</td>
<td>Insoluble</td>
</tr>
</tbody>
</table>

Fig. 7.4: PTU asymmetric membranes left) before hydrogen peroxide crosslinking and right) after hydrogen peroxide crosslinking.
FTIR analysis

FTIR spectrum in Fig.7.5 was recorded for PTU and crosslinked PTU membrane to confirm the occurrence of the chemical reaction. The peak in the PTU spectra at 925 cm\(^{-1}\) is attributed to the C=S bond which breaks after crosslinking reaction and that explains the disappearance of that peak. A decrease in the intensity of the peak around 1343 cm\(^{-1}\) where C-N bond is presented in the crosslinked PTU membrane due to the crosslinking reaction. The appearance of 1687 cm\(^{-1}\) peak in the crosslinked PTU spectra prove the success of the crosslinking reaction where C=N is formed. A noticeable broadening in the N-H peak at 3389 cm\(^{-1}\) due to the formation of C=N on the expense of N-H.
Fig. 7.5: FTIR analysis of pristine and hydrogen peroxide crosslinked PTU.
Performance

Crosslinked PTU membranes with hydrogen peroxide were carefully tested for solvent permeances that are shown in Table. 7.2. The rejection performances for these membranes were not possible to measure since the membranes suffered from brittleness and they were detaching from the support.

The water permeance of crosslinked PTU membranes has dropped to almost half the value for pristine PTU. Permeance of THF through crosslinked PTU was relatively high compared to permeances of solvents such as DMF, DMSO and DMAc which are considered good solvents for PTU. This might be an indication that the crosslinked PTU membranes are stable however still suffer from swelling.

Table 7.2: Permeances of different solvents through hydrogen peroxide crosslinked asymmetric PTU membranes.

<table>
<thead>
<tr>
<th>Membrane condition</th>
<th>Solvent</th>
<th>Permeance (L/m².h.bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine PTU membrane</td>
<td>Water</td>
<td>172</td>
</tr>
<tr>
<td>H₂O₂ crosslinked PTU membrane</td>
<td>Water</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>THF</td>
<td>114</td>
</tr>
<tr>
<td></td>
<td>DMF</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>NMP</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>DMAc</td>
<td>4</td>
</tr>
</tbody>
</table>
7.6.2 Crosslinking with α, α Dibromo-p-xylene (DBX)

Crosslinking PTU membranes with α, α Dibromo-p-xylene (DBX) was successful, membranes have shown excellent chemical stability towards DMSO, DMF and THF.

$^{13}$C NMR analysis

The sucess of the chemical reaction was confirmed by the $^{13}$C NMR. Fig. 7.6 on the right the NMR spectra represent pristine PTU polymer and on the left the crosslinked PTU polymer. The chemical shifts identified on the pristine PTU polymer are the CH$_2$ peak at 42 ppm. The aromatic rings are located at the chemical shifts of 123, 130 and 138 ppm. The C-O bond is identified at the 154 ppm chemical shift where as the C=S is located around 182 ppm chemical shift. Regarding the crosslinked PTU polymer, a new peak located at the 163 ppm is assigned to the C=S bond after chemical reaction occurance, an integration of these peaks shows that within 24 hours the reaction achieved 60% crosslinking degree. The C-S bond formed after crosslinking is assigned to the 30 ppm chemical shift.
On the contrary of the H$_2$O$_2$ crosslinked PTU membranes, DBX crosslinked PTU membranes showed excellent mechanical stability where membranes were flexible and resilient and stable chemically and mechanically.

**FTIR**

Fig. 7.7 shows the FTIR spectrum of pristine and PTU and DBX crosslinked PTU membranes. The pristine PTU shows a strong absorption band at 1113 cm$^{-1}$ (C=S) and (3271 cm$^{-1}$, 1612 cm$^{-1}$, 815 cm$^{-1}$) for aromatic C-H stretching, bending and aromatic C=C present in the polymer backbone. Absorption bands at 1343 cm$^{-1}$ represents the aliphatic C-N stretch. Crosslinked PTU shows slight shift in the C=S absorption band from 1113 cm$^{-1}$ to 1150 cm$^{-1}$ which reveals the interaction between DBX and the sulfur in Thiourea group. Splitting of the peak at around 1356 cm$^{-1}$ for crosslinked PTU membrane indicate
a change occurred at the C-N bond due to the reaction. A weak new bond appeared in the crosslinked PTU membrane compared to the pristine one at 810 cm\(^{-1}\) which correspond to the new C-S bond formed after the reaction. Also the addition of DBX to the polymer backbone shows a new peak at 1612 cm\(^{-1}\), which corresponds to the aromatic group present in the crosslinker and the aromatic C-H stretch at 3284 cm\(^{-1}\) was shifted and broadened for the crosslinked membranes. All the above data suggests the occurrence of crosslinking reaction between DBX and the thiourea group of the PTU membranes.

Fig. 7.7: FTIR spectra of pristine and crosslinked PTU membranes.
SEM

SEM surface images were taken for pristine and crosslinked asymmetric PTU membranes. Fig. 7.8 shows a porous morphology for both pristine and crosslinked PTU membranes with around 80 nm pore diameter. This indicates no change on the morphology after crosslinking.

![SEM images of PTU and DBX crosslinked PTU membranes](image)

Fig. 7.8: SEM surface images of left) PTU membrane and right) DBX crosslinked PTU membrane.

Solvent permeances

Asymmetric PTU membranes prepared via non solvent induced phase separation were chemically crosslinked with DBX dissolved in ethanol under heat with temperature of 80 °C for 24 hours with 2:1 mole ratio of DBX to PTU polymer. The crosslinked membranes were stable in harsh solvents like DMSO and DMF. Solvent permeances were measured through these membranes and they are summarized in Table 7.3.
Table 7.3: Solvent permeances through asymmetric crosslinked PTU membranes.

<table>
<thead>
<tr>
<th></th>
<th>Dodecane permeance (L/m².h.bar)</th>
<th>DMSO permeance (L/m².h.bar)</th>
<th>DMF permeance (L/m².h.bar)</th>
<th>Ethanol permeance (L/m².h.bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBX crosslinked asymmetric PTU</td>
<td>6</td>
<td>55</td>
<td>65</td>
<td>141</td>
</tr>
</tbody>
</table>

7.6.3 TFC dual bath DBX crosslinked PTU membranes

TFC PTU membranes prepared via dual bath precipitation were chemically crosslinked with DBX dissolved in ethanol under heat with temperature of 80 °C for 24 hours with 2:1 mole ratio of DBX to PTU polymer.

These membranes unlike asymmetric DBX crosslinked PTU membranes are in the nanofiltration range due to the formation of dense skin layer. Reactive Green dye (MW = 1400 g/mol, size = 1.7 nm, charge = -6) in DMSO was tested through these membranes and showed 90% rejection with a permeance of 0.4 L/m².h.bar when they were precipitated in 90/10 % IPA/water first bath. Higher permeance can be obtained when 80/20 % first bath composition used however on the expense of rejection performance Table 7.4.

Table 7.4: Permeance and rejection values of Reactive Green/DMSO for dual bath TFC crosslinked PTU membranes.

<table>
<thead>
<tr>
<th></th>
<th>Water permeance (L/m².h.bar)</th>
<th>20 ppm RG/DMSO permeance (L/m².h.bar)</th>
<th>Rejection (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTU</td>
<td>172</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Crosslinked asymmetric PTU</td>
<td>157</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>Crosslinked 90/10 % 1 min dual bath PTU</td>
<td>2.3</td>
<td>0.4</td>
<td>90</td>
</tr>
<tr>
<td>Crosslinked 80/20 % 1 min dual bath PTU</td>
<td>7</td>
<td>5.8</td>
<td>76</td>
</tr>
</tbody>
</table>
SEM images

Dual bath precipitated PTU membranes cross-section images were compared with pristine PTU. 90/10 % first bath cross-section membrane shown on the right side of Fig. 7.9 shows a skin dense layer of around 600 nm (far right) where pristine PTU membrane cross-section shown on the left show rather skin porous layer.

Fig. 7.9: SEM cross-section images of left) PTU membrane and right) 90/10% 1 min dual bath precipitated PTU membrane.

7.6.4 Performance of anion exchanged DBX crosslinked asymmetric PTU membranes

Anion exchanged DBX crosslinked PTU membranes were prepared as filters with the potential to remove sulfur components form solvents. XPS analysis was provided to judge whether the exchange efficiency is higher in water or DMSO. From the XPS analysis it is clear that the exchange in water is better, where the fluorine percentage is 2 times higher although it was expected that the exchange will proceed better in DMSO due to the swelling of the chains of the polymer Table 7.5.
Table 7.5: XPS results of pristine, crosslinked PTU and anion exchanged PTU membranes.

<table>
<thead>
<tr>
<th></th>
<th>Carbon (%)</th>
<th>Nitrogen (%)</th>
<th>Oxygen (%)</th>
<th>Fluorine (%)</th>
<th>Sulfur (%)</th>
<th>Bromine (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTU</td>
<td>63</td>
<td>9.3</td>
<td>25.9</td>
<td>0</td>
<td>1.8</td>
<td>0</td>
</tr>
<tr>
<td>DBX crosslinked PTU</td>
<td>79.2</td>
<td>9.9</td>
<td>6.7</td>
<td>0</td>
<td>3.1</td>
<td>1.1</td>
</tr>
<tr>
<td>Anion exchange in H₂O</td>
<td>73.2</td>
<td>9.5</td>
<td>11.2</td>
<td>2.4</td>
<td>3.2</td>
<td>0.5</td>
</tr>
<tr>
<td>Anion exchange in DMSO</td>
<td>74.8</td>
<td>9.3</td>
<td>11.4</td>
<td>1.3</td>
<td>3.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Sulfur removal

The exchange was carried out in water as well as DMSO solvents. 200 ppm DBT (Dibenzothiophene) in Dodecane was used as a test solution, DBT chemical structure is presented in Fig. 7.10. Permeance was recorded to be 2 L/m².h.bar. The anion exchanged crosslinked PTU membranes will facilitate the permeance of DBT hence the permeate will be enriched with sulfur. Feed, permeate and retentate samples were collected and tested using GC-MS for the determination of the dibenzothiophene concentration. Permeate samples of anion exchanged PTU membranes were 3.2 times higher in sulfur concentration when compared with the permeate of the pristine PTU membranes.

Fig. 7.10: Chemical structure of dibenzothiophene (DBT) used as a model to represent the sulfur compound.
These first results are preliminary, but additional experiments could not be carried out in the time frame of this PhD work. Future tests should show if increasing the residence time between sulfur and membrane will result in enhanced removal of sulfur. To accomplish that, membranes with dense top layer are preferred; we suggest the use of dual bath TFC PTU membranes for this type of application. Also the type of ionic liquid used for the anion exchange affect heavily on the sulfur removal.
7.7 References:


8  CHAPTER 8: Crosslinked poly (ether block amide) composite membranes for organic solvent nanofiltration applications

8.1  Abstract

Poly (ether block amide) - Pebax® - based membranes are well described for gas separation applications. But only a few publications exist for their application in pressure driven liquid applications like ultrafiltration and nanofiltration. Here we use the commercially available Pebax® 1657 for the preparation of membranes for the filtration of organic solvents. Porous polyacrylonitrile membranes were coated with Pebax® 1657 which was then crosslinked. Toluene diisocyanate (TDI) was used as a crosslinker agent for the coating. Reaction time and crosslinker concentration were optimized for the aimed application. The Pebax® coating and the impact of the TDI on the resulting crosslinked membranes were investigated by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and differential scanning calorimetry (DSC). SEM analysis shows a uniform thin coating of the PEBAX that covers the pores of the PAN membranes. FTIR and DSC analysis confirm the crosslinking reaction. Crosslinked Pebax® membranes show high stability toward ethanol propanol, acetone and even dimethylformamide (DMF). In the case of DMF applications, the standard PAN was replaced by crosslinked PAN developed in our laboratory.

In order to increase the membranes permeances, graphene oxide (GO) nanosheets were

incorporated in the Pebax® coating. These GO containing membranes showed strongly increased permeances for selected solvents.

8.2 Introduction

Polymeric membranes found their way into conventional industrial separation processes, such as gas separation and water purification due to their mechanical robustness, structural diversity and relatively low fabrication cost \(^1\)\(^-\)\(^2\). In the last few years, the interest in developing polymeric membranes for solvent resistant nanofiltration is growing. Solvent-stable nanofiltration membranes are rapidly gaining attention due to their potential to replace distillation in various industries, such as petrochemistry, food and pharmaceutical industries, which involve the use of a large amount of aggressive polar aprotic solvents \(^3\)\(^-\)\(^6\).

Organic solvent nanofiltration membranes require high resistivity towards solvents and a molecular weight cut off (MWCO) of 200-1000 g/mol. Easy processability is important to facilitate industrial manufacture and commercialization. The most studied polymer for these applications is polyimide (PI). This polymer exhibits good chemical stability towards some solvents and its resistivity could further be improved by chemical crosslinking. The Livingstone group achieved high fluxes and outstanding rejection performances using thin film composite membranes prepared on crosslinked PI supports \(^7\)\(^-\)\(^{16}\). The search for further polymers that can be implemented in this area is still going on and recently many polymers found their way into OSN such as polythiosemicarbazide (PTSC), polybenzimidazole (PBI) and other polyazoles \(^17\)\(^-\)\(^19\).
Commercially available poly (ether block amide) resins are known under the trademark Pebax®. They are thermoplastic elastomer block copolymers, which combine linear chains of rigid polyamide segments interspaced with flexible polyether segments. Through the proper combination of polyether and polyamide segments a wide range of grades are available. Fig. 8.1 show the general structure of any Pebax® polymer grade. Polyamide (PA) represents the crystalline polyamide “hard segment” that promotes mechanical stability and it can be nylon-6 or nylon-12. Polyether (PE) represents the amorphous polyether “soft segment” that provides good solvent affinity such as poly (ethylene oxide) or poly (tetramethylene oxide).

Fig. 8.1: General chemical structure of Pebax®

Pebax® membranes have been investigated in ultrafiltration, nanofiltration, pervaporation, solvent filtration and gas separation processes. The first use of Pebax® composite membranes for aqueous ultrafiltration was reported by Nunes et al. in 1995, where dense hydrophilic coatings were applied on PVDF support 20. Nanofiltration membranes were also obtained by in situ interfacial polymerization of trimesoylchloride and different amines inside a dense layer of Pebax® 21. Other studies reported the use of Pebax® membranes for the pervaporation separation of aqueous isopropanol and aqueous ethyl butyrate 22 and ethanol recovery from aqueous solutions 23. Zwijnenberg et al. used
Pebax® membranes to separate different vegetable oil/solvent mixtures, which is an important separation process in the oleochemical industry. The use of Pebax® membranes for carbon dioxide separation was described in an MTR Inc. patent in 1990. It was shown later, that the addition of polyether homopolymer increases the CO2 permeance to a large extend. The moderate separation of CO2/CH4 mixtures using Pebax®1657 was improved by crosslinking thin film composite membranes of Pebax®1657 with toluene diisocyanate (TDI). The crosslinking occurs through the formation of urethane linkages between carbonyl group of the crosslinker and the hydroxyl end-groups of polyether segments.

Graphene oxide (GO) is an oxidized form of graphene nanosheets, which has a variety of oxygen-containing groups together with a laminar structure, providing the potential for membrane separations. The use of these nanosheets in water purification and solvent filtration processes is discussed in recent publications. Polymer/GO mixed matrix membranes have been prepared for separation of gaseous and liquid mixtures. GO membrane preparation sometimes depends on using an aqueous environment where GO nanosheets are dispersed in water and processed using either dip coating, spin coating or filtration followed by drying. These methods highly depend on stacking the nanosheets of the GO. Recent work discusses a methodology for fabricating membranes that involve GO assembly in polymeric environment. The key concept of this method is the construction and utilization of favorable molecular interactions between GO and the polymer leading to well-defined laminates.

In this work, thin film composite membranes were prepared by dip coating using Pebax®1657 solution on PAN support. The goal is the application in organic solvent
nanofiltration since Pebax®1657 shows good stability to a number of solvents. In order to enhance this stability and to increase the rejection performance, the Pebax®1657 layer was crosslinked using toluene diisocyanate. It was expected that the crosslinking would improve chemical stability as well as lower the swelling of the dense layer. Also, graphene oxide nanosheets were incorporated in the dense layer for further enhancement of the membranes performance. The last part of this work discusses the possibility of expanding the application of these membranes to filter harsh solvents such as DMF. In order to study this, Pebax®1657 coating was applied on crosslinked PAN support, which was previously reported to tolerate DMF.

8.3 Materials

PAN powder was supplied by Kelheim Fibers GmbH, Germany, molecular weight higher than 100.000 g/mol. Polypropylene support was purchased from Sojitz Europe, type HOP-80HCF. Arkema Specialty Polyamides kindly supplied the Pebax® 1657 grade. Toluene diisocyanate (TDI), DMF, 1-propanol, graphene oxide (GO) dispersion, hydrazine hydrate solution and acetone were purchased from Sigma Aldrich. Hexane and ethanol were purchased from VWR Chemicals. Fisher Scientific provided Brilliant Blue (BB) dye.
8.4 Methods

8.4.1 Fabrication of thin film composite of PAN/ crosslinked Pebax® 1657

Pebax® 1657 (PEO = 60%, Polyamide 6 = 40%) pellets were dissolved with 1% concentration in 70:30 % of ethanol/water solution at 75 °C under stirring for 3 hours. PAN membranes were dip coated with the solution for 3 minutes then left to dry at room temperature, the procedure is shown in Fig. 8.4 a. Crosslinking of membranes was achieved by immersing them in a solution of 1% or 2% TDI/hexane for 30 and 60 minutes at room temperature, Fig. 8.2 shows the crosslinking reaction.

![Crosslinking chemical reaction of Pebax® 1657.](image)

Fig. 8.2: Crosslinking chemical reaction of Pebax® 1657.
8.4.2 Fabrication of thin film composite of PAN/ crosslinked Pebax® 1657/GO

Method 1: Pebax® 1657 pellets were dissolved with 1% concentration in 70:30 % of ethanol/water solution at 75 °C under stirring for 3 hours with the addition of GO/water dispersion of 1.5, 3, 6 and 8.9 ml (4 mg/ml). PAN membranes were dip coated with the solutions for 3 minutes then left to dry at room temperature. Crosslinking of membranes was achieved by immersing them in a solution of 2% TDI/hexane for 30 minutes at room temperature. It was expected that the graphene oxide nanosheets would form hydrogen bonding with the Pebax® chain, crosslinking with TDI will form a cage like structure as shown in Fig. 8.3 and the procedure is illustrated in Fig. 8.4 b.
Fig. 8.3: Crosslinking chemical reaction of Pebax® 1657 with the presence of GO sheets and possible hydrogen bonding.

Method 2: Pebax® 1657 pellets were dissolved with 1% concentration in 70:30 % of ethanol/water solution at 75 °C under stirring for 3 hours with the addition of GO/water dispersion of 3, 6 and 8.9 ml (4 mg/ml). Sheets of PAN membranes were fixed on a glass plate and the Pebax®/GO solutions were cast using a casting knife with 100µm gap. Membranes were then left to dry at room temperature. Illustration of the procedure is given in Fig. 8.4 c. Crosslinking of membranes was achieved by immersing them in a solution of 2% TDI/hexane for 30 minutes at room temperature.
8.4.3 Fabrication of thin film composite of crosslinked PAN (X PAN)/crosslinked Pebax\textsuperscript{®} 1657.

Mesoporous support membranes were fabricated from PAN polymer via phase inversion. A solution of 12\% PAN was prepared in DMF at 70 °C under constant mechanical stirring for 12 h. The obtained homogenous solution was left overnight to obtain an air bubble free solution. The solution was cast on a polypropylene support on a continuously operating casting machine with a casting thickness of 150 µm at a casting speed of 2 m/min. Cast films were immersed in a water bath at room temperature where the precipitation occurs. Airtime before immersion into the water bath was about 3 s. The wet membranes were then transferred to a hot water bath (90 °C) for 45 min to remove excess solvents. The PAN membranes were crosslinked at 85 °C for 6 h in an aqueous 20\% hydrazine hydrate solution in order to enhance the chemical stability. The crosslinked membranes were finally washed and dried.

The crosslinked PAN membranes were then dip coated with 1\% solution of Pebax\textsuperscript{®} 1657 for 3 min and dried followed by crosslinking with TDI as previously described. The procedure is illustrated in Fig. 8.4 d.
Fig. 8.4: Membranes preparation procedure (a) preparation of PAN/X-Pebax® 1657 membranes. (b) Preparation of PAN/X-Pebax® 1657/GO membranes via dip coating. (c)
Preparation of PAN/X-Pebax®1657/GO membranes via casting. (d) Preparation of X-PAN/X-Pebax®1657 membranes.

8.5 Membrane characterization

Scanning electron microscopy (SEM)

The surface and cross-section of the membranes were characterized by scanning electron microscopy. For the analysis of the membrane’s surface samples were prepared by mounting a small membrane square on to SEM stubs. The cross-section images were obtained by fracturing the membrane samples in liquid nitrogen. The samples were then sputtered with a 5 nm thick Iridium coating using an Emitech K575x sputter coater under an argon atmosphere to achieve the necessary conductivity. The microscopic analyses were performed at 5 kV using scanning electron microscope (Quanta 200).

Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectra were recorded on a Nicolet iS10 FTIR spectrometer with a Smart iTR Attenuated Total Reflectance (ATR) sampling accessory in the range of 3500-500 cm⁻¹ at room temperature. The samples were fixed between a diamond plate and pressure tower with the separating layer facing the beam. Membranes were dried prior to FTIR measurements. Spectra of different membranes prepared were compared.
Differential scanning calorimetry (DSC)

DSC thermogram of the synthesized Pebax® 1657 and crosslinked Pebax® 1657 membranes were recorded on a DSC Q 2000 instrument in the temperature range of 25–200 °C at a heating rate of 10 °C/min in nitrogen atmosphere.

Contact Angle measurement

Contact angle measurements were performed with an Easy-Drop Instrument (manufactured by Kruess) at room temperature using the drop method, in which a drop of water was deposited on the surface of a piece of membrane using a micropipette. The contact angle was measured automatically by a video camera in the instrument using drop shape analysis software. Three measurements on different membrane pieces were performed. All membranes were dried prior to measuring their contact angle.

8.6 Nanofiltration experiments

All nanofiltration experiments were carried out at 25 °C in a stirred-dead end filtration cell. The effective membrane area was 12.6 cm², permeate samples for flux and rejection measurements were collected after obtaining steady state condition. Rejection studies were carried out using a feed solution of 5ppm Brilliant blue dye in ethanol or 10ppm Brilliant blue in DMF. Analysis of the dye was done with a UV Vis/near IR (Perkin Elmer Lambda 1050) spectrophotometer.
Solvent permeance ($J$) was determined by measuring the permeate volume ($V$) per unit area ($A$) per unit time ($t$) per unit pressure ($P$) according to equation 8.1:

$$J = \frac{V}{A \times t \times P}$$

(8.1)

The rejection ($R_i$) of dyes was calculated from equation 8.2, where $CP_i$ and $CF_i$ correspond to the permeate and the feed dye concentrations, respectively.

$$R_i = \left(1 - \frac{CP_i}{CF_i}\right) \times 100\%$$

(8.2)

Each filtration experiment reported was at least repeated three times with three membrane coupons.

### 8.7 Results and Discussion

8.7.1 Scanning electron microscopy (SEM)

SEM for PAN and PAN / Pebax® 1657 membranes

SEM images for PAN and Pebax® coated PAN are presented in Fig. 8.5. The image of the PAN support shows the surface with open pores of approximately 30 nm in diameter. Pebax® coated PAN membranes on the other hand shows no pores using same scale and magnification, which proves the formation of thin dense layer on top. Cross-section
image of the Pebax® coated membranes shows the distinctive dense layer on top with a thickness of ~ 100 nm.

Fig. 8.5: SEM images of a) surface and c) cross-section of PAN, and b) surface and d) cross-section of PAN coated with Pebax® 1657.
8.7.2 Fourier transform infrared spectroscopy (FTIR)

FTIR of PAN and Pebax® 1657 membranes

FTIR spectra for bare PAN and PAN coated with Pebax® are shown in Fig. 8.6. Looking at the PAN spectrum, the peak at 2920 cm⁻¹ represent the C-H bond stretching while the peak at approximately 2252 cm⁻¹ speaks for the triple bond between C and N. The characteristic peaks at 1459 cm⁻¹ and 1080 cm⁻¹ are appointed to the C-H and N-N linkages. According to the Pebax® spectrum, the observed peak at 1094 cm⁻¹ is attributed to the stretching vibration of the C-O-C bond. 3297 cm⁻¹ peak corresponds to the –N-H-linkages while the peaks at 1637 and 1732 cm⁻¹ are assigned to H-N-C=O group and O-C=O group, respectively.
Fig. 8.6: FTIR spectra of PAN and Pebax® 1657 membranes.

FTIR of PAN/crosslinked Pebax® 1657 membranes

Fig. 8.7 demonstrates the FTIR spectra of Pebax® and crosslinked Pebax® with different concentration and reaction time. Comparing the spectra, it can be seen that there are two additional peaks for the crosslinked Pebax®; one is at approximately 1600 cm⁻¹ that represents the C=C aromatic from the crosslinker, whereas the other peak is at 875 cm⁻¹ corresponding to the C-H aromatic. The other highlighted peaks reveal either higher
intensity for the crosslinked Pebax like the peak at 3300 cm$^{-1}$, which corresponds to the N-H linkage, or broadening that is clearly seen in the 1750 cm$^{-1}$, which is attributed to the C=O bond. Also shifting of one of the already existing peaks in the non-crosslinked Pebax® at 1250 cm$^{-1}$ can be noticed and it represents the C-O bond. Splitting of one peak is also noted around 2875 cm$^{-1}$ which is attributed to the C-H stretching.

Fig. 8.7: FTIR spectra of Pebax® 1657 and crosslinked Pebax® 1657 membranes for different time interval and concentration of TDI.
FTIR of PAN/crosslinked Pebax<sup>®</sup> 1657/GO membranes

Method 1: Pebax<sup>®</sup> / GO membranes via dip coating were prepared with different GO loading of (2%, 3.8%, 7% and 10%). It was noticed that concentrations higher than 2% did not give a uniform distribution on the surface. Therefore only 6 mg GO loading (GO-6) was tested. Fig. 8.8 Shows the FTIR spectra of Pebax<sup>®</sup> 1657 and Pebax<sup>®</sup> 1657 / GO -6. No additional peaks are noticed in the Pebax<sup>®</sup> 1657/GO-2% spectra which demonstrate the absence of chemical bond generating. Only a slight shift to lower frequency of two peaks can be observed; one is at 3299 cm<sup>-1</sup>, which represents the –N-H- and the other is at 1639 cm<sup>-1</sup> which is assigned to H-N-C=O. Hydrogen bonds between different groups of Pebax<sup>®</sup> and GO can be formed.
Fig. 8.8: FTIR spectra of Pebax® 1657 and Pebax® 1657/GO membranes.

Fig. 8.9 Demonstrates the IR spectra for the Pebax® 1657 membranes loaded with GO before and after crosslinking. The same additional peaks can be noticed in the crosslinked Pebax® without GO and also same shifting, broadening, splitting and higher intensity of the peaks in crosslinked Pebax® 1657 / GO compared to the already existing peaks in Pebax® 1657 / GO.
Fig. 8.9: FTIR spectra of Pebax® 1657/GO and Pebax® 1657/GO crosslinked membranes with 2% TDI for 30 min.

FTIR of crosslinked PAN/crosslinked Pebax® 1657 membranes

The IR spectra of PAN and crosslinked PAN are displayed in Fig. 8.10 the crosslinked PAN spectra prove that crosslinking reaction has happened. Additional peaks of N-H are located at 3340 cm⁻¹ and C=N located at 1550 cm⁻¹. The characteristic peak at 1088 cm⁻¹ in the PAN spectra can be attributed to the C-N bond but the same peak in crosslinked PAN corresponds to the N-N additional bond. At around 1600 cm⁻¹ higher intensity was spotted for the crosslinked PAN and it represents the C-C bond corresponding to the
crosslinker.

Fig. 8.10: FTIR spectra of PAN and XPAN support membranes.

8.7.3 Differential scanning calorimetry (DSC)

An indicator for the degree of crosslinking could be obtained from the DSC analysis, Fig. 8.11 in the DSC graph for Pebax® 1657 two endothermic peaks are evident, one occurs at 50 °C and the other at 165 °C. These peaks can be attributed to the fusion of the crystalline fraction of the blocks of PE and PA, respectively. Comparing the pristine Pebax® graph with crosslinked Pebax®, the endothermic peak attributed to the crystalline fraction of PE shows a shift to higher values after crosslinking Table 8.1 whereas the
peak assigned for PA remains the same at 165 °C for all crosslinking conditions. This suggests that the carbonyl groups of TDI interact with the polyether blocks.

Fig. 8.11: DSC analysis of crosslinked Pebax® 1657 membranes.
Table 8.1: Crosslinking degree indication obtained from the shift of PE peak.

<table>
<thead>
<tr>
<th></th>
<th>Pebax® 1657</th>
<th>X-Pebax® 1% TDI 30 min</th>
<th>X-Pebax® 1% TDI 60 min</th>
<th>X-Pebax® 2% TDI 30 min</th>
<th>X-Pebax® 2% TDI 60 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature of Peak of PE (°C)</td>
<td>50</td>
<td>60</td>
<td>66</td>
<td>75</td>
<td>78</td>
</tr>
<tr>
<td>Indication of the crosslinking degree (%)*</td>
<td>-</td>
<td>20</td>
<td>32</td>
<td>50</td>
<td>56</td>
</tr>
</tbody>
</table>

* Indication of the crosslinking degree is calculated based on \( D\% = \frac{(X_a - X_b)}{X_a} \times 100\% \), where \( X_a \) and \( X_b \) represent temperature before and after crosslinking respectively.

8.7.4 Contact Angle measurement

Analyzing the crosslinking reaction, the introduction of additional PA segments causes the 1657 grade to shift to a more hydrophobic stage, which leads to lower water permeance. Fig. 8.12 Shows contact angle measurements for both crosslinked and non-crosslinked membranes. Observing a water drop on a dry piece of a Pebax® 1657 membrane, the drop gets absorbed within seconds into the membrane matrix leaving a wet spot. To measure the advancing contact angle a video was taken and stopped at the first moment when the drop was shaped on the surface. The drops on the crosslinked Pebax® 1657 membranes kept their shape much longer.
8.8 Nanofiltration experiments

8.8.1 Performance of PAN/crosslinked Pebax® 1657 membranes

The permeance of Pebax® 1657 coated PAN was 8 times reduced compared to PAN supports. Results are summarized in Table 8.2. However the formed Pebax® layer is incapable of rejecting Brilliant Blue (BB) dye in solvents, which swell the Pebax® like acetone and ethanol.
Table 8.2: Permeances and rejection values of PAN, Pebax® 1657 and crosslinked Pebax® 1657 membranes for different marker/solvent mixtures.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Permeance L/m².h.bar</th>
<th>Rejection %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN</td>
<td>153 ± 5</td>
<td>0</td>
</tr>
<tr>
<td>PAN - Pebax® 1657 1% 3 min</td>
<td>20 ± 3</td>
<td>0</td>
</tr>
<tr>
<td>PAN - Pebax® 1657 1% 3 min 1% TDI 30 min</td>
<td>0.85 ± 0.01</td>
<td>50 ± 6</td>
</tr>
<tr>
<td>PAN - Pebax® 1657 1% 3 min 1% TDI 60 min</td>
<td>0.67 ± 0.017</td>
<td>70 ± 5</td>
</tr>
<tr>
<td>PAN - Pebax® 1657 1% 3 min 2% TDI 30 min</td>
<td>0.1 ± 0.005</td>
<td>95 ± 3</td>
</tr>
<tr>
<td>PAN - Pebax® 1657 1% 3 min 2% TDI 60 min</td>
<td>No permeance</td>
<td>-</td>
</tr>
<tr>
<td>PAN - Pebax® 1657 1% 3 min 2% TDI 30 min</td>
<td>0.1 ± 0.004</td>
<td>95 ± 3</td>
</tr>
<tr>
<td>PAN - Pebax® 1657 1% 3 min 2% TDI 30 min</td>
<td>0.1 ± 0.01</td>
<td>100</td>
</tr>
<tr>
<td>PAN - Pebax® 1657 1% 3 min 2% TDI 30 min</td>
<td>0.1 ± 0.006</td>
<td>95 ± 3</td>
</tr>
<tr>
<td>X PAN - Pebax® 1657 1% 3 min 2% TDI 30 min</td>
<td>1 ± 0.013</td>
<td>95 ± 5</td>
</tr>
</tbody>
</table>

Crosslinking tests were performed with Pebax® membranes to optimize crosslinking time and concentration. Table 8.2 summarizes the results and Fig. 8.13 presents the UV spectra of feed, permeate and retentate of BB/ethanol for these membranes. With increasing time and concentration of crosslinking, the membranes became tighter and the permeance decreased with increasing rejections. Using 1% crosslinker concentration reduced the permeance considerably although the rejection of dye was only 50% even
when increasing the reaction time to one hour. Raising the concentration of TDI to 2% enhanced the performance of the membranes. We were able to get 95% rejection of Brilliant Blue in ethanol with acceptable permeance when the reaction time was 30 minutes. However, when the reaction time was extended to one hour the membranes became very dense to a point were no permeate could be collected even at a high pressure of 20 bar. To compare the performance of our Pebax composite membranes with other membranes we used data of a recent detailed review on OSN membranes published by the Livingston group. Taking data from this review we plotted permeance versus rejection for different markers in DMF, acetone and ethanol. We added the performance data of our Pebax composite membranes. These plots are now shown in the Fig. 8.14.
Fig. 8.13: UV-Vis spectra of feed, permeate and retentate of Brilliant blue/ethanol mixture filtered through crosslinked Pebax® 1657 membranes with different time and concentration of TDI.
According to the results obtained the best concentration and reaction time for crosslinking with TDI is 2% and 30 minutes respectively. Membranes also were tested for other solvents such as 5ppm BB/acetone and 5ppm BB/1-propanol and all showed around 95% rejections to BB dye with permeances similar to the BB/ethanol solution. We tested two additional solutes in ethanol: Protoporphyrin IX dimethyl ester (MW=590.71g/mol) and Rose Bengal (MW=1017.64 g/mol). Rejection was around 60% for the Protoporphyrin and 100% for Rose Bengal.
Organic solvent nanofiltration membranes could be used in the food industry, especially for recovering solvent from edible oil in the process of extraction oil from seeds. This process involves the use of solvent to extract oil from seeds; solvent recovery is conventionally done by distillation, which could be replaced by less energy consuming nanofiltration.

The average molecular weight of olive oil is 850 ~ 900 g/mol. \(^{34}\) Pebax\(^{®}\) coated PAN membranes were crosslinked with 2\% TDI for 30 min and tested for 10\% Olive oil/Acetone separation.

The membranes exhibit complete rejection of oil as shown in the UV spectra of feed, permeate and retentate in Fig. 8.15 with a permeance of 0.1 L/m\(^2\).h.bar.

![Fig. 8.15: UV-Vis spectra of feed, permeate and retentate of olive oil/acetone mixture filtered through crosslinked Pebax\(^{®}\) 1657 membrane.](image)
Pebax® membranes generally suffer from swelling especially in water and methanol. Extensive swelling is not desirable since it leads to lower selectivities. Crosslinked Pebax® membranes were tested for swelling; first the water permeance of an initially dry Pebax® membrane was measured, and then the membrane was soaked in water for 20 hours before it was tested again. The same procedure was followed for the crosslinked Pebax® membrane. The results are presented in Table 8.3.

Table 8.3: Water permeance values with flux increase% for Pebax® 1657 and crosslinked Pebax® 1657 membranes soaked in water for different time intervals.

<table>
<thead>
<tr>
<th></th>
<th>Pebax® 1657</th>
<th>Crosslinked Pebax® 1657 (2% TDI 30 min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Permeance</td>
<td>Flux increase</td>
</tr>
<tr>
<td>Performance at t = 0 hr</td>
<td>33</td>
<td>-</td>
</tr>
<tr>
<td>Performance at t = 20 hr</td>
<td>49</td>
<td>48</td>
</tr>
<tr>
<td>Performance at t = 40 hr</td>
<td>49</td>
<td>48</td>
</tr>
</tbody>
</table>

The results show almost 50% flux increase for non-crosslinked Pebax® membranes after 20 hour exposure to water; this was the equilibrium swelling since it did not change after 40 h exposure. Crosslinked membranes however, showed the same performance in terms of permeances before and after the water exposure proving that crosslinked membranes do not show excessive swelling.

8.8.2 Performance of PAN/ crosslinked Pebax® 1657 /GO membranes

Method 1: Pebax® 1657/GO-2% membranes were crosslinked and tested with
ethanol/Brilliant Blue rejection and compared to crosslinked Pebax® 1657 membranes without GO. Table 8.4 shows the calculation for incorporation of GO in Pebax solution. The ethanol/BB flux has doubled for membrane with graphene oxide compared to GO-free membranes without sacrificing selectivity. See Table 8.5. Graphene oxide sheets create extra channels for ethanol increasing the permeance without compromising rejections.

Table 8.4: Calculations of GO loading in Pebax® 1657/GO membranes

<table>
<thead>
<tr>
<th>Water/GO dispersion (4 mg/ml)</th>
<th>GO/Water dispersion (ml)</th>
<th>Go loading in solution (mg)</th>
<th>Go loading in solution (wt%)</th>
<th>GO loading in Pebax layer (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 ml water/GO - 8.9 ml water</td>
<td>0</td>
<td>0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>1.5 ml water/GO - 7.4 ml water</td>
<td>1.5</td>
<td>6</td>
<td>0.02</td>
<td>2.0</td>
</tr>
<tr>
<td>3 ml water/GO - 1.5 ml water</td>
<td>3</td>
<td>12</td>
<td>0.04</td>
<td>3.8</td>
</tr>
<tr>
<td>6 ml water/GO - 2.9 ml water</td>
<td>6</td>
<td>24</td>
<td>0.08</td>
<td>7.4</td>
</tr>
<tr>
<td>8.9 ml water/GO - 0 ml water</td>
<td>8.9</td>
<td>35.6</td>
<td>0.1</td>
<td>10.6</td>
</tr>
</tbody>
</table>

Table 8.5: Permeance and rejection values of crosslinked Pebax® 1657/GO membranes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Permeance L/m² h bar</th>
<th>Rejection %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN - Pebax® /GO-0% - 2% TDI 30 min</td>
<td>0.1 ± 0.01</td>
<td>95 ± 3</td>
</tr>
<tr>
<td>PAN - Pebax® /GO-2%* Dip coating -2% TDI 30 min</td>
<td>0.2 ± 0.021</td>
<td>95 ± 5</td>
</tr>
<tr>
<td>PAN - Pebax® /GO-3.8%* Casting - 2% TDI 30 min</td>
<td>1.9 ± 0.012</td>
<td>95 ± 4</td>
</tr>
<tr>
<td>PAN - Pebax® /GO-7.4%* Casting - 2% TDI 30 min</td>
<td>0.2 ± 0.005</td>
<td>95 ± 5</td>
</tr>
<tr>
<td>PAN - Pebax® /GO-10.6%* Casting - 2% TDI 30 min</td>
<td>No permeance</td>
<td>-</td>
</tr>
</tbody>
</table>

* GO percentages are calculated in relation to the Pebax layer.
Method 2: Pebax® / GO membranes via casting were prepared with different GO loadings of (3.8%, 7.4% and 10.6%). It was noticed that a uniform distribution of GO is possible using this method. GO-3.8%, GO-7.4% and GO-10.6% membranes were crosslinked with 2% TDI for 30 min and tested for ethanol/Brilliant Blue rejection, Table 8.5. GO-3.8% loading showed best results in terms of permeance value; all membranes showed the same high rejection. It was noticed that increasing the GO concentration reduced the permeance of membranes because of the high density of sheet stacking.

8.8.3 Performance of crosslinked PAN/ crosslinked Pebax® 1657 membranes

When the crosslinked Pebax layer is prepared on a standard PAN support, the composite membrane cannot be used in solvents like DMF and NMP, which dissolve the PAN. To overcome this problem we used a crosslinked PAN membrane described previously. A 0.001% BB/DMF solution was filtered through these membranes and the permeance was 1 L/ m² h bar with a rejection of 95%. It should be mentioned that the dry crosslinked PAN membranes are slightly brittle and should be handled carefully. They are mechanically stable in wet state. The ability in filtering DMF solution through crosslinked PAN/ crosslinked Pebax® 1657 membranes shows that crosslinked Pebax is suitable for applications harsh solvents

8.9 Conclusion

Pebax/PAN composite membranes have been prepared for the filtration of aqueous and organic liquids. The Pebax layer was crosslinked with toluene diisocyanate (TDI)
crosslinker to enhance the chemical stability and to increase its selectivity. The influence of crosslinker concentration and reaction time on membrane performance was studied. Best results were obtained with 2% TDI concentration and 30 min reaction time. Crosslinked Pebax/PAN membranes showed a MWCO of 800 g/mol and an ethanol flux of 0.1 L/m².h.bar. An almost 20 fold increase of the ethanol flux could be obtained by addition of graphene oxide nanosheets to the Pebax coating solution. The optimum GO concentration was 3.8 wt.% in relation to Pebax layer using casting method.

In order to increase the overall membrane solvent stability, a previously developed crosslinked PAN membrane was used as support. The crosslinked Pebax membranes on crosslinked PAN were stable in DMF; they showed a DMF permeance of 1 L/m².h.bar and a 95% rejection of Brilliant Blue in DMF.
8.10 References


9 CHAPTER 9: Towards greener organic solvent nanofiltration membranes

Calcium Alginate thin film composite membranes.

9.1 Introduction

Membrane-based separation processes have gained significant attention in industrial applications due to their distinct advantages over traditional separation processes like distillation and extraction. Such advantages are smaller footprint, lower costs of the equipment used and improved energy efficiency 1-4.

NF membranes have pore diameters in the range of 0.5–2 nm combined with a molecular weight cutoff of MWCO 200 - 2000 g/mol and NF is a pressure-driven separation process without phase transition 5. OSN has a high potential to become one of the best available technologies among the separation techniques in organic media due to 6 (i) low energy requirements, (ii) low solid waste generation, (iii) simple scale-up, (iv) stability in harsh environments allowing wide flexibility (pH, T, solvents) and (v) mild operating conditions (T, p).

Polymeric membranes must be solvent stable and preserve their separation characteristics in organic solvents in order to be used in the OSN. The two main types of polymeric membranes are integrally skinned asymmetric membranes and the thin film composite (TFC) membranes. Various chemically stable polymeric materials have been used to prepare OSN membranes by phase inversion either as NF membranes or UF supports for OSN membranes. Such materials are polyacrylonitrile (PAN) 7-8, polyimide (PI) 9-18, polythiosemicarbazide (PTSC) 19, polybenzimidazole (PBI) 20, polyaniline (PANI) 21-22,
polysulfone (PSf)/sulfonated poly (ether-ether ketone) (SPEEK) blends \(^{23}\), poly (ether-ether ketone) (PEEK) \(^{24-25}\) and copolyazole \(^{26}\).

The second group of membranes are TFC membranes, which consist of a thin separating layer cast on top of a chemically different porous support. Coating and interfacial polymerization are the main methods to prepare such membranes \(^{27-31}\). Different strategies are proposed to make OSN greener by following some of the principles of green chemistry such as using greener solvents for casting or coating, using low toxicity chemicals, minimizing the number of steps in membranes production to reduce waste, using renewable, environment friendly or degradable materials for membrane formation and minimizing energy in preparing casting solutions \(^{32}\).

Cellulose and its derivatives are one of the most abundant organic materials; they are inexpensive, biodegradable and sustainable polymers as they conserve natural resources through the use of biomass feedstock. Cellulose does not melt or dissolve in ordinary solvents because of the strong hydrogen bonds between its chains. This qualifies cellulose as a very good candidate for organic solvent separation applications \(^{33-35}\).

Another example of biopolymers is chitosan; it is one of the most used polysaccharides and the second most abundant natural polymer after cellulose. Chitosan exhibits excellent resistance to most organic solvents and it is used in pervaporation and OSN \(^{36-37}\). Sodium alginate (NaAlg) is a natural polysaccharide product extracted from the cell wall of brown seaweed and it is the water-soluble salt of alginic acid. Alginate is an unbranched binary copolymer of 1–4 linked \(\beta\)-D- mannuronic acid (M) and \(\alpha\)-L guluronic acid (G). In principle, alginate is built of G-G blocks, G-M blocks, and M-M blocks Fig 9.1. These blocks can be found in different ratios and in different molecular weights in alginate
preparations leading to different physical and chemical characteristics\textsuperscript{38-39}. The major concern in SA use is its swelling in the presence of hydrophilic solvents such as water. NaAlg is a potential candidate for pervaporation applications. However, crosslinking is essential to increase resistivity to water as well as enhance the mechanical strength. A number of crosslinking agents were reported including glutaraldehyde \textsuperscript{40-41}, toluene diisocyanate (TDI) \textsuperscript{42}, hexanediamine or jeffamine \textsuperscript{43-46} and divalent cations such as calcium salts through ionic crosslinking \textsuperscript{47}. In this work sodium alginate thin film composite membranes were prepared using polyacrylonitrile (PAN) and crosslinked PAN supports, these membranes were tested for several solvents. To achieve higher permeances another approach was followed where free-standing nanofilms were prepared and deposited on alumina support \textsuperscript{48}.

\begin{center}
\textbf{Fig. 9.1:} the chemical structure of sodium alginate polymer with mannuronic (M) and guluronic (G) acid blocks.
\end{center}
9.2 Membranes preparation

First a solution of sodium alginate (NaAlg polymer) was prepared by dissolving NaAlg in water and let it stir for 3 hours. Even a low concentration of 0.5% alginate results in a viscous solution, and the preparation is facile since it is carried out at room temperature. Two types of membranes were prepared: one is a composite membranes and the other is a free-standing nanofilm on alumina support.

9.2.1 Thin film composite membranes.

Composite membranes were prepared by casting of 1 or 0.5 % NaAlg solution on top of PAN or crosslinked PAN (XPAN). After casting the membranes were left to dry at room temperature or they were precipitated in an acetone bath or in water containing calcium chloride for a certain time. The calcium ions act as crosslinkers, the reaction is presented in Fig. 9.2. The preparation procedure is illustrated in Fig. 9.3.

Fig. 9.2: Chemical crosslinking reaction of NaAlg polymer and CaCl$_2$ salt solution.
9.2.2 Freestanding membranes

Free-standing NaAlg membranes were prepared by spin coating. 1% polymer solution was spin coated with 1000 rpm and acceleration of 1000 rpm/s on a glass slide for 1 min. After coating the glass plate was immersed in 5% CaCl$_2$/water solution for 5 min where precipitation of the polymer occurs due to chemical crosslinking reaction and CaAlg membranes were formed. After 5 min reaction the glass plate is transferred to pure water to stop further crosslinking. After detachment of the film from the glass plate, an alumina support (Anodisc 25, Whatman Ltd, 200 nm pore size) was used to pick up the nanofilm. Fig. 9.4 describes the preparation procedure.
9.3 Membrane characterization

9.3.1 FTIR analysis

The FTIR spectra were recorded on a Nicolet iS10 FTIR spectrometer with a Smart iTR Attenuated Total Reflectance (ATR) sampling accessory in the range of 500 – 3500 cm\(^{-1}\) at room temperature. The samples were fixed between a diamond plate and pressure tower with the separating layer facing the beam. Membranes were dried prior to FTIR measurements. Spectra of different membranes prepared were compared.

9.3.2 SEM images

The surface of the studied membranes was characterized by high-resolution scanning electron microscope (Magellan) at 2 kV. The samples for cross-section images were obtained by fracturing the membrane in liquid nitrogen. Prior to the SEM imaging the samples were sputtered with 3 nm thick Iridium coating using Quorum Q150T S sputter coater under an argon atmosphere to achieve the necessary conductivity.
Magellan was also used to take the cross-section SEM images of the freestanding membranes; the samples were fractured carefully without liquid nitrogen since the support is brittle. A Helios Nanolab 400S dual beam SEM equipped with electron beam (field emission source), focused ion beam (FIB) and through-the-lens secondary electron detector (TLD) was used to examine the freestanding membranes cross-section. To dissipate charging during focused ion beam cutting of membrane and subsequent imaging of cross-section face with electron beam, membranes were coated with 7 nm of Pt/Pd inside a K575X sputter coater (Quorum Technologies). Two-steps coating with platinum was used to protect the top surface layer from ion beam-induced damage during subsequent cross-sectioning steps. The membrane surface was first coated with 200 nm of platinum using e-beam and additional 1200 nm of platinum coating using FIB. Subsequently, membranes were cross-sectioned using FIB. The cross-sectioned face of the membranes were imaged using TLD at 5 KV, 52 degree stage tilt angle and 3.9 mm working distance.

9.3.3 AFM analysis

The surface topographies were analyzed by AFM on an ICON Veeco microscope operating in the tapping mode using commercial silicon TM AFM tips (MPP 12100).

9.3.4 Contact angle measurements

Contact angle measurements were performed with an Easy-Drop Instrument (manufactured by Kruess) at room temperature using the drop method, in which a drop of
water was deposited on the surface of a piece of membrane using a micropipette. The contact angle was measured automatically by a video camera in the instrument using drop shape analysis software. Three measurements on different membrane pieces were performed. All membranes were dried prior to measuring their contact angle.

9.3.5 Nanofiltration experiments

All nanofiltration experiments were carried out at 25 °C in a stirred dead-end filtration cell. The effective membrane areas were 12.6 and 4 cm² for thin film composite and free-standing membranes respectively. Permeate samples for flux and rejection measurements were collected after obtaining steady state condition. Rejection studies were carried out using a feed solution of 20 ppm vitamin B12 (MW = 1355 g/mol, size = 1.7 nm, charge = neutral) in the solvents methanol, DMF, DMSO and NMP. The rejection of vitamin B12 was monitored using a NanoDrop 2000/2000c spectrophotometer (Thermo Fisher Scientific).

Solvent permeance (J) was determined by measuring the permeate volume (V) per unit area (A) per unit time (t) per unit pressure (P) according to equation 9.1:

\[ J = \frac{V}{(A \cdot t \cdot P)} \]  
(9.1)

The rejection (Rᵢ) of dyes was calculated from equation 9.2, where CPᵢ and CFᵢ correspond to the permeate and the feed dye concentrations, respectively.

\[ Rᵢ = \left(1 - \frac{CPᵢ}{CFᵢ}\right) \times 100\% \]  
(9.2)
Each filtration experiment reported was at least repeated three times with three membranes.

9.4 Characterization results and discussion

The Fourier transform infrared (FTIR) spectra of the sodium alginate (NaAlg) and calcium alginate (CaAlg.) were recorded and compared in Fig. 9.5. Spectrum of sodium alginate showed important absorption bands regarding hydroxyl, ether and carboxylic functional groups. Stretching vibrations of O–H bonds of NaAlg appeared in 3344 cm$^{-1}$ shift. Stretching vibrations of aliphatic C–H were observed at 2932 cm$^{-1}$. Observed bands in 1602 and 1413 cm$^{-1}$ were attributed to asymmetric and symmetric stretching vibrations of carboxylate salt ion, respectively. The bands at 1092 and 1031 cm$^{-1}$ were attributed to the C–O stretching vibration of pyranose ring and the C–O stretching with contributions from C–C–H and C–O–H deformation. Calcium alginate spectrum showed changes in comparison with IR spectrum of NaAlg. Absorption region of stretching vibrations of O–H bonds in CaAlg appeared narrower than NaAlg. This difference arises from the participation of hydroxyl and carboxylate groups of alginate to the calcium forming a chelate structure and a consequent decrease in hydrogen bonding between hydroxyl functional groups. Asymmetric stretching vibration of carboxylate ion shifted to lower wave numbers 1080 and 1021 cm$^{-1}$. When calcium ions replaced sodium ions in the sodium alginate, the charge density, the radius and the atomic weight of the cation were changed and hence, this shifting should be expected.
Fig. 9.5: FTIR- analysis of sodium and calcium alginate membranes.

SEM surface images of PAN support, NaAlg coated PAN, CaAlg crosslinked membranes are presented in Fig. 9.6. PAN porous supports have a pore size of around 50 nm. NaAlg coated PAN membranes were not showing any visible pores at the same magnification. This observation did not change whether the membranes were precipitated in acetone or left to dry. The same morphology was obtained for NaAlg membranes that were crosslinked with calcium chloride.
Fig. 9.6: SEM surface images of up left) PAN support, up right) 1% NaAlg coated PAN precipitated in acetone, bottom left) 1% NaAlg coated PAN dried at room temperature and bottom right) 1% NaAlg precipitated in 5% CaCl₂ for 5 min.

Series of cross-section SEM images were obtained for the free-standing membranes prepared via spin coating then fixed on alumina support. Fig. 9.7 shows a thin layer of alginate polymer with 1% concentration and crosslinked for 5 min in 5% CaCl₂ crosslinker bath sitting on top of a highly porous alumina support.
Fig. 9.7: SEM cross-section images of 1% NaAlg spin coated on glass plate then immersed in 5% CaCl₂/water bath for 5 min. the freestanding membrane is mounted on alumina support.

FIB SEM technique was used to get high-resolution images of the cross-section of the free-standing membranes without disturbing the nanofilm Fig. 9.8.
Fig. 9.8: FIB SEM cross-section images of 1% NaAlg spin coated immersed in 5% CaCl₂/water bath for 5 min placed on alumina support.

AFM height images and corresponding height profile of a section of alginate nanofilm on alumina support is presented in Fig. 9.9 the roughness of the surface of the nanofilm was measured to be 18.2 nm. The thickness of the nanofilm was found to be around 200 nm.

Fig. 9.9: AFM height image and corresponding height profile of 1% NaAlg spin coated then immersed in 5% CaCl₂/water bath for 5 min.

Contact angles were measured of the PAN support and a CaAlg coated PAN. Fig. 9.10 shows a contact angle of around 44° of the PAN support; the membrane coated with 1% NaAlg crosslinked with 5% CaCl₂ for 30 min has a contact angle of 25° indicating a more hydrophilic surface. Contact angle for NaAlg membrane was not possible to measure since the membrane dissolves in water.
Fig. 9.10: Contact angle measurement of water drop on a) PAN support, and b) 1% NaAlg crosslinked with 5% CaCl₂ for 30 min film on PAN support.

9.5 Nanofiltration performance

Composite membranes were prepared via casting of NaAlg/water solution on PAN or XPAN support, afterwards the cast films were left to dry at room temperature or precipitated in a crosslinking bath consisting of calcium chloride dissolved in water for half hour then left to dry. Fig. 9.11 shows UV analysis of feed, permeate and retentate samples of VB12 in methanol and DMF solvent. Two types of alginate thin film composite membranes with two different concentrations were prepared on PAN and tested; another is prepared on a crosslinked PAN support to test the VB12/DMF mixture. A coating with 1% NaAlg leads to dense layers that are capable of rejecting more than 98% of the VB12/methanol and VB12/DMF. However, with 0.5% alginate the rejection is slightly lower. Table 9.1 summarizes the permeance values for the prepared membranes. Using 0.1% alginate concentration apparently is not enough to form defect free dense layers; the rejection did not exceed 34%. Alginate thin film composite
membranes prepared by drying and without crosslinking either showed no flux when 1% concentration was used or very low rejection of 30% for 0.5% alginate concentration.

Fig. 9.11: UV-Vis analysis of feed, permeate and retentate samples of VB12 in methanol and DMF solvents for alginate thin film composite membranes on PAN and XPAN supports.
Table 9.1: Permeance and rejection values of alginate thin film composite membranes.

<table>
<thead>
<tr>
<th>Membrane Type</th>
<th>20 ppm VB12/MeOH Permeance (L/m².h.bar)</th>
<th>20 ppm VB12/MeOH Rejection (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% NaAlg on PAN crosslinked 5% CaCl2 30 min</td>
<td>1.27 ± 0.2</td>
<td>&gt;98</td>
</tr>
<tr>
<td>0.5% NaAlg on PAN crosslinked 5% CaCl2 30 min</td>
<td>1.46 ± 0.3</td>
<td>&gt;85</td>
</tr>
<tr>
<td>0.1% NaAlg on PAN crosslinked 5% CaCl2 30 min</td>
<td>22.93 ± 5</td>
<td>34</td>
</tr>
<tr>
<td>1% NaAlg on PAN Dry</td>
<td>No flux</td>
<td>-</td>
</tr>
<tr>
<td>0.5% NaAlg on PAN Dry</td>
<td>17.19 ± 2</td>
<td>30</td>
</tr>
<tr>
<td>0.1% NaAlg on PAN Dry</td>
<td>33.44 ± 4</td>
<td>0</td>
</tr>
<tr>
<td>20 ppm VB12/DMF Permeance (L/m².h.bar)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1% NaAlg on XPAN crosslinked 5% CaCl2 30 min</td>
<td>0.21 ± 0.1</td>
<td>&gt;98</td>
</tr>
<tr>
<td>0.5% NaAlg on XPAN crosslinked 5% CaCl2 30 min</td>
<td>0.85 ± 0.3</td>
<td>&gt;80</td>
</tr>
</tbody>
</table>

The performance of alginate composite membranes in DMF was outstanding however a crosslinked support was necessary. A free-standing ultrathin alginate film was prepared as described above. Fig. 9.12 show the alginate nanofilm fixed on a 2 cm diameter metal wire ring. And Fig. 9.13 shows the alginate free-standing nanofilm fixed on alumina support.
Fig. 9.12: Photograph of 1% NaAlg nanofilm crosslinked in 5% CaCl₂/water mixture for 5 min.

Fig. 9.13: Photograph of 1% NaAlg nanofilm crosslinked in 5% CaCl₂/water mixture for 5 min fixed on alumina support.
Permeances of different solvents were measured for the alginate nanofilm membranes on alumina support and plotted against the combined solvent property which is a parameter that combined the effect of viscosity $\eta$, solvent size (diameter) $d_m$ and the solubility parameter $\delta_p^{49-50}$. In Fig. 9.14 Methanol, with viscosity of $0.49 \times 10^{-3}$ Pa·s, solubility parameter due to dipole force ($\delta_p$) of 12.3 MPa$^{1/2}$ and diameter of 0.51 nm gave the highest permeance of $48$ L/m$^2$.h. bar. THF ($0.43 \times 10^{-3}$ Pa·s, 5.7 MPa$^{1/2}$, 0.62 nm) gave the second highest permeance of $34$ L/m$^2$.h. bar. Nonpolar toluene ($0.52 \times 10^{-3}$ Pa·s, 1.4 MPa$^{1/2}$, 0.70 nm) surprisingly gave a permeance of $21$ L/m$^2$.h. bar.

![Fig. 9.14: Plot of solvent permeances against the combined solvent properties ($\delta_p/d_m^{2*}\eta$) (Pa$^{0.5}$/m$^2$.Pa.s) for alginate nanofilm on alumina support.](image)

The alginate free-standing membranes show high permeances for many solvents which indicates the chemical stability of these membranes. The solvent permeances of the alginate nanofilms supported by porous alumina are much higher than the permeances of the alginate/PAN composite membranes. The porosity of the alumina support is much
higher and we have no pore penetration due to the preparation method. Filtration of methanol solvent through alginate free-standing membrane for longer time periods was measured and a flux decline of 39% was noticed after 20-hour filtration for such membranes Fig. 9.15.

Fig. 9.15: Pure methanol permeance over time through alginate freestanding membrane.

Alginate free-standing membranes were tested for the Reactive Green dye (MW= 1400, size = 1.7 nm, charge = -6) in methanol, a complete rejection was achieved, the UV analysis of feed, permeate and retentate is presented in Fig. 9. 16. When the as-prepared alginate membranes were tested with the Reactive Green/methanol mixture the permeance was unexpectedly low with 0.06 L/m².h.bar. To enhance the permeance, water was first filtered through the same membrane; water here can act as a swelling solvent or as activation solvent. After filtration the same membrane was washed with methanol and left to dry. After this activation step the Reactive Green/methanol mixture was again
filtered and now a 20 times higher permeance of 1.17 L/m².h.bar was obtained. Reactive Green is negatively charged, for comparison the neutral vitamin B12, which has same size and similar MW like Reactive Green, was used as a neutral marker in methanol. More than 90% rejection was achieved and the UV analysis is presented in Fig 9.17.

Fig. 9.16: UV analysis of feed, permeate and retentate of Reactive Green dye in methanol filtered through alginate freestanding membrane.

The advantages of preparing free-standing membranes is the possibility of laminating it on a more chemically stable or larger pores supports such as alumina as well as avoiding pore penetration which happens during coating step in forming thin film composite membranes. Alginate free-standing membranes supported by porous alumina were used
to filter vitamin B12 marker is harsh solvents such as DMSO, DMF and NMP. Fig. 9.17 exhibits the UV analysis and Table 9.2 summarize the permeance values.

Fig. 9.17: UV analysis of feed, permeate and retentate of Vitamin B12 in methanol, DMF, DMSO and NMP filtered through alginate freestanding membrane.

Table 9.2: Permeance and rejection values of vitamin B12 in different solvents tested through alginate freestanding membranes.

<table>
<thead>
<tr>
<th>Membrane Type</th>
<th>Solvent</th>
<th>20 ppm VB12/solvent Permeance (L/m².h.bar)</th>
<th>20 ppm VB12/solvent Rejection (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% NaAlg crosslinked 5% CaCl₂ 5 min</td>
<td>MeOH</td>
<td>0.82 ± 0.2</td>
<td>&gt;90</td>
</tr>
<tr>
<td>1% NaAlg crosslinked 5% CaCl₂ 5 min</td>
<td>DMF</td>
<td>0.25 ± 0.02</td>
<td>&gt;70</td>
</tr>
<tr>
<td>1% NaAlg crosslinked 5% CaCl₂ 5 min</td>
<td>DMSO</td>
<td>0.15 ± 0.05</td>
<td>&gt;76</td>
</tr>
<tr>
<td>1% NaAlg crosslinked 5% CaCl₂ 5 min</td>
<td>NMP</td>
<td>0.11 ± 0.03</td>
<td>&gt;80</td>
</tr>
</tbody>
</table>
The rejection of vitamin B12 in methanol using alginate free-standing membrane was about 90% with a flux of 0.82 L/m².h.bar. Composite membranes, which are made by laminating a free-standing film on an open, highly porous support, usually show higher solvent fluxes than membranes prepared by solution coating. High permeances were obtained with a number of different pure solvents (Fig. 9.14). However for the membranes where solvent/solute mixtures were tested lower permeances were observed. Nanofilm folding, which results in additional flow resistance might have happened during handling that caused the lower performance. It was also noticed that the flux of Vitamin B12/methanol was one order of magnitude lower than pure methanol. This reduction is caused by the compaction effect as well as the solute-solvent-membrane interaction. 70%, 76% and 80% rejection was achieved with Vitamin B12 in DMF, DMSO and NMP respectively. Although these rejections are not high enough it is evident that alginate membranes can tolerate harsh solvents and it should be possible to achieve a higher rejection with careful optimization of polymer concentration, crosslinker concentration, crosslinking time and nanofilm handling.

To test the stability of the alginate/alumina membrane in more detail, the 2% NaAlg membrane crosslinked with 5% CaCl₂ for 5 min was first tested with water, then with different solvents and finally with water again. Filtration of different solvents was performed at 15 bar. The cell was depressurized after the end of each 3h filtration to change solvent and pressurized again for testing. Fig. 9.18 shows the filtration of different solvents using the same membranes. The stable performance for each solvent indicates that a steady state was reached and no compaction was encountered. Water
filtration was performed at the beginning and the end of the study giving the same performance, which confirms the high chemical stability of alginate membranes toward harsh solvents. Permeances were 20 times lower than membranes prepared with 1% alginate polymer indicating denser to layer.

Fig. 9.18: Solvent filtration using the same free-standing alginate membrane with 2% NaAlg and 5% CaCl₂ 5 min crosslinker on alumina support.
9.6 Conclusions

The fabrication of membranes for OSN on large scale requires large amounts of solvents and the use of sometimes-expensive synthetic polymers and additives. Here we report the utilization of a cheap, biodegradable, renewable and environment friendly polymer as a membrane for OSN making the membrane fabrication process more sustainable. Alginate polymer used in this project is a water-soluble polymer, which allows the substitution of conventional, harsh solvents by greener solvents. The amount of liquid waste generated during the membrane fabrication process can be reduced drastically. In addition the fast crosslinking reaction of this polymer takes place in water and at room temperature. In addition non-toxic calcium chloride is used as a crosslinker with no organic solvent needed making the process safer and reduce the energy consumption. In this project, membranes were prepared using reaction induced phase separation where the alginate is precipitated and crosslinked in the same step, which minimizes toxic waste, energy consumption and costs. In terms of performance alginate membranes proved to be chemically stable in harsh solvents with a MWCO of around 1300 g/mol. Optimization of conditions is still required to achieve higher performances.
9.7 References:


10 CHAPTER 10: Conclusions and recommendations

10.1 Introduction

Chapters 3 through 9 highlighted the search and modification of polymers to serve as filtration media for harsh organic solvent purification from impurities or solute concentration in the presence of solvents. In this chapter, the main conclusions of each project will be summarized and discussed. In addition, future recommendations and strategies, which can be added to this work, will be briefly outlined.

10.2 Conclusions and future recommendations

Desirable properties of membranes for organic solvent nanofiltration are (i) outstanding chemical stability of membrane in wide range of solvents, (ii) high temperature resistivity, (iii) MWCO values of 200 g/mol or more, (iv) membrane materials with low swelling and compaction, (v) high permeance, (vi) cheap, biodegradable, abundant polymers and (vii) easy to scale up membrane process. The ultimate goal is to combine all these objectives in one outcome membrane.

10.2.1 Diamine type for better, functionalized polymers.

Chapter three tackles the synthesis and characterization of two polymers that have good potential in OSN. This chapter deals with condensation polymerization between di-isothiocyanate (-NCS) and diamine monomers. There are many different monomers that can be used for this reaction and each monomer results in a new polymer with different functionalities for better polymer solution preparation, better membrane preparation and
possibilities of chemical modifications. The use of bulky monomers results in an hindered packing of polymer chains resulting in open structures. Using di-diisocyanate (\(-\text{NCO}\)) monomer instead of the monomer mentioned above can result in more mechanically stable polymers, Table 10.1 and Table 10.2 summarizes suggested options of different monomers.

Table 10.1: Diamine monomers that can be used in polymer synthesis.

<table>
<thead>
<tr>
<th>Diamine monomer Name</th>
<th>Chemical structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,4’-Diaminodiphenylmethane</td>
<td><img src="image1" alt="Chemical structure" /></td>
</tr>
<tr>
<td>P-Phenylenediamine</td>
<td><img src="image2" alt="Chemical structure" /></td>
</tr>
<tr>
<td>4-Aminophenyl sulfone</td>
<td><img src="image3" alt="Chemical structure" /></td>
</tr>
<tr>
<td>4,4’-(9-Fluorenylidene) dianiline</td>
<td><img src="image4" alt="Chemical structure" /></td>
</tr>
<tr>
<td>4,4’-(Hexafluoroisopropylidene) bis (p) phenyleneoxy) dianiline</td>
<td><img src="image5" alt="Chemical structure" /></td>
</tr>
<tr>
<td>3,3,3’,3’-tetramethyl-2,2’,3,3’-tetrahydro-1,1’-spiro[indene]-6,6’-diamine</td>
<td><img src="image6" alt="Chemical structure" /></td>
</tr>
<tr>
<td>4,4’-(1,1’-Biphenyl-4, 4’-diylidioxy) dianiline</td>
<td><img src="image7" alt="Chemical structure" /></td>
</tr>
<tr>
<td>4,4’-(1,3-Phenylenedioxy) dianiline</td>
<td><img src="image8" alt="Chemical structure" /></td>
</tr>
</tbody>
</table>
Table 10.2: Diisothiocyanate and Diisocyanate monomers that can be used in polymer synthesis.

<table>
<thead>
<tr>
<th>Diisothiocyanate/Diisocyanate monomer Name</th>
<th>Chemical structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,4’-(perfluoropropane-2, 2-diyl) bis (isothiocyanatobenzene)</td>
<td><img src="image" alt="Chemical structure" /></td>
</tr>
<tr>
<td>4,4’ sulfonylbis (isothiocyanatobenzene)</td>
<td><img src="image" alt="Chemical structure" /></td>
</tr>
<tr>
<td>9,9-bis (4-isothiocyanatophenyl)-9H-fluorene</td>
<td><img src="image" alt="Chemical structure" /></td>
</tr>
<tr>
<td>Bis (4-isocyanatophenyl) methane</td>
<td><img src="image" alt="Chemical structure" /></td>
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</tbody>
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10.2.2 Thin film composite membranes (TFC):

10.2.2.1 TFC via interfacial polymerization:

TFC membranes consist of an ultra-thin “separating top layer” on top of a chemically different porous support. This preparation technique gives more freedom to get a better overall membrane by designing each layer independently for a specific application. Solvent flux is entirely proportional to the top layer thickness if the support does not create any resistance to solvent flux hence the thinner the top layer the higher the flux.

The forth chapter discussed the preparation of thin film composite membranes where the dense selective layer is formed by interfacial polymerization. Diaminopiperazine
monomer reacted with TMC to form a polyamide top layer on crosslinked PTSC support. Diaminopiperazine resulted in higher permeances coupled with relatively higher MWCO values when compared with other diamine monomers. A recent publication discusses the careful preparation of free-standing interfacially polymerized layers using MPD diamine to achieve low MWCO’s in the range of 200 g/mol \(^1\) with high permeabilities omitting the compaction effect from the support beneath.

Microporous organic materials with well-defined pore structures are excellent candidates for highly permeable and selective membranes such as metal–organic frameworks (MOFs) \(^2\) and porous organic cages \(^3\). However, the fabrication of defect-free membranes is technically challenging. Interfacially polymerized polymers of intrinsic microporosity (PIMs) \(^4\) have contorted, rigid backbones resulting in Hindered packing, owing to the shape and rigidity of the component monomers. Interconnected voids of less than 2 nm are created that behave as micropores \(^5\).

Triptycene functionalized aqueous/organic phase monomers:

An emerging strategy for introducing free volume and rigidity into a polymer matrix is the incorporation of iptycenes into the polymer chain. Iptycenes are a unique class of \([2,2,2]\)-ring systems in which the bridges are aromatic rings \(^6\). The simplest member of this class is triptycene, first synthesized in 1942, in which three benzene rings are bridged together about a \([2,2,2]\) tricyclic ring system (Fig. 10.1) \(^7\). Free volume and rigidity are added on two fronts. Firstly, a rigid three-dimensional geometry with a high-energy barrier to molecular deformation creates void spaces between the aromatic bridges and internal to the triptycene moiety. Secondly, the bulky nature of the moiety prevents
efficient packing of both discrete molecules and polymer chains.

Fig. 10.1: Chemical structure of Triptycene moiety.

Previously we mentioned the functionalization of Triptycene with brome Fig. 10.2 we used the brominated triptycene as a crosslinker for the RIPS method. This component could also serve as an organic phase monomer for the preparation of interfacial polymerization triptycene functionalized polyamine layers with high performance.
This brominated triptycene monomer can also undergoes amination reaction to produce aqueous phase monomer.

10.2.2.2 Thin film composite via coating:

Chapter seven and chapter nine feature the preparation of thin film composite membranes via coating. TFC membranes with Pebax coating layers on a PAN support were prepared to filter ethanol/marker mixtures after crosslinking with toluene diisocyanate. Crosslinked Pebax membranes were solvent resistant and successfully survived DMF filtration when prepared on top of crosslinked PAN support. Crosslinking of Pebax TFC membrane with dialkyl halides is also possible and worth being investigated. Contorted alkyl halides crosslinkers would be a good choice to get higher free volume that will allow higher
permeances Fig. 10.3. Sodium alginate coated support membranes also are chemically stable membranes to many solvents. Fillers can be added to the alginate layer to increase the permeance of these membranes. Mixed matrix membranes consisting of metal organic frameworks MOF’s in situ grown into the alginate layer where zinc salts are used as a crosslinker and later then the alginate layer is post treated with a MOF ligand solution.

![Chemical structure of 6,6'-bis(bromomethyl)-3,3,3',3'-tetramethyl-2,2',3,3'-tetrahydro-1,1'-spirobiindene.](image)

Fig. 10.3: Chemical structure of 6,6'-bis(bromomethyl)-3,3,3',3'-tetramethyl-2,2',3,3'-tetrahydro-1,1'-spirobiindene.

10.2.3 Asymmetric membranes

Chapter five explored the possibility of using skinned asymmetric membranes as OSN. PTSC asymmetric ultrafiltration membranes were tailored down to the nanofiltration range using a simple chemical crosslinking reaction with a silane agent. The resulting mixed matrix membranes were chemically stable and had a MWCO of 1300 g/mol. A similar approach can be used to crosslink PTU polymer with GPTMS. (3-Bromopropyl)
trimethoxysilane agent (BPTMS) (Fig. 10.4) is another example of a silane agent that can be used as a crosslinker where the crosslinking reaction attacks the piperazine group and it is at room temperature relatively fast. However heat is needed to achieve the Si-O-Si bond.

Fig. 10.4: Chemical structure of (3-Bromopropyl) trimethoxysilane agent (BPTMS).

10.2.3.1 Cyclodextrin functionalized films via RIPS method:

Chapter six discusses the novel combination of two known phase separation methods in polymer science to form composite membranes. PTSC membranes were crosslinked with alkyl halide crosslinker in a good solvent and the phase separation there was initiated via chemical reaction. The type of crosslinker was proved to affect the outcome dense layer thickness and as a result the permeance value was affected to Fig. 10.5. Also by choosing certain functionalized crosslinkers specific chemical groups that is needed for certain separation can be incorporated. The incorporation of such functionalization is specifically in the dense selective layer where it is needed.
Cyclodextrines are torus-shaped biological super molecules with hydrophilic external surface and a hydrophobic cavity. Because of the molecular-size level, affinity to specific compounds, controllable cavity diameter and easy modification, cyclodextrines are an ideal candidate to form membranes with tunable solvent and solute permeation properties. Using functionalized cyclodextrines (Fig. 10.6) as a crosslinkers in the preparation of RIPS membranes could result in specific incorporation of theses truncated cone molecules in the selective layer for better performances ⁹.
10.2.4 Construction of upper-bond plot for OSN:

In the emerging field of OSN, membranes selection is often based upon the molecular weight cut off (MWCO) values to meet specific application. The MWCO value is the interpolating molecular weight value corresponding to the 90% rejection. However, there is uniformity within the industry, as the techniques for obtaining MWCO values are often not disclosed. Differing methods might lead to inconsistencies, and the selection of a suitable membrane often necessitates the screening of many membranes.

A method that enables the comparison of the MWCO in different solvents would be highly advantageous. Whilst standardized methods have been developed for aqueous NF systems using salts and sugars, a standardized method has yet to be proposed for use in organic solvent systems. Many markers have been used throughout the years to characterize OSN membranes such as PEG’s, dyes and alkanes, however theses markers are different in size, charge and shape and that give inconsistency in comparison. With
uniformly increasing MW, the use of homologous polymers or oligomers are ideal for membrane characterization. As an example styrene oligomers of 200-1000 g/mol are inert molecules that are unlikely to have chemical interactions with the membrane polymer. Many factors must be considered when constructing an upper-bond curve for OSN; the marker shape, size and charge, the filtration solvent and the type of membrane used (thin film composite, asymmetric or freestanding). Livingston group has already initiated the construction of such curves, Fig. 10.7. This curve is summarizing regions of TFC, TFN and ISA membranes using styrene oligomers as a marker in acetone.

![Upper bound curve](image)

**Fig. 10.7:** The permeance of acetone versus rejection of α-methyl styrene dimer (236 g/mol) for TFC, TFN and ISA membranes (Adopted from reference 5).
10.3 References


