

Incorporation of POSS into PVDF water filtration membranes

by

Jonathan Karl Sierke

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Abstract

The use of pressure-driven water filtration using polymeric water filtration membranes is an important technology that has been adopted globally for the purification of water. One polymer, which has favourable properties for use as water filtration membranes is polyvinylidene difluoride (PVDF), due to the high chemical stability and good mechanical properties of PVDF. Two common issues faced with using polymeric water filtration membranes is compaction and biofouling, which reduce the efficiency of the process.

In this thesis, the research is focused on the incorporation of Polyhedral Oligomeric Silsesquioxane (POSS) into PVDF water filtration membranes to reduce the effects of membrane compaction. To combat biofouling, preliminary work has also been conducted on the incorporation of eugenyl methacrylate (EgMA) (an antibacterial agent) into PVDF water filtration membranes.

The first part of this thesis (Chapter 3) investigates PVDF water filtration membranes incorporating 3,3,3-trifluoropropyl POSS (TFP POSS). These TFP POSS/PVDF membranes were investigated by attenuated total reflectance – Fourier transform infrared spectroscopy (ATR-FTIR), scanning electron microscopy (SEM), tensile tests, and stirred cell experiments. The results of the analyses of these membranes indicated that TFP POSS was successfully incorporated into the PVDF membranes, but did not provide improvements in mechanical properties of the membranes, and did not improve the compaction resistance of the membranes either.

In order to provide compaction resistance to the PVDF membranes, a method of cross-linking PVDF with POSS was devised. This method uses thiol-ene addition of octa(3-mercpatopropyl) POSS (thiol POSS) with the alkenes on dehydrofluorinated PVDF (d-PVDF).

The next part of the thesis (Chapter 4) investigated the synthesis of thiol POSS using 3-mercaptopropyltrimethoxysilane (MPTMS). After examining different reaction conditions, a novel method of synthesising thiol POSS was developed, which afforded thiol POSS in a yield of 19.2 %. The structure of thiol POSS was confirmed

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with ¹H, ¹³C, and ²⁹Si nuclear magnetic resonance (NMR) spectroscopies, as well as ATR-FTIR spectroscopy. Following this, the reactivity of thiol POSS to thiol-ene addition reactions using different alkenes and different catalysis was examined. The results of the thiol-ene addition reactions indicated that thiol POSS reacted readily when using 2,2'-azobis(2-methylpropionitrile) (AIBN), or benzophenone/UV-irradiation as catalysts. On the other hand, using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a catalyst provided more selectivity, allowing an organic-solvent soluble octa(EgMA) POSS derivative to be produced.

Following the successful synthesis and modification of thiol POSS with thiolene addition, the dehydrofluorination of PVDF using DBU was investigated, as well the thiol-ene addition of thiols of d-PVDF (Chapter 5). Analysis of PVDF after treatment with DBU in solution (by ATR-FTIR spectroscopy) indicated that, under the conditions used, a treatment time of 4 h provided the largest quantity of alkenes on d-PVDF. Moreover, d-PVDF was found to react readily with thiols, either when the thiols were added together with DBU, or using benzophenone/UV-irradiation with thiols as a post-treatment.

Cross-linked PVDF membranes were then produced using benzophenone/UVirradiation with thiol POSS and d-PVDF, with thiol POSS loadings of 0-10 wt% examined. Analysis of these membranes (Chapter 6) by tensile tests indicated that the Young's modulus was highest for the membrane with 10 wt% of thiol POSS, and that this membrane also showed improved compaction resistance during pure water filtrations.

Finally, preliminary work on investigating the biofouling resistance of EgMA-POSS modified PVDF membranes, membranes incorporating thiol POSS and EgMA was conducted (Chapter 6). EgMA, a known antibacterial, was successfully incorporated into the membranes by benzophenone/UV-irradiation (as indicated by ATR-FTIR spectroscopy). However, bacterial adhesion tests performed on these membranes indicated that changes in the surface morphology of the membranes played a larger role in the extent of bacterial adhesion.

Declaration

'I certify that this thesis does not incorporate without acknowledgement any material previously submitted for a degree or diploma in any university; and that to the best of my knowledge and belief it does not contain any material previously published or written by another person except where due reference is made in the text.'

09/10/2017

J.K. Sierke

Date

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List of abbreviations

| AFM | Atomic Force Microscopy |
|--------------------------------|---|
| Ag ₂ NCN | Silver cyanamide |
| AIBN | 2,2'-Azobis(2-methylpropionitrile) |
| Al ₂ O ₃ | Aluminium oxide |
| AMA | Allyl methacrylate |
| AMMRF | Australian Microscopy and Microanalysis Research Facility |
| ATR-FTIR | Attenuated total reflectance – fourier transform infrared |
| ATRP | Atom transfer radical polymerisation |
| ВНТ | 2.6-Di- <i>tert</i> -butyl-4-methylphenol |
| BSA | Bovine serum albumin |
| СА | Cellulose acetate |
| CA-POSS | POSS covalently bound to cellulose acetate |
| CDCl ₃ | Deuterated chloroform |
| CHCl ₃ | Chloroform |
| CNT | Carbon nanotubes |
| COSY | Homonuclear correlation |
| CuBr | Copper(I) bromide |
| D ₆ -DMSO | Deuterated dimethyl sulfoxide |
| DBTDL | Dibutyltin dilaurate |
| DBU | 1,8-Diazabicyclo[5.4.0]undec-7-ene |
| DI water | Deionised water |
| DMA | Dynamic mechanical analysis |
| DMAc | N,N-dimethylacetamide |
| DMAPS | 2-(N-3-sulfopropyl-N,N-dimethyl ammonium)ethyl |
| | methacrylate |
| DMF | N,N-dimethylformamide |
| DMPA | 2,2-dimethoxy-2-phenylacetophenone |
| DMSO | Dimethyl sulfoxide |
| E. aerogenes | Enterobacter aerogenes |
| E. coli | Escherichia coli |
| EG POSS | Ethylene glycol POSS |
| EgMA | Eugenyl methacrylate |
| EPS | Extracellular polymeric substances |
| EtOH | Ethanol |
| Fe ₃ O ₄ | Iron oxide |
| FTIR | Fourier transform infrared |
| GO | Graphene oxide |
| НА | Humic acids |
| HAsO4 ²⁻ | Hydroarsenate |
| HCl solution | Hydrochloric acid solution |
| НСРМА | 2-hydroxy-3-cardanylpropyl methacrylate |
| HDT | 1,6-hexanedithiol |
| НМВС | Heteronuclear multiple bond correlation |
| HMQC | Heteronuclear multiple-quantum correlation |

| IEP | Isoelectric point |
|---|---|
| IPA | isopropanol |
| КСІ | Potassium chloride |
| KCN | Potassium cyanide |
| M ⁺¹ X ₂ -L | Metal catalyst complexed with a ligand after oxidation with |
| | halogeninitiator |
| MA POSS | Methacrylate POSS |
| MA-POSS | Methacyloxypropyl heptacyclohexyl POSS |
| MEHQ | 4-methoxyphenol |
| MF | Microfiltration |
| Mg(OH) ₂ | Magnesium hydroxide |
| MPA | 3-mercaptopropionic acid |
| MPTES | 3-mercaptopropyl triethoxysilane |
| MPTMS | 3-mercaptopropyl trimethoxysilane |
| MWCNT | Multi-walled carbon nanotubes |
| MX-L | Metal catalyst complexed with a ligand |
| N ₂ | Nitrogen gas |
| Na ₂ HPO ₄ ,2H ₂ O | Sodium phosphate dibasic dihydrate |
| NaCl | Sodium chloride |
| | Sodium phosphate monohasic dihydrate |
| | Sodium hydroxide |
| | National Contro of Excellence in Decalination |
| NE | National Centre of Excenence in Desaination |
| | Non-colvent induced phase congration |
| | Non-solvent induced phase separation |
| | N-methyr pyrrondone |
| | Nacional inagricultas |
| | Nanoparticles |
| | Nanowires |
| | Overnight |
| | Octa(3-hydroxy-3-methylbutyldimethylsilyloxy) POSS |
| | |
| | |
| OMPOSS | Octamethyl POSS |
| OP POSS | Octaphenyl POSS |
| РА | Polyamide |
| PAN | Polyacrylonitrile |
| PBS | Phosphate buffered saline |
| PC | Polycarbonate |
| PE | Polyethylene |
| PEG | Poly(ethylene glycol) |
| PEG POSS | POSS derivative with PEG arms |
| PEGMA | Poly(ethylene glycol) methyl ether methacrylate |
| PES | Polyethersulfone |
| PET | Polyethylene terephthalate |
| PHI POSS | 1,2-propanediol heptaisobutyl POSS |
| PLA | Polylacticacid |
| POSS | Polyhedral oligomeric silses quioxane |
| РР | Polypropylene |

| ppm | Parts per million |
|--------------------------------|--|
| Psf | Polysulfone |
| PSNT | Phosphorylated SiO ₂ nanotube |
| PTFE | Polytetrafluoroethylene |
| p-TSA | p-toluenesulfonic acid |
| PVDF | Polyvinylidene difluoride |
| PVDF-Bz | PVDF with benzoxamine pendant groups |
| PVDF-g-PAMA | PVDF grafted with poly(allyl methacrylate) |
| PVP | Poly(vinylpyrrolidone) |
| PWF | Pure water flux |
| PWF _f | Final pure water flux |
| PWFi | Initial pure water flux |
| RAFT | Reversible addition-fragmentation chain transfer |
| RO | Reverse osmosis |
| ROS | Reactive oxygen species |
| S. aureus | Staphylococcus aureus |
| S. epidermidis | Staphylococcus epidermidis |
| S. mutans | Streptococcus mutans |
| SBA-15 | Type of mesoporous SiO ₂ particle |
| SEM | Scanning electron microscopy |
| SeO ₃ ²⁻ | Selenite |
| SeO4 ²⁻ | Selenate |
| SiO ₂ | Silicon oxide |
| SNT | SiO ₂ nanotube |
| TDI | Toluene-2,4-diisocyanate |
| TEA | Triethylamine |
| TEM | Transmission electron microscopy |
| TEP | Transparent exopolymer particles |
| TFC | Thin-film composite |
| TFP POSS | 3,3,3-Trifluoropropyl POSS cage mixture |
| Tg | Glass transition temperature |
| THF | Tetrahydrofuran |
| Thiol POSS | Octa(3-mercaptopropyl) POSS |
| TiO ₂ | Titanium oxide |
| TIPS | Thermally induced phase separation |
| T _m | Melting temperature |
| TMP | Transmembrane pressure |
| TMS | Tetramethylsilane |
| UF | Ultrafiltration |
| USA | United States of America |
| UTDR | Ultrasonic time-domain reflectometry |
| UV | Ultraviolet |
| UV-Vis | Ultraviolet-visible |
| wt% | Weight percent |
| ZnO | Zinc oxide |
| ZrO ₂ | Zirconium oxide |
| δ | Chemical shift |

٦

Chapter 1 Introduction

1.1 Necessity of water

Having a source of clean water is important for human health.^[1-4] A report prepared by the National Bureau of Economics, USA, indicated that filtration and chlorination of water is associated with ~50 % of the total reduction of mortality, ~75 % of the infant mortality reduction, and ~66 % of the child mortality reduction in major cities in the USA in the 20th century.^[6] Access to clean water is intrinsically linked to human health, with lack of clean drinking water leading to increased incidences of diarrhoeacausing infections,^[7] or exposure to lead.^[8] Water quality also impacts on agriculture, with high levels of boron, for example, reducing crop yields.^[9]

However, many readily available water sources are unsuitable for use by humans, and can contain a range of different contaminants.^[3,4] Contaminants include sodium chloride (when in high concentrations) and other ionic salts, heavy metals (such as lead, chromium, copper, and others), micro-organisms (such as cyanobacteria, water-borne parasites, pathogenic bacteria, and viruses), as well as other inorganic species from soil run-off (such as dirt, clay, etc) and organic species from decayed organic materials. Another potential issue with available water sources are pollutants introduced by human activity.^[3, 4, 10-12] This can occur due to pesticide, herbicide, or fertilizer use, the use of pharmaceuticals (such as antibiotics) entering the water way, and pollutants introduced from industrial processes. Furthermore, the chemicals used for water treatment can also result in harmful pollutants entering the water source.

In order to meet the growing need for clean water, especially with the effect of climate change expected to increase the scarcity of water,^[13] there is a need for methods to purify these water sources so that they can be safely used. One of the prominent techniques to purify water is through the use of water filtration membranes.

1.2 Water filtration membranes

The use of water filtration membranes to purify water has wide utility as a method of water purification.^[14-16] The use of water filtration membranes for water treatment is due to the technique being one of the most effective techniques for the purification of water.^[14-17]

There are several advantages for using water filtration membranes for water treatment compared to conventional treatments. One advantage is that they are capable of removing multiple contaminants at a time, whereas conventional water treatments usually target specific contaminants.^[14] The use of water filtration membranes can also reduce the amounts of chemicals used in water treatment, as filtration through water filtration membranes is a physical process of removing contaminants, whereas some conventional methods are chemical-based.^[16]

The general technique is performed by applying external pressure to a solution (called the feed solution), forcing the solution through a porous material, called a membrane. The membrane acts as a semi-permeable barrier, allowing water to pass through while preventing undesired contaminants from passing through. The solution that is yielded from this process (called the filtrate or permeate) is purified water. A simplified schematic of this process is presented in Figure 1.1.



Figure 1.1 – Simplified schematic of the process of water filtration using water filtration membranes. By applying pressure to the feed solution, the solution is forced to pass through the membrane, which acts as a semi-permeable barrier. This separates the water from the contaminant, yielding purified water as the filtrate/permeate.

The pore size dictates the type of contaminant the water filtration membranes can remove from solution. Based on the pore size, water filtration membranes are categorized into four different types; microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). The different types of membranes with their respective pore size ranges, and the materials that they can remove, can be found in Table 1.1.

3

Table 1.1 - The pore size ranges and typical species rejected of different types ofmembranes. Taken from ref.^[15]

Table has been removed due to Copyright restrictions

As can be seen in Table 1.1, the smaller the pore size of the membrane, the smaller the species that that the membrane can remove from solution. For example, while MF membranes are only capable of removing larger species, such as bacteria, yeasts, and fungi, RO membranes are able to remove inorganic ions, such as sodium chloride, as well.

However, another important parameter to take into consideration is how fast water passes through the membrane or how fast the filtration process can produce purified water (known as the flux). In literature, the relationship between the mean pore size of the membrane, r_m , and the water flux of the membrane, J, has been described by the following equation;^[18-20]

Equation has been removed due to Copyright restrictions

Where Q is the flow rate of water, A is the area of the membrane being tested, TMP is the transmembrane pressure (the pressure drop from the feed-side of the membrane to the permeate side of the membrane), A is the area of the membrane being tested, ε is the membrane porosity (percentage of the volume of pores/empty

space compared to the total volume of the membrane), l is the thickness of the membrane, and η is the viscosity of water.

The important point of the above equation is that $J \propto r_m^2$, which indicates that the water flux of a water filtration membranes is greatly affected by the mean pore size. This is important, as it means that there is a trade-off between flux and the species the membrane can effectively remove from solution. For the most efficient use of water filtration membranes, ideally the pore size of the membrane should be as large as possible, yet still has a high removal of the desired species from solution. The pore size of a given membrane is controlled by the conditions used to fabricate the membrane, which is discussed in the following section.

1.3 Techniques of Membrane fabrication

There are numerous methods by which polymeric membranes can be formed, including phase separation, interfacial polymerisation, stretching, track-etching, and electrospinning (a review of these different methods can be found in ref.^[21]). A summary of the different methods used to fabricate polymeric membranes, in terms of ease of fabrication and the resulting membrane performance and properties, is presented in Table 1.2.

Table 1.2 - Comparison of fabrication parameters, and the resulting membraneperformance and properties, of different methods used to form polymericmembranes. Taken from ref.^[21]

Table has been removed due to Copyright restrictions

Out of the fabrication methods used, phase inversion is one of the more common methods used to fabricate polymeric membranes in literature.^[21] Within phase inversion, there exists four different types, namely non-solvent induced phase separation (NIPS), thermally induced phase separation (TIPS), evaporation induced phase separation, and vapour induced phase separation.^[21-24] Out of all these methods, NIPS is the more common method to fabricate polymeric membranes, ^[21-24] and was the method chosen to fabricate polymeric membranes in this thesis.

1.3.1 Non-solvent induced phase separation

Fabricating water filtration membranes by NIPS is a straight forward method to perform. First, the polymer is dissolved using a good solvent for the polymer, with polymer concentrations typically ranging from 10-20 % by weight.^[25-28]. Co-additives such as poly(ethyleneglycol) (PEG)^[22, 24, 25] or poly(vinylpyrrolidone) (PVP)^[22, 24, 26] are usually included in the solution as well, as pore forming agents. This solution (polymer, solvent, and co-additives) is referred to as the casting solution.

Second, the casting solution is cast on to a glass plate (to fabricate unsupported membranes), or on to backing material, such as non-woven fabrics (to fabricate supported membranes). To ensure that the casting is reproducible, the casting solution is cast at a specific film thickness. This is done using a device such as a Doctor's blade, a casting knife, or a film applicator.

Third, the cast polymer-solution film is then immersed into a coagulation bath, which is filled with an appropriate solvent. The solvent in the coagulation bath needs to be a non-solvent for the polymer, while also being fully miscible with the solvent used to form the casting solution. Upon contact between the polymersolution film and the non-solvent of the coagulation bath, the exchange of the nonsolvent with the organic solvent of the polymer solution film leads to the polymer precipitating. This results in the formation of the membrane as a porous polymeric film.

Finally, the "as formed" membrane is soaked and/or washed, usually with the solvent used in the coagulation bath. This is done to remove the residual solvent (used to dissolve the polymer), as well as residual pore forming agent.

The process by which the polymer precipitates and forms the membrane is referred to as demixing. Demixing of the polymer from the solution phase occurs due to the exchange of the solvent (used to dissolve the polymer in the casting solution) with the non-solvent (solvent in the coagulation bath), which results in the polymer precipitating.^[29-31] The demixing process is controlled by the rate at which solvent and non-solvent exchange occurs.^[29-32] This is important, as the membrane morphology (and subsequently, its filtration properties) changes depending on the demixing process, as outlined in the following text.

For the situation where rapid demixing occurs once the polymer-solution film is immersed in the coagulation bath, the membrane forms an asymmetric morphology, with a dense skin-layer at the top with a layer of macrovoids (see Figure 1.2, left image).^[26-28, 31-33] When delayed demixing occurs, the formation of macrovoids is suppressed, and the cross-section of the membrane shows a more sponge-like morphology which is more homogenous (see Figure 1.2, right image).^[26-28, 31-33]

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Figure 1.2 – Scanning electron microscopy (SEM) images of the cross-sections of PVDF membranes with asymmetric morphology (left) and with sponge-like morphology (right). Taken from the work of Kuo et al.^[33]

Control of the membrane morphology can be achieved by controlling the rate of the demixing process, which can be done by altering the key parameters of the NIPS process. Changing the casting solution composition (solvent, polymer concentration, addition of additives/additive concentration),^[22, 24-28, 31] changing the time of exposure of the cast polymer-solution film before immersion in the coagulation bath,^[24, 28] as well as changing the coagulation bath composition (solvent and temperature)^[24, 27, 28, 33, 34] are all ways that can be used to produce membranes with different morphologies. This allows polymeric membranes to be prepared with different pore sizes^[24-26, 28, 33] (which controls the separation properties of the membrane), which allows the membrane to be tailored for a specific application.

A good example of the different membrane morphologies produced can be found in the work of Cheng et al.^[27] In their work, they compared the morphologies of polyvinylidene difluoride (PVDF) membranes formed using the same casting solution composition, but changed the coagulation bath composition. They compared the morphologies of PVDF membranes formed using a coagulation bath of 100 % water, or with a coagulation bath of 75 % DMF and 25 % water (by volume). Scanning electron microscopy (SEM) images of the membrane cross-sections and membrane top-surfaces are presented in Figure 1.3. To note is that in the crosssectional images, the top-surface is facing the bottom of the image. It can be seen that the membrane produced using the coagulation bath of 100 % water resulted in the membrane having the asymmetric morphology, possessing a layer of finger-like macrovoids sitting atop a porous, spongey-layer (Figure 1.3, A-1), while the topsurface is dense and shows little pores (Figure 1.3, A-2). In comparison, the membrane produced using the coagulation bath of 75 % DMF and 25 % water by volume shows a more homogenous cross-section (Figure 1.3, B-1), and the top-surface has a similar structure to the membrane cross-section (Figure 1.3, B-2).

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Figure 1.3 – SEM images of PVDF membranes prepared in either a coagulation bath of 100 % water (A-1 – membrane cross-section, A-2 – membrane topsurface) or a coagulation bath of 75 % DMF and 25 % water by volume (B-1 – membrane cross-section, B-2 – membrane top-surface). From the work of Cheng et al.^[27]

1.4 Issues with water filtration membranes – flux decline

Although the use of water filtration membranes is an important method of water purification, during the filtration the water flux declines, due to several different issues which are outlined in the following. The flux decline results in the filtration being less efficient, requiring longer filtration times to achieve the desired volume of water, or increased operating pressure to maintain the desired rate of water output. Three of the main issues that cause flux decline during filtration are fouling (compounds/materials adhering to the membrane surface), biofouling (microorganisms forming biofilms on the membrane surface), and membrane compaction (compression of the membrane). The combined effects of these mechanisms of flux decline can result in the shutdown of RO plants in extreme cases,^[35] and can mean that increasing the operating pressure no longer results in an increase in flux.^[36, 37] Therefore understanding these mechanisms of flux decline (fouling, biofouling, and compaction) is important, and are discussed individually in the following sections.

1.4.1 Fouling

Fouling of membranes during water filtration refers to the process whereby various substances in the solution (referred to as foulants) accumulate on the membrane surface and/or plug the pores of the membranes.^[38-40] This greatly increases the hydraulic resistance of the membrane, resulting in severe decline in the flux.^[38-40] There are many different substances that can foul water filtration membranes, including biopolymers (such as humic acids (HA), polysaccharides, proteins), particles (dirt, dust, sand, etc), fats, oils.^[38-40] For RO and NF membranes, precipitation of ionic salts on the membrane is an additional source of fouling.^[41, 42]

Since almost any substance in solution can act as a foulant, preventing fouling completely is very difficult. Therefore, there has been continued research into understanding the fouling process, to identify ways to mitigate (as much as possible) the flux decline of water filtration membranes due to fouling. Several key factors have been identified which can affect the fouling of membranes, which are discussed in some detail in the following section.

1.4.1.1 The membrane surface

The properties of the membrane surface have been shown to greatly affect the initial fouling of polymeric membranes. The main properties of the membrane surface that govern the fouling potential includes the surface hydrophobicity, the surface roughness, and the surface charge. However, once adhesion of foulants occurs, the surface properties of the membrane play less of role on the flux decline after long periods of filtration, ^[37, 43, 44] though still greatly effects how rapid the flux decline is.

1.4.1.1.1 Surface Hydrophobicity

The hydrophilicity of a membrane surface has been demonstrated to affect the fouling potential of polymeric membranes. Generally, more hydrophilic membrane surfaces show less fouling than hydrophobic membrane surfaces, showing less flux decline during the filtration due to fouling.^[45-49] Moreover, membranes with more hydrophilic surfaces also show greater improvements in flux recovery after cleaning the membrane after fouling.^[50] The improvement in fouling resistance with more hydrophilic membrane surfaces is attributed to the formation of ordered layers of water at the membrane surface, which provides a repulsive interaction for foulants attempting to adhere to the membrane.^[51] As most of the polymeric materials used to make membranes, such as PVDF, polysulfone (Psf), and polyethylene (PE) are hydrophobic in nature, these membranes show greater amounts of fouling compared to membranes with more hydrophilic properties, such as cellulose and cellulose acetate (CA).^[50, 52] Modification of the membrane surface with a hydrophilic layer is also a common method to reduce fouling, as well as improve the recovery of the water flux after cleaning.^[46, 53, 54]

1.4.1.1.2 Surface Roughness

The surface roughness of the membrane also plays a large role on the fouling of membranes (and potentially, has the largest effect on fouling compared to the surface hydrophobicity and surface charge).^[55, 56] Li et al.^[55] subjected different commercial RO membranes (with differing surface properties) to filtration under different conditions (ionic strength, pH, bovine serum albumin (BSA), sodium alginate, initial operating pressure). It was found that the membrane with highest surface roughness (as measured by atomic force microscopy (AFM)) typically showed the largest flux reduction, regardless of other conditions examined. This was attributed to be due to the larger surface area of the membrane surface providing more area for foulants to adhere, while also foulants deposited in valleys on the membrane surface become more difficult to dislodge by the flow of the solution. A schematic of this mechanism is presented in Figure 1.4. The correlation between higher surface roughness with increased fouling has been observed with other foulants, such as colloids, ^[49, 56, 57] BSA, ^[37] and bacteria, ^[58, 59]. Modelling has indicated that fouling from colloidal particles is worsened by rough surfaces, due to the valleys producing localised sites of favourable adhesion/reduced repulsion. However, this
does depend on the size of the valleys relative to the size of the particles in question.^[60, 61]

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Figure 1.4 – Diagram of the effect of the membrane surface (patterned shape) roughness on the adhesion of foulant (coiled lines), with the arrows showing the direction of water flow. With a smooth surface (a) the foulant is more exposed to the water flow, preventing the foulant from accumulating excessively on the surface as the foulant gets dislodged. With a rougher surface (b), more foulant accumulates on the surface, due to a combination of greater surface area to adhere to, as well as foulants depositing in valleys, which protects from the water flow. Taken from Li et al.^[55]

1.4.1.1.3 Surface charge

The surface charge of the membrane can play a significant role in the fouling potential of the membrane. Many of the foulants present in natural waters (particularly organic foulants, such as proteins, nucleic acid, humic acids, and polysaccharides) possess a charge in solution, though this is often pH dependent.^[37, 47] The surface charge of a membrane can often provide a source of electrostatic repulsion, reducing the extent of fouling from these charged species.^[37, 47, 49, 62] However, this is only if the membrane surface and the foulant both possess the same charge. If the membrane surface and foulant possess opposing charges, due to electrostatic attraction, the extent of fouling is worsened.^[49] The extent of which the surface charge of membrane affects the fouling process also depends on the solution being filtered. This is because the presence of dissolved ionic compounds can mask the charge both of the foulant and the membrane surface, resulting in worse fouling.^[37, 46, 63] Not only do the ionic salts mask the surface charge of the membrane from the foulant, but it also reduces the electrostatic repulsion between foulant molecules, allowing the foulant to form a more dense fouling layer on the membrane surface.^[37, 46, 63]

In the case of mixed foulants, which are oppositely charged in solution at the same pH, increasing ionic strength can reduce the extent of fouling. Shielding of the charge lessens the electrostatic attraction.^[64]

1.4.1.2 Foulant and solution properties

Although the membrane surface does play a significant role in the fouling of polymeric membranes, the properties of the foulants and the composition of the solution being filtered play a large role as well. Some of the key properties include the isoelectric point (IEP) of the foulant and the pH of the solution, the presence of divalent cations, as well as the presence of microorganisms. These points are discussed in the following.

1.4.1.2.1 The isoelectric point

The IEP is the pH at which, for a given substance, the net charge is zero.^[65] Many foulants (particularly organic foulants) are known to typically produce worse fouling at the pH of their IEP,^[37, 64] and show increased forces of adhesion to membrane surfaces at their IEP.^[66] This is due to the charge repulsion between the membrane surface ^[64] ^[37, 49] and the foulant being minimised, which allows the foulant to more readily to adhere to the membrane surface.^[37, 64, 66] At their IEP, proteins and humic acids are able to more quickly form a fouling layer, as the charge repulsion between the foulant to more the foulant molecules are minimised.^[64] The molecules also typically possess more compact shapes,^[63] allowing the foulants to form more dense fouling layers.

1.4.1.2.2 Divalent cations

The presence of Ca²⁺ or Mg²⁺ cations in solution can also result in worsening of organic fouling, ^[37, 47, 55, 62, 67-71] due to the formation of calcium-complexes. ^[46, 68, 71] These can be mitigated by the inclusion of a competing ligating agent, such as ethylenediaminetetraacetate. ^[68, 69] The presence of Ca²⁺ can form complexes between the membrane surface and the foulant, such as that observed between a cellulose UF membrane and dextran. ^[72] The same study did not show a similar effect with Ca²⁺ concentration on flux decline with a polyethersulfone UF membrane, which may be due to the different functional groups of the different polymers. ^[72]

1.4.1.2.3 Microorganisms

Microorganisms in the solution (such as algae and bacteria) are a large source of fouling in water filtration, the cells acting as foulant particles.^[73-76] Many microorganisms also produce extracellular polymeric substances (EPS), which are a mixture of polysaccharides, proteins, and nucleic acids,^[77] and are a significant source of fouling as well.^[73, 76, 78] The lysing of algae cells (either by hydrodynamic shear, or simply to cell death overtime) results in much worse fouling, due to the release of the cellular contents which are much more varied in size and in terms of chemical properties compared to the cells alone.^[73, 74] Microorganisms adhering to the membrane surface can also form biofilms on the membrane surface which also causes flux decline, which is referred to as biofouling, which is discussed in detail in section 1.4.2.

1.4.1.3 Synergistic effects of foulants

Many studies have focused on the effects of single foulants, which although does provide important data, is not reflective of most water sources, which typically contain multiple foulants.^[14, 79] Studies have shown for example, that the combination of polysaccharides with proteins results in worse flux decline during filtration compared to either the polysaccharide or protein alone.^[46, 55, 62] Similarly, the fouling effect of two different proteins combined, BSA and lysine, was found to produce far more flux decline than with the individual proteins alone.^[64] The combination of silica nanoparticles with humic acids also produced more rapid and typically greater flux decline than with the individual foulants alone.^[70] Other examples can be found in literature demonstrating the greater fouling of membranes with combinations of foulants, as compared to single foulants in solution.^[48, 80, 81]

The synergistic effect of foulants is attributed to several different effects. The first is that the adhesion of foulants to the membrane surface masks the underlying surface chemical properties of the membrane surface, which can allow other foulants to adhere more readily, resulting in worse fouling.^[64, 70, 80] Another is that the combination of differently sized foulants can produce a more densely packed fouling layer on the membrane surface, which leads to thicker foulant layers, and greater flux decline.^[70, 81] Adhesion of organic foulants to colloids has also been indicated as a source of increased fouling, by altering the surface properties of the colloid particles

such that the repulsive forces between colloid particles is reduced.^[80] Finally, foulants with opposite charges in solution can produce worse fouling due to electrostatic attraction between the two different foulants, such as that observed with BSA and lysine.^[64]

1.4.2 Biofouling

Biofouling of polymeric membranes occurs when microorganisms establish a biofilm on the membrane surface, resulting in reduced water permeation, or increased TMP to maintain the flux.^[48, 82, 83] Though similar to organic fouling, biofouling differs in that the source of the fouling comes from the microorganisms themselves, and are typically much more difficult to remove once the biofilm has been established. ^[58, 84, 85] The following sections discuss the formation of biofilms on polymeric membranes, the membrane surface properties that resist cell attachment, and strategies used to manage biofouling.

1.4.2.1 Biofilm formation

The formation of a biofilm begins when microorganisms attach to the membrane surface, which then secretes EPS to form the biofilm.^[86, 87] The biofilm plays a large role in improving the survival of the microorganism, improving the acquisition of nutrients, as well as protecting the microorganism from antimicrobial substances.^[86, 87]

An important facilitator of biofilm formation found in natural waters is known as transparent exopolymer particles (TEP).^[88] TEP is similar to EPS, comprising of polysaccharides, proteins, and nucleic acids.^[89-91] TEP exists as transparent microscopic particles in water, ranging in size from 0.4-200 µm.^[89-91] TEP acts not only as a fouling agent that causes flux decline,^[90, 92] but also acts as a platform for bacterial colonies to grow in natural waters,^[89] and has been implicated as increasing the attachment of cells to the surfaces of membranes.^[91, 92] There is evidence that TEPs are also major contributors to the biofilm formation, acting as a major constituent of the initial biofilm.^[88, 92]

1.4.2.2 Membrane surface properties that minimise cell attachment

As with fouling, membranes which are more hydrophilic, smoother, and more negatively charged (if the cells are negatively charged) typically show reduced rates

of cell attachment and biofouling.^[48, 51, 93] Membranes with high salt rejection (such as RO and NF membranes) can also undergo more rapid cell attachment, due to the localised increase in salt concentration at the membrane surface, which reduces electrostatic repulsion.^[51] As with fouling, the adhesion of foulants to the membrane surface masks the surface properties of the underlying membrane surface, which can either reduce or increase the rate of cell attachment. For example, in one study, exposing a membrane to BSA or sodium alginate could actually reduce the rate of cell attachment.^[71] In another study, exposing the membrane to BSA or humic acid solutions increased the flux decline due to biofouling. However, exposing the membrane to sodium alginate reduced the flux decline due to biofouling.^[83] Similarly, exposing the membrane to more complex mixtures of foulants, such as sterilised bacterial broth^[58] or trypic soy broth,^[43] led to greater biofilm coverage on the membrane surface,^[58] thicker biofilms,^[43] and produced larger reductions in the membrane flux (compared to a membrane not exposed to the foulants before the filtration).^[43] These results corroborate with research examining biofouling with TEP,^[91, 92] which together indicates that the composition of the foulants plays an important role in facilitating cell adhesion, which cannot be modelled with single foulants.

Unfortunately, even using membranes that possess favourable surface properties to resist cell adhesion, cells are still able to attach to the membrane surface. This is due to the membrane surface not being completely homogenous, with localised heterogeneities allowing cells to adhere. Once these cells are adhered to the membrane surface, they then act as focal points for other cells to attach.^[51, 71] This observation is significant as it implies that even with membrane surfaces that have been tailored to reduce cell attachment, the membrane will still undergo biofouling, though at a slower rate. Therefore, understanding how to manage biofouling is an important part of using water filtration membranes.

1.4.2.3 Managing biofouling

Since cell adhesion cannot be prevented entirely, managing biofouling through cleaning treatments is important to maintain the membrane performance. However, removal of the biofilm is difficult, as biofilms are not removed well with common cleaning methods used to remove foulants, such as the washing with surfactants,

and/or alkaline or acidic solutions.^[58, 84, 85] Moreover, biofilms have been demonstrated to improve the survival of the cells to many different types of disinfection.^[84, 94-97] This is problematic, as incomplete removal (and disinfection) of the biofilm leads to the biofilm being re-established more quickly.^[58, 85, 96]

A common method to control biofouling is by chemical means, such as hypochlorite treatment, which has been shown to be effective at removing biofilms.^[58, 84, 96] However, hypochlorite has been shown to degrade polymeric membranes (including PVDF membranes),^[98-101] and also introduce toxic by-products into the water.^[102-107] Other biocidal treatments, such as with chlorine dioxide, chloramines, and ozone also produce toxic by-products.^[102, 104-107] UV-irradiation can also be used to control biofouling water treatment systems,^[108] as well as chlorine from water,^[109] though the use of UV to clean membranes is limited, as excessive UV exposure is known to degrade polymeric membranes.^[110, 111]

So far, the best way to control biofouling is prevent the formation of the biofilm in the first place, by pre-treating the feed water to remove microorganisms before they reach the membrane. Autopsies of RO membranes from a desalination plant in Ceuta after ~8 years of operation were found to be free of biofilms, due to a combination of chlorination disinfection of the feed water before entering the RO line in the desalination plant, as well as weekly cleaning of the RO membranes with a biocidal agent, 2,2-dibromo-3-nitrosilpropionamide (author possibly meant 2,2-dibromo-3-nitroilopropanamide).^[112] In a pilot plant set-up designed to mimic the pre-treatment lines of an open sea water intake RO installation, continuous dosing of chlorine into the raw seawater was found to be able to prevent biofilm growth on the pipes and tank walls, whereas intermittent high chlorine dosages every 15 days was ineffective. Continuous chlorination also provided lower total aerobic bacteria counts in the permeate.^[113] Though these methods do reduce the burden of the chemical treatment on the polymeric membrane, these methods do use large amounts of chemicals to be effective.

1.4.3 Compaction

Membrane compaction refers to the process whereby the membrane deforms under the applied pressure during the filtration, resulting in reductions in water flux. The effect of compaction is most easily observed during the filtration of pure water,

where a notable decline in the pure water flux (PWF) occurs over time.^[114-118] The membranes before and after filtration generally show signs of physical compression as well, such as collapsed macrovoids in membrane cross-sections,^[116, 118, 119] or reductions in membrane thickness.^[114, 117-119]

1.4.3.1 General effect of compaction on flux

The effects of compaction during the filtration shows an asymptotic-like trend on the membrane flux. At the start of the filtration, there is a rapid decline in the flux, with the rate of flux decline then decreasing quickly with time (particularly within the first hour of the filtration), until a relatively stable flux is achieved.^[114, 120, 121]

Another general characteristic of compaction of polymeric membranes it that there shows both a reversible (recoverable) and irreversible (permanent deformation) on the membrane flux.^[114, 118] This is attributed to the viscoelastic behaviour of polymers, with reversible compaction demonstrating the elastic response, while irreversible compaction due to relaxation and creep of the polymer.^[122] From an application standpoint, the extent of reversible and irreversible compaction that a membrane experiences at a given pressure is not as important as the overall extent of compaction, as the loss of flux affects the efficiency of the filtration regardless of whether the compaction is reversible or not. However, it is important to know what factors can cause compaction, and the effects of compaction of the filtration performance of the membranes.

1.4.3.2 Understanding compaction

Towards understanding how the membrane deforms with the decline in flux due to compaction, Peterson et al.^[114] developed a method of measuring the membrane thickness during filtration, using ultrasonic time-domain reflectometry (UTDR). The set-up and basic principle of function is described in Figure 1.5. A simplified explanation is provided, however readers are encouraged to see the paper^[114] for a more in-depth explanation. The mode of action of the UTDR is as follows. An ultrasonic transducer is affixed to the top of a high-pressure cross-flow cell, which produces an acoustic signal. As the signal travels through the cross-flow cell, the acoustic signal is partially reflected back to the transducer at the interfaces of materials with different acoustic impedances. By knowing the speed of the acoustic signal was sent and

the reflected signal is received can be used to calculate the distance of the transducer to that interface. During the filtration, any thickness change in the membrane due to compaction results in a change in the time delay of sending and receiving the acoustic signal, as the distance of the transducer to the membrane/pure water interface will change. Assuming the other components of the cross-flow cell do not show any appreciable change in thickness during the filtration, the change in the time delay of the acoustic signal allows the determination of the thickness change of the membrane using the equation below;

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Where Δl = the change in membrane thickness, c = speed of the acoustic signal through pure water (1500 m.s⁻¹), and Δt = the measured change in the time delay of sending the acoustic signal and receiving the reflected acoustic signal.

Using UTDR, both the changes in membrane thickness and the flux can be measured simultaneously, allowing a correlation to be made between changes in membrane thickness and the flux. UTDR can also measure the change in membrane thickness due to recovery from compaction after the pressure is released, which also allows an understanding of not only how the membrane thickness responds to changes in pressure, but also how this affects the flux of the membrane.

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Figure 1.5 – Diagram describing the set-up and principle of the measurement using ultrasonic time domain reflectometry (UTDR) for measuring changes in membrane thickness during cross-flow filtration. An ultrasonic transducer is affixed to the top of the high pressure cross-flow cell (left image) for transmitting and receiving the ultrasonic signals. At the interface of surfaces of materials with different acoustic impedance, the ultrasonic signal is partially reflected. In this situation, a partial reflection of the ultrasonic signal occurs at the interface of the top aluminium plate and feed solution (producing signal A), the interface of the feed solution and membrane surface (producing signal B), and the interface of the bottom membrane surface and the porous support (providing signal C). As the thicknesses of the aluminium plates, porous support, and feed solution do not vary during the filtration, the change the arrival time of signal B can be used to calculate the distance of the transducer to the membrane surface in real-time. This allows a measurement of the membrane thickness during the filtration. Image taken from Peterson et al.^[114]

Through the studies using UTDR and others, the understanding of membrane compaction has greatly improved. Compaction of polymeric membranes causes a significant loss of membrane flux, though the flux decline is variable, ranging from 35-57 %,^[123] 14-70 %^[117] 43-62 %,^[123] 20-40 %,^[124] or 17-50 %^[115] during the filtrations of pure water. Therefore, understanding the factors that affect the compaction behaviour of polymeric membranes is required if the filtration process using these membranes is to be as efficient as possible, while maintaining the required output.

1.4.3.3 Pressure-dependence of compaction

The effect of transmembrane pressure on the flux can be described using a modified form of Darcy's Law;^[122, 125]

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Where J is the flux through the membrane, TMP is the transmembrane pressure, μ is the solution viscosity, and R_m is the hydraulic resistance of the membrane (each membrane has its own value of R_m). Assuming the other factors remain constant,

Darcy's Law predicts that *J* will increase linearly with increasing TMP. However, when using polymeric membranes to filter pure water, it has been observed that the measured flux does not show a linear increase with increasing TMP, and instead the flux is typically lower than that predicted with Darcy's Law. Controlling the other factors (*TMP*, μ) indicates that the hydraulic resistance of the membranes must be changing during the filtration, which is attributed to membrane compaction. In comparison, using a rigid, α -alumina ceramic membrane for the filtration did not show this effect in the TMP range of 5-75 kPa.^[125] Several studies^[122, 125, 126] have used the following equation to describe the changes in the membrane hydraulic resistance with TMP;

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Where $R_{m,0}$ is the initial membrane hydraulic resistance (before the membrane is compacted), k_c is a constant, and n is the compressibility factor. Typically, the stabilised flux (the flux of the membrane after compaction) of polymeric membranes follows the above relation well when $n \approx 0.8$.^[122, 125, 126] Replacing R_m in the equation for flux yields the following equation;

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Converting the flux, J, to the water permeability, k (dividing the flux by the TMP) yields the following relationship;

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The water permeation can be thought of as the efficiency of the filtration process with respect to pressure. The above equation for k is significant, as this indicates that although increasing the TMP (done by increasing the operating pressure) will increase the flux, the water permeation will decrease with increasing pressure. It should be noted that the above equations apply only once the hydraulic resistance of the membrane has effectively stabilised (in other words, the membrane has reached its compaction limit at the given TMP). However, this relationship does not work well with low TMPs (TMPs < 20 kPa),^[125] as the morphology (and porosity) of the membrane also plays a role in the compaction behaviour of the membrane (covered

in Section 1.4.3.4).^[122] These results are corroborated by other researchers, which have also found that increasing the operating pressure/TMP results in greater reductions in water permeability,^[118, 125, 127] or greater percentages of flux decline during filtration.^[121, 126]

Higher pressures do not just increase the overall extent of compaction, higher pressures also result in more irreversible compaction.^[127] This effect can be observed from the results of experiments conducted by Stade et al.^[118] using UTDR (see Figure 1.6). As can be seen in Figure 1.6, compacting the same membranes at 5 bar of pressure for 2.5 h, and then measuring the permeability at 1 bar again, shows a significant reduction in permeability at 1 bar before and after compaction at 5 bar. This indicates that the membranes underwent greater quantities of irreversible compaction at 5 bar of pressure than at 1 bar of pressure.

It is interesting to note that the effect of pressure on thickness of the membranes does not always show a similar trend to the changes in permeability. Studies have shown that some polymeric membranes show greater reductions in membrane thickness with increasing pressure, ^[118, 119, 121, 127] such as with the UC030 membrane in Figure 1.6, this is not always the case. As discussed in the following section, the compaction behaviour of polymeric membranes also depends on the morphology of the membranes.

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Figure 1.6 – Effect of pressure on membrane compaction using UTDR, measuring the changes in membrane thickness (left graph) and permeability (right graph) of three different commercial membranes. The measurements on the membranes involved first measuring the stabilised thickness/permeability at 1 bar of pressure, then after 2.5 h at 5 bar, the flux and thickness was remeasured at 1 bar. Image from Stade et al.^[118]

1.4.3.4 Influence of membrane morphology on compaction

The membrane morphology plays a large role not only in the filtration properties of the membrane, but also on the compaction behaviour of the membranes. Modelling of the compaction behaviour of polymeric membranes^[128] has indicated that membranes with tortuous pore morphologies, such as polymeric membranes formed by NIPS,^[128] tend to show greater susceptibility to compaction the larger the membrane porosity. While the membrane permeability is typically higher with a larger membrane porosity, the increased susceptibility to compaction can cause the membrane to have a lower permeation at higher pressures. This has been demonstrated experimentally, by the work of Stade et al.^[118] using a combination of UTDR and SEM. In their work the compaction performance of three different commercial flat sheet polymeric UF membranes designated as UC030 (regenerated cellulose top-layer with polyethylene terephthalate (PET) backing), UH030 (hydrophilic polyethersulfone (PES) top-layer with a PE/polypropylene (PP) backing), and UP020 (PES top-layer with a PE/PP backing) were compared. Examining the SEM images of the membrane cross-sections before filtration (Figure 1.7) shows that the UC030 membrane possesses the largest macrovoids in the membrane cross-section (Figure 1.7, left image), some almost spanning from the top-surface to the bottom of the membrane. The cross-sections of the UH030 and UP020 membranes (Figure 1.7, middle and right image, respectively) possess much smaller macrovoids in comparison.

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Figure 1.7 – SEM images of membrane cross-sections studied in the work of Stade et al.^[118] before UTDR experiments. Membranes are commercially sourced, and are designated UC030 (leftimage), UH030 (middle image), and UP020 (right image). Taken from Stade et al.^[118]

Analysis of these membranes by UTDR, giving both the membrane thickness with the measured pure water permeability, are shown in Figure 1.8. It can observed

that with 1 bar of pressure, the UC030 membrane showed a far higher pure water permeability than the either the UH030 or UP020 membranes (Figure 1.8, dashed lines). Upon increasing the pressure to 3 bar however, the pure water permeability of UC030 dropped to become slightly lower than both the UH030 or UP020 membranes. Moreover, the difference in the pure water permeabilities of the different membranes increased the greater the applied pressure.

In terms of membrane thickness (also from the UTDR experiments, Figure 1.8, solid lines), the UC030 membrane always showed a larger reduction in membrane thickness than the other two membranes. The UC030 membrane was also observed to become more compacted with increasing pressure, while the other membranes do not show a significant reduction in membrane thickness.

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Figure 1.8 – Results of UTDR experiments, providing simultaneous pure water permeability (dashed lines) and membrane thickness (solid lines) measurements of three different commercial membranes (UC030, UH030, and UP020) with increasing operating pressures. Experiment involved measuring the pure water permeability and membrane thickness at 1 bar until stabilisation was reached, then repeating the process for sequentially higher pressures. After the measurements at 7 bar, the pressure was reduced to 0.15 bar to examine compaction recovery in terms of membrane thickness. Taken from Stade et al.^[118]

Correlating the SEM images of the membrane cross-sections (Figure 1.7), and the results of the UTDR experiments (Figure 1.8), it can be asserted that the larger macrovoid size has resulted in greater membrane compaction, both in terms of

reduction in membrane pure water permeability, as well as much greater reductions in membrane thickness. The large change in pure water permeability of the UC030 membrane from increasing the pressure from 1 to 3 bar (Figure 1.8) is attributed to the collapse of the macrovoids in the membrane cross-section. This can be observed in SEM images of the cross-sections of the different membranes (Figure 1.9), where there is a noticeable compression of the macrovoids of the UC030 membrane, while the UH030 and UP020 membranes show much less change.

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Figure 1.9 - SEM images of membrane cross-sections studied in the work of Stade et al.^[118] after UTDR experiments. Membranes are commercially sourced, and are designated UC030 (leftimage), UH030 (middle image), and UP020 (right image). Scale bar is 25 μm. Images sourced form Stade et al.^[118]

The results of this study agreed with those conducted by others. The membranes with cross-sections with larger-sized macrovoids, and larger membrane porosities, tended to show greater susceptibility to compaction, in terms of reduction of pure water permeability^[116, 122, 123] and in the reduction in the membrane thickness.^[114, 116, 122]

1.4.3.5 Compression of the skin-layer

The work of Stade et al.^[118] also highlighted an important characteristic of membrane compaction in that compaction of the skin-layer of the membrane plays a large role in the loss of pure water permeability.^[114] Examining the results of the UTDR experiments again (see Figure 1.8), it can be observed that all three membranes examined show reductions in pure water permeability with increasing pressure. This is despite the UH030 and UP020 membranes showing minimal changes in overall membrane thickness with increasing pressure. The UC030 membrane, on the other hand, gave a very different result, showing larger and larger reductions in membrane thickness with increasing pressure (Figure 1.8). However, while the UC030 membrane shows a large reduction in pure water permeability from increasing the pressure from

1 to 3 bars, the reduction in permeability beyond 3 bars is a similar rate to the UH030 and UP020 membranes.

The reason the changes in the membrane thickness do not correlate with reduction in permeability is due to the structure of the pores in the skin-layer. The pores in the skin layer are not perfectly straight channels, but are actually tortuous and winding. As the channels of individual pores are orientated in random directions, they can be orientated such that as the skin-layer is compacted, the walls of the pores become pressed closer together. This effectively reduces the pore size in the skin-layer, restricting the flow of water through the membrane (see Figure 1.10).^[128] This effect can also result in changes in the retention/rejection behaviour of the membranes, which is discussed in the following sections.

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Figure 1.10 – General schematic of the compaction of a polymeric water filtration membrane with tortuous pore channels. The changes caused by compaction are highlighted in red. Of particular note is the compression of the pore channels in the skin-layer. Image reproduced from the work of Handge.^[128]

1.4.3.6 Changes in retention due to compaction

The rejection behaviour (how much of a particular contaminant a membrane removes from the solution) of water filtration membranes is an important characteristic, as it directly determines the quality of the permeate produced. In some cases, compaction has resulted in changes of the rejection properties of the membranes.^[118] Stade et al.^[119] examined the rejection of PEG of four different commercial membranes, before and after compaction at 7 bar at different temperatures of the solution for 15 h. In their work, it was found that after compaction, all the membranes displayed increased rejection of PEG compared to before compaction, by + 4-12 percentage points, depending on the membrane used. In a different study, Han et al.^[129] noted a reduction in the average pore size

distribution (as measured with gas-liquid displacement experiments) of three different commercial membranes after compaction. The reduction in the pore size of the membranes varied depending on the membrane tested, with the reduction varying from ~0.025-0.13 μ m. Increased rejection during filtration due to membrane compaction has been demonstrated to occur with RO and NF membranes as well.^[117, 130]

1.5 Common polymers used to fabricate membranes

There are several different polymers commonly used to fabricate water filtration membranes. These polymers can be grouped into several different categories; fluorinated polymers, such as polytetrafluoroethylene (PTFE) and PVDF; semi-aromatic polymers, such as Psf, PES, and polycarbonate (PC); ethylene polymers, such polyacrylonitrile (PAN), PP and PE; and finally CA. Each of these polymers possess different chemical stabilities and mechanical properties, which are compared in the following text.

1.5.1 Comparison of chemical stability

During the lifetime of a water filtration membrane, the membrane will be exposed to different chemical conditions. Due to fouling and biofouling (or measures taken to reduce them), membranes are commonly cleaned with acidic and/or alkaline solutions, and disinfectants,^[40, 131, 132] which damage polymeric membranes.^[98, 100, 131] Therefore, the chemical stability of the polymer used to fabricate the membrane needs to be considered, to ensure the longevity of the membrane.

A comparison of the chemical stabilities of different polymers can be found in Table 1.3. It should be kept in mind that this data is a simplistic overview of the chemical stability, and cannot be used to gauge how well a polymer will perform to specific chemicals. The data does give an idea of the general stability of the different polymers.

As can be seen, the fluorinated polymers, particularly PTFE, are the most chemically stable, followed by the semi-aromatic polymers (Psf, PES, and PC). Except for PAN, the chemically stability of the ethylene polymers (PP and PE) is lower again compared to the semi-aromatic polymers, while CA has the lowest chemical stability out of all the polymers compared.

 Table 1.3 – Comparison of chemical stabilities* of different polymers commonly used to fabricate polymeric water filtration membranes (Data from ref.^[5])

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1.5.2 Comparison of mechanical properties

The mechanical properties of the polymer used to fabricate the membranes also needs to be considered, as the membrane needs to able to withstand the pressures applied during the filtration.

A comparison of the mechanical properties of the different polymers used to fabricate polymeric membranes can be found in Table 1.4. As can be observed, the moduli (tensile modulus and flexural modulus) and tensile strength of the fluorinated polymers (PTFE, PVDF) tend to be lower than the others (excluding PE). However, the compressive strength of PVDF, PES, and PC are the highest of the polymers examined (with the data provided), while PFTE, PP, and CA are the lowest.
 Table 1.4 - Comparison of different mechanical properties of various polymers commonly used to fabricate polymeric membranes (Data from ref.^[5])

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Based on the combination of the chemical stability and mechanical property data, PVDF was chosen as the material to fabricate polymeric membranes in this thesis. PVDF possesses high chemical stability, while having similar mechanical properties to the other polymers used to fabricate polymeric membranes. Although PTFE is more chemically stable than PVDF, PTFE has poorer mechanical properties. PTFE is also more difficult to work with, as it has very limited solubility in organic solvents, noted to be only soluble in perfluorokerosene at 350 °C.^[5] Further information regarding the properties of PVDF is discussed in the following text.

1.6 PVDF

PVDF is a semi-crystalline semi-fluorinated polymer with a simple repeating unit of (- CH_2-CF_2-) (see Figure 1.11).



Figure 1.11 - Repeating unit of the PVDF homopolymer

PVDF is typically synthesised by free-radical polymerisation of the monomer, vinylidene difluoride (VDF), either by aqueous emulsion or suspension polymerisation, though other methods of polymerisation have also been reported (a review on the polymerisation on the can be found in ref^[133]). The following discusses the key characteristics of PVDF, including crystallinity, thermal properties, chemical resistance, and UV stability.

1.6.1 Crystallinity

PVDF is a semi-crystalline polymer, meaning it possesses regions of ordered polymer chains (known as the crystalline phase) and regions of disordered polymer chains (known as the amorphous phase). The crystallinity of PVDF is a defining feature of this polymer, as this is what gives rise to PVDFs electroactive properties, such as pyroelectricity and piezoelectricity.^[134, 135]

Research has indicated that the crystalline regions of PVDF can possess different phases based on orientation of the side groups (fluorine and hydrogen atoms) along the polymer backbone, as well as relative to other polymer chains. The type of crystal phase is important as only some of the crystal phases of PVDF are electroactive. Four different crystalline phases of PVDF have been identified in literature, designated as α -phase, β -phase, γ -phase and δ -phase (also named phase II, I, III and IV respectively).^[134, 135] The type of crystal phase present in PVDF-based materials strongly depends on processing conditions, additives used and posttreatment.^[134, 135]

The two most common phases of PVDF observed experimentally are the α -phase and the β -phase.^[134] The α -phase represents a polymer chain where the pendant units are at an alternating trans-gauche-trans-gauche (TGTG') orientation along the polymer backbone (see Figure 1.12), such that the resulting crystal phase is non-polar and non-electroactive.^[134-136] This phase is often present in most PVDF materials (as it the most stable form thermodynamically under non-stressed conditions)^[134] and occurs in all PVDF materials crystallised from the melt (regardless of temperature)^[137] and is also the predominate crystal phase from PVDF films cast from solvent dried at 110 °C or above.^[137, 138] In comparison, the β -phase, which has all trans orientation (see Figure 1.12) along the PVDF backbone, giving rise to a permanent dipole within the crystal. The β -phase is perhaps the most studied of the

PVDF crystal phases, as it provides PVDF with electroactive properties yet can be easily formed by either; mechanical stretching of PVDF materials with α -phase crystals; from the melt under specific conditions (such as applying an electrical potential); from PVDF films cast from solution and dried at 70 °C or below; or using nucleating additives.^[134, 135, 137]

The γ -phase is also polar and electroactive but is difficult to obtain experimentally as it requires melt crystallisation at high temperatures (near the melting point (155-165 °C) of the α -phase)^[137] and slow cooling rates, and yields PVDF with a mixture of α - and γ -phase crystallites.^[134] In the γ -phase, the orientation is also trans-gauche-trans-gauche like the β -phase, however the polymer chain is staggered (see Figure 1.12).

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Figure 1.12 – Schematic representation of the three main crystal phases found in PVDF; a) the α -phase, b) the β -phase, and c) the γ -phase (reproduced from ref^[134]).

The last major phase of PVDF, the δ -phase, is a polar form of the α -phase. Although the orientation of pendant units along the PVDF polymer chain is the same as for the α -phase (TGTG'), the difference in the packing of the polymer chains is such that a dipole moment exists due to out-of-plane interactions, which are cancelled out in the α -phase (see Figure 1.13). The δ -phase is obtained by pulsing α -phase PVDF with a strong electric field, but unlike the β -phase does not require thermal annealing.^[136] This allows smooth films of δ -phase PVDF to be made which are suitable for use as

capacitors, whereas other PVDF films can be rough (and short circuit) due to being too rough.^[136]

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Figure 1.13 – Schematic diagram of the PVDF polymer chain packing in the unit cell of the α -phase and δ -phase (taken from ref^[136]). Grey spheres represent carbon atoms, red spheres represent fluorine atoms and blue spheres represent hydrogen atoms, and grey lines represent covalent bonds.

1.6.2 Thermal properties

In terms of thermal properties, PVDF possesses a glass transition temperature (T_g) at -35 °C^[139, 140] and a melting temperature (T_m) starting at approx. 158 °C^[139] (PVDF can exhibit different melting transitions in the 158 – 200 °C depending on the crystallinity present^[140]). PVDF also possesses high thermal stability, having an onset of thermal degradation at 375 °C in air by thermal gravimetric analysis.^[139, 140] This allows PVDF to be melt cast and annealed at high temperatures without requiring special precautions.

1.6.3 Chemical Resistance

Strong chemical resistance is a characteristic of PVDF, but rarely is any real detail given in literature. Yet understanding what chemicals PVDF is capable of tolerating is essential to using it in a given application. In this regard, the manufacturers^[141-143] of PVDF have provided detailed information regarding the chemicals that PVDF is capable of resisting though little detail is given as to the mechanism of degradation. According to the manufacturers specifications, PVDF is resistant to a wide range of different chemicals, but does lack resistance to some chemicals. These chemicals are separated into chemical antagonists (chemicals which chemically degrade PVDF), and

swelling/solvating agents, chemicals which don't chemically degrade PVDF, but are noted to swell or dissolve PVDF.

1.6.4 Chemical antagonists

This section covers chemicals that degrade PVDF by chemical reaction, attacking the polymer backbone. Largely the use of these chemicals should be avoided where exposure to PVDF can occur, though they can be used as methods of modifying PVDF if used in a controlled fashion.

1.6.4.1 Strong bases

Despite being considered as a chemically resistant polymer, PVDF is well known to be degraded by strong bases.^[144-147] This causes chemical degradation of the PVDF backbone by the process known as dehydrofluorination, removing HF to produce alkenes.^[148, 149] With strong bases, this process occurs at room temperature, and even if the base is heavily diluted.^[148] On the other hand, weaker bases such as sodium carbonate require high temperatures to cause chemical degradation.^[141-143] While small amounts of exposure do not affect mechanical properties of PVDF to a large degree, too much dehydrofluorination breaks down the PVDF material, causing it become brittle and mechanically weak.^[144, 148] Ideally, exposure to strong bases should be minimised, whether for cleaning or for chemical modification, to avoid damaging PVDF to a significant degree.

1.6.4.2 Amines

Amines have also been identified as causing chemical degradation of PVDF.^[141-143] Notably, PVDF is degraded by less substituted amines, such as ammonia and monoalkyl amines (such as ethylamine and *n*-butylamine) at room temperature, yet raised temperatures are required for more substituted amines (i.e., diethyl- and triethylamine) to cause degradation.^[141-143] Recent work conducted by Sun et al.^[150] showed similar observations, with PVDF films more readily reacting with the primary amine, monoethanolamine, than the secondary amine, diethanolamine, when immersed in solutions of the amines and heated. Under similar conditions, PVDF films showed limited reactivity with a tertiary amine, 2-amino-2-methyl-1-propanol.

1.6.4.3 Other chemical antagonists

Other notable chemical antagonists^[141-143] of PVDF include sodium and potassium metals, fuming nitric acid and fuming sulphuric acid. PVDF only has a limited resistance to concentrated (90 %) hydrogen peroxide, hypochlorous acid, and fluorine gas, and is recommended for exposure at room temperature only for these agents.

1.6.5 Swelling/Solvating agents

This section discusses chemicals that do not chemically degrade PVDF, but are capable of swelling and/or solvating PVDF. While this does not damage the PVDF, it does cause PVDF to lose structural integrity, and may cause the PVDF to be dissolved away completely, which is problematic particularly if PVDF is being used as a coating.

Good solvents for PVDF are largely limited to dipolar aprotic solvents, such as amides. Commonly used solvents for PVDF include N,N-dimethyl formamide (DMF), (NMP), N-methyl pyrrolidone dimethyl sulfoxide (DMSO) and hexamethylphosphoramide. These solvents are capable of forming stable solutions of PVDF even at room temperature.^[151] Other solvents can be used to dissolve PVDF, but typically require elevated temperatures, and can also have the issue of the PVDF gelling and/or crystallising out of solution on cooling. These solvents are typically esters, aldehydes, ketones or ethers, either aliphatic or cyclic, with common examples including ethyl acetate, diethyl phthalate, acetaldehyde, methyl ethyl ketone, acetone and tetrahydrofuran (THF).^[151, 152] While a number of esters and ketones have been identified as solvating PVDF, PVDF tends to be able resist aldehydes and ethers with larger aliphatic chains.^[141-143] These solvents are used to fabricate PVDF membranes by TIPS.^[153]

1.6.6 UV stability

PVDF shows good stability to UV irradiation, with a thin PVDF film showing only minor changes after 10 weeks of irradiation with a xenon lamp.^[154] In comparison, other polymers used in water filtration membranes typically show significant signs of degradation when exposed to UV-irradiation for long periods of time. Two studies^[110, 111] comparing different polymeric membranes demonstrated that the PVDF is one of the more stable polymeric membranes to UV-photodegradation, with PTFE, PAN, PC, and polyamide (PA) RO membranes showing similar stability. On the other hand,

membranes consisting of CA, PP, Psf, or PES showed significant degradation under the same conditions. The semi-aromatic polymers, Psf and PES, are known to undergo scission of the polymer chain under UV-irradiation.^[155, 156] The UV-photodegradation susceptibility of polymeric membranes is complicated by the fact that other additives can accelerate the photodegradation of the membranes. The presence of TiO₂ nanoparticles (NPs) can result in more rapid degradation of PVDF membranes due to the photocatalytic properties of TiO₂ NPs,^[157, 158] and commercial hydrophilised PVDF membranes were shown to undergo more UV-degradation than hydrophobic PVDF membranes.^[110] Nonetheless, PVDF is a good choice as a polymer for applications where UV-exposure is an issue, such as for photocatalytic membranes, or UVcleaning/disinfection.

1.7 Improving the properties of PVDF membranes to resist flux decline

Despite the desirable properties of PVDF (good chemical stability, high thermal stability, high UV stability), PVDF water filtration membranes suffer from fouling (and biofouling) due to its hydrophobic nature, and PVDF membranes undergo compaction. To combat these mechanisms of flux decline, studies have incorporated inorganic fillers into PVDF membranes. The next sections discuss in detail the types of inorganic fillers incorporated into PVDF water filtration membranes, and the benefits that this provides.

1.7.1 Incorporation of Inorganic fillers in PVDF water filtration membranes

The incorporation of inorganic fillers in PVDF water filtration membranes has received wide attention in literature as a method of changing these membranes to possess more desirable properties. The main benefits of incorporating inorganic fillers include increasing the hydrophilicity of the membranes to improve resistance to fouling (as well as improve recovery from fouling with cleaning), and improve the mechanical properties of the membranes to better resist compaction. Incorporating inorganic materials can provide other desirable properties to membranes as well. This includes providing antibacterial properties to membranes to reduce biofouling, or photocatalytic activity. Photocatalytic membranes can break down organic materials in solution with exposure to the appropriate radiation, as well as degrade organic foulants on the membrane surface. This provides a chemical free method to clean PVDF membranes.

Common inorganic fillers include particles and NPs of metal oxides (SiO₂,^[159-168] Al₂O₃,^[169-173] Fe₃O₄,^[174] ZnO,^[175-179] ZrO₂,^[180, 181] TiO₂,^[158, 182-190]), metal salts (Mg²⁺ salts,^[191] or Ca²⁺ salts^[192-196]), Ag(0) metal,^[197, 198] and aluminosilicate materials (zeolites,^[199-202] clay particles,^[203-208] and halloysite nanotubes^[209]). Particles with unusual morphologies (instead of simple spherical particles), such as nanowires (NWs),^[187, 198] and mesoporous particles^[164, 210] have also been incorporated, and have been demonstrated to beneficial to the membrane properties as well.

A different strategy to incorporate inorganic materials into PVDF water filtration membranes is to use a carbon-based template, such as graphene oxide (GO),^[211-215] or multiwalled carbon nanotubes (MWCNTs)^[216, 217] as a template. Reviews on the literature studying composite water filtration membranes can be found in refs.^{[221-223][218-220]}

The following discusses the benefits of incorporating inorganic fillers into PVDF water filtration membranes. The benefits of incorporating inorganic fillers into PVDF water filtration membranes include improvements in hydrophilicity and fouling resistance, as well as improvements in mechanical properties. Incorporation of inorganic fillers has also lead to the production of membranes with antibacterial or photocatalytic properties.

1.7.1.1 Improving fouling resistance and flux recovery with cleaning

A large focus on the incorporation of inorganic fillers into PVDF membranes is to improve the fouling resistance of the membranes. This is typically done by examining the flux decline during the filtration of a solution containing a foulant, as well as examining the recovery of the PWF after fouling and cleaning of the membrane. The improvements in fouling resistance are attributed to the increase in membrane hydrophilicity^[158, 160, 162, 169-171, 176-178, 181, 183, 187, 188, 191-193, 197-200, 204, 209, 212-216, 221-227] with the inclusion of inorganic fillers, and/or reductions in membrane surface roughness.^[158, 193, 209, 213, 215, 216]

The improvements in antifouling properties of PVDF membranes has been demonstrated with the inclusion of particles of many different materials, such as Ag(0),^[197] Al_2O_3 ,^[169-171] aluminosilicate materials ($clay^{[203, 204]}$, halloysite nanotubes^[209]), Ca^{2+} salts,^[192, 193] Fe_3O_4 ,^[174] $Mg(OH)_2$,^[191] SiO_2 ,^[159] TiO_2 ,^[158, 182-184]

zeolites,^[199] ZnO,^[175-178] and ZrO₂.^[180, 181] These composite membranes have been demonstrated to have reduced flux decline during filtration to a multiple of different foulants. These include solutions containing foulants such as BSA,^[171, 175, 182, 188, 199] HA,^[158, 183, 184, 228] and oil-water emulsions,^[209] but also solutions containing mixtures of foulants, such as reclaimed river water, ^[175, 177] whey solution,^[203] dairy solution,^[204] and *E. coli* solutions.^[191, 228] Moreover, these composite membranes show an improved flux recovery after fouling and cleaning of the membranes (compared to membranes without inorganic filler). This has been demonstrated for fouling from BSA,^[159, 171, 174, 188, 197, 199] whey solution,^[203] an oil-water emulsion,^[209] synthetic wastewater,^[176] and from petroleum refinery effluent.^[180] This coincides with the membranes showing a reduction in the amount of foulant that absorbs to the membrane surface,^[169, 170, 178, 188, 191] as well as reductions of bacterial cell adhesion.^[191, 197, 228]

For example, the incorporation of ZnO NPs into PVDF membranes^[176] allowed ~100 % flux recovery after fouling from the filtration of synthetic wastewater followed by washing with water. Moreover, the high flux recovery was maintained over 3 cycles of filtration of synthetic wastewater and washing, whereas the membrane without ZnO NPs showed a continuous decline in flux with more cycles.

There has also been significant research into improving the antifouling performance of PVDF membranes by the incorporation of inorganic fillers with more complex morphologies and chemistries. Examples of some of the particles with unusual morphologies incorporated into PVDF water filtration membranes include mesoporous TiO₂^[210] or SiO₂,^[164] NWs of TiO₂^[187] or Ag(0),^[198] and hollow SiO₂ microspheres.^[229] Examples of chemically modified inorganic fillers that have been incorporated into PVDF membranes include lysine-modified SiO₂,^[160] PEG-modified SiO₂,^[161] poly(methyl methacrylate)-*b*-poly(2-hydroxyethyl methacrylate)-modified SiO₂,^[162] polydimethylsiloxane-modified SiO₂,^[163] ionic-liquid modified TiO₂,^[185] and zeolites that have undergone exchange with Ag⁺ ions.^[200, 201]

Incorporation of hybrid fillers (fillers consisting of different materials with an inorganic component) have also been incorporated to improve the fouling resistance of the membranes as well. These hybrid fillers can be produced from hybrids of different inorganic materials (examples include layered double hydroxides of zinc-

aluminium^[224] or magnesium-aluminium,^[226] SiO₂-Al₂O₃,^[230] and TiO₂-halloysite nanotubes^[227]), but can also be produced from hybrids of inorganic materials with carbon allotropes, such as GO (examples include Fe₃O₄-GO,^[211] SiO₂-GO,^[212, 213] Ag-GO,^[214] and TiO₂-reduced GO^[215]) and MWCNTs (examples include ZrO₂-MWCNT,^[216] and SiO₂-MWCNTs^[217]). The antifouling performance of PVDF membranes have also been improved by incorporation of far more complex inorganic fillers, such as sulfonated ZrO₂-shell/void/TiO₂ core NPs,^[221-223] or Y_xFe_yZr_{1-x-y}O₂-coated core shell TiO₂ NPs,^[225] but also with incorporation of simple mixtures of TiO₂ NPs and Al₂O₃ NPs.^[231]

Similar to the more simple inorganic fillers discussed previously, the PVDF membranes incorporating these more complex inorganic fillers have demonstrated improved antifouling performance to multiple foulants, by reduction of the flux decline during filtration (of solutions containing BSA,^[160, 164, 187, 200, 201, 210-214, 226, 227, 230] HA,^[160] oil-water emulsions,^[232-238] or oily wastewater^[221-223]), as well as increased flux recovery after fouling and washing the membrane (from membranes fouled by BSA,^[160-163, 185, 198, 201, 211-215, 226, 227, 229, 230] HA,^[160, 163, 198, 224, 229] oil-water emulsions,^[216, 232-238] oily wastewater,^[221-223, 225], or whey solution^[226]). These composite membranes have also shown reduced adsorption of proteins (BSA^[160, 163, 198, 224, 226, 227] and lysozyme^[224]) to the membrane, and reduced bacterial adhesion as well.^[201]

The incorporation of more complex inorganic fillers can provide better improvements in the membrane antifouling performance when compared to PVDF membranes incorporating their simpler counterparts.^{[160, 161, 163, 164, 200, 211, 212, 215, 217, ^{221-223, 227, 232-238]} For example, the inclusion of 5 wt% of lysine-modified SiO₂ NPs^[160] reduced the flux decline from either BSA or HA fouling from 38-45 % to 4-5 %, and increased the flux recovery of the cleaning from 55-62 % to 95-97 % compared to the control membrane, whereas the membrane incorporating 5 wt% of unmodified SiO₂ NPs showed similar results to the control membrane. PVDF membranes incorporating zeolites that have undergone exchange with Ag⁺ ions^[200] were found to undergo less flux decline during the filtration of a BSA solution, the flux decline decreasing from 45.7 to 30.1 %, compared to 38.4 % for the membrane incorporating SiO₂ NPs or sulfonated ZrO₂-shell/void/TiO₂ core NPs (at the same loading) revealed that the}

membrane incorporating sulfonated ZrO₂-shell/void/TiO₂ core NPs was more hydrophilic (water contact angle of 33.9°, compared to 56.7°), and showed better antifouling performance to an oil-water emulsion, showing a cumulative PWF recovery of 91.11 % after 5 cycles of oil-water filtration and cleaning (compared to 77.14 %).

Inorganic fillers can, however, result in undesirable changes to the fouling performance of membranes, such as increasing the surface roughness,^[169, 170, 192, 214, 226, 227] or increasing the fouling potential. For example, causing increased adsorption and flux decline during filtration of anionic poly(acrylamide) solutions with PVDF membranes incorporating mixtures of TiO₂ and Al₂O₃ NPs.^[236]

1.7.1.2 Improving mechanical properties

Numerous studies have demonstrated that the incorporation of inorganic fillers can improve the mechanical properties of membranes. Typically, the tensile properties of membranes are used as the benchmark for determining whether mechanical properties are improved or not. Although tensile tests do not provide direct evidence for the compaction resistance of the membrane, tensile tests do provide a general understanding of how the filler has impacted the response of the membrane to mechanical deformation. All kinds of inorganic materials, such as TiO₂,^[186-190] Al₂O₃,^[172, 173] ZnO,^[176, 177, 179], Ag(0),^[198] zeolites,^[200-202] clays,^[205-208] SiO₂,^[159, 164-168] Ca²⁺-based particles, ^[193-196] as well as hybrid materials ^[217, 230, 239, 240] have been noted to improve the tensile properties of PVDF membranes. At an optimum loading, the inclusion of filler has been found in numerous cases to beneficial to all the tensile properties examined.^{[159, 164-166, 168, 173, 177, 179, 186, 189, 190, 193, 195, 196, 200, 202, 206, 208, 212, 230,} ^{239, 241]} Examples of this include the incorporation of TiO₂-carbon hybrid aerogel particles into PVDF membranes,^[241] which increased the tensile strength from 1.47 MPa to 1.76 MPa, increased the % elongation at break from 10.55 % to 20.83 %, and increased the Young's modulus from 29.69 MPa to 46.08 MPa. The incorporation of 1 wt% of SiO₂-decorated GO into PVDF membranes^[212] was found to increase the tensile stress and % elongation at break from ~1.55 MPa to ~2.4 MPa and ~8.1 % to ~10.8 %, respectively. In comparison, 1 % of GO reduced the tensile stress at break to ~1.4 MPa, and also reduced the % elongation at break to ~7.5 %. Incorporation of

0.1 wt% of ZnO NPs into PVDF membranes^[179] increased the tensile strength from ~1.55 MPa to 2.16 MPa and the % elongation at break from 20.35 % to 40.83 %.

For some fillers, the incorporation into the PVDF membranes results in a trade-off of different tensile mechanical properties.^[205] In some cases, the filler causes the membrane to become more brittle, decreasing the % elongation at break, yet increasing the tensile strength.^[172, 176, 187, 194, 198, 201, 217] Conversely, in some cases the membranes show improvements in the % elongation at break, but show decreases in the tensile strength.^[173, 188, 240]

However, in yet other cases, the mechanical properties of membranes are simply reduced with inclusion of filler materials, with some studies noting decreases in all tensile mechanical properties examined, regardless of loading of the filler. ^[167, 170, 206, 207, 224] For example, the inclusion of zinc-aluminium layered double hydroxide particles into PVDF membranes^[224] decreased both the tensile strength and the % elongation at break, and decreased these properties further with increasing particle loading. Incorporation of γ -Al₂O₃ NPs into PVDF membranes^[170] decreased the tensile stress with all loadings of γ -Al₂O₃ NPs examined, while % elongation at break was comparable for the control and with 2 wt% of γ -Al₂O₃ NPs, however 1 wt% and 4 wt% of the filler significantly decreased the % elongation at break.

The use of inorganic fillers with non-standard morphologies, such as NWs, ^[187] mesoporous particles, ^[164] or nanotubes, ^[165, 166] can show better improvements in mechanical properties than their spherical counterparts (when compared in the same study). The incorporation of TiO₂ NWs at 5 wt% into PVDF membranes^[187] was found to increase the tensile strength from 1.67 MPa to 2.23 MPa, and increase the % elongation at break from 36.91 % to 59.01 %. In comparison, while inclusion of 5 wt% of TiO₂ NPs did increase the tensile strength to 2.28 MPa, the membranes became more brittle, the % elongation at break decreasing to 18.03 %. The addition of either SiO₂ NPs or SBA-15 particles (type of mesoporous SiO₂ particle) to PVDF membranes^[164] was found to increase the tensile strength from ~0.150 MPa to ~0.175 MPa with the lowest loadings of 0.04 wt% of either particle. However, while the inclusion of SiO₂ NPs did not really change the % elongation at break up to 0.14 wt%, the inclusion of SBA-15 particles increased the % elongation at break up to 0.07 wt% loading, increasing from ~33 % to ~48 %. Incorporation of three different fillers,

namely SiO₂ NPs, SiO₂ nanotubes (SNTs), or phosphorylated SiO₂ nanotubes (PSNTs), into PVDF membranes^[165, 166] was found to effect the tensile properties of the membranes differently. While incorporation of either one of the three fillers examined provided improvements to the tensile strength and % elongation at break, the use of PSNTs provided larger improvements. At the same mass ratio for each filler, the tensile strength of the membranes increased from 1.18 MPa to 1.52 MPa (with SiO₂ NPs), 2.03 MPa (with SNTs) and 2.76 MPa (with PSNTs), and the % elongation at break of the membranes increased from 10.6 % to 12.0 % (with SiO₂ NPs), 15.7 % (with SNTs), and 22.4 % (with PSNTs).

The mechanism of how fillers improves the mechanical properties of polymeric materials (including polymeric membranes) has been indicated to be strongly dependent on the strength of interfacial interactions between the filler particles and the polymer.^[165, 166, 168, 205, 242-246] When the material is subjected to stress, part of the force is transferred to the filler particle.^[168, 242, 243] In cases where the filler particle material possesses greater strength and/or Young's modulus than the polymer of the material, this results in reduced deformation of the material.^[244] Interactions between the filler particles and the polymer chains can also lead to the polymer chains becoming more rigid or stiff, which in turn provides a mechanical enhancement to materials.^[165, 166, 172, 187, 205, 206, 246, 247] As these mechanisms of reinforcement rely on filler particle-polymer interactions, chemical modification of the surface of the filler can increase the strength of interactions between the polymer and the filler, and therefore can provide better improvements to mechanical properties.^[165, 166, 212, 243] Particles with complex morphologies can provide higher surface areas per particle for interaction with the polymer, which can also provide greater improvements in mechanical properties than standard spherical particles. [164-166, 187]

1.7.1.3 Improving compaction resistance

Incorporation of inorganic fillers into PVDF membranes cannot only improve/alter the tensile properties of the membranes, but can also improve the compaction resistance of the membranes. Typically, this is demonstrated by comparing the flux decline during the filtration of pure water at the same pressure, ^[194, 222, 225, 241, 248] or by comparing the change in PWF with increasing TMP.^[174] For example, the inclusion

of 0.5 wt% (loading of the casting solution) of calcium stearate particles into flat sheet PVDF membranes^[194] was found to reduce the flux decline to membrane without filler, after 50 mins of pure water measurement at an operating pressure of 1379 kPa. PVDF membranes with 65 wt% or 70 wt% of Fe₃O₄ particles^[174] were found to show a more linear trend with flux increasing when the TMP was varied from 0.1 MPa to 0.4 MPa, whereas membranes with \leq 60 wt% tended to show a clear drop in the PWF, particularly at 0.4 MPa. Incorporation of TiO₂-carbon hybrid aerogel particles^[241] into PVDF membranes reduced the flux decline during the pure water filtration to ~14 %, compared to ~42 % for the unfilled membrane.

1.7.1.4 Antibacterial membranes

Addition of antibacterial properties to membranes is favourable, as the membranes can better resist biofouling. As mentioned in the previous section on biofouling (see section 1.4.2), making a membrane that can prevent the adhesion of any and all bacterial cells is virtually impossible. This is due to the combination of membrane surfaces always having some level of heterogeneity to which at least some cells can adhere to, [51, 71] and the adhesion of foulants to the membrane surface promoting cell adhesion.^[43, 91, 92] To make PVDF water filtration membranes that are inherently antibacterial with inorganic materials, typically silver-based materials are incorporated. In recent literature, this has been done by incorporation of pure Ag nanomaterials (such as Ag(0) NPs,^[197] silver lactate NPs,^[249] or cysteine-modified Ag(0) NWs^[198]), by incorporation of zeolites which have undergone ion exchange to incorporate Ag⁺ ions^[200, 201, 250] (followed by reduction as well), ^[251] or by incorporation of Ag-decorated GO.^[214, 239] These membranes have been demonstrated to possess antibacterial properties to E. coli, S. aureus, Salmonella, E. aerogenes, increasing the zone of inhibition, [197, 200, 214, 239, 249] and reducing the viable cell count when immersing the membrane in the solution^[198, 201, 250, 251] and during filtration.^[201, 239] Moreover, incorporation of these materials can improve the fouling resistance of the membranes, and has been demonstrated to reduce fouling from BSA^[197, 198, 200, 201, 214] and HA,^[198] as well as reduce the adhesion of bacterial cells to the membrane surface.[197, 250]

The bactericidal mechanism of silver nanomaterials is has been demonstrated to result from their ability to damage the membrane of bacterial cells, which results

in cell lysis.^[252-256] A number of different mechanisms have been proposed by which this occurs. One mechanism proposed is that Ag⁺ ions are released from the silver nanomaterial, which is then uptaken by the bacterial cell,^[252, 253, 257] which inhibit important enzymes for cellular respiration and/or cell transport, resulting in the death of the bacterial cells.^[253, 256, 258] Silver nanoparticles have also been shown to directly interact with, and disrupt bacterial cell membranes,^[253-256] and also be uptaken into bacterial cells,^[253-255] where the silver nanoparticle can then release Ag⁺ ions into the cells.^[252, 253] The production of reactive oxygen species (ROS) has also been implicated in the antibacterial mechanism of silver nanomaterials, produced as free radicals from the surface of the silver nanomaterials.^[254]

One issue with incorporation of these Ag-materials is that Ag⁺ ions leach from the membranes into the solution, ^[197, 239] and although Ag⁺ ions are regarded as relatively non-toxic to humans,^[259, 260] there are concerns regarding their toxicity on the environment.^[261, 262] Leaching of Ag⁺ ions also diminishes the fouling resistance and antibacterial properties of the membranes.^[197, 251] The rate of leaching can be partially mitigated using reduced forms of silver (Ag(0)),^[251] or silver lactate NPs with amine-modified halloysite nanotubes,^[249] although this does not mitigate the leaching completely. Further work is needed to assess the long-term performance of these membranes both to long filtration times, and to different cleaning regimes, to examine how long the antibacterial and antifouling properties of these membranes can be maintained at a useful level.

1.7.1.5 *Photocatalytic membranes*

The addition of photocatalytic properties (typically under UV irradiation) is a common property usually provided by TiO₂-based materials,^[157, 158, 183, 210, 263-270] although other materials do possess photocatalytic activity, such as ZnO NPs,^[179] or silver cyanamide (Ag₂NCN) particles.^[271]

Under non-filtration conditions (such as in photocatalytic reactors), these membranes demonstrate improved degradation of organic materials with UV-irradiation. Organic materials successfully degraded using these photocatalytic membranes include organic dyes,^[210, 241, 272] oils,^[223, 268] bisphenol A,^[267] and nonylphenol,^[270] indicating these membranes could be used for removing chemical pollutants from wastewaters, for example.

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The photocatalytic properties of these membranes have also been demonstrated to provide benefits during filtration as well. With UV-irradiation, the flux decline due to fouling can be reduced, and can also increase the removal of the organic components in the solution, which has been demonstrated using HA^[158, 183, 266] and steroidal estrogens,^[265] offering a way to both reduce fouling, as well as provide an additional method (besides rejection) of purifying water. For example, during the crossflow filtration of HA with a membrane incorporating TiO₂ NPs, the flux decline was reduced from 56 % to 28 % with UV-irradiation,^[183] though UV-irradiation had no effect when using a membrane without TiO₂ NPs. In a separate study, the use of membranes with TiO₂ NPs increased the removal of 17β -estradiol (steroidal estrogen) from 28.3 to 73.1 % under UV-irradiation (comparing membranes without and with TiO₂ NPs, respectively).^[265]

Finally, the photocatalytic effect of these membranes offers an effective method to remove foulants adhered to the membrane surface and improve flux recovery. This has been demonstrated with methylene blue, ^[263] HA, ^[183, 266, 269] oleic acid, ^[157] and foulants from reclaimed wastewater. ^[179] These photocatalytic membranes also demonstrate antibacterial properties to *E. coli* under UV-irradiation, in zone of inhibition tests. ^[264] For example, the PWF recovery of a membrane fouled with methylene blue reached ~100 % after UV irradiation for 1 h, ^[263] and reached ~90 % for a membrane fouled with HA after UV-irradiation for 480 min. ^[183] The ability to degrade organic materials as well as bacterial cells offers a method of removing biofilms, which are difficult to remove with standard cleaning practices. ^[58, 95, 96]

However, the UV-catalysed photoactivity of these membranes does result in degradation of the membrane overtime.^[157] Long UV-treatment times (12 h) was found to reduce the HA rejection of a membrane incorporating TiO₂ NPs. This was attributed to be due to photocatalysed degradation of the membrane surface.^[158] Further work is needed to understand the rate of degradation and the effect it has on the usable lifetime of these photocatalytic membranes, which will ultimately decide whether this is cost-effective. In that regard, PVDF membranes incorporating Ag₂NCN particles are particularly interesting, as the material is photoactive in visible light (> 420 nm), and showed limited degradation of the membrane after 5 cycles of

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photodegradation experiments of the organic dye, acid blue I, as determined by Xray diffraction.^[271]

1.7.1.6 Problems with inorganic fillers

Currently, a large issue with incorporation of inorganic particles into PVDF membranes is controlling the particle aggregation, which diminishes and/or prevents any further improvements in the membrane properties.^[161, 164, 168, 170, 187, 194, 199, 205, 210, 214, 217, 226, 239] Though the compatibility of the inorganic fillers with polymers can be improved by modification^[161, 164, 168, 187, 207] (including forming particles with unusual morphologies, or hybrid materials) this usually requires lengthy and/or multiple steps to do so.^[161, 164, 168, 187, 207-210, 213, 223, 225, 227, 241]

A different kind of inorganic-based filler that can overcome this issue is known as polyhedral oligomeric silses quioxane (POSS), which is discussed in further detail in the next section.

1.7.2 Polyhedral Oligomeric Silsesquioxane

Polyhedral oligomeric silsesquioxanes (POSS) are a class of organic-inorganic hybrid materials, which are defined by the presence of Si-O-Si bridges in the molecules, and possess a general molecular formula of $[RSiO_{3/2}]_n$ where the R = H, alkyl, or alkyloxy. ^[273, 274] A common form of POSS is a cage-like structure, where each silicon atom in the molecule is bonded to each other by oxygen bridges, and each silicon atom has an R-group. This POSS is referred to as a completely condensed cage, and n (from the molecular formula, $[RSiO_{3/2}]_n$) = 6, 8, 10, or 12, though n = 8 is the most widely available form.^[275, 276] Another common form of the cage-like POSS is an incompletely condensed cage structure, where (compared to the completely condensed form) one of the silicon atoms is missing, and the adjacent silicon atoms have silanol groups.^[275, 276] A schematic picture of both the completely and incompletely condensed POSS cages can be found in Figure 1.14.



Figure 1.14 – Schematic depictions of completely and incompletely condensed POSS cages. R = H, alkyl, alkoxy

POSS (both completely and incompletely condensed cages) is typically synthesised by the hydrolysis and condensation of trichloro- or trialkoxysilanes. Incompletely condensed POSS cages can also undergo corner capping, where a trichloro- or trialkoxysilane is used to complete the cage. This allows completely condensed POSS cages to possess a mixture of different R-groups, with one R-group being different to the other seven. Extensive reviews of the synthesis of various POSS can be found in literature.^[273, 274] Research has indicated that incorporation of POSS into polymeric matrices can be used to alter the properties of the material.^[277-279] Compared to other inorganic fillers used in PVDF water filtration membranes, POSS possess three main advantages;

- POSS is fully soluble in appropriate solvents (solubility varying according to Rgroup(s) on the POSS cage);^[280-288]
- 2) POSS cages with different R-groups are commercially available, which gives a choice to match the compatibility of POSS with the chosen polymer;^[275, 276]
- 3) POSS can be more easily chemically modified, as there are a range of commercial POSS bearing R-groups^[208, 213, 223, 241] with functional moieties (eg., Si-H, hydroxyl, amine, thiol, alkenes, etc) which can be used both to change the properties of the POSS, as well as covalently attach POSS to polymers. ^[280-283, 285-293]

1.7.2.1 Naming conventions for POSS

For ease of writing, the word 'POSS' is typically used to describe that the chemical structure of a compound that possesses the Si-O-Si bridged cage-like structure, either condensed or fully condensed (in this thesis, POSS refers to the cage-like structure,

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typically with n = 8 unless otherwise specified). The most distinguishing feature is therefore the R-groups on each of the Si atoms in the cage-like structure. If all the Rgroups are the same, it is named by the R-group first (often with the prefix octa- or octakis-, though sometimes this is left out), followed by POSS. The carbon bonded to the Si atom of the POSS cage always has the '1' position. For example, if for a particular POSS cage, all the R-groups are isobutyl groups, or all phenyl groups, the resulting POSS is named octaisobutyl POSS or octaphenyl POSS respectively.

For POSS cages with different R-groups, with the most common being one Rgroup being different to the all the other R-groups on the same POSS cage, the POSS is named by the odd R-group first, followed by the other R-groups (often with heptapreceding the name), finishing with POSS. For example, if a POSS cage has a 3aminopropyl group, and seven isobutyl groups, the POSS would be named 3aminopropyl heptaisobutyl POSS.

Finally, for incompletely condensed POSS cages, the name is preceded by trisilanol to designate the incomplete condensation of the POSS cage, followed by the R-group name, finishing with POSS. For example, for an incompletely condensed POSS cage where all the R-groups are isobutyl groups, the POSS would be named trisilanol heptaisobutyl POSS.

1.7.3 Incorporation of POSS into polymeric systems

Incorporation of POSS into polymers to form composites has been shown to be able to provide improvements to material, such as improving the mechanical properties,^[284, 285, 287, 289-291, 294-297] or improving the thermal stability.^[284, 285, 287, 290, 291] Due to the solubility of POSS, POSS can be incorporated into various polymers by dissolving the POSS in the molten polymer,^[294-297] in the liquid monomers (before polymerisation),^[289, 290] or by dissolving the polymer/monomers and POSS together in an appropriate solvent.^[284, 287, 291] As with the other inorganic fillers previously discussed in section 1.7.1, poor compatibility of the POSS with the polymer matrix can lead to severe aggregation of POSS, and can actually worsen the material properties.^[295, 298] It has been demonstrated that the compatibility of POSS cage.^[295, 296, 298, 299] Covalent attachment of the POSS cage to the polymer can also improve the dispersion of POSS, and reduce aggregation of POSS in the polymer matrix compared
to blending,^[280-282, 285] which can provide better improvements to the material properties.^[281, 285] Moreover, POSS bearing functional groups on multiple arms provides the opportunity as a cross-linker, combining the benefit of POSS reinforcement with covalent cross-linking, which can improve the mechanical properties further.^[289, 299] Reviews on POSS-polymer composites can be found in literature.^[277-279] The following two sections discuss examples of POSS-polymer composite materials and their properties, with section 1.7.3.1 focusing on POSS-polymer composites produced by blending, while section 1.7.3.2 discusses examples of POSS-polymer composites produced using covalent attachment of the POSS cage to the polymer.

1.7.3.1 Blended POSS-polymer materials

Incorporation of POSS by blending into polymeric matrices is the simplest method to incorporate POSS into polymers. Blending POSS into polymeric materials has been shown to be able to improve the mechanical properties, compared to the same polymers without POSS. Misra et al.^[294] formed blends of nylon-6 with either octaisobutyl POSS or trisilanol heptaphenyl POSS, and found that either POSS preferentially concentrated to the surface of the film. Analysis by nanoindentation indicated that the resulting nanocomposites showed increased surface hardness, from 24 MPa to 157-166 MPa with 10 wt% of either POSS, and the storage modulus (also from nanoindentation) increased, particularly near the top surface. In comparison, Wahab et al.^[284] incorporated octa(3-hydroxypropyl-1-dimethylsiloxy) POSS into poly(amic acid) by blending, and found that the POSS was well-dispersed throughout the polymer matrix. This resulted in a reduction of transmittance of the polymer film, improvements in thermal stability and increased hydrophilicity, and although POSS did not alter the surface hardness, the modulus (as measured by nanoindentation) improved with POSS loading.

Blending POSS into PP, PET, or polylactic acid (PLA) has also shown improvements in mechanical properties. Comparing the effect of blending one of three different POSS, octamethyl POSS (OMPOSS), octaisobutyl POSS (OIB POSS), and octaisooctyl POSS (OIO POSS), into PP Baldi et al.^[295] found that only OM POSS had reinforcement effect, increasing the elastic modulus from 1450 MPa to 1650 MPa with 10 wt% loading. OIB POSS and OIO POSS typically reduced the elastic modulus.

However, all three materials incorporating POSS were found to be more brittle, reducing the tensile strength and the % elongation at break with POSS loading.

In a similar study, Lim et al.^[296] compared the effect of blending either OM POSS, OIB POSS, or octaphenyl POSS (OP POSS) on the mechanical properties of PET, finding that all three POSS increased the tensile strength and % elongation at break with 0.5 wt% loading, though reduced these properties with increasing loading of POSS thereafter. Out of the three POSS examined, OIB POSS provided the largest enhancement in mechanical properties, which was attributed to the more favourable solubility parameters of OIB POSS with PET.

Blending a POSS derivative with PEG arms (PEG POSS) into PLA (with or without trially lisocyanurate included), Jung et al.^[297] found that with 15 wt% loading of PEG POSS, that although the tensile strength was slightly reduced, the composite material was much less brittle, greatly increasing the % elongation at break from 8 % to 309-323 %, and the toughness of the material from ≤ 5 MJ.m⁻³ to $\sim 68-75$ MJ.m⁻³.

1.7.3.2 Covalently bound POSS-polymer materials

There are numerous examples of POSS-polymer composite materials produced by covalent attachment of the POSS cage. For example, Liu et al.^[283] tethered 3-aminopropyl heptaisobutyl POSS to PA, by reaction of the amine group of the POSS with maleimide side groups of the PA (see Figure 1.15). It was found that POSS was homogenously dispersed as small aggregates throughout the PA matrix. Incorporation of POSS to PA increased the Young's modulus of the materials, from 560-695 MPa to 1078-1270 MPa (as compared to the same PA without POSS), though the materials with POSS were found to be more brittle than the materials without POSS.

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Figure 1.15 – Attachment of POSS to PA, by the amine group of POSS adding across the alkenes of maleimide groups on the PA, with p-toluenesulfonic acid (p-TSA) as the catalyst. Taken from Liu et al.^[283]

Hebda et al.^[289] formed covalently attached POSS-polyurethane foams, as either pendant groups (using 1,2-propanediol heptaisobutyl POSS (PHI POSS)) or as a crosslinking agent (using octa(3-hydroxy-3-methylbutyldimethylsiloxy) POSS (OCTA POSS)). Both of these POSS possess hydroxyl groups, which can attach to isocyanate groups of the monomers used to produce the polyurethane foams (see Figure 1.16).

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Figure 1.16 – Synthesis of polyurethane foams incorporating POSS, by reaction of the hydroxyl groups of POSS (PHI-POSS or OCTA-POSS) with the isocyanate groups of the isocyanate. Taken from Hebda et al.^[289]

Incorporation of PHI POSS increased the compressive strength of the foam with increasing POSS loading up to 15 wt%, increasing the compressive strength (in the

growth direction of the foam) from 331.4 kPa to 469.5 kPa. Incorporation of OCTA POSS also increased the compressive strength of the foam to 523 kPa with 5 wt% loading, but foams with higher loadings of OCTA POSS showed reductions in compressive strength. The difference in mechanical enhancement provided by PHI POSS and OCTA POSS was that the PHI POSS formed a homogenous dispersion of POSS crystallites throughout the foam at all loadings examined, providing reinforcement throughout the foam. Incorporation of 10 and 15 wt% of OCTA POSS into the polyurethane foam formed larger, less homogenously dispersed crystallites, which weakened the foam integrity.

Other studies have used POSS as a cross-linker as well, such as in a cyanate ester resin,^[290] a UV-cured Psf-methacrylate-methacylamide resin,^[291] to cross-link a poly(aryl ether ketone),^[287] and into a polybenzoxamine resin.^[285] These cross-linked POSS-polymer composite materials have been demonstrated to have improved properties when compared to similar materials without POSS, such as improved mechanical properties,^[285, 287, 290, 291] or improved thermal stability.^[285, 290, 291] Notably, incorporation of POSS as a cross-linker could also increase the glass transition temperature of the material,^[285, 287, 290] meaning that the material maintained its mechanical integrity at higher temperatures.^[285, 291]

1.7.3.3 Incorporation of POSS into polymeric water filtration membranes

Despite the wide research into the incorporation of POSS into polymeric materials, there is currently few studies involving the incorporation of POSS into water filtration membranes in pressure driven filtrations.

Several studies have investigated blending different POSS into the PA layer of thin-film composite (TFC) membranes, by adding the POSS to either the organic solution layer or the aqueous solution layer used to interfacially polymerise the PA. POSS examined have been octa(trimethylammonium chloride) POSS,^[300] OP POSS,^{[286, ^{292]} or octa(poly(ethylene glycol)) POSS,^[292] with results indicating that incorporation of these POSS by blending can increase the water flux^[286, 300] and hydrophilicity^{[286, ^{300]} of the membranes, and while still providing good salt rejection properties.^[286, 292, 300]}}

These studies also investigated the incorporation of POSS containing primary amine groups, which are capable of participating in the PA interfacial polymerisation, and covalently binding to the PA layer. ^[286, 292, 293] The POSS with amine groups examined were octa(aminophenyl) POSS, octa(ammonium chloride propyl) POSS, or 3-aminopropyl hepta(isobutyl) POSS. The incorporation of 3-aminopropyl hepta(isobutyl) POSS was found to produce a more hydrophobic PA TFC membrane, and in comparison to a control PA TFC membrane without POSS, reduced the water flux by 85 %, and also reduced the salt rejection from 98-99 % to 95.9 %. In comparison, Duan et al.^[286] found that membranes incorporating octa(aminophenyl) POSS or octa(ammonium chloride propyl) POSS were more hydrophilic and had higher water fluxes, with comparable rejection properties to the control membrane without POSS. Varying the reaction conditions during the PA interfacial polymerisation using octa(ammonium chloride propyl) POSS (reaction time, base concentration, or POSS concentration) altered the membrane water flux and rejection properties,^[286, 293] and could increase the PWF further while maintaining a similar salt rejection.^[286] Optimising the loading of octa(ammonium chloride propyl) POSS into PA TFC membranes at 1 wt% could maintain a similar PWF and similar rejection of various salts as the control membrane without POSS. However, the PA TFC membranes with octa(ammonium chloride propyl) POSS showed increased rejection of selenium oxide (SeO₃²⁻ and SeO₄²⁻) and HAsO₄²⁻ salts, as well reduce the adsorption of these salts to the membrane surface.^[292]

TFC membranes have also been produced by UV-initiated polymerisation of a combination of methacyloxypropyl POSS (mixture of n = 8, 10, and 12 cage sizes) and methacrylate-terminated PEG, by coating the mixture onto a Psf UF membrane and curing with UV-irradiation.^[301] This TFC membrane displayed good water permeability and high rejection of organic dyes. This method was also used to introduce antifouling coatings on the Psf membrane. By including PEG (without methacrylate groups) in the coating mixture, and extracting it with water after curing the coating, caused the rejection capabilities of the membrane. Compared to the uncoated Psf membrane, the coated membranes showed superior antifouling performance, showing less flux decline during the filtration of BSA solution or an oil-water emulsion.

Kim et al.^[302, 303] also formed anti-fouling coatings onto Psf membranes, by atom transfer radical polymerisation (ATRP), using an octa-bromo POSS initiator, octakis(2-bromo-2-methylpropionoxypropyldimethylsiloxy) POSS, to create star polymers.

ATRP works by a metal catalyst complexed with a ligand (MX-L), in this case CuBr complexed with N, N, N', N'', N''-pentamethyldiethylenetriamine, undergoing oxidation (becoming M⁺¹X₂-L) to remove the bromine from the initiator. This forms a radical, which can polymerise monomer. The oxidised metal complex (M⁺¹X₂-L) can cap the radical with a bromine group, while undergoing reduction back to MX-L. This reversible exchange of the bromine group allows the polymer to be formed, while minimising the concentration of radicals at any given time. This reduces the rate of radicals combining, which irreversibly terminates the polymerisation.^[304, 305]

The star polymers used for the coatings consisted of copolymers of poly(ethylene glycol) methyl ether methacrylate (PEGMA), with either methylacryloxypropyl hepta(cyclohexyl) POSS,^[302] or with 2-hydroxy-3-cardanylpropyl methacrylate^[303] (a derivative of cardinol, a bio-sourced molecule) (see Figure 1.17). The latter star polymer with PEGMA and 2-hydroxy-3-cardanylpropyl methacrylate was also cross-linkable by UV-irradiation, owing to the long alkyl chain with alkenes on the 2-hydroxy-3-cardanylpropyl methacrylate monomer.

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Figure 1.17 – Synthesis of star polymers using an octa-functional bromine POSS, by polymerisation (by ATRP) of; a combination of polyethyleneglycol methacrylate (PEGMA) and methacyloxypropyl heptacyclohexyl POSS (MA-POSS) (top image); or a combination of PEGMA and 2-hydroxy-3-cardanylpropyl methacrylate (HCPMA) (bottom image). Taken from Kim et al.^[302, 303]

Application of either of the star polymers by spin coating onto the Psf membranes (followed by UV-irradiation for the star polymer with 2-hydroxy-3-cardanylpropyl methacrylate) reduced the PWF, but in return made the membrane surface more hydrophilic and oleophobic. This was found to improve the fouling resistance of the membranes to both BSA and an oil-water emulsion, greatly reducing the flux decline due to fouling during the filtration (as compared to the uncoated Psf membrane). UV-irradiation was found to be necessary for the coating using the star polymer with 2-hydroxy-3-cardanylpropyl methacrylate, as otherwise the coating was removed by washing with water.

Incorporation of POSS into the bulk of the membrane material, rather than as a thin film or coating, has also been demonstrated to provide improvements to water filtration membranes. Worthley et al.^[288] incorporated a POSS-CA additive into CA RO membranes. The CA-POSS additive was synthesised by coupling the amine group of aminopropyl heptaisobutyl POSS to the hydroxyl groups of CA using toluene-2,4-diisocyanate (see Figure 1.18). Figure has been removed due to Copyright restrictions

Figure 1.18 – Synthesis of a covalently bound CA-POSS material, using TDI as the bridge between POSS and CA, using dibutyltin dilaurate (DBTDL) as the catalyst. Taken from Worthley et al.^[288]

At 1 wt% of POSS in the membrane, the membrane incorporating the CA-POSS additive showed a homogenous dispersion throughout the membrane by SEM, whereas blending CA with unmodified aminopropyl heptaisobutyl POSS lead to the formation of large, micron-sized aggregates. Thickness measurements (by SEM) of the membranes before and after filtration at 1000 kPa, incorporation of 0.5 wt% of the POSS-CA additive reduced the physical compaction of the membranes from 42 % to 0.1 %, indicating that the incorporation of CA-POSS improved the compaction resistance of CA membranes.

Sun et al.^[306] first synthesised, and then incorporated a POSS with ethylene glycol arms (EG POSS) into PVDF UF membranes in loadings of 0-2 wt% of the casting solution. It was found that higher loadings of EG POSS created more hydrophilic membranes, and reduced the adhesion of BSA more, though there was a more variable effect on mechanical and filtration properties. In terms of tensile properties, the optimal EG POSS loading for tensile strength was 1.5 wt%, and was 1 wt% for the % elongation at break, decreasing with higher EG POSS loadings. For filtration properties, the incorporation of EG POSS typically produced concurrent changes in

the PWF and the BSA rejection, increasing the PWF while decreasing the BSA rejection, or vice versa (depending on EG POSS loading).

1.8 Thesis aim

The results of these studies indicate that the incorporation of POSS into water filtration membranes, either by blending or covalent attachment of the POSS, is a promising avenue to improve the properties of water filtration membranes. The focus of this thesis is therefore to incorporate POSS into PVDF water filtration membranes, both by blending and covalent attachment, to assess the effect POSS has on the properties of the membranes. The main focus is to determine if the POSS can improve the mechanical properties of the PVDF membranes, to improve the resistance of the membranes towards membrane compaction.

Chapter 2 contains the experimental details, including methods of organic synthesis used, membrane preparation, and techniques used for analysis. The following chapters then discuss the results of these experiments and analyses, focusing on specific topics.

Previous research has shown that incorporation of 3,3,3-trifluoropropyl POSS (TFP POSS) has improved the mechanical properties of PVDF materials. However the incorporation of TFP POSS has not been examined for use in PVDF water filtration membranes, where TFP POSS may provide improvements in compaction resistance. Chapter 3 therefore examines the effect of blending of TFP POSS into PVDF water filtration membranes, and how TFP POSS changes the properties of the PVDF membranes, particularly the mechanical and compaction properties of the membranes.

Octa(3-mercaptopropyl POSS) (Thiol POSS) was identified as a POSS compound that can be easily modified using thiol-ene addition with alkenecontaining molecules. Using thiol POSS in this way offers a simple strategy to tailor POSS compounds to maximise compatibility of POSS with different polymers (including PVDF), as well as attach thiol POSS to alkene-containing polymers (such as dehydrofluorinated PVDF, which is discussed in the following paragraph). Chapter 4 is therefore focused on the synthesis and modification of thiol POSS by thiol-ene addition chemistry. Due to the difficulty in replicating literature methods of

synthesising thiol POSS, a novel method of synthesising thiol POSS was devised in thesis. Novel POSS compounds were then developed using thiol-ene addition chemistry of thiol POSS with a variety of different alkenes. This work demostrates a simple method to be able to functionalise thiol POSS with different organic groups, so as to be able to optimise the compatibility of POSS compounds with different polymers, as well offering insight into the reactivity of thiol POSS under different catalytic conditions.

Direct functionalisation of PVDF using thiols is a potential way to modify PVDF to optimise the properties of PVDF, as well as a method to cross-link PVDF with thiol POSS. Cross-linking PVDF with thiol POSS should provide improved mechanical properties, as well as improved compaction resistance to PVDF membranes. However, there is limited literature on modifying PVDF with thiols directly, and using simple procedures. Chapter 5 therefore examines the modification of PVDF with thiols, using а combination of dehydrofluoratination (using 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) to produce alkenes on PVDF), and thiol-ene addition, to attach thiols to PVDF. Two different methods of modification of PVDF with thiols were examined, either by adding thiols as co-additives with DBU, or by post-treatment of dehydrofluorinated PVDF with UV-catalysed thiol-ene addition. This work offers a novel methods to be able to modify PVDF with thiols under different catalytic conditions, as well as demonstrates the ability to modify dehydrofluorinated PVDF with thiols by UV-catalysed thiol-ene addition as a post modification step.

Cross-linking polymers is has been shown to be able to improve mechanical properties of polymeric materials, and should provide similar improvements to PVDF membranes for the purpose of reducing membrane compaction. However, currently there is no literature on cross-linking PVDF for forming water filtration membranes. Chapter 6 therefore examines cross-linked PVDF membranes, produced by UV-catalysed thiol-ene addition of dehydrofluorinated PVDF with thiol POSS. Preliminary results on a second type of PVDF membrane produced using UV-catalysed thiol-ene addition with thiol POSS is also examined, where eugenyl methacrylate (EgMA), a known antibacterial monomer, has been incorporated into the membrane. The antibacterial EgMA is known to impart antibacterial properties to materials when

incorporated, but has so far not been examined for use in water filtration membranes, where it may provide anti-biofouling properties.

Finally, Chapter 7 contains the overall conclusions of this work, and future directions.

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Chapter 2 Materials and methods

2.1 Synopsis

This chapter of the thesis covers the details of the chemicals used and the methodology used for the experimental work. This chapter is split into three sections. Section 2.2 covers the details of the chemicals used, including their sources and any details regarding how they were used. Section 2.3 covers the experimental details regarding the synthesis of materials, including details of organic synthesises as well as the preparation of the PVDF membranes. Finally, section 2.4 covers the details of the methods of both sample preparation and instrumentation used for sample analysis, including relevant calculations and equations.

2.2 Chemicals

The following chemicals listed in Table 2.1 were used as received, while chemicals that required additional preparation/purification can be found after Table 2.1.

| Name | CAS No. | Grade | Supplier |
|--|----------------|--------------------------------------|------------------|
| 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) | 6674-22-2 | ≥99.0% | Sigma Aldrich |
| 1-dodcanethiol | 112-55-0 | ≥ 98 % | Sigma Aldrich |
| 2,2'-azobis(2-methylpropionitrile) solution (AIBN solution) | 78-67-1 (AIBN) | 0.2 M solution of AIBN in toluene | Sigma Aldrich |
| 2-allyloxy ethanol | 111-45-5 | 98 % | Sigma Aldrich |
| 3-mercaptopropionic acid | 107-96-0 | ≥ 99 % | Sigma Aldrich |
| 3-mercaptopropyltrimethoxysilane (MPTMS) | 4420-74-0 | 95 % | Sigma Aldrich |
| 6-bromo-1-hexene | 2695-47-8 | 95 % | Sigma Aldrich |
| 6-chloro-1-hexene | 928-89-2 | 96 % | Sigma Aldrich |
| Acetone | 67-64-1 | ≥ 99.9% | Chem- Supply |
| Allyl alcohol | 107-18-6 | ≥ 99 % | Sigma Aldrich |
| Ammonium chloride | 12125-02-9 | ACS reagent, ≥ 99.5 % | Sigma Aldrich |

Table 2.1 – List of chemicals that were purchased and used as received in this work

| Benzophenone | 119-61-9 | 99 % | Sigma Aldrich |
|---|------------------------------|--|-------------------------|
| Bovine Serum Albumin (BSA) | 9048-46-8 | Fraction V, ≥ 96 %, lyophilized powder | Sigma Aldrich |
| Chloroform (CHCl₃) | 67-66-3 | 99.8% | Chem- Supply |
| Chloroform-d₁ (CDCl₃) | 865-49-6 | ≥ 99.8 atom%, containing 0.5 wt% of silver foil as a stabiliser | Sigma Aldrich |
| Diethylether | 60-29-7 | ≥ 98 % | Vetec Fine Chemicals |
| Dimethyl sulfoxide-d ₆ (D ₆ -DMSO) | 2206-27-1 | "100 %", 99.96 atom% | Sigma Aldrich |
| Ethanol (EtOH) | 64-17-5 | ≥ 99.9% | Chem- Supply |
| Eugenol | 97-53-0 | 99 % | Sigma |
| Formaldehyde (37 wt% solution) | 50-00-0 (Formaldehyde) | containing 10-15 % of methanol as stabiliser | Sigma Aldrich |
| Gluteraldehyde (50 wt% solution) | 111-30-8 (gluteraldehyde) | containing ≤ 0.5 % of methanol | Sigma Aldrich |
| Hydrochloric acid solution (concentrated HCl soltuion) | 7647-01-0 | 37 %, ACS grade | Scharlau |
| Isopropanol (IPA) | 64-17-5 | ≥ 99.9 % | Chem- Supply |
| Magnesium sulfate | 7487-88-9 | ≥ 97 % | Sigma Aldrich |
| Methanol (MeOH) | 67-56-1 | ≥ 99.9% | Chem- Supply |
| <i>N,N</i> -Dimethylacetamide (DMAc) | 127-19-5 | ≥ 99.5% | Chem- Supply |
| <i>N,N-</i> Dimethylformamide (DMF) | 68-12-2 | 99.8% | Sigma Aldrich |
| n-butylamine | 109-73-9 | 99 % | Sigma Aldrich |
| Polyvinylidene difluoride (PVDF) | 24937-79-9 | Solef 1015 | Solvay |
| Poly(vinylpyrrolidone)(PVP) | 9003-39-8 | PVP10 | Sigma Aldrich |
| Potassium chloride | 7447-40-7 | ACS reagent, 99.0-100.5 % | Sigma |
| Sodiumacetate | 127-09-3 | ≥ 99 % | Sigma Aldrich |
| Sodium chloride | 7647-14-5 | BioXtra, ≥ 99.5 % | Sigma Aldrich |
| Sodium phosphate dibasic dihydrate | 10028-24-7 | ≥ 99.5 % | Riedel-de- Haën |
| Sodium phosphate monobasic dihydrate | 13472-35-0 | ≥ 99.0% | Fluka |
| Styrene | 100-42-5 | 99.5% for analysis, stabilised | Acros Organics |

| Tetrahydrofuran (THF) | 109-99-9 | anhydrous, ≥ 99.9 %, contains 250 ppm of BHT as inhibitor | Sigma Aldrich |
|---|-------------|--|--------------------|
| Tetramethylsilane (TMS) | 75-76-3 | NMR grade, A.C.S. reagent, ≥99.9 % | Sigma Aldrich |
| Toluene | 108-88-3 | anhydrous, 99.8% | Sigma Aldrich |
| Triethylamine | 121-44-0 | for synthesis | Merck |
| Trifluoropropyl POSS cage mixture (TFP POSS) | 851814-19-2 | ≥ 97 % | Hybrid Plastics |

The following chemicals required additional preparation before use.

2,2'-azobis(2-methylpropionitrile) (AIBN) (CAS # - 78-67-1), was purchased from Merck and recrystallised twice from ethanol and stored in a refrigerator prior to use by another researcher in our laboratories.

Methacryloyl chloride (CAS # - 920-46-7), 97 %, stabilized with 200 ppm MEHQ; distilled at atmospheric pressure under N₂, keeping the 97-98 °C fraction then storing the collected fraction in a freezer at -20 °C under N₂.

MilliQgrade H_2O (MilliQ water) was obtained using a Labconco Waterpro[®] PS water purification system. The system is fed deionised water and passes through a carbon cartridge followed by three deionisation cartridges to yield MilliQ grade water. The system was flushed with water for at least 5 minutes and only once the digital display gave a measured resistance of 18.2 M Ω was the water collected for use.

Phosphate Buffered Saline (PBS) tablets were purchased from Sigma Aldrich. When dissolved in 200 mL of purified water, gives a 0.01 M phosphate buffer solution with 0.0027 M of KCl and 0.137 M of NaCl at pH 7.4 at 25 °C (according to manufacturer's specifications).

2.3 Synthesis of materials and casting of PVDF membranes

2.3.1 Casting of TFP POSS/PVDF blended membranes

The trifluoropropyl POSS (TFP POSS)/PVDF water filtration membranes were cast by hand and the membranes formed by the non-solvent induced precipitation and solidification (NIPS) process. The results and discussion of the analyses of the TFP POSS/PVDF membranes can be found in Chapter 3.

Firstly, to form the casting solution, PVDF, TFP POSS and poly(vinylpyrrolidone) (PVP) were added into a small glass bottle and dissolved with DMAc using a magnetic stirrer (quantities used are listed in Table 2.2). The bottle was then flushed with N₂, sealed and heated in a water bath at 60 °C overnight with slow stirring. The next morning (after approx. 16 h) the stirrer bar was removed; the bottle was flushed with N₂, resealed and placed in an oven at 60 °C for at least 4-6 h to remove any air bubbles.

The casting solution was then hand cast by a Doctors Blade set at 200 µm onto clean glass plates (previously washed with DI water and a sponge, followed by rinsing with acetone then ethanol and allowed to air dry, and finally wiped down with Kim wipes© to remove any dust). The membranes were then formed by NIPS by immediately precipitating the cast polymer film in DI water baths at room temperature. After 1h the bath water was changed over (with DI water), and this was repeated at least 3 more times over 24 h. The membranes were then stored in glass jars filled with 10% methanol:DI water solution (10:90 volume ratio, v/v) to prevent bacterial growth.

| Wt% of TFP | Mass of | Mass of | Mass of | Mass of |
|------------|--------------|----------|---------|----------|
| POSS* | TFP POSS (g) | PVDF (g) | PVP (g) | DMAc (g) |
| 0 | 0.0000 | 4 | 1 | 15 |
| 1 | 0.0404 | 4 | 1 | 15 |
| 2 | 0.0816 | 4 | 1 | 15 |
| 5 | 0.2105 | 4 | 1 | 15 |
| 10 | 0.4444 | 4 | 1 | 15 |
| 20 | 1.0000 | 4 | 1 | 15 |
| 50 | 4.0000 | 4 | 1 | 15 |

Table 2.2 - Composition of polymer solution used to cast PVDF membranes with different weight percent (wt%) of trifluoropropyl POSS (cage mixture).

*Wt% calculated relative to PVDF (Not including PVP or DMAc)

The results and discussion of the analyses of the TFP POSS/PVDF membranes can be found in Chapter 3.

2.3.2 Synthesis of Eugenyl methacrylate

Eugenyl methacrylate was synthesised according to literature methods.^[1, 2]

Under N₂ atmosphere with stirring, triethylamine (15.69 mL, 11.3909 g 0.1226 mol) was added to a solution of eugenol (15.57 mL, 16.8053 g, 0.1023 mol) in diethyl
ether (150 mL), which was then cooled on an ice bath for 30 min. While still on the ice bath, methacryloyl chloride (11.0 mL, 11.7700 g, 0.1126 mol) was added in 1 mL aliquots at 5 minute intervals. Once the final aliquot of methacryloyl chloride was added, the solution was kept on the ice bath for an additional 30 min, after which the ice bath was removed and the solution stirred at room temperature for 24 h. The solution was then filtered under vacuum to remove triethylammonium chloride precipitate, and then the filtrate washed 3 times (~33 mL each) with dilute HCl solution (3 drops of concentrated HCl solution to 100 mL of Dl water). The filtrate was then washed 3 times (~33 mL each) with a ~0.1 M solution of sodium carbonate (~10.85 g, 0.1024 mol in 100 mL of Dl water); and then washed twice with Dl water (50 mL). The diethyl ether was then removed via rotary evaporation, and the remaining liquid placed in the freezer (with boiling sticks) to crystallise the product. The resulting crystals were then collected and washed using a chilled solution of 1:9 DI water:methanol mixture and then dried in a vacuum oven under minimum pressure at RT overnight. Yield 78.1 %.

¹**H-NMR** (400 MHz, CDCl₃) δ (ppm) - 2.09 (s, 3H), 3.40 (d, *J* = 8 Hz, 2H), 3.82 (s, 3H), 5.09 – 5.15 (m, 2H), 5.75 (m, 1H), 5.94 – 6.04 (m, 1H), 6.37 (m, 1H), 6.78 – 6.81 (m, 2H), 6.99 (d, *J* = 8 Hz, 1H); ¹³**C-NMR** (100.58 MHz, CDCl₃) δ (ppm) - 18.55, 40.19, 56.02, 112.98, 116.19, 120.80, 122.67, 127.08, 135.84, 137.23, 138.34, 138.97, 151.17, 165.68

2.3.3 Synthesis of octa(3-mercaptopropyl) POSS (Thiol POSS)

Octa(3-mercaptopropyl) POSS (thiol POSS) was synthesised by hydrolysis and condensation of 3-mercaptopropyltrimethoxysilane (MPTMS). The results and discussion involving the synthesis of thiol POSS (covering the material presented in Sections 2.3.3) can be found in Chapter 4.

2.3.3.1 Synthesis of thiol POSS using literature method (methanol) (trial 1)

Based on the methods found in refs.^[3, 4] To a 25 mL two-neck round bottom flask under N₂ with a stirrer bar, 12 mL of methanol and 1 mL of concentrated HCl solution (~37 %) were added together and stirred, followed by 0.5 mL of MPTMS. The reaction was then refluxed at 90 °C for 24 h, forming an oily precipitate. After allowing to cool to room temperature, the methanol was carefully decanted and the precipitate washed with ethanol several times and dried in an oven at 60 °C. The product was

soluble in chloroform, and was analysed by ¹H and ²⁹Si NMR spectroscopy, as well ATR-FTIR spectroscopy.

¹**H-NMR** (400 MHz, CDCl₃) δ (ppm) - 0.73 (t, *J* = 7.9 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, *J* = 8 Hz, 0.4H), 1.36 (m, 1H), 1.69 (m, 2H), 2.52 (m, 2H), 3.49 (m), 3.77 (q, *J* = 7 Hz); ²⁹**Si-NMR** (79.50 MHz, TMS) δ (ppm) - -57.92, -59.69, -61.00, -66.03, -66.09, -66.12, -67.08, -67.93, -67.97, -67.98, -68.01, -68.11, -68.18, -68.39, -68.58, -68.76, -68.93; **ATR-FTIR** (cm⁻¹) 3000-2800 (C-H), 2522 (S-H), 1087, 1065, 1038 and 1002 (Si-O), 920 (Si-OH)

2.3.3.2 Synthesis of thiol POSS with varying solvent and temperature (Trials 2-5)

As previous method (Section 2.3.3.1) did not produce the desired thiol POSS in adequate purity, and so reaction conditions were varied by using different solvents and temperatures

2.3.3.3 Synthesis of thiol POSS in methanol at room temperature (Trial 2)

To a 25 mL two-neck round bottom flask under N₂ and with stirrer bar (with condenser attached if conducted above room temperature), 12 mL of methanol and 1 mL of concentrated HCl solution (~37 %) added together and stirred, followed by 0.5 mL of MPTMS. The reaction was left to stir at room temperature. Within 24 h, the solution became slightly opaque and formed an oily precipitate. To ensure completion of the reaction, the solution was left stirring for a total of 96 h, after which the methanol was carefully decanted, and the remaining precipitate washed with ethanol several times and dried in an oven at 60 °C. The product was soluble in chloroform, and was analysed by ¹H and ²⁹Si NMR spectroscopy.

¹H-NMR (400 MHz, CDCl₃) δ (ppm) - 0.73 (m, 2H), 1.38 (m, 1H), 1.70 (m, 2H), 2.54 (m, 2H), 3.52 (m, 0.3H);
 ²⁹Si-NMR (79.50 MHz, TMS) δ (ppm) - -59.71, -66.04, -66.11, -67.10, -67.99, -68.00, -68.13, -68.39, -68.60, -68.95

2.3.3.4 Synthesis of thiol POSS in acetone at 90 °C (Trial 3)

To a 25 mL two-neck round bottom flask under N₂ and with stirrer bar (with condenser attached if conducted above room temperature), 12 mL of acetone and 1 mL of concentrated HCl solution (~37 %) added together and stirred, followed by 0.5 mL of MPTMS. The reaction was then refluxed at 90 °C. Within 10-15 min, the solution turned opaque, and with a further 3-5 min formed a white powdery precipitate. The reaction was left refluxing overnight, after which the solution had turned a deep red.

The heating was then removed and the solution allowed to cool to room temperature. The precipitate was filtered under gravity and washed with acetone x3 which removed the red colour, leaving an off-white precipitate. This was found to be insoluble in chloroform, and was not analysed further.

2.3.3.5 Synthesis of thiol POSS in acetone at room temperature (Trial 4)

To a 25 mL two-neck round bottom flask under N_2 and with stirrer bar (with condenser attached if conducted above room temperature), 12 mL of acetone and 1 mL of concentrated HCl solution (~37 %) added together and stirred, followed by 0.5 mL of MPTMS. The reaction was left to stir for 6 h at room temperature, during which time a significant amount of white precipitate had formed. The solution was filtered under gravity and air dried for 4 h. The precipitate was then stirred in chloroform overnight, filtered under gravity to remove insoluble precipitate, and then the chloroform removed under a stream of N_2 , leaving no residue. Analysis was not continued further.

2.3.3.6 Synthesis of thiol POSS in ethanol at 90 °C (Trial 5)

To a 25 mL two-neck round bottom flask under N₂ and with stirrer bar (with condenser attached if conducted above room temperature), 12 mL of ethanol and 1 mL of concentrated HCl solution (~37 %) added together and stirred, followed by 0.5 mL of MPTMS. The reaction was refluxed at 90 °C for 48 h, after which heating was removed. On cooling to room temperature, a white precipitate formed and the flask was placed in the freezer overnight. The white precipitate formed was recovered by filtration under gravity and washed with ethanol x3 and then and dried in an oven at 60 °C. The product, which was a white powder (rather than oil or waxy solid) was then analysed by ¹H and ²⁹Si NMR spectroscopy.

¹H-NMR (400 MHz, CDCl₃) δ (ppm) - 0.78 (m, 2H), 1.39 (t, J = 8 Hz, J = 8 Hz, 0.4H), 1.58 (s (broad)), 1.73 (quin, J = 8.3 Hz, 2H), 2.57 (q, J = 7.4 Hz, 2H); ²⁹Si-NMR (79.50 MHz, TMS) δ (ppm) - -67.10

Repetitions of Trial 5 was unable to reproduce a white powder, instead producing a clear, transparent oil. The solvent was carefully decanted into a beaker to leave the clear oil in the reaction flask, and the clear oil was discarded. The decanted solution was allowed to cool to room temperature, precipitating an oily/waxy solid. The

product was soluble in chloroform, and was analysed by ¹H and ²⁹Si NMR spectroscopy.

¹**H-NMR** (400 MHz, CDCl₃) δ (ppm) - 0.75 (m, 2H), 1.22 (t, J = 7.0 Hz, 0.15H), 1.36 (t, J = 8.0 Hz, 1H), 1.70 (m, 2H), 2.54 (m, 2H), 3.79 (m, 0.09H); ²⁹**Si-NMR** (79.50 MHz, TMS) δ (ppm) - -57.88, -58.85, -61.00, -65.76, -65.85, -66.02, -66.11, -67.07, -67.93, -67.97, -68.01, -68.18, -68.38, -68.76, -68.93

2.3.3.7 Synthesis of thiol POSS in ethanol with varying water/HCI/MPTMS concentration

The previous trials at synthesising thiol POSS were unable to do so in adequate purity. The synthesis of thiol POSS in ethanol at 90 °C (Section 2.3.3.6) had shown promise, but was not reproducible. Further experiments were therefore conducted using ethanol, but altering the amount of HCl acid, water and MPTMS added. To a 100 mL two-neck round bottom flask under N₂ and with stirrer bar (with condenser attached if conducted above room temperature) specific quantities of the following were added as listed in Table 2.3; ethanol, concentrated HCl solution (~37%), DI water and MPTMS. The reaction was then refluxed at 90 °C (unless otherwise specified). Small volumes of solvent (~10 mL) were removed at certain time intervals, placed into sample vials and allowed to cool to room temperature to precipitate any product. If the reaction produced any precipitate while refluxing it was stopped and allowed to cool to room temperature.

| etnanoi | | | | | | | | |
|------------|---------------|----------------------|---------------------|-----------------|-------------------------|-----------------------------------|--|--|
| Trial # | MPTMS (mL) | Conc. HCl (mL) | DI water (mL) | Ethanol (mL) | Reaction Time (h) | Product | | |
| 6 | 3 | 8 | 0 | 72 | 24 | Oily material | | |
| 7 | 3 | 4.5 | 1.5 | 72 | 24 | Mixture of crystalline/waxy solid | | |
| | | | | | 48 | Mixture of crystalline/waxy solid | | |
| | | | | | 72 | Mixture of crystalline/waxy solid | | |
| 8 | 3 | 3 | 3 | 72 | 24 | Crystalline | | |
| | | | | | 48 | Mixture of crystalline/waxy solid | | |
| | | | | | 72 | Mixture of crystalline/waxy solid | | |
| 9 3 | | 1.5 | 4.5 | 72 | 24 | Crystalline | | |
| | | | | | 48 | Mixture of crystalline/waxy solic | | |
| | | | | | 120 | Mixture of crystalline/waxy solid | | |
| 10 | 3 | 0.75 | 5.25 | 72 | 24 | Crystalline | | |
| | | | | | 48 | Crystalline | | |
| | | | | | 72 | Oily material | | |
| 11 | 3 | 0.5 | 5.5 | 72 | 48 | Crystalline | | |
| 12 | 3 | 0.25 | 5.75 | 72 | 60 | Crystalline | | |
| | | | | | 84 | Mixture of crystalline/waxy solid | | |
| 13 | 3 | 0.75 | 19.4 | 58 | 24 | Oily material | | |
| 14 | 3 | 0.75 | 0 | 77.25 | 24 | No product | | |
| | | | | | 48 | No product | | |
| | | | | | 72 | No product | | |
| | | | | | 96 | No product | | |
| | | | | | 264 | No product | | |
| 15 | 3 | 0 | 6 | 72 | 24 | No product | | |
| | | | | | 48 | No product | | |
| | | | | | 72 | No product | | |
| | | | | | 96 | No product | | |
| | | | | | 264 | No product | | |
| 16 | 4.5 | 0.75 | 5.25 | 72 | 24 | Mixture of crystalline/waxy solid | | |
| | | | | | 48 | Oily material | | |

 Table 2.3 - Volumes of reagents used in different trials to synthesise thiol POSS in

 ethanol

2.3.3.8 Bulk Synthesis of thiol POSS

Based on the results in Section 2.3.3.7, Table 2.3, trial # 10 was chosen to be scaled up as it gave good quality product (crystalline material) in a relatively good timescale.

To a 500 mL two-neck round bottom flask under N₂ with a stirrer bar and condenser, 240 mL of ethanol, 2.5 mL of concentrated HCl solution (~37 %) and 17.5 mL of DI water were added and placed in an oil bath heated at ~90 °C. Once refluxing, 10 mL of MPTMS was added and the reaction refluxed for 48 h. The oil bath was then removed and the solution was allowed to cool to room temperature overnight, during which time white, crystalline precipitate formed. The reaction solution was

carefully decanted into another 500 mL round-bottom flask, allowing the precipitate to be collected. The precipitate was washed with ethanol and dried in an oven at 60 °C. The decanted reaction solution was further refluxed on an oil bath ~90 °C for 48 h before allowing to cool to room temperature overnight again, forming more crystalline precipitate. The precipitate was recovered as before. This process of refluxing and cooling to room temperature was repeated until a total of 4 lots of precipitate was obtained; attempting to reflux for a further 48 h yielded an oily precipitate and so the reaction was not continued. The individual fractions were analysed by ¹H and ²⁹Si NMR spectroscopy; fraction 1 was also analysed by ATR-FTIR spectroscopy.

Fraction 1 – Yield = 0.4837 g (7.1 %) ¹H NMR (400 MHz, CDCl₃) δ (ppm) - 0.74 (t, J = 8.3 Hz, 2H), 1.36 (t, J = 8 Hz, 1H), 1.70 (quin, J = 8.1 Hz, 2H), 2.52 (q, J = 7.5 Hz, 2H); ²⁹Si NMR (79.50 MHz, TMS) δ (ppm) - -67.09; ATR-FTIR (cm⁻¹) - 3000-2800 (C-H), 2522 (S-H), 1080 and 1002 (Si-O)

Fraction 2 - Yield = 0.3189 g (4.7 %) ¹H NMR (400 MHz, CDCl₃) δ (ppm) - 0.75 (t, J = 8.2 Hz, 2H), 1.36 (t, J = 8 Hz, 1H), 1.70 (quin, J = 15.5 Hz, 7.5 Hz, 2H), 2.54 (q, J = 7.3 Hz, 2H); ²⁹Si NMR (79.50 MHz, TMS) δ (ppm) - -67.07

Fraction 3 - Yield = 0.3068 g (4.5 %) ¹H NMR (400 MHz, CDCl₃) δ (ppm) - 0.74 (t, J = 8.2 Hz, 2H), 1.37 (t, J = 8 Hz, 1H), 1.70 (quin, J = 15.5 Hz, 7.5 Hz, 2H), 2.54 (q, J = 7.4 Hz, 2H); ²⁹Si NMR (79.50 MHz, TMS) δ (ppm) - -67.08

Fraction 4 - Yield = 0.2059 g (3.0 %) ¹H NMR (600 MHz, CDCl₃) δ (ppm) - 0.74 (t, J = 8.2 Hz, 2H), 1.36 (t, J = 8 Hz, 1H), 1.70 (quin, J = 15.5 Hz, 7.7 Hz, 2H), 2.53 (q, J = 7.4 Hz, 2H); ²⁹Si NMR (99.36 MHz, TMS) δ (ppm) - -67.08

The combined yields of the 4 fractions was 1.3153 g (19.2 %).

The results and discussion involving the synthesis of thiol POSS (covering the material presented in sections 2.3.3, 2.3.3.7, and 2.3.3.8) can be found in Chapter 4.

2.3.4 Thiol-ene addition chemistry with thiol POSS

This section of the materials and methods chapter covers the methodologies employed to modify thiol POSS by thiol-ene addition chemistry, catalysed by either AIBN with heating, or DBU, or a combination of UV-light with benzophenone. The

results and discussion of the experiments undertaken to modify thiol POSS by thiolene addition (sections 2.3.4) are presented in Chapter 4.

2.3.5 General method for AIBN catalysed thiol-ene addition

Under N₂, thiol POSS (0.0500 g, 4.91 x 10^{-2} mmol) and AIBN (0.0065g, 3.96 x 10^{-2} mmol, 0.1 mol equiv. to thiol groups) was dissolved in toluene (0.25 mL). Alkene (1.1 mol equiv. to thiol groups) was then added and the flask placed in an oil bath at 80 °C for 4 h. The oil bath was then removed and the solution was exposed to air. Product was recovered by precipitating in an approx. 10 fold excess of an appropriate solvent, and the reaction flask rinsed with chloroform into the same precipitation solve nt. These were then left to settle overnight at room temperature, after which the solvent was carefully decanted, the product carefully washed with another volume of solvent and decanted, and the flasks dried for 4 h at 60 °C at minimum pressure in a vacuum oven. Specific solvents and quantities for each experiment are listed in the following.

2.3.5.1 Allyl alcohol

The reaction of thiol POSS and allyl alcohol (29 μ L, 4.26 x 10⁻¹ mmol) was conducted according to the method in Section 2.3.5. The reaction mixture separated into a 2phase mixture with toluene on top and a transparent yellow, viscous oil on bottom. This oil was then precipitated into n-hexane. The final product was a white solid after precipitation. Yield 0.0625 g (86 %). This octa(allyl alcohol) POSS product was soluble in D₆-DMSO and ¹H, ¹³C, COSY, HMQC and HMBC NMR spectra were taken.

¹**H NMR** (400 MHz, D₆-DMSO) δ (ppm) - 0.74 (t, *J* = 8 Hz, 2H), 1.18 (dd, *J* = 12 Hz, *J* = 8 Hz, 0.4H), 1.56-1.68 (m, 4H), 2.48–2.52 (m, 4H), 2.69–2.81 (m, 0.23H), 3.22–3.28 (m, 0.11H), 3.45 (q, *J* = 8 Hz, 2H), 4.45 (t, *J* = 4 Hz, 1H), 4.76 (t, *J* = 4 Hz, 0.07H); ¹³**C NMR** (100.58 MHz, D₆-DMSO) δ (ppm) - 10.48, 10.57, 18.09, 22.62, 23.18, 32.19, 32.49, 33.56, 36.05, 41.39, 59.39, 65.86

2.3.5.2 2-Allyloxyethanol

The reaction of thiol POSS and 2-allyloxy ethanol (46 μ L, 4.30 x 10⁻¹ mmol) was conducted according to the method in Section 2.3.5. The reaction mixture separated into a 2-phase mixture with toluene on top and a transparent reddish, viscous oil on bottom. This oil was then precipitated into n-hexane. The final product was a colourless transparent oil. Yield 0.0831 g (92 %). This octa(allyloxy ethanol) POSS

product was soluble in CDCl₃ and 1 H, 13 C, COSY, HMQC and HMBC NMR spectra were taken.

¹**H NMR** (400 MHz, CDCl₃) δ (ppm) - 0.71 (broad, 2H), 1.24 (d, *J* = 4 Hz, 0.27H), 1.64 (quin, *J* = 8 Hz, 2H), 1.75 (m, 0.16H), 1.83 (quin, *J* = 8 Hz, 2H), 2.04 (broad, 0.17H), 2.49 (t, *J* = 4 Hz, 2H), 2.56 (t, *J* = 8 Hz, 2H), 2.64 (m, 0.28H), 2.76 (m, 0.68H), 2.92 (m, 0.26H), 3.39–3.43 (m, 0.11H), 3.49–3.55 (m, 4H), 3.60 (m, 0.21H), 3.67 (broad, 2H); ¹³**C NMR** (100.58 MHz, CDCl₃) δ (ppm) - 11.31, 11.42, 16.69, 18.55, 22.43, 22.63, 23.07, 23.39, 23.53, 28.16, 28.67, 29.34, 29.61, 33.52, 34.89, 39.55, 49.42, 55.01, 61.67, 69.26, 69.70, 72.09, 72.27, 72.39, 75.83

2.3.5.3 6-chloro-1-hexene

The reaction of thiol POSS and 6-chloro-1-hexene (57 μ L, 4.31 x 10⁻¹ mmol) was conducted according to the method in Section 2.3.5. The solution was then added to methanol to precipitate the product. The final product was a colourless transparent oil. Yield 0.0778 g (81 %). This octa(chlorohexene) POSS product was soluble in CDCl₃ and ¹H, ¹³C, COSY, HMQC and HMBC NMR spectra were taken.

¹**H NMR** (400 MHz, CDCl₃) δ (ppm) - 0.73 (broad, 2H), 1.26 (d, *J* = 8 Hz, 0.10H), 1.43 (broad, 4H), 1.55–1.68 (overlap, 4H), 1.77 (quin, *J* = 8 Hz, 2H), 1.87 (broad, 0.20H), 2.47–2.53 (m, 4H), 2.66 (t, *J* = 8 Hz, 0.66H), 3.52 (t, *J* = 8 Hz, 2H); ¹³**C NMR** (100.58 MHz, CDCl₃) δ (ppm) - 11.06, 11.43, 11.55, 16.77, 21.59, 22.50, 22.65, 23.16, 24.45, 26.60, 28.22, 29.58, 31.98, 32.33, 32.57, 32.74, 33.17, 35.01, 36.39, 36.54, 39.79, 41.08, 44.90, 45.06, 52.43, 55.15

2.3.5.4 6-bromo-1-hexene

The reaction of thiol POSS and 6-bromo-1-hexene (53 μ L, 3.97 x 10⁻¹ mmol) was conducted according to the method in Section 2.3.5. The solution was then added to methanol to precipitate the product. Yield 0.0749 g (66 %). This octa(bromohexene) POSS product was soluble in CDCl₃ and ¹H, ¹³C, COSY, HMQC and HMBC NMR spectra were taken.

¹H NMR (400 MHz, CDCl₃) δ (ppm) - 0.73 (broad, 2H), 1.25 (broad, 0.10H), 1.43 (broad, 4H), 1.55–1.70 (overlap, 4H), 1.86 (quin, J = 8 Hz, 2H), 2.48–2.53 (m, 4H), 2.66 (t, J = 8 Hz, 0.11H), 2.79 (t, J = 8 Hz, 0.08H), 3.40 (t, J = 8 Hz, 2H); ¹³C NMR (100.58 MHz,

CDCl₃) δ (ppm) - 11.01, 11.44, 11.71, 22.53, 22.69, 23.17, 23.30, 26.70, 27.69, 27.89, 28.10, 28.28, 29.56, 31.98, 32.74, 33.87, 35.02, 36.54

2.3.6 1,8-diazabicycloundec-7-ene (DBU) catalysed thiol-ene addition

2.3.6.1 Styrene

Under N₂, thiol POSS (0.0500 g, 4.91 x 10⁻² mmol), styrene (0.05 mL, 4.32 x 10⁻¹ mmol, 1.1 mol equiv. to thiol groups) and toluene (0.25 mL) were stirred together until dissolved. DBU (1 μ L, 6.69 x 10⁻³ mmol) was then injected into the solution and the solution left to stir for 24 h at room temperature. After which the solution was precipitated into methanol (approx. 10 fold excess) and left overnight to settle. The solution was then decanted, and the solid white product washed overnight in another volume of methanol. After decanting the solid white product was then dried for 4 h at 60 °C at minimum pressure in a vacuum oven. The product (a white solid) was found to be insoluble in common organic solvents (methanol, toluene, acetone and chloroform), so analysis was not continued.

2.3.6.2 Eugenyl methacrylate (EgMA)

Under N₂, thiol POSS (0.0500 g, 4.91 x 10^{-2} mmol), EgMA (0.10 g, 4.32 x 10^{-1} mmol, 1.1 mol equiv. to thiol groups) and toluene (0.25 mL) were stirred together until dissolved. DBU (1 µL, 6.69 x 10^{-3} mmol) was then injected into the solution. The solution was then left to stir for 24 h at room temperature. After which solution was precipitated into methanol (approx. 10 fold excess) and left overnight to settle. The solution was decanted, and washed again overnight in another volume of methanol. After decanting for the second time the product (a lightly yellow oil) was then dried for 4 h at 60 °C at minimum pressure in a vacuum oven. Yield 0.0796 g (56 %). This octa(EgMA) POSS product was soluble in CDCl₃ and ¹H, ¹³C, COSY, HMQC and HMBC NMR spectra were taken.

¹**H NMR** (400 MHz, CDCl₃) δ (ppm) - 0.78 (t, *J* = 8 Hz, 2H), 1.21–1.29 (m, 0.33H), 1.41 (d, *J* = 8 Hz, 3H), 1.72 (q, *J* = 8 Hz, 2H), 2.60 and 2.65–2.70 (t and m respectively, 3H), 2.88–3.02 (m, 2H), 3.37 (d, *J* = 8 Hz, 2H), 3.79 (s, 3H), 5.08–5.12 (m, 2H), 5.91–6.01 (m, 1H), 6.75–6.78 (m, 2H), 6.95–6.97 (m, 1H); ¹³**C NMR** (100.58 MHz, CDCl₃) δ (ppm) - 11.39, 16.95, 23.21, 35.50, 35.64, 40.15, 40.40, 55.93, 112.89, 116.18, 120.77, 122.59, 137.18, 138.18, 138.99, 150.99, 173.44

2.3.6.3 Styrene (10% DBU)

Under N₂, thiol POSS (0.0500 g, 4.91 x 10^{-2} mmol), styrene (0.05 mL, 4.32 x 10^{-1} mmol, 1.1 mol equiv. to thiol groups) and toluene (0.25 mL)were stirred together until dissolved. DBU (6.5 µL, 4.35 x 10^{-2} mmol) was then injected into the solution and the solution left to stir for 24 h at room temperature. After which the solution was precipitated into methanol (approx. 10 fold excess) and left overnight to settle. The solution was then decanted, and the solid white product washed overnight in another volume of methanol. After decanting the solid white product was then dried for 4 h at 60 °C at minimum pressure in a vacuum oven. The product (a white solid) was found to be insoluble in common organic solvents (methanol, toluene, acetone and chloroform), and so analysis was not continued further.

2.3.7 General method for UV catalysed thiol-ene addition (without benzophenone)

To a glass sample vial, thiol POSS was dissolved in toluene, followed by alkene. The solution was then exposed to UV-light from a UV cabinet (5 x 8 W UV-tubes at a wavelength of ~365 nm). The reaction was left for 4 h in air and at room temperature. Toluene was removed under a stream of N₂, and then dried in a vacuum oven overnight at 80 °C at minimum pressure (~30 mbar). Specific quantities are listed for each reaction below.

2.3.7.1 2-allyloxyethanol

The reaction of thiol POSS and 2-allyloxy ethanol (42 μ L, 3.93 x 10⁻¹ mmol) was conducted according to the method in Section 2.3.7. Yielded a white solid after drying. Analysis by ¹H NMR spectroscopy indicated no reaction had occurred. This sample was not analysed further.

2.3.7.2 6-chloro-1-hexene

The reaction of thiol POSS and 6-chloro-1-hexene (55 μ L, 4.16 x 10⁻¹ mmol) was conducted according to the method in Section 2.3.7. Yielded a white solid after drying. Analysis by ¹H NMR spectroscopy indicated the reaction was incomplete, with only ~34 % of thiols successfully undergone the reaction. This sample was not analysed further.

2.3.7.3 6-bromo-1-hexene

The reaction of thiol POSS and 6-bromo-1-hexene (55 μ L, 4.16 x 10⁻¹ mmol) was conducted according to the method in Section 2.3.7. Yielded a white solid after drying. Analysis by ¹H NMR spectroscopy indicated the reaction was incomplete, with only ~8 % of thiols successfully undergone the reaction. This sample was not analysed further.

2.3.7.4 Styrene

The reaction of thiol POSS and styrene (46 μ L, 4.00 x 10⁻¹ mmol) was conducted according to the method in Section 2.3.7. Yielded a white solid after drying. Analysis by ¹H NMR spectroscopy indicated the reaction was incomplete, with only ~16 % of thiols successfully undergone the reaction. This sample was not analysed further.

2.3.7.5 Eugenyl methacrylate (EgMA)

The reaction of thiol POSS and EgMA (92.2 mg, 3.97×10^{-1} mmol) was conducted according to the method in Section 2.3.7. Formed a transparent, yellow film on the bottom of the flask. After drying, product was unable to be solubilised in chloroform, and was not analysed further.

2.3.8 General method for UV catalysed thiol-ene addition (with benzophenone)

To a glass sample vial, thiol POSS and benzophenone was dissolved in toluene, followed by alkene. The solution was then exposed to UV-light from a UV cabinet (5 x 8 W UV-tubes at a wavelength of ~365 nm). The reaction was left for 4 h in air and at room temperature. Toluene was removed under a stream of N₂, and then the sample was dried in a vacuum oven overnight at 80 °C at minimum pressure (~30 mbar). Specific quantities are listed for each reaction below.

2.3.8.1 2-allyloxyethanol

The reaction of thiol POSS and 2-allyloxy ethanol (42 μ L, 3.93 x 10⁻¹ mmol) was conducted according to the method in Section 2.3.8. Yielded a transparent oil after drying. Analysis of the crude material by ¹H NMR spectroscopy indicated the reaction had gone to completion. This sample was not analysed further.

¹**H NMR** (400 MHz, CDCl₃) δ (ppm) - 0.71 (broad, 2H), 1.25 (d, J = 4 Hz, 0.18H), 1.65 (quin, J = 8 Hz, 2H), 1.83 (quin, J = 8 Hz, 2H), 2.05 (broad, 0.17H), 2.49 (t, J = 4 Hz, 2H),

2.56 (t, *J* = 8 Hz, 2H), 2.63 (m, 0.16H), 2.78 (m, 0.32H), 2.91 (broad, 1H), 3.39–3.43 (m, 0.11H), 3.49–3.60 (m, 4H), 3.68 (broad, 2H)

2.3.8.2 6-chloro-1-hexene

The reaction of thiol POSS and 6-chloro-1-hexene (55 μ L, 4.16 x 10⁻¹ mmol) was conducted according to the method in Section 2.3.8. Yielded a transparent oil after drying. Analysis of the crude material by ¹H NMR spectroscopy indicated the reaction had gone to completion. This sample was not analysed further.

¹**H NMR** (400 MHz, CDCl₃) δ (ppm) - 0.72 (broad, 2H), 1.26 (d, *J* = 8 Hz, 0.12H), 1.42 (broad, 4H), 1.55–1.69 (overlap, 4H), 1.76 (quin, *J* = 8 Hz, 2H), 2.47–2.52 (m, 4H), 2.66 (broad, 0.31H), 3.52 (t, *J* = 8 Hz, 2H)

2.3.8.3 6-bromo-1-hexene

The reaction of thiol POSS and 6-bromo-1-hexene (55 μ L, 4.16 x 10⁻¹ mmol) was conducted according to the method in Section 2.3.8. Yielded a slightly yellowish oil after drying. Analysis of the crude material by ¹H NMR spectroscopy indicated the reaction had gone to completion. This sample was not analysed further.

¹**H NMR** (400 MHz, CDCl₃) δ (ppm) - 0.71 (broad, 2H), 1.42 (broad, 4H), 1.55–1.70 (overlap, 4H), 1.84 (quin, *J* = 8 Hz, 2H), 2.46–2.52 (m, 4H), 2.66 (broad, 0.29H), 3.39 (t, *J* = 8 Hz, 2H)

2.3.8.4 Styrene

The reaction of thiol POSS and Styrene (46 μ L, 4.00 x 10⁻¹ mmol) was conducted according to the method in Section 2.3.8. Yielded a white solid after drying. Analysis of the crude material by ¹H NMR spectroscopy indicated the reaction had gone to completion. This sample was not analysed further.

¹H NMR (400 MHz, CDCl₃) δ (ppm) - 0.76 (broad, 2H), 1.59 (broad, 0.19H), 1.71 (broad, 1.43H), 1.92 (broad, 0.47H), 2.54 (broad, 1.69H), 2.75 (broad, 1.54H), 2.88 (broad, 1.55H), 3.09 (broad, 0.27H), 7.26 (m, 4.27H)

The results and discussion of the experiments undertaken to modify thiol POSS by thiol-ene addition (Section 2.3.4) are presented in Chapter 4.

2.3.9 Dehydrofluorination of PVDF with DBU, and covalent attachment of nucleophiles

This section of the materials and methods chapter covers the methodologies employed to chemically modify PVDF by using dehydrofluorination with DBU to induce the formation of alkenes. Two different thiols (1-dodecanethiol and 3mercaptopropionic acid) as well as n-butylamine were investigated as model nucleophiles to attach to PVDF, either during the dehydrofluorination reaction by adding the nucleophiles with DBU, or by post-modification of dehydrofluorinated PVDF with the thiols by UV-light catalysed thiol-ene addition. The results and discussion of the results of these experiments (Sections 2.3.9 and 2.3.10) are presented in Chapter 5.

2.3.9.1 DBU treated PVDF (5%) in THF

PVDF powder (1 g, 15.62 mmol of repeat units) was dissolved in THF by refluxing at 80 °C under an atmosphere of N₂ until a transparent solution was obtained. DBU (0.11 mL, 0.736 mmol) was added and the solution was left refluxing at 80 °C overnight. The solution (with any precipitate) was added to 200 mL of ethanol, filtered under gravity, washed with ethanol again and dried overnight at 60 °C.

2.3.9.2 DBU treated PVDF (1%) in THF

PVDF powder (1 g, 15.62 mmol of repeat units) was dissolved in THF by refluxing at 80 °C under an atmosphere of N₂ until a transparent solution was obtained. DBU (0.02 mL, 0.134 mmol) was added and the solution was left refluxing at 80 °C overnight. The solution (with any precipitate) was added to 200 mL of ethanol, filtered under gravity, washed with ethanol again and dried overnight at 60 °C.

2.3.9.3 DBU + 1-dodecanethiol treated PVDF in THF

Same as the method used for DBU treated PVDF (1 mol%) in THF (Section 2.3.9.2) except 1-dodecanethiol (0.37 mL, 1.545 mmol) was added right before adding DBU.

2.3.9.4 DBU + 1-dodecanethiol + AIBN treated PVDF in THF

Same as method used for DBU treated PVDF (1%) in THF (Section 2.3.9.2) except 1dodecanethiol (0.37 mL, 1.545 mmol) and AIBN (0.2 M solution in toluene, 0.78 mL, 1.562 mmol) were added before adding DBU.

2.3.9.5 DBU + n-butylamine treated PVDF in THF

Same as method used for DBU treated PVDF (1%) in THF (Section 2.3.9.2) except nbutylamine (0.15 mL) was added before adding DBU.

2.3.9.6 Dehydrofluorination of PVDF with 10 % DBU in DMAc

PVDF powder (2 g, 31.23 mmol of repeat units) was dissolved in 20 mL of DMAc at room temperature under N₂. DBU (0.48 mL, 3.210 mmol) was added and the solution left stirring at room temperature overnight. Samples were taken at timed intervals and precipitated in 75-100 mL of ethanol, filtered, washed with ethanol and dried in an oven at 60 °C overnight. Overnight, the polymer solution became a soft, black solid, which was then washed and soaked in ethanol overnight several times and dried in the oven at 60 °C overnight. The soft solid shrunk but continually 'wept' liquid, and was again soaked several times in ethanol overnight and dried overnight again at 60 °C. This yielded a shrunken, hard but brittle black solid.

2.3.9.7 DBU + 1-dodecanethiol (1:5 mol ratio) treated PVDF in DMAc

Same as the method used for DBU treated PVDF (10 mol%) in DMAc (Section 2.3.9.6) except 1-dodecanethiol (3.75 mL, 15.66 mmol) was added prior to addition of DBU.

2.3.9.8 DBU + 1-mercaptopropionic acid treated PVDF in DMAc

PVDF powder (1 g, 15.62 mmol of repeat units) was dissolved in 10 mL of DMAc at room temperature under N₂. 1-mercaptopropionic acid (0.14 mL, 1.607 mmol) was added followed by DBU (0.24 mL, 1.605 mmol). After 24 h stirring at room temperature, a sample was taken and precipitated and washed with ethanol and dried at 60 °C overnight. To the remaining polymer solution another aliquot of 1-mercaptopropionic acid (0.14 mL, 1.607 mmol) was added, and left to stir for another 48 h at room temperature, with samples taken at 24 h after the addition of the extra portion of 3-mercaptopropionic acid (48 h after the reaction was initially started) and at the end of the 48 h (72 h after the reaction was initially started). The polymer was then recovered by precipitating in ethanol, washing with ethanol and drying overnight at 60 °C.

2.3.9.9 Dehydrofluorination of PVDF by DBU (10 %) in DMAc (bulk)

PVDF powder (30 g, 468.48 mmol of repeat units) was dissolved in 450 mL of DMAc at room temperature under N_2 . DBU (7.2 mL, 48.15 mmol) was added and the

solution left stirring at room temperature for 4 h. After this time, the solution was poured into two stirred 2.5 L beakers of ethanol (~1.5 L of ethanol each), which precipitated a black solid. This was left to stir for 1 h, then the precipitate was recovered by filtration using a water aspirator. The recovered precipitate was then continuously washed with fresh ethanol until the ethanol filtrate was colourless to the naked eye. The solid was then allowed to air dry overnight, followed by drying overnight in an oven at 60 °C. It should be noted that to avoid forming a single black solid, the precipitate was disturbed and separated using a plastic spatula, as otherwise it was difficult to break off or cut the black polymer for further experimentation. The resulting product was a hard, brittle black solid, referred to as d-PVDF.

2.3.10 UV-catalysed reactions of dehydrofluorinated PVDF (d-PVDF)

The following experiments involve modification of dehydrofluorinated PVDF (d-PVDF) using DBU (Section 2.3.9.9)) by UV-catalysed thiol-ene addition with either 1dodecanethiol or 3-mercaptopropionic acid.

2.3.10.1 UV-irradiation only

d-PVDF solid (0.1 g) was dissolved in 1.5 mL of DMAc at room temperature under N₂ with stirring in a sealed glass vial. The cap was then removed and the vial placed in a UV cabinet (5 x 8 W UV-tubes at a wavelength of ~365 nm) 1 h with UV-light. The polymer was then recovered by precipitation in ~100 mL of ethanol, filtered and washed with ethanol, followed by drying in an oven at 60 °C overnight.

2.3.10.2 UV-irradiation with benzophenone

Method similar to Section 2.3.10.1, however benzophenone (0.0142 g, 0.0781 mmol) was dissolved in DMAc with the d-PVDF.

2.3.10.3 UV-irradiation with double benzophenone

Method similar to Section 2.3.10.1, however benzophenone (0.0285 g, 0.1562 mmol) was dissolved in DMAc with d-PVDF and treated with UV-irradiation for 4 h (instead of 1 h).

2.3.10.4 UV-irradiation with 1-dodecanethiol

Method similar to Section 2.3.10.1, however 1-dodecanethiol (0.19 mL, 0.7808 mmol) was added to the DMAc/d-PVDF solution prior to UV-irradiation.

2.3.10.5 UV-irradiation with 1-dodecanethiol and benzophenone

Method similar to Section 2.3.10.2, however 1-dodecanethiol (0.19 mL, 0.7808 mmol) was added to the DMAc/d-PVDF/benzophenone solution prior to UV-irradiation.

2.3.10.6 UV-irradiation with 3-mercaptopropionic acid

Method similar to Section 2.3.10.1, however 3-mercaptopropionic acid (0.07 mL, 0.7808 mmol) was added to the DMAc/d-PVDF solution prior to UV-irradiation.

2.3.10.7 UV-irradiation with 3-mercaptopropionic acid and benzophenone

Method similar toSection 2.3.10.2, however 3-mercaptopropionic acid (0.07 mL, 0.7808 mmol) was added to the DMAc/d-PVDF/benzophenone solution prior to UV-irradiation.

2.3.10.8 UV-irradiation with double 3-mercaptopropionic acid

Method similar to Section 2.3.10.6, however the quantity of 3-mercaptopropionic acid was doubled (0.14 mL, 1.5612 mmol) and was treated by UV-irradiation for 4 h (instead of 1 h).

2.3.10.9 UV-irradiation with double the quantities of 3-mercaptopropionic acid and benzophenone

Method similar to 2.3.10.3, however 3-mercaptopropionic acid (0.14 mL, 1.5612 mmol) was added to the DMAc/d-PVDF/benzophenone solution prior to UV-irradiation for 4 h.

The results and discussion of the dehydrofluorination experiments of PVDF (Section 2.3.9) as well as the modification of d-PVDF by UV-catalysed thiol-ene addition (Section 2.3.10) can be found in Chapter 5.

2.3.11 Casting of cross-linked PVDF membranes

Cross-linked PVDF membranes were produced by combining dehydrofluorinated PVDF (d-PVDF) and thiol POSS and irradiating the hand cast polymer film (before coagulation in the water bath) with UV-light for 1 h (with benzophenone as a photocatalyst and PVP as pore-forming agent) to cause thiol-ene addition of thiol

POSS with d-PVDF. The results and discussion of the analyses of these membranes can be found in Chapter 6.

Firstly, d-PVDF (3.4 g, 17 wt% (synthesised using the method found in Section 2.3.9.9)) and PVP (1 g, 5 wt%) were dissolved in DMAc (16.7 mL, ~15.6 g, 78 wt%) in brown glass bottles under N_2 (with a magnetic stirrer) by stirring and heating at ~60 °C overnight (~16 h). The bottles were then placed in an oven at 80 °C for 2 h and then removed, and then stirred magnetically for ~4 h before using further.

In a separate glass vial, benzophenone (0.0505 g) and thiol POSS were added together and dissolved in THF (0.5 mL), and once completely dissolved (takes ~1 min), were added to the above d-PVDF/PVP/DMAc solutions in brown glass bottles, and stirred for 1 h. After this time, the resulting solution was cast on to a flat glass plate with a thickness of ~250 μ m by hand using a Doctor's Blade, and then placed in a UV cabinet (5 x 8 W UV-tubes at a wavelength of ~365 nm) and irradiated with UV-light for 1 h. The glass plate with the cast polymer film was then removed and immediately precipitated in a coagulation bath of DI water at room temperature. After 1 h, the coagulation bath water was replaced with fresh DI water, which was repeated several times over a 24 h period. Finally, the membranes were stored in 10 % IPA/water (v/v, IPA:water) to prevent bacterial growth. Quantities of each reagent in the final casting solution used for each membrane in this study are listed in Table 2.4.

| Wt% of Thiol POSS* | Thiol POSS (g) | d-PVDF (g) | PVP (g) | DMAc volume (mL) (mass (g)) | Benzophenone (g) |
|--------------------------|-------------------|---------------|---------|--------------------------------|---------------------|
| 0 | 0 | 3.4 | 1 | 16.7 (~15.6 g) | 0.0505 |
| 1 | 0.0343 | 3.4 | 1 | 16.7 (~15.6 g) | 0.0505 |
| 5 | 0.1789 | 3.4 | 1 | 16.7 (~15.6 g) | 0.0505 |
| 10 | 0.3778 | 3.4 | 1 | 16.7 (~15.6 g) | 0.0505 |

 Table 2.4 – Quantities of reagents used in the casting solution to produce crosslinked PVDF membranes

*Wt% calculated relative to PVDF (Not including PVP or DMAc)

The results and discussion of the analyses of the cross-linked PVDF membranes with thiol POSS can be found in Chapter 6.

2.3.12 Casting of EgMA-POSS modified PVDF membranes with Eugenyl Methacrylate

EgMA-POSS modified PVDF membranes were produced using a combination of DBUmodified PVDF (d-PVDF), thiol POSS, and EgMA, reacted together with UV-irradiation and benzophenone as a photocatalyst to provide radicals (as well as PVP as pore forming agent). The results and discussion of the analyses of these membranes can be found in Chapter 6.

To cast EgMA-POSS modified membranes, first d-PVDF (3.4 g, 17 wt% (synthesised using the method found in Section 2.3.9.9)) and PVP (1 g, 5 wt%) were dissolved in DMAc (16.7 mL, ~15.6 g, 78 wt%) in brown glass bottles under N₂ (with a magnetic stirrer) by stirring and heating at ~60 °C overnight (~16 h). The bottles were then placed in an oven at 80 °C for 2 h and then removed, and then stirred magnetically for ~4 h before using further.

In a separate glass vial, benzophenone (0.0505 g), thiol POSS, and EgMA(see footnote¹) were added together and dissolved in THF (0.5 mL), and once completely dissolved (takes ~1 min), were added to the above d-PVDF/PVP/DMAc solutions in brown glass bottles, and stirred for 1 h. After this time, the solution was cast on to flat glass plate with a thickness of ~250 µm by hand using a Doctor's Blade, and then placed in a UV cabinet (5 x 8 W UV-tubes at a wavelength of ~365 nm) and irradiated with UV-light for 1 h. The glass plate with the cast polymer film was then removed and immediately precipitated in a coagulation bath of DI water at room temperature. After 1 h, the coagulation bath water was replaced with fresh DI water, which was repeated several times over a 24 h period. Finally, the membranes were stored in 10 % IPA/water (v/v, IPA:water) to prevent bacterial growth. Quantities of each reagent in the final casting solution used for each membrane in this study are listed in Table 2.5.

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¹With high quantities of EgMA (10-20 wt%), to avoid solubility issues in THF, EgMA was added to d-PVDF/PVP/DMAc solution (instead of in the thiol POSS/benzophenone/THF solution), and allowed to stir for ~1 h before adding the thiol POSS/benzophenone/THF solution.

| Name | d- PVDF (g) | PVP (g) | DMAc volume (mL) (mass (g)) | Thiol-POSS (g) (wt%*) | EgMA (g) (wt%*) | Benzop henone (g) |
|----------------|-------------------|------------|--------------------------------------|--------------------------|--------------------|-------------------------|
| 0 thiol POSS - | 3.4 | 1 | 16.7 | 0 | 0 | 0.0505 |
| 0 EgMA | | | (~15.6 g) | (0 wt%) | (0 wt%) | |
| 10 thiol POSS | 3.4 | 1 | 16.7 | 0.3778 | 0 | 0.0505 |
| - 0 EgMA | | | (~15.6 g) | (10 wt%) | (0 wt%) | |
| 10 thiol POSS | 3.4 | 1 | 16.7 | 0.3778 | 0.0343 | 0.0505 |
| - 1 EgMA | | | (~15.6 g) | (10 wt%) | (1 wt%) | |
| 10 thiol POSS | 3.4 | 1 | 16.7 | 0.3778 | 0.1789 | 0.0505 |
| - 5 EgMA | | | (~15.6 g) | (10 wt%) | (5 wt%) | |
| 10 thiol POSS | 3.4 | 1 | 16.7 | 0.3778 | 0.3778 | 0.0505 |
| - 10 EgMA | | | (~15.6 g) | (10 wt%) | (10 wt%) | |
| 10 thiol POSS | 3.4 | 1 | 16.7 | 0.3778 | 0.8500 | 0.0505 |
| - 20 EgMA | | | (~15.6 g) | (10 wt%) | (20 wt%) | |

 Table 2.5 – Quantities of reagents used in the casting solution to produce EgMA

 POSS modified PVDF membrane

*Wt% relative to d-PVDF only

The results and discussion of the analyses of the EgMA-POSS modified PVDF membranes with thiol-POSS and EgMA (Section 2.3.12) can be found in Chapter 6.

2.4 Sample preparation, analysis, and instrumentation

2.4.1 Nuclear Magnetic Resonance (NMR) Spectroscopy

Solution NMR spectroscopy experiments (both 1D and 2D NMR experiments) were performed using either a 400 MHz or 600 MHz Bruker Avance III Spectrometers. All experiments were performed at room temperature in solution, using either CDCl₃ or D_6 -DMSO as the solvent.

Solution ¹H (400.00 or 600.01 MHz) NMR spectra were collected using the solvent signal as the reference – 7.27 ppm for CDCl₃ and 2.50 ppm for D_6 -DMSO.

Solution ${}^{13}C$ (100.57 or 150.86 ppm) NMR spectra were collected using the solvent signal as the reference – 77.16 ppm for CDCl₃ and 39.52 ppm for D₆-DMSO.

Solution ²⁹Si (79.53 or 119.29 ppm) NMR spectra were collected using the internal standard, tetramethylsilane (TMS) as the reference, taken as 0.00 ppm.

2.4.2 ATR-FTIR Spectroscopy

Attenuated total reflectance - Fourier transform infrared (ATR-FTIR) spectra were collected using a Thermo Nicolet Nexus 870 FTIR spectrometer with ATR attachment with a diamond window, taken with a resolution of 2 cm⁻¹ and with 32 scans (after taking a background). Solid samples were placed on the window, and carefully pressed against the window using a clamp. For liquid samples, one drop of the liquid was placed on the window, and then a Teflon cover was placed on top.

2.4.3 Scanning Electron Microscopy (SEM)

SEM images of membrane surfaces and cross-sections were taken on either a FEI Phenom SEM or a FEI F50 Inspect SEM, using a voltage of 5 kV and a working distance of 10 mm. Samples were stuck onto SEM stubs using carbon tape, and coated with 5 nm of platinum using a Quorumtech K757X sputter coater with a film thickness monitor.

2.4.3.1 Membrane surfaces

Samples used for imaging of membrane surfaces were prepared by soaking a sample of the membrane in either ethanol (EtOH) or isopropanol (IPA) for 1 h, and then allowing it to air dry overnight before being stuck to the SEM stub.

2.4.3.2 Membrane cross-sections

Samples used for imaging of membrane cross-sections were prepared using a modified cryo-snap method.^[5] After soaking membrane strips in either EtOH or IPA for 1 h, the membrane strips were then placed in test tubes filled with DI water. The membrane strips were placed such that they were extended across the length of the test tube as much as possible. The test tubes were then slowly immersed in liquid N₂. As the liquid in the test tube was observed to freeze the test tube was lowered further, which was continued until all the liquid was frozen and the liquid N₂ level had reached the same height as the liquid level in the test tube. After leaving the test tube immersed at this depth for 1 minute, the test tube was then removed from the liquid N₂, wrapped in several layers of paper towel, before being carefully smashed with a hammer. Once a clean break of the sample had been obtained, the frozen membrane was soaked in IPA until fully defrosted, and then left to air dry overnight. Finally, the membrane sample was stuck between two pieces of brass with carbon tape before being stuck to the SEM stub, so that the cross-section was facing upwards.

2.4.4 Pure water flux (PWF)

The pure water flux (PWF) and BSA rejection of the membranes fabricated in this work were measured using a Sterlitech UHP 76 450 mL dead-end stirred cell equipped with a Sterlitech 5 gallon 316 stainless steel pressure vessel to act as external reservoir. To measure the filtration performance of the membranes, the set-up was pressurised with high purity nitrogen gas. A schematic of the set-up can be seen in Figure 2.1.



Figure 2.1 - Schematic of the set-up of the filtration apparatus used in this work. 1
= N₂ canister; 2 = 5 gallon pressure vessel; 3 = stirred cell; 4 = hotplate-stirrer; 5 = jack; 6 = collection bottle; 7 = balance. A = N₂ canister opening; B = pressure regulator; C = N₂ outlet from pressure vessel to stirred cell. Z1 = pressure gauge for internal N₂ canister; Z2 = pressure gauge for exiting N₂ pressure; Z3 = pressure gauge for outlet N₂ pressure; Z4 = pressure gauge of N₂ pressure of pressure vessel.

Before measuring the PWF, membranes were soaked in IPA for 0.5 h, and then MilliQ water for a further 0.5 h. During the soaking periods, the pressure vessel (2) was filled with MilliQ water, connected to the N₂ canister (1), and pressurised by opening the tap of the N₂ canister (A), and adjusted to the desired pressure using the pressure regulator (B) (using the pressure gauge Z3 as the pressure reading). After the membrane soaking periods were completed, the membrane was then assembled into the stirred cell (3), and the stirred cell filled with MilliQ water and connected to the pressure vessel (2). The tap (C) connecting the pre-pressurised pressure vessel (2) to the stirred cell (3) was then opened, allowing water to flow from the pressure vessel to the stirred cell. The applied pressure forced the water to flow through the membrane within the stirred cell and into a collection vessel (6). The mass of water collected was recorded with time using the balance (7), which was connected to a computer which measured the mass at 1 minute intervals.

Measuring the PWF was conducted over 3 h. For the first hour, the membrane was placed under pressure (with the set-up in Figure 2.1), and the PWF measured for 1 h (referred to as Phase 1). After 1 h of measuring the PWF the pressure was then released, and the stirred cell disconnected from the set-up and emptied, leaving a thin-layer of water to keep the membrane hydrated. The stirred cell (with the membrane still fixed inside) was left for 1 h, referred to as the Recovery Phase. After being left for 1 h, the stirred cell was filled with MilliQ water, placed back into the set-up (Figure 2.1), and the PWF measured again at the same pressure for 1 h (referred to as Phase 2). Immediately after completing the Phase 2 of PWF measurements, the pressure was released, and the stirred cell emptied, ready for BSA rejection measurements.

2.4.4.1 Calculations

$$PWF = \frac{\Delta V}{\Delta t.A}$$

Where PWF = pure water flux, ΔV = change in volume of permeate in litres (L) over a period of time, Δt , in hours (h), and A = effective membrane surface area in m² (0.00385 m² for the stirred cell used).

The initial PWF (PWF_i) was taken as the PWF after 1 min of filtration, while the final PWF (PWF_f) was taken as the average of the last 5 measurements before the 1 h mark was reached.

The % flux change_x (the change in PWF over the 1 h period, where x denotes the Phase number the PWF measurement was taken (x = 1 or 2)) was calculated using the equation below;

% flux change_x =
$$\left(\left(\frac{PWF_{xf}}{PWF_{xi}}\right) - 1\right) * 100$$

Where PWF_{xi} = initial PWF of phase x, PWF_{xf} = final PWF of phase x.

The % *flux recovery*, the change in PWF between the end of Phase 1 and Phase 2 of the PWF measurements, was calculated using the equation below;

% flux recovery
$$= \left(\frac{PWF_{2i}}{PWF_{1f}}\right) * 100$$

Where PWF_{1f} = the final PWF of the Phase 1 of PWF measurements, and PWF_{2i} = the initial PWF of the Phase 2 of PWF measurements.

The error (E) in these measurements was taken as the standard error of the mean, calculated using the equation below (using Microsoft Excel);

$$E = \frac{STDEV.S(range)}{SQRT(COUNT(range))}$$

2.4.5 Rejection of Bovine Serum Albumin (BSA)

2.4.5.1 Preparation of Phosphate buffered saline (PBS) solution

10 mM phosphate buffered saline (PBS) was prepared by adding NaCl (14.9606 g), KCl (0.4026 g), NaH₂PO₄.2H₂O (0.5928 g), and Na₂HPO₄.2H₂O (2.8834 g) to clean and dry 2 L glass Schott bottle, which was then filled to the 2 L mark with MilliQ water. A stirrer bar was then added, and the solution was stirred magnetically until all solids had dissolved. The resulting PBS solution was kept at room temperature and used within one week of production, or otherwise discarded, so as to prevent interference from bacterial growth.

2.4.5.2 Preparation of Bovine Serum Albumin (BSA) solution

For BSA rejection experiments, a 0.2 g.L⁻¹ BSA solution in 10 mM PBS was prepared 1 h prior use. To a clean and dry measuring cylinder, BSA (0.0700 g) was added, and then made to a volume of 350 mL using the pre-prepared 10 mM PBS solution. A stirrer bar was added, and the solution was stirred magnetically until the BSA solution was to be used.

2.4.5.3 BSA rejection measurement

Immediately after the PWF measurement of the membrane was complete, the pressure was released, the stirred cell emptied, and rinsed 3 times with the prepared 0.2 g.L⁻¹ BSA solution (using ~50 mL of the solution). The stirred cell was then filled with the remaining BSA solution, and a ~20 mL sample was taken for measurement of the initial BSA concentration. The stirred cell was then connected directly to the N₂ canister, and pressurised to the same pressure used for the PWF measurement. Initially, ~50 g of the solution permeate was collected and discarded, then ~150 g of permeate was then collected. The pressure was then released, and after collecting the BSA solution samples from the permeate and from the solution remaining in the

stirred cell, any remaining solution was discarded. All glassware and the stirred cell were thoroughly rinsed with DI water, cleaned with Pyroneg solution, and then rinsed thoroughly with DI water again. Glassware used to collect samples of BSA solution for analysis were rinsed with MilliQ water before being dried in an oven at 80 °C, while the stirred cell was rinsed thoroughly with EtOH, and either allowed to air-dry, or if used again that day, rinsed with MilliQ water for the next membrane.

2.4.5.4 BSA concentration measurements

The BSA concentration of the starting BSA solution (sample taken from the stirred cell prior to filtration) and in the permeate were measured using an Agilent Cary 60 UV-Vis Spectrophotometer. The UV-Vis absorbance of the solutions was measured at a wavelength of 278 nm (note²) in 2.5 mL UV cuvettes macro (dimensions - 12.5 x 12.5 x 45 mm) BRAND[®], using the 10 mM PBS solution used to make the BSA solution as the blank. 5 samples of the initial BSA solution and the permeate solution were measured with 3 scans per sample. From the measured absorbance the BSA concentration of the solutions were measured using a pre-established BSA calibration curve using standard solutions of BSA in 10 mM PBS solution, with BSA concentrations ranging from 0.0096-2 g.L⁻¹. The resulting calibration curve can be seen in Figure 2.2. As can be seen the calibration curve shows a linear trend of UV-Vis adsorption with BSA concentration across the whole range of BSA concentrations tested, indicating that UV-Vis is an appropriate technique to measure the BSA concentration in solution. The fitted trend line (y(UV-Vis absorption at 278 nm) =0.6535.x(BSA concentration in g.L⁻¹)) was used to calculate the BSA concentration in solution.

 $^{^{\}rm 2}$ Wavelength was chosen by running a UV-Vis spectrum of the BSA solution



Figure 2.2 – UV-Vis calibration curve of BSA concentration and UV-Vis adsorption measured at 278 nm. The standard BSA solutions in concentrations ranging from 0.0096-2 g.L-1 were prepared in 10 mM PBS solution, and the PBS solution was used as the blank.

2.4.5.5 Calculations

The concentration of BSA (C_{BSA}) was calculated using the equation below;

$$C_{BSA} = \frac{y}{m}$$

Where y = absorbance of the solution at 278 nm, and the slope of the trend-line (obtained from Figure 2.2), m = 0.6535 L.g⁻¹.

The BSA rejection was calculated using the equation below;

$$BSA \ rejection = \left(\left(\frac{C_{BSAp}}{C_{BSAs}}\right) - 1\right) * 100$$

Where C_{BSAs} = the concentration of BSA in the initial solution, and C_{BSAp} = the concentration of BSA in the permeate.

The error (E) in these measurements was taken as the standard error of the mean, calculated using the equation below (using Microsoft Excel);

$$E = \frac{STDEV.S(range)}{SQRT(COUNT(range))}$$

2.4.6 Bacterial Adhesion Tests

To assess the anti-biofouling performance of the membranes, membrane pieces were soaked in a nutrient solution for 1-6 days to promote growth of bacteria in the solution. The membrane pieces were then removed, and after applying a fixing treatment to the membrane, the number of bacterial cells was counted on the membrane top-surface using SEM. Prior to this experiment, all glassware was rinsed with ethanol and left to air dry before use.

2.4.6.1 Biofouling of membranes

The method of measuring bacterial adhesion on the surfaces of membranes by soaking the membranes in nutrient solution is based on literature methods.^[6, 7] First, membranes were soaked in ethanol and allowed to air-dry overnight, before being cut into ~ 1 x 1 cm squares. Each membrane was then immersed in its own bottle containing 80 mL of nutrient solution (sodium chloride (1g), ammonium chloride (20 mg), sodium acetate (100 mg), magnesium sulphate (20 mg), and sodium dihydrogen phosphate dihydrate (13 mg) dissolved in 500 mL of MilliQH₂O), and left for 1, 2, 4, or 6 days before being removed. After the desired amount of immersion time was completed, the membrane square was removed from the nutrient solution and swirled briefly in ~20 mL of PBS buffer solution (made using commercial PBS tablets) to dislodge loosely bound bacteria. Following this the membrane square was placed in a fixing solution (consisting of 4 wt% of formaldehyde (by adding ~10.81 g of 37 wt% formaldehyde solution), and glutaraldehyde (by adding 2 mL of 50 wt% glutaraldehyde solution), made up to 100 mL with PBS buffer solution (made using commercial PBS tablets)) for 30 min. Following the fixing procedure, the membranes were then dehydrated by serial immersion in 50 %, 75 %, 90 %, and then 100 % ethanol/water solutions (v/v, ethanol:water) for ~20 min each before allowing to air dry overnight. After fixing the dried membrane square to an SEM stub using carbon tape, and then sputter coating with 5 nm of platinum, the membranes were then ready for bacterial cell counting.

Chapter 2

2.4.6.2 Bacterial cell counting by SEM

To gain an approximation of the number of bacteria cells on the membrane surface, the membrane was first observed at the lowest magnification (x45, with a working distance of 10 mm). After finding the approximate centre of the membrane, 8 places around the centre in a circular pattern were marked, and then images are taken at all of these places at x2400 magnification, for a total of 9 images (centre plus 8 places around centre).





The number of bacterial cells on each SEM image was counted using ImageJ software. For SEM images with low numbers of bacterial cells on the membrane surface, the "Cell Counter" plugin was used, which allows one to mark each cell with a number observed on the image manually with the mouse, while keeping a tally of the number of cells marked. For SEM images with large numbers of bacterial cells on the membrane surface, the "Analyze Particles" function was employed, which is capable of counting the number of particles in the SEM image. The following protocol was employed to calculate the number of bacterial cells using the "Analyze Particles" function;

1. The image is loaded into ImageJ

- 2. The image scale is set by drawing a line over the SEM scale bar on the image, and specifying the 'known distance' as 50, and the units as μm
- 3. Placing a rectangle over the bottom part of the SEM image, covering the scale bar and other SEM information, and choosing the 'fill' option. This is done to remove this part of the SEM image from being counted.
- 4. Using the "Threshold" function, the image is converted to black and white, so as to be able to use the "Analyze Particles" function. Visually, the best settings for the "Threshold" option of the SEM images were;
 - a. Threshold method Intermodes
 - b. Threshold colour B & W (black and white)
 - c. Colour space HSB
 - d. Dark background box ticked
 - e. The brightness of the image is adjusted so as to emphasise the bacterial cells on the membrane surface while limiting the appearance of features from the membrane surface
- 5. The "Make binary" process is then chosen, followed by the "Watershed" process, the latter which is able to separate bacterial cells that appear joined together in the image, which would otherwise be counted as a single cell, or not counted at all for being outside the size range
- 6. The "Analyse Particles" option is chosen, and the following settings are used;
 - a. Size (µm²) 0.20 3.00
 - b. Pixel units box not ticked
 - c. Circularity 0 1
 - d. Show count masks
 - e. The following boxes are ticked Display results, Summarize, Add to Manger, In situ Show
 - f. Ok is selected
- 7. The pop-up image with the count masks shown is visually compared to the original image to check if the count appears to be realistic. If not, the analysis is restarted, with adjustments made to the settings (mainly altering the "Threshold" brightness settings) or by covering over membrane surface features that are too bright.
- 8. If the analysis is considered acceptable, the number of bacterial cells within each SEM image is taken as the 'count' from the Summary pop-up window which appears, which is recorded on an Excel spreadsheet

The mean bacterial cell count on the membrane surface was calculated as the average of the total bacterial cell count of the 9 images (each image covers a 0.1146

x 0.1245 mm area, for a surface area of 0.0142677 mm^2).

2.4.6.3 Calculations

Calculations were carried out in Microsoft Excel 2016.

First, the mean bacteria count, μ , was calculated with the equation below;

$$\mu = AVERAGE(range)$$

Second, the standard deviation of the bacteria count, *SD*, was calculated with the equation below;

$$SD = STDEV.S(range)$$

Third, outliers in the bacterial cell counts were determined to be individual counts outside the limits of the mean bacteria count $\pm 2 * SD$, equation below;

$$Limits = \mu \pm 2 * SD$$

The outliers determined with above equation were then excluded from the calculations, and the process was repeated until no more outliers remained, giving the final mean bacteria count, μ , and the standard deviation, *SD*. It should be noted that no more than one individual bacterial cell count was excluded using this method.

The error of the mean bacteria count was calculated as the standard error of the mean, using the equation below;

$$E = \frac{STDEV.S(range)}{SQRT(COUNT(range))}$$

The mean bacteria count per unit area, μ_A , (the value reported in the this work) was calculated with the equation below;

$$\mu_A = \frac{\mu}{A}$$

Where A = the membrane surface area covered by the SEM image, which was determined to be 0.0142677 mm².

The error of the bacteria count per unit area, E_A , (the reported error value) was then calculated using the error of the mean bacteria count, E, using the equation below;

$$E_A = \mu_A * \left(\frac{E}{\mu}\right)$$

2.4.7 Stress/strain experiments

The tensile properties of membranes were tested using a TA Instruments Q800 Dynamic Mechanical Analyser (DMA). To run tensile tests, the membranes were first

cut into strips ~6 mm wide and ~30 mm long, using a scalpel and ruler. The width and thickness of the strips were measured using digital calipers. The strips were then mounted into the tension film clamp of the DMA with a load torque of 0.0113 N.m (0.1 ln.lbs⁻¹). To run the tensile tests, the DMA was run in 'controlled force' mode using the 'stress/strain' test. After applying a pre-load force of 0.1-0.3 N to straighten out the membrane strip completely, the effective length of the membrane strip (distance between the upper and lower clamps) was measured by the DMA instrument. To start the run, the sample was equilibrated at 25 °C for 5 min, after which a force ramp of 1 N.min⁻¹ was applied to the membrane strip until the strip broke. The data from the stress/strain experiment were analysed using TA Universal Software. The experiment was repeated for at least 3 samples, and the results averaged for each membrane type. The error in the values was taken as the standard error of the mean, calculated with the equation below (using Excel);

$$E = \frac{STDEV.S(range)}{SQRT(COUNT(range))}$$

To illustrate how the different tensile parameters (Young's modulus, stress at break, and % strain at break), a simplified stress-strain curve with these parameters marked are presented in Figure 2.4.



% Strain

Figure 2.4 - Illustration of the results of a typical stress-strain experiment. The blue curve is the sample, with the stress (force applied) to the sample with the change in % strain (change in sample length (as a percentage) due to the applied stress) measured by the instrument. From this curve, the Young's modulus (slope of the line before necking), % stress at break (stress achieved when the sample broke), and the % strain at break (how much the sample was stretched at breakage).

2.4.8 Pore size distribution

The pore size distribution of membranes were determined by imaging the surface of the membrane using SEM, and then using ImageJ software to count the number of pores as well as their sizes. For each membrane, three random places on the membrane surface were imaged at a magnification of 8000x. The following protocol was used to calculate the pore sizes and counts, using the "Analyze Particles" function;

- 1. The image is loaded into ImageJ
- 2. The image scale is set by drawing a line over the SEM scale bar on the image, and specifying the 'known distance' as 20, and the units as μm
- 3. Placing a rectangle over the bottom part of the SEM image, covering the scale bar and other SEM information, and choosing the 'fill' option. This is done to remove this part of the SEM image from being counted.
- 4. Using the "Threshold" function, the image is converted to black and white, so as to be able to use the "Analyze Particles" function. Visually, the best settings for the "Threshold" option of the SEM images were;

- a. Threshold method Intermodes
- b. Threshold colour B & W (black and white)
- c. Colour space HSB
- d. Dark background box not ticked
- e. The brightness of the image is adjusted so as to emphasise the pores on the membrane surface while limiting the appearance of features from the membrane surface
- 5. The "Make binary" process is applied
- 6. "Set Measurements" is selected, and Feret's Diameter box is ticked to be included in the results
- 7. The "Analyse Particles" option is chosen, and the following settings are used;
 - a. Size (μm^2) 0.01 infinity
 - b. Pixel units box not ticked
 - c. Circularity 0 1
 - d. Show count masks
 - e. The following boxes are ticked Display results, Summarize, Add to Manger, In situ Show
 - f. Ok is selected
- 8. The pop-up image with the count masks shown is visually compared to the original image to check if the count appears to be realistic. If not, the analysis is restarted, with adjustments made to the settings (mainly altering the "Threshold" brightness settings) or by covering over membrane surface features that are too bright.
- 9. If the analysis is considered acceptable, the results table is saved as a .csv document

The pore radius (r_p , in nm) of each pore is calculated from the Feret's Diameter (which is in μ m) of the pore as determined by ImageJ, using the following equation in Excel;

$$r_p = \left(\frac{Feret's \ Diameter \ (\mu m)}{2}\right) * \ 1000$$

The data from the three images for each membrane is combined, and the histogram plotted in Origin Pro 9 software.

2.5 References

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Chapter 3 TFP POSS/PVDF blended membranes

3.1 Synopsis

This chapter covers the analysis of PVDF membranes blended with 3,3,3trifluoropropyl POSS (TFP POSS) produced via non-solvent induced precipitation. It was found by ATR-FTIR spectroscopy that increasing the relative quantity of TFP POSS in the casting solution increased the relative quantity of TFP POSS to PVDF in the resulting membrane. The addition of TFP POSS was found to have no appreciable effect on the tensile mechanical properties (Young's Modulus and % Strain at break) of the membranes, but did produce changes in the surface and cross-sectional morphology of the membranes. The pure water flux (PWF) values of the membranes did not change significantly with inclusion of TFP POSS, and the rejection of BSA was maintained at approximately 90 %.

3.2 Introduction

Incorporation of POSS as a nanofiller into different polymers has been shown, in some instances, to provide improvements in mechanical properties.^[1-3] POSS is desirable as a nanofiller in polymeric membranes as it is readily soluble in organic solvents and so should readily be able to be incorporated into the membrane fabrication process. So far, there has been relatively few studies on incorporating POSS into PVDF to form nanocomposites, and only three studies published so far on incorporating POSS into PVDF water filtration membranes. The following outlines those studies.

Previous studies on incorporation of POSS into PVDF films (non-membrane) have included; fluorooctyl-POSS, fluorodecyl-POSS and methyl-POSS into PVDF by melt blending in a microcompounder;^[4] methacryloxypropyl-POSS incorporated by melt blending,^[5, 6] trifluoropropyl heptaisobutyl POSS incorporated by dissolution and solution evaporation,^[7], the fusion of MWCNTs coated in acryloxypropyl-POSS (grown by ATRP from the surface of MWCNTs functionalised with bromo-initiator groups) incorporated into PVDF films prepared by dissolution, solution evaporation and then thermo-compression at 220 °C,^[8] and finally, multiple studies on

trifluoropropyl-POSS (TFP POSS) incorporated into PVDF by dissolution in DMF followed by drying at 70 °C under vacuum.^[9-13]

In a report published in 2005 by the Air Force Research Lab (Edwards AFB, California, USA) three different POSS cages, namely fluorooctyl-POSS, fluorodecyl-POSS and methyl-POSS were added into PVDF by melt blending in a microcompounder at 180 °C at 100 rpm for 3 min, and then the nanocomposite was molded into the desired shape for analysis.^[4] Incorporation of any of the three POSS used into PVDF, at either 5 and 10 wt% loading, was found to slightly reduce the elastic modulus and stress at yield as compared to unfilled PVDF. Addition of POSS to PVDF did produce significant changes in the hydrophilicity of the PVDF nanocomposite, with water contact angle increasing from 73.2° for unfilled PVDF up to 110.6, 110.8 and 94.6° (for fluorooctyl-POSS, fluorodecyl-POSS and methyl-POSS respectively (all at 10 wt% loading).

Incorporating methacryloxypropyl-POSS into PVDF films has previously been conducted by melt blending the two in a batch mixer at 200 °C at 200 rpm for 10 min. Analysis by SEM revealed that with the conditions of PVDF film preparation used showed that large agglomerate formation of POSS was suppressed at small loadings of POSS (1 wt% or less) but formed large agglomerates if greater than 1 wt% of POSS was used. Analysis by dynamic mechanical analysis (DMA) of the resulting nanocomposite indicated that the addition of methacryloxypropyl-POSS to PVDF did not cause any significant change in storage or loss moduli of the polymer films, but the presence of methacryloxypropyl-POSS did reduce the viscosity of the liquid-melt-blend, as measured by rheometry.^[5, 6]

Incorporating trifluoropropyl heptaisobutyl POSS into PVDF films has been performed by dissolution of the POSS and PVDF in DMF at room temperature, followed by solvent evaporation under vacuum at 70 °C.^[7] Analysis of the surface morphology by optical microscopy showed that at all weight percentages of POSS used (3, 5 and 8 wt%) micron-sized aggregates of POSS in the PVDF matrix were produced. Nanoindentation studies of the POSS-PVDF nanocomposites revealed that the maximum loading of POSS (8 wt%) produced a larger reduction of hardness and elastic modulus with indentation depth as compared to other nanocomposites and
PVDF without POSS, but otherwise did not produce a significant change in the mechanical properties.

Perhaps the most unusual POSS-based additive used in PVDF was based on a combination of POSS and CNTs, and using this POSS-CNT additive in PVDF films.^[8] This POSS-CNT fusion was accomplished by first chemically bonding a bromo-ester to the walls of MWCNTs, followed by applying ATRP to polymerise acryloxypropyl-POSS. This produced a cross-linked and covalently bound shell of acryloxypropyl-POSS around the outside of the MWCNTs, with the thickness of the POSS shell controllable by adjusting grafting density of the bromo-ester initiator on the surface of the MWCNTs. To form the nanocomposite, PVDF and the POSS-CNT were dissolved in DMAc, dried under vacuum at 100 °C for three days then thermocompressed at 220 °C to produce the nanocomposite PVDF films. While dielectric properties of nanocomposite PVDF films were examined, largely the analysis focused on synthesis of the POSS-CNT additive (and products of the various steps leading up to it) with very little analysis provided on the nanocomposite PVDF films themselves. This prevents any real conclusion to be made on the advantages of this POSS-CNT additive as compared to unmodified MWCNTs, such as effect on CNT dispersion or mechanical properties. However, this does appear to be a promising method to modify CNTs to improve compatibility of CNTs with polymer matrices.

Out of all the studies regarding incorporation of POSS into PVDF, the most studied has involved formation of 3,3,3-trifluoropropyl-POSS (TFP POSS) in PVDF nanocomposites.^[9-13] This has been typically achieved by dissolution of TFP POSS and PVDF in DMF and then removing the solvent under vacuum at 70 °C, producing films approx. 70 µm thick. It was found that the optimal loading (out of the ones used) of 3 wt% of TFP POSS improved the Young's modulus (increased from 1.53 to 2.10 GPa), yield strength (increased from 28.3 to 37.6 MPa), fracture strength (increased from 33.1 to 44.8 MPa) and hardness (increased from 0.60 to 0.81 GPa) while slightly reducing % fracture strain (decreased from 14.2 to 11.8 %). Increasing the TFP POSS loading further was shown to reduce these properties, and at 8 wt% loading gave mechanical properties equivalent, or weaker than, the PVDF control while further reducing the % fracture strain.^[9] TFP POSS was found to disperse well in the PVDF

matrix showing no large aggregates by optical microscopy,^[9] as well as forming homogeneous solutions in DMF.

For incorporation of POSS into PVDF membranes currently there are only three studies. The first was published in 2009 and involved grafting POSS onto PVDF, and then forming membranes containing 0, 0.5, 1 and 2 wt% of POSS.^[14] This was accomplished by grafting an amino-functionalised POSS (aminopropyl heptaisobutyl POSS) via Michael addition to PVDF modified with alkenes (introduced by alkaline treatment), and then confirmed attachment by Raman spectroscopy. XPS of the resulting membranes also confirmed the presence of POSS. However, the properties (ie., mechanical, rejection, water flux, etc) of the membranes were not analysed, giving no indication of the effect the POSS had on the resulting nanocomposite properties.

The second study on incorporating POSS into PVDF membranes, published in 2012, was conducted by dissolution of PVDF in DMAc at 70 °C for 24 h, followed by addition of acetone and epoxycyclohexyl heptaisobutyl POSS, which was mixed for a further 24 h at room temperature.^[15] The resulting solution was electrospun into nanofibres to form nanofibre mats. To compare, a nanocomposite film was prepared by casting the POSS-PVDF solution onto a glass slide and the solvents removed under vacuum at 80 °C for 12 h. Analysis of the morphologies by SEM of the POSS-PVDF nanocomposites revealed that the presence of POSS suppressed bead-formation of the resulting nanofibres and reduced size dispersity as compared to neat PVDF nanofibres. While electrospinning produced a homogeneous dispersion of the POSS throughout the PVDF nanofibre, the film produced by simple casting of the PVDF-POSS onto a glass slide followed by solvent evaporation produced micron-sized aggregates, indicating that the electrospinning process is critical to suppressing POSS aggregation in this case. Blending POSS into the PVDF nanofibres also produced a significant improvement in the tensile properties of the PVDF nanofibre mats, approximately doubling the Young's modulus from 35 ± 8 to 70 ± 9 MPa as well as increasing the stress at yield almost three-times from 1.3 ± 0.2 to 3.0 ± 0.5 MPa. The nanofibre mats were not assayed for potential use as water filtration membranes.

The third study on incorporating POSS into PVDF membranes was published in 2015 and involved forming a blended POSS-PVDF nanocomposite membrane using

POSS chemically modified to have polyethylene glycol side-groups.^[16] This involved a two-step procedure of partially oxidising vinyl-POSS with a mixture of hydrogen peroxide and sulphuric acid to produce epoxide groups, and then reacting the epoxide groups with the hydroxide groups of polyethylene glycol using NaOH. Addition of this POSS material (designated EG-POSS) to PVDF membranes was shown to improve the membrane hydrophilicity (water contact angle decreased from 83.1° (no POSS) to 75.0° (2 wt% EG-POSS)), membrane fouling potential (BSA adsorption decreased from approx. 5.75 mg/g (no POSS) to a minimum of around 2.5 mg/g (1-2)wt% of EG-POSS) and membrane tensile properties (tensile strength increased from approx. 2.6 MPa (no POSS) to a maximum of approx. 3.4 MPa (1.5 wt% EG-POSS), but decreased to approx. 3.2 MPa with 2 wt% EG-POSS). The addition of EG-POSS to these membranes also produced changes in the membrane morphology, increasing the effective pore size from approx. 11.4 nm (no POSS) to 16.1 nm with 0.5 wt% of EG-POSS (also reached the highest pure water flux with lowest retention of BSA). This also produced membranes with a more dense macroporous structure. Increasing the EG-POSS loading beyond 0.5 wt% in the PVDF membranes caused the water flux to decrease and BSA retention to increase due to a decrease in the pore size.

While the EG-POSS has shown promising results for the improvements in PVDF water filtration membranes, it would be preferable to use a commercially available POSS, rather than needing to synthesise one.

3.3 Chapter Aim

The choice of POSS to use as a nanofiller in PVDF water filtration membranes requires that the POSS be soluble in similar solvents to PVDF, be water insoluble, compatible with PVDF and ideally be available in large quantities so enough membrane can be produced to perform water filtration experiments. Based on the literature examined and commercial availability, TFP POSS was deemed to be a promising candidate as it has been shown to be soluble in DMF, provides improvements in mechanical properties and is commercially available from Hybrid Plastics Inc. in quantities of up to 100 g. In this work, TFP POSS has been blended into PVDF to produce water filtration membranes (see Figure 3.1 for details) to see if TFP POSS can produce a similar improvement in mechanical properties as it has for PVDF films cast by solvent evaporation. If so, this should lead to more mechanically robust water filtration membranes which should be able to better resist the effects of membrane compaction and reduce flux lost.



Figure 3.1 - Process of forming blended PVDF/TFP POSS membranes, by adding TFP POSS to the membrane casting solution. Note that the schematic of TFP POSS only shows the smallest cage size of the TFP POSS cage mixture for simplicity, however larger POSS cage sizes are also present.

3.4 Results and Discussion

3.4.1 Casting of blended PVDF/TFP POSS membranes

The casting method for PVDF membranes was based on the method used in refs.^[17-19] Initially the casting solutions (DMAc solutions of PVDF, TFP POSS and PVP) were allowed to cool to room temperature before casting but this caused a precipitate to form in the solutions. The temperature of the casting solutions were therefore maintained at 60 °C in an oven before being cast onto glass plates. This was also found to reduce the viscosity of the polymer solutions which made them easier to cast. The detailed method of casting PVDF/TFP POSS membranes can be found in Chapter 2, Section 2.3.1.

While the casting solutions with 0-20 wt% of TFP POSS (relative to PVDF) formed clear, slightly yellowed solutions, the casting solution containing 50 wt% of TFP POSS was cloudy (likely due to incomplete dissolution of the TFP POSS). Pouring out this solution revealed it was inhomogeneous, consisting of viscous globs in a

runny liquid fraction. As a result this casting solution was difficult to spread across the glass plate and did not form a useable membrane upon precipitation in the water bath. However, it was kept for analysis by ATR-FTIR spectroscopy. Otherwise, all the casting solutions containing 0-20 wt% of TFP POSS produced useable membranes.

It was observed that with increasing quantities of TFP POSS a difference in the flow behaviour of the polymer solutions. The solution containing no TFP POSS was highly viscous and, when spread across the glass plate using the doctors blade, only spread approximately 2/3 the length of the glass plate. With increasing TFP POSS concentration, the solution was found to spread further and further along the glass plate, suggesting that addition of TFP POSS reduced the viscosity of the polymer solution. A similar observation was made in a study adding octamethyl POSS (OM POSS) to the melt of high density polyethylene, which found that addition of methyl-POSS decreased the viscosity of the polymer melt at low loadings (0.25-0.50 wt%).^[20] This was attributed to dispersed octamethyl POSS cages acting as a lubricant by interfering with chain entanglement and increasing free volume. In this work the addition of TFP POSS may be interfering with PVDF polymer chain entanglement in solution, increasing the free volume to allow the casting solution to be spread more easily and cover more of the glass plate.

3.4.2 ATR-FTIR spectroscopy studies

The ATR-FTIR spectra of the starting materials, PVDF and TFP POSS, and the PVDF/TFP POSS blended membranes are presented in Figure 3.2 and Figure 3.3 respectively, with the peak assignments listed in Table 3.1. The ATR-FTIR spectra are largely dominated by signals due to PVDF, with all spectra containing a weak signal corresponding to the C-H stretch at 3027 cm⁻¹ and 2984 cm⁻¹, as well as a strong signal at 1402 and 1383 cm⁻¹ corresponding to the C-H bending mode of PVDF. A series of relatively strong signals in the 1350-800 cm⁻¹ region appear due to C-F stretching and bending modes of PVDF as well. The presence of the signal at 1665 cm⁻¹ is attributed to residual PVP (specifically, C=O signal from PVP) trapped in the membrane polymer matrix.^[21, 22]



Figure 3.2 - Overlayed ATR-FTIR spectra of pristine TFP POSS and PVDF. Offset is a close-up of the 2800-3200 cm⁻¹ region of the ATR-FTIR spectra.

The addition of 1 wt% of TFP POSS introduces a very weak signal at 2918 cm⁻¹ which increases in intensity with increasing wt% of TFP POSS. At 20 wt% of TFP POSS the signal at 2953 cm⁻¹ becomes observable (at 1-10 wt% of TFP POSS, this signal is obscured by the C-H peak of PVDF at 2984 cm⁻¹) (Figure 3.3). Despite the strongest signals of TFP POSS being present in the 1500-700 cm⁻¹ region, changes in this region of the ATR-FTIR spectrum cannot be easily observed due to overlap with the signals from PVDF. Only at 5 wt% of TFP POSS can a slight shoulder on the 1172 cm⁻¹ (C-F peak of PVDF) peak at 1127 cm⁻¹ due to the Si-O backbone of the POSS cage be observed (Figure 3.3). Similarly, the shoulder at 1027 cm⁻¹ only appears at 5 wt%. Including the signal at 1067 cm⁻¹, these three signals become more intense with increasing wt% of TFP POSS relative to the PVDF signal at 1172 cm⁻¹ until at 50 wt% the signals at 1127 cm⁻¹ and 1067 cm⁻¹ become more intense than the signal at 1172 cm⁻¹. Other changes include the decrease in the C-H bend intensity at 1402 cm⁻¹ due to PVDF and the appearance of peaks at 1208 cm⁻¹ and 1316 cm⁻¹, also due to the increasing wt% of TFP POSS in the membrane.



Figure 3.3 - ATR-FTIR spectra of PVDF membranes containing different loadings of TFP POSS. Peaks labelled are for those of TFP POSS present in the membranes. Offset is a close-up of the 2800-3200 cm⁻¹ region of the ATR-FTIR spectra.

Qualitatively, this shows that increasing wt% of POSS in the polymer solution used to cast the membranes does increase the quantity of TFP POSS in the final membrane. This is also backed by the presence of PVP in the membranes, which is completely water soluble yet is not completely removed from the membranes during precipitation and washing.

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| Wavenumber (cm ⁻¹) | PVDF | TFP POSS | Assignment | Ref. |
|--------------------------------|------|----------|---|------|
| 3027 (vw) | х | | C-H stretch | |
| 2984 (vw) | х | | C-H stretch | |
| 2953 (vw) | | х | C-H stretch | |
| 2918 (vw) | | х | C-H stretch | |
| 1431 (w) | х | | CH ₂ bending | [23, |
| | | | | 24] |
| 1402 (s) | х | | CH ₂ bending | [24] |
| 1383 (m) | х | | CH ₂ bending | [24] |
| 1274 (m) | х | | C-F out of plane deformation (β- | [25] |
| | | | phase) | |
| 1269 (w) | | х | C-H bending | |
| 1208 (m) | | х | C-H bending | |
| 1205 (s) | х | | CF ₂ assymmetric stretch | [24] |
| 1180 (vs) | х | | CF ₂ symmetric stretch | [24] |
| 1148 (s) | х | | CF ₂ symmetric stretch | [24] |
| 1127 (vs) | | х | Si-O-Si | [26] |
| 1069 (m) | х | | CF ₂ symmetric stretch | [24] |
| 1067 (s) | | х | C-F | [26] |
| 1027 (s) | | х | C-F | [26] |
| 974 (m) | х | | C-H out-of-plane deformation (α - | [25] |
| | | | phase) | |
| 898 (m) | | х | | |
| 874 (vs) | х | | Amorphous polymer | [24] |
| 839 (s) | х | | CH ₂ rocking (β or α -phase) | [25] |
| 796 (m) | х | | CH ₂ rocking (γ-phase) | [25] |
| 762 (s) | х | | CF ₂ bending and scelete bending | [25] |
| | | | (α-phase) | |
| 614 (m) | х | | CF ₂ bending and skeletal bending | [25] |
| | | | (α-phase) | |

 Table 3.1 - IR vibration assignments for PVDF and TFP POSS

*vw = very weak, w = weak, m = medium, s = strong, vs = very strong

3.4.3 SEM of membrane cross-sections

Figure 3.4 (a-f) shows the SEM images of the PVDF membranes containing different loadings of TFP POSS. The addition of TFP POSS produces gradual changes in the membrane morphology with increasing wt% of TFP POSS. Without TFP POSS (Figure 3.4 (a)), the membrane has a very open macroporous structure sitting below a layer of smaller voids. When the loading of TFP POSS is low (1 and 2 wt%, Figure 3.4 (b) and (c)) these two layers merge together, forming macrovoids that start from the membrane surface and extend to the bottom of the membrane. At 5 wt% of TFP POSS (Figure 3.4 (d)), the morphology changes again with the macrovoids now having a more regular oval/tear drop shape with a very small layer of small pores sitting atop a macroporous layer (similar to the cross-section of the membrane with 0 wt% of TFP POSS (Figure 3.4 (a)), however the macrovoids have a more regular shape). Increasing

the TFP POSS loading from 5 to 10 wt% (Figure 3.4 (e)) causes the macrovoids to become similar in size, but when the TFP POSS loading is increased to 20 wt% (Figure 3.4 (f)) the macrovoids become distinctly tear drop shaped, typically starting at the membrane surface but extend to different depths within the membrane. Overall, the macrovoids vary in size but mostly all possess the teardrop shape.

The change in morphologies of the PVDF membranes can be attributed to changes in the membrane formation process. It is known the rate of PVDF precipitation during the phase inversion process has a significant effect on the membranes morphology, with rapid demixing producing membranes dominated by large macrovoids, whereas delayed demixing produces a more sponge-like porestructure.^[17, 27, 28] As the only variable that was changed during these experiments was the content of TFP POSS in the casting solution, the TFP POSS must be causing these changes in membrane morphology. TFP POSS is insoluble in water and would therefore not be expected to be extracted out of the polymer-solution film upon immersion in the water bath. This is consistent with ATR-FTIR spectra (see Figure 3.3), which shows that TFP POSS is in the final membranes. At low quantities of TFP POSS (1-2 wt%) in the casting solution, the effect of TFP POSS on the phase inversion process is not very significant, causing the membrane morphologies of the 0, 1 and 2 wt% TFP POSS membranes to remain similar. At 5 wt% TFP POSS, TFP POSS acts to suppress macrovoid formation, which becomes more pronounced with increasing TFP POSS content. As all the membranes exhibit an asymmetric morphology (dense skin-layer with a macroporous layer underneath) liquid-liquid demixing is the dominant process during membrane formation as opposed to crystallisation of PVDF. Crystallisation of PVDF only predominates when the conditions are used to precipitate the PVDF are very slow (such as using a coagulant bath comprised of alcohols or of water-solvent (good solvents for PVDF) mixtures). [28, 29]



Figure 3.4 - SEM images of the cross-sections of PVDF membranes containing (a) 0 wt%, (b) 1 wt%, (c) 2 wt%, (d) 5 wt%, (e) 10 wt% and (f) 20 wt% of TFP POSS. Scale bar is 150 μm.

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TFP POSS is thought to accomplish this by inhibiting precipitation of PVDF during the phase inversion process. It is hypothesised that the presence of TFP POSS physically gets in the way of PVDF chains merging during the precipitation process. This delays the demixing process which in turn produces the membrane morphologies observed.



Figure 3.5 - Thickness of PVDF membranes with different loadings of TFP POSS (wt%) as measured by SEM of the membrane cross-sections.

The membrane thickness also varies with wt% of TFP POSS added (see Figure 3.5). With no TFP POSS the membrane has an average thickness of 186 ± 4.3 μ m. With the addition of TFP POSS at 1 and 2 wt%, the membrane thickness increases to 226 ± 1.7 μ m and 224 ± 6.0 μ m respectively. Increasing the TFP POSS loading to 5 wt% leads to the membrane thickness significantly decreasing to 135 ± 3.5 μ m, but the membrane thickness then increases with higher content of TFP POSS, with membrane thickness measured as 140 ± 3.8 μ m and 155 ± 1.6 μ m for membranes containing 10 wt% and 20 wt% of TFP POSS respectively

3.4.4 SEM of membrane surfaces

Figure 3.6 (a-f) shows the typical SEM images of the top surfaces of the PVDF membranes containing different loadings of TFP POSS. The PVDF membrane without TFP POSS (0 wt%, Figure 3.6 (a)) has pores (dark spots) randomly dotted across the membrane surface but otherwise has no other distinct features. At 1 wt% of TFP POSS (Figure 3.6 (b)), a distinct zigzag-like pattern can be seen on the membrane surface, a feature which is shared with membranes containing TFP POSS loadings between 1-10 wt% (Figure 3.6 (b-e)). The zigzag-like pattern appears as a linear aggregation of pores, creating valleys on the membrane surface. When the loading of TFP POSS is increased to 20 wt% (Figure 3.6 (f)) the pores form straight lines on the membrane surface.



Figure 3.6 - Typical SEM images of the surfaces of PVDF membranes containing (a) 0 wt%, (b) 1 wt%, (c) 2 wt%, (d) 5 wt%, (e) 10 wt% and (f) 20 wt% of TFP POSS. Scale bar is 20 μm.

Here we propose two different hypotheses for this surface patterning phenomena. It is known that POSS cages tend to have a high affinity for themselves, causing POSS to form large aggregates when attempting to disperse them in polymeric systems.^[7, 30] Here it is proposed that once the polymer casting solution (PVDF/TFP POSS in DMAc solution) is cast onto the glass plate, exposure to the atmosphere (causing cooling and exposure to atmospheric moisture) causes TFP POSS to start aggregating, forming regions of higher concentrations of TFP POSS. Upon immersion in the coagulation bath, these regions of higher TFP POSS concentration precipitate more slowly due to TFP POSS inhibiting PVDF precipitation, creating depressions on the surface allowing pores to form more readily. This creates the valleys of pores on the PVDF membrane surface.

An alternative hypothesis for the surface patterning observed by SEM is that it is due to the separation/segregation of PVP during membrane casting. PVP is a hydrophilic polymer and is completely water soluble. When the casting solution is cast onto the glass plate by the Doctors blade (but before immersion in the coagulation bath), the exposure of the surface to the atmosphere allows water to be absorbed into the polymer film. As both PVDF and TFP POSS are highly fluorinated compounds they have favourable interactions with one another,^[31] but not with water. PVP, being hydrophilic, has strong interactions with water but weaker interactions with PVDF or TFP POSS. It is proposed that as water is absorbed into the cast polymer film, PVP is slowly drawn to these regions with higher water content, while hydrophobic interactions cause the PVDF and TFP POSS to draw away from the water and towards each other. When immersed in the water coagulation bath, the regions containing the higher concentration of PVP collapse as PVP is drawn out into the water. This creates the depressions observed, as the regions containing more PVDF and TFP POSS precipitate, forming the taller regions. It is thought that this process begins as soon as the casting solution is drawn across the glass plate and exposed to the atmosphere, causing the PVP-segregated regions (on the film surface) to form semi-parallel to the edge of the Doctors blade. As segregation of the PVP (or absorption of water) drives segregation of the TFP POSS/PVDF, the TFP POSS/PVDF regions form parallel to the PVP-rich regions. This creates the linear alignment of pores during precipitation in the water bath, creating the linear "valleys" observed on the surfaces of membranes containing TFP POSS (Figure 3.6 (b-f)).

The cross-sections of the membranes containing TFP POSS under SEM (Figure 3.4 (b-f)) do not show any kind of similar pattern to the surface. This is thought to be due to a combination of slow diffusion of water deeper into the polymer thin film, as well as rapid precipitation of the polymer upon immersion in the water coagulation bath, which does not give enough time for this region segregation to occur.

It should also be noted that no large aggregates (expected range of $1-5 \,\mu m$)^[15] of TFP POSS can be observed in the SEM images of the membrane surfaces or crosssections, which has occurred when films of PVDF have been produced by solvent evaporation^[15] which indicates that TFP POSS is well-dispersed throughout the membrane. This is particularly impressive for the membrane containing 20 wt% of TFP POSS, as nearly a fifth of the membrane (by weight) is TFP POSS. This can be explained by a combination of factors. The TFP POSS used in this work is known to have good compatibility with PVDF (due to trifluoropropyl arms of TFP POSS)^[9] and in previous studies has been shown to be homogenously dispersed in PVDF films formed by solvent evaporation.^[9] Another factor is the preparation method of the polymer composite, as the preparation method can greatly alter the dispersion of POSS in polymer matrices. For example, one study showed that POSS aggregation in polymers of (covalently bound) polyethylene-POSS is suppressed when the polyethylene-POSS is precipitated from xylene solution by addition of acetone, as compared from crystallisation from xylene.^[30] Another study showed that electrospinning of PVDF (to form nanofibres) suppressed POSS aggregate formation and gave homogeneous dispersions of POSS as compared to a film cast by solvent evaporation.^[15] The results of these studies indicate that rapid precipitation of the polymer, or rapid removal of solvent, leads to better dispersion of POSS in polymer matrices. As the PVDF/TFP POSS membranes in this work were formed by NIPS, it is proposed that due to the rapid rate at which PVDF precipitates prevents TFP POSS from forming large aggregates in the PVDF.

3.4.5 Stress-Strain Experiments

The results of the stress-strain experiments for the PVDF/TFP POSS membranes with different loadings of TFP POSS are shown in Figure 3.7. The value of the Young's Modulus (black squares) was found to not change significantly with increasing wt% of TFP POSS in the membranes, with all values being well within the error (standard

deviation) of the other data points. The % Strain at break (Figure 3.7) shows a small reduction when testing the membrane with 10 wt% of TFP POSS but again is well within the error limit of the other data points. The combination of these results indicates that addition of TFP POSS to the membranes has not altered the overall tensile properties significantly. While it would be desirable for TFP POSS to have a reinforcing effect as an additive to these membranes, it is very interesting to see that even with high quantities of TFP POSS (10 and 20 wt% in particular) the resulting membrane does not become brittle (or in other words, the % Strain at break drop significantly). Polymer nanocomposites becoming more brittle due to addition of nanofillers (including TFP POSS if the PVDF film is prepared by solvent evaporation)^[9] is a common issue,^[32, 33] yet has been avoided in the PVDF-TFP POSS membranes prepared in this work. This can be explained by TFP POSS being dispersed well within the PVDF, ^[9] as well as due to the membrane preparation method, as discussed in the previous section.



Figure 3.7 – Young's modulus, % strain at break, and stress at break of TFP POSS/PVDF blended membranes

3.4.6 Pure Water Flux (PWF)

The method used to perform the pure water flux experiments can be found in Chapter 2, section 2.4.4. To summarise the method briefly – membranes to be tested were first soaked in IPA for 30 min and then MilliQ water for 30 min to prime the membrane. Following this the membrane PWF was measured for 1 h under 200 kPa of pressure (referred to as Phase 1), then the pressure was released and the membrane allowed to recover for 1 h (referred to as the Recovery Phase). The membrane was then rinsed in MilliQ water before again being tested at 200 kPa for a further hour (referred to as Phase 2). It was proposed that by comparing the flux measurements between Phase 1 and Phase 2 of the experiment should theoretically allow an indirect measure of the extent of reversible compaction.

3.4.6.1 Initial and final PWFs

The initial and final PWFs of both Phase 1 and Phase 2 of the PWF experiments are presented in Figure 3.8. In the Phase 1 of the PWF measurements, the initial PWF (see Figure 3.8, red columns) of the membrane with no TFP POSS was the highest, averaging 1401 \pm 206 L.m⁻².h⁻¹. The average initial PWF of the Phase 1 PWF measurements of the membranes with added TFP POSS was lower (relative to the membrane with 0 wt% of TFP POSS) at any of the loadings examined in this work, ranging between 808-1039 L.m⁻².h⁻¹, with 20 wt% of TFP POSS giving the lowest initial PWF. However, the extent of error prevents making any conclusive results with regards to the effect of different loadings of TFP POSS on PWF.

The final PWF of the membranes, or the PWF measured at the end of phase 1 of the experiment, after being subjected to 200 kPa for 1 h, are also shown in Figure 3.8 (fuchsia columns). The final PWF shows a similar trend in the data to the initial PWF of the same membranes (Figure 3.8), with the membrane containing 0 wt% of TFP POSS having (on average) the highest final PWF of 991 ± 170 L.m⁻².h⁻¹. The membranes containing 1-20 wt% of TFP POSS gave (on average) lower PWF values in the range 465-711 L.m⁻².h⁻¹. Again, the variability in the measurements prevents any conclusive remarks to be made in terms of comparing the effect of increasing TFP POSS loading has had on the final PWF.

After the 1 h recovery phase, the PWF of the membranes were tested again at 200 kPa (Phase 2). The results of phase 2 of the PWF measurements are also presented in Figure 3.8.

The average initial PWF from phase 2 of the PWF measurements of the membranes (Figure 3.8, green columns) showed a similar trend to the initial PWFs of phase 1, with the membrane with 0 wt% TFP POSS having a typically higher initial PWF than membranes containing TFP POSS. The same trend can be said for the final PWF values of phase 2 (Figure 3.8, light blue columns), the values which are also reduced relative to the initial PWF values. This effect was also observed in phase 1 PWF measurements.



Figure 3.8 – Pure water flux (PWF) of PVDF membranes containing different loadings of TFP POSS, as measured from the PWF measurements of Phases 1 and 2 (run at 200 kPa at room temperature)

3.4.6.2 Compaction

The effect of membrane compaction can be quite clearly observed in Figure 3.8, as the PWF of membranes in both Phase 1 and Phase 2 of the PWF measurements is

observed to decrease over the 1 h period (comparing the initial and final PWF measurements from the same phase). As the water used is MilliQ grade water, the concentration of contaminants should be far too low to have an observable effect over this time. The reduction in PWF (from both Phase 1 and 2) is presented in Figure 3.9. On average, the membranes containing 0 and 1 wt% of TFP POSS showed the least reduction in PWF from the Phase 1 of the PWF measurements (Figure 3.9, red columns), with flux changes of -30 ± 3.7 -4.0 %. The % flux change showed a greater decrease from Phase 1 PWF measurements (greater flux reduction of PWF) with increasing wt % of TFP POSS, reaching -39 ± 8.1 % for 10 wt% of TFP POSS, and then decreasing slightly to -34 ± 5.0 % with 20 wt% of TFP POSS. Again, however, the large variability in the measurements (especially for the membranes containing 5-20 wt% of TFP POSS) makes any it difficult to ascertain if this result is accurate.

After the 1 h recovery phase, the membranes were observed to undergo further compaction during Phase 2 of the PWF measurements, the PWF again decreasing during the 1 h period (see Figure 3.9, green columns). Compared to the % flux change observed in Phase 1, the % flux change from Phase 2 PWF measurements is much reduced, ranging from -6.9 to -15.4 %, as compared to -30 to -39 % flux change from Phase 1 PWF measurements. The difference in the % flux change between Phases 1 and 2 of the PWF measurements is expected. When a membrane undergoes compaction, it has both a reversible and irreversible component.^[34-36] Before PWF measurements start in Phase 1, the membrane is not compacted at all, and once the pressure is applied to start the PWF measurement, the membrane compacts and the PWF value declines. Once the pressure is released at the end of Phase 1, the membrane recovers from compaction, and would continue to do so overtime during the recovery phase. The membrane still does not recover the flux lost due to irreversible compaction, though does (or should) recover at least some of the flux lost due to reversible compaction. When the pressure is reapplied in Phase 2 of PWF measurements the membrane undergoes further compaction but as the total amount a membrane can be compacted is finite for a given pressure (and the membrane is already compacted), the amount of irreversible compaction should be less, though still shows further PWF reduction due to the reversible compaction.



Figure 3.9 - % Flux change between the initial and final PWF of PVDF membranes containing different loadings of TFP POSS, during Phase 1 and 2 of the PWF measurements (run at 200 kPa at room temperature)

3.4.6.3 Flux Recovery

The design of the PWF measurements offers two ways to measure indirectly the effect the addition of TFP POSS has on the compaction behaviour of the PVDF membranes. The first is to compare the differences in the initial and final PWF values of PWF measurements of the same Phase, in other words, the % flux change (which was done in the previous section). The % flux change represents the effect of both reversible and irreversible compaction. The other measure of compaction behaviour of the membranes is from comparing the PWF value of the membranes before and after the recovery phase – that is, compare the final PWF value from Phase 1 to the initial PWF value of PMF value of PMF measurements. In this work, this value is represented as the % flux recovery, and provides an insight into the reversibility of the compaction of the membranes. The limitation of this method of measurement is

that the recovery period is restricted to 1 h, and therefore does not necessarily represent the overall extent of reversible compaction, only the amount of compaction that is reversed in 1 h.

The % flux recovery values are shown in Figure 3.10. Based on the averages of the % flux recovery, PVDF membranes containing 0 and 1 wt% TFP POSS showed very little PWF recovery after the 1 h recovery phase, and actually gave negative values of -3.2 ± 7.7 % and -7.0 ± 10.6 % for 0 and 1 wt% of TFP POSS respectively. The membranes containing 5-20 wt% of TFP POSS, on average, did show some PWF recovery, giving values of 26.9 ± 16.4 %, 41.9 ± 12.6 %, and 42.9 ± 14.0 % for membranes containing 5, 10 and 20 wt% of TFP POSS respectively. This can be explained due to the changes in membrane morphology, rather than a reinforcement effect by TFP POSS. At 0-2 wt% of TFP POSS, the membrane cross-section is dominated by large macrovoids (see Figure 3.4(a-c)). Polymeric membranes with this morphology tend to resist compaction at lower pressures, but when a high enough pressure is reached the macrovoids collapse and the PWF is significantly reduced. [34] When 5 wt% or higher loadings of TFP POSS are used, the macrovoids of the membrane are suppressed and produces are denser, more sponge-like morphology (see Figure 3.4 (d-f)). Polymeric membranes with this morphology tend to show compaction proportional to the applied pressure, though the compaction tends to be more reversible as well.^[34]





Figure 3.10 - % Flux recovery of PVDF membranes containing different loadings of TFP POSS, comparing the final PWF of phase 1 with the initial PWF of phase 2, after the 1 h recovery phase

3.4.7 BSA Rejection

Another important factor for water filtration membranes is what the membrane can remove from solution, or prevent from passing through the membrane. This is referred to as rejection, and is the primary factor for deciding what a particular membrane can be used for. For example, membranes used for reverse osmosis need to be able to reject dissolved monovalent ions such as sodium and chloride. To compare the rejection properties of the membranes used in this work, Bovine Serum Albumin (BSA) was chosen as it is a well-studied model protein for measuring UF membrane performance.^[18, 32, 37]

The results of the BSA rejection experiments can be found in Figure 3.11. All the membranes tested showed ~90 % rejection of BSA regardless of loading of TFP POSS, indicating that TFP POSS has not produced significant changes in the separation

properties of the resulting membranes. The rejection experiment also verifies that addition of TFP POSS still produces workable membranes for water filtration.



Figure 3.11 - Rejection of BSA for PVDF membranes containing different loadings of TFP POSS

3.5 Conclusions

TFP POSS has been successfully incorporated into PVDF membranes by solution blending followed by phase-inversion to form porous water filtration membranes. Analysis by ATR-FTIR spectroscopy indicated that increasing TFP POSS content in the casting PVDF solution increased the TFP POSS content in the resulting membranes cast from these solutions. Analysis by SEM of the membrane cross-sections revealed that, while all membranes were asymmetric in morphology, membranes with low loadings (<5 wt%) of TFP POSS produced thicker membranes with large macrovoids. When 5 wt% or higher of TFP POSS was used, the macrovoids were suppressed and became more tear-drop shaped with increasing TFP POSS loading. Inclusion of TFP POSS into the membranes was also found to change the surface morphology, with the pore arrangement changing from a random distribution to an aligned formation, forming a zigzag pattern with pores forming a valley on the membrane surface when

the TFP POSS loading was between 1-10 wt%. When the TFP POSS loading was increased to 20 wt% the surface formed a line of pores. Up to 20 wt% of TFP POSS also did not produce large aggregates of POSS and appeared to be well distributed through the membrane. Tensile testing of the membranes indicated that inclusion of TFP POSS did not produce significant changes to the Young's modulus or % strain at break, which shows that while TFP POSS does not strengthen the membrane, TFP POSS doesn't significantly reduce the mechanical strength or cause the membranes to become brittle either. PWF experiments indicate that while inclusion of TFP POSS, on average, reduced the PWF of the membranes, there was otherwise no significant change in PWF values or compaction behaviour of the membranes. There was also found to be no real change in the rejection of BSA, with all membranes having greater than 90 % rejection of BSA. These results indicate that TFP POSS does not act as a particularly good nanofiller for PVDF membranes formed by phase inversion in a water bath.

3.6 References

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Chapter 4 Synthesis and thiol-ene addition of thiol POSS

4.1 Synopsis

Octa(3-mercaptopropyl) POSS (thiol POSS) is a very useful POSS derivative, as it possesses eight thiol arms. These thiols allow thiol POSS to be readily modified by thiol-ene addition, whereby the thiols of thiol POSS add across alkenes. This allows POSS derivatives to be synthesised to provide good compatibility with PVDF (such as attaching fluoroalkyl chains), or to be used to cross-link PVDF.

In this work, thiol POSS was synthesised by hydrolysis and condensation of 3mercaptopropyltrimethoxysilane (MPTMS) under acidic conditions. The method of synthesising thiol POSS was adapted from literature, which was determined through experiments with different conditions, such as varying MPTMS, HCl solution, and DI water concentration, solvent, and temperature. The resulting method yielded thiol POSS as a crystalline solid in a yield of 19.2 %. The structure was confirmed by ¹H and ²⁹Si NMR spectroscopies, and ATR-FTIR spectroscopy.

Following the successful synthesis of thiol POSS, the thiol-ene addition reactions of thiol POSS with various alkenes using different catalytic conditions was examined. Thiol POSS was found to react readily with the alkenes such as allyl alcohol, 2-ethoxy ethanol, 6-chloro-1-hexene, and 6-bromo-1-hexene using 2,2'-azobis(2-methylpropionitrile) (AIBN) or benzophenone/UV-light as catalysts, as determined by ¹H NMR spectroscopy. Styrene was also found to react with thiol POSS readily with benzophenone/UV-light as the catalyst, whereas eugenyl methacrylate (EgMA) was found to form an insoluble material with thiol POSS with UV-light catalysis. However, when using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as the catalyst, thiol POSS was found to form a soluble material with EgMA. However, thiol POSS did not successfully react with styrene using DBU.

These results indicated that AIBN or benzophenone/UV-light as a catalyst provided the most reliable method to react thiol POSS in thiol-ene addition reactions.

Part of this work (synthesis of thiol POSS, and thiol-ene addition reactions of thiol POSS using AIBN or DBU as catalysts) has been published in Inorganic Chemistry Communications, vol. 60 (2015), pages 41-43.

4.2 Introduction

The use of POSS as a nanofiller to alter the thermal and mechanical properties of polymeric matrixes has been well-established in literature.^[1-3] However, one of the key problems with using POSS is aggregation of the POSS cages. The aggregation of POSS within a polymeric matrix usually results in the resulting polymer composite to become excessively brittle, and can in some cases, lead to poorer mechanical properties than the same polymer material without POSS.^[4-7] Aggregation of POSS within a polymeric matrix is controlled, in part, on the compatibility of the POSS cage with the polymer. The compatibility of a POSS cage is largely governed by the organic groups on the POSS cage.^[6, 8, 9] Covalently attaching POSS to the polymer also aids in dispersion of POSS within the polymeric matrix.^[10-13]

Octa(3-mercaptopropyl) POSS (thiol POSS) is particularly interesting, as it possesses eight thiol groups. Thiols have significant utility in organic chemistry, as thiols can be readily reacted with alkenes, in a reaction referred to as thiol-ene addition (see Figure 4.1).



Figure 4.1 – Generic scheme of a thiol-ene addition reaction

Thiol-ene addition (also known as thiol-ene "click") is a versatile reaction, the reaction capable of reacting many different thiols with a wide variety of different alkenes, typically catalysed with bases, radical sources, or UV-light.^[14, 15] This reaction is typically high yielding, can use 1:1 mol ratio of reagents (ratio of alkenes and thiols), and is typically stable to limited amounts of air,^[16] making thiol-ene reactions an excellent choice for modifying thiol POSS.

Several different methods of synthesising thiol POSS can be found in literature. All of the methods to synthesise thiol POSS use similar methodologies,

using HCl acid to induce hydrolysis and condensation of a silane, such as 3mercaptopropyltrimethoxysilane (MPTMS) (see Figure 4.2);



Figure 4.2 – Synthesis of thiol POSS by hydrolysis and condensation of MPTMS under acidic conditions

A common method to synthesise thiol POSS^[17-23] is by combining MPTMS (15 mL), concentrated HCl solution (30 mL) and methanol (360 mL), and refluxing the mixture at 90 °C for 36 h. This provided thiol POSS as a viscous liquid, in a yield of 87 %.

By a different method, Xu et al.^[24] synthesised thiol POSS by combining MPTMS (0.2 mL), deionised (DI) water (5.4 mL), concentrated HCl solution (0.4 mL), and ethanol (40 mL), and then heating the mixture for 60 °C for 36 h. This method also yielded thiol POSS as a viscous fluid, in a slightly lower yield of 62 %.

Dumitriu et al.^[25] synthesised thiol POSS without heating, by combining 7.46 g of MPTMS (7.46 g), concentrated HCl solution (15 mL), and methanol (250 mL), and leaving the reaction to stir for a month. This method gave a modest yield of 18 %.

Finally, one method to synthesise thiol POSS^[26, 27] used 3mercaptopropyltriethoxysilane (MPTES) rather than MPTMS, by combining MPTES (23 mL), DI water (2.7 mL), concentrated HCl solution (0.2 mL), and ethanol (20 mL), and heating the mixture at 60 °C for 36 h. The resulting thiol POSS was obtained as a viscous liquid, but the yield was not provided.

Therefore, the first method $^{[17-23]}$ mentioned was used in this work, as it gave the highest yield of thiol POSS of 87 %, and also used the shortest reaction time of 36 h.

4.3 Chapter Aim

The focus of this chapter is on the synthesis of thiol POSS, and the modification of thiol POSS with different alkenes under different catalytic conditions. The purpose of this work is to provide a method of synthesising thiol POSS in a reliable manner, as well as provide an understanding of the reactivity of thiol POSS with different alkenes and different catalysts.

This work was done to examine whether it would be possible to form a soluble eugenyl methacrylate (EgMA)-functionalised POSS, which should possess antibacterial activity, and impart antibacterial activity when blended into PVDF membranes. In literature, it has been indicated that when attempting to polymerise EgMA in solution with radicals that the reaction mixture must kept at low conversions of EgMA to avoid forming insoluble materials.^[28]

The other purpose is to investigate whether thiol POSS would be able to covalently attach to dehydrofluorinated PVDF (PVDF treated with base to introduce alkenes (discussed further in Chapter 5), and potentially be used as a cross-linking agent. This should provide PVDF membranes with stronger mechanical properties, and hence reduce flux due to compaction during filtration.

4.4 Results and discussion – Synthesis of thiol POSS

The full experimental details regarding the synthesis of thiol POSS can be found in Chapter 2, Section 2.3.3. The following discusses observations of different experiments to synthesise thiol POSS, as well as the analysis of the products of the reactions. An overview of the different reaction conditions examined to synthesise thiol POSS, as well as the general outcome of the reaction condition used, is presented in Figure 4.3.



 st difficulty in reproducing result when using 6/0 volumes of concentrated HCl solution/water

Figure 4.3 – General overview of the reaction conditions trialled to synthesise thiol POSS using MPTMS. The numbers represent the volumes (in mL) of concentrated HCl solution/water added to the reaction. The volume of MPTMS added was 3 mL unless otherwise indicated, and the reaction volume was maintained at ~81 mL.

4.4.1 Synthesis of thiol POSS – effect of solvent

4.4.1.1 Synthesis of thiol POSS by literature method (in methanol)^[17-23] (Trial 1)

Synthesis of thiol POSS was conducted by hydrolysis and condensation of MPTMS under acidic conditions.^[17-23] The resulting product was a white, viscous oil. Analysis by ¹H NMR spectroscopy (Figure 4.4) confirmed the presence of the propyl arm (signals at 0.73 (1), 1.69 (2) and 2.52 (3) ppm) and thiol (signal at 1.35 ppm (4)) with integrals of 2:2:2:1 as would be expected. The signals are very broad, which may indicate the presence of multiple species. The signal at 3.50 ppm is attributed to unhydrolysed methoxy-groups^[29] and the signals at 1.20 (triplet) and 3.78 ppm (quartet) are attributed to ethoxy-groups.^[30]



Figure 4.4 - ¹H NMR spectrum of thiol POSS synthesised by literature method ^[17-23] in methanol. (Taken on 400 MHz NMR spectrometer in CDCl₃).
 For further analysis, the ²⁹Si NMR spectrum was also taken (Figure 4.5).

The spectrum is dominated by a large signal at -67.08 ppm which is attributed to the desired thiol POSS. However, a multitude of additional signals also appear in the -65 to -69 ppm region, indicating the presence of multiple products. Pure, symmetrical POSS compounds typically only have 1 signal in when analysed by ²⁹Si NMR spectroscopy,^[31] as the electronic environments of all the silicon atoms are identical. Signals at -57.92, -59.70 and -60.99 ppm are potentially due to silanol groups.^[32]



Figure 4.5 - ²⁹Si NMR spectrum of thiol POSS synthesised by literature method ^[17-23] in methanol (taken on 400 MHz NMR spectrometer in CDCl₃ using TMS as an internal standard)

This information indicates that the literature method^[17-23] of synthesising thiol POSS has produced multiple condensation by-products. This method does produce organic solvent soluble compounds. Further reactions were conducted based on this methodology but with different solvents and temperatures.

4.4.1.2 Synthesis of thiol POSS in methanol at room temperature (Trial 2)

The next attempt at synthesising thiol POSS was conducted using the same conditions as the previous reaction, except the reaction temperature was maintained at room temperature (instead of refluxing). Leaving the reaction for 96 h produced a white, oily precipitate which stuck to the sides of the flask, allowing the reaction solution to be decanted. After washing the precipitate several times with methanol and drying, the precipitate was then analysed by ¹H and ²⁹Si NMR spectroscopies. These spectra are very similar to those obtained previously, with the ¹H NMR spectrum (Figure 4.6) displaying signals for the propyl arm (signals at 0.74 (1), 1.70 (2) and 2.54 (3) ppm) and thiol (signal at 1.37 ppm (4)) with integrals of 2:2:2:1. The signals are again quite broad, and the signal at 3.51 ppm (attributed to un-hydrolysed methoxy-groups^[29]) again indicated that other condensation products had formed.



Figure 4.6 - ¹H NMR spectrum of thiol POSS synthesised in methanol at room temperature (Taken on 400 MHz NMR spectrometer in CDCl₃).

This was confirmed by ²⁹Si NMR spectroscopy (Figure 4.7), with the spectrum again showing a strong signal at -67.10 ppm, but also displaying multiple other signals (-59.71 ppm, -66.04 ppm, -66.11 ppm, -67.99 ppm, -68.00 ppm, -68.13 ppm, -68.39 ppm, -68.60 ppm, -68.95 ppm) due to the presence of other condensation products other than thiol POSS.


Figure 4.7 - ²⁹Si NMR spectrum of thiol POSS synthesised in methanol at room temperature (taken on 400 MHz NMR spectrometer in CDCl₃ using TMS as an internal standard)

As this reaction did not produce thiol POSS in the desired purity, different solvents were then trialled to synthesise thiol POSS.

4.4.1.3 Synthesis of thiol POSS in acetone (Trials 3 and 4)

The next trials at synthesising thiol POSS were carried out in acetone, both at reflux (90 °C) and at room temperature. Refluxing the reaction at 90 °C rapidly produced a large quantity of white solid within 5 min. Refluxing the reaction further up to 24 h did not noticeably produce any more solid, but did cause the solution to change to a red-colour. The cause of the colour change of the solution is not known, but possibly occured due to the formation of by-products involving acetone. It is known thiols will attack the carbonyl group of ketones and aldehydes^[33] (Figure 4.8).



Figure 4.8 – Potential by-products formed during the synthesis of thiol POSS in acetone^[33]

At room temperature in acetone, the reaction proceeded much more slowly, taking at least 1 h before producing any white solid. After 4 h, a significant amount of white solid precipitated, and the reaction was left for another 2 h. As no more precipitate formed in this time, the reaction was assumed to have reached completion. The solution did not undergo any colour change, as occurred when refluxing acetone at 90 °C.

Both attempts at synthesising thiol POSS in acetone (at room temperature and at 90 °C) were unsuccessful, as both of the white solids produced in either reaction were insoluble in chloroform. Moreover, after stirring the solid in chloroform, filtering off the insoluble material and then evaporating the chloroform, no residue remained. This indicates that the reaction failed to produce the desired thiol POSS and instead produced larger particles.

The cause of the faster rate of precipitate formation in acetone as compared to methanol is not clear. The reaction of alkoxysilanes to form siloxane bonds occurs in two separate steps. Firstly, alkoxy groups are hydrolysed by water to produce silanols, followed by condensation of the silanol groups to produce siloxane bridges. Currently, there are limited studies comparing the influence of different organic solvents on the rates of hydrolysis and condensation of alkoxysilanes (particularly condensation). It is known that the rate of hydrolysis of methyltriethoxysi lane (under acid catalysis) is almost three times faster in methanol than acetone,^[34] but this information is of limited use, as it provides no understanding on the rate of condensation of the silane in the different solvents. Also, the difference in reaction conditions may not make this study comparable to the experiments conducted in this work. It is therefore proposed, under the conditions used here, that the rate of condensation of MPTMS is faster in acetone than methanol, causing the reaction to proceed uncontrolled and forming insoluble siloxane materials. This occurs because when the reaction is conducted in methanol, the excess methanol hinders the reaction(s) via the chemical equilibrium, as methanol is produced as a by-product during the hydrolysis and condensation process of MPTMS (see Figure 4.9). When the reaction is conducted using acetone as the solvent, the reaction is uninhibited, as acetone does not participate in the hydrolysis/condensation of MPTMS. This leads to a rapid production of siloxane bonds uncontrollably, leading to larger particles

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forming when using acetone as the solvent. As the reaction in acetone does not produce the desired thiol POSS, and also produces significant quantities of insoluble materials, experiments using acetone as a solvent were not continued.



Figure 4.9 – Simplified hydrolysis and condensation of a trialkoxysilane

4.4.1.4 Synthesis of thiol POSS in ethanol at 90 °C (Trial 5)

The next attempt at synthesising thiol POSS was carried out in ethanol, refluxing at 90 °C for 48 h. Unlike the previous trials at synthesising thiol POSS in methanol and acetone, no precipitate formed during reflux. On cooling to room temperature, a white precipitate did form, but unlike in the previous trials it was crystalline in appearance. Analysis by ¹H NMR spectroscopy (Figure 4.10) confirmed the presence of the propyl arm (signals at 0.78 (1) (triplet), 1.73 (2) (quintet) and 2.57 ppm (3) (quartet) and thiol (signal at 1.39 ppm (4) (triplet)) with integrals of 2:2:2:1, as expected. Unlike the previous ¹H NMR spectrum of the product from the synthesis of thiol POSS in methanol (Figure 4.4),^[24] the signals were significantly less broad and the correct coupling pattern was observed.



Figure 4.10 - ¹H NMR spectrum of thiol POSS synthesised in ethanol at 90 °C (1st attempt) (taken on 400 MHz NMR spectrometer in CDCl₃)

Analysis by ²⁹Si NMR spectroscopy (Figure 4.11) shows only the one signal at -67.10 ppm and no other major signals, confirming that the material was the desired thiol POSS, with low amounts of impurities.

Exp 25.5 octathiol POSS (EtOH syn).002.001.1r.esp



Figure 4.11 - ²⁹Si NMR spectrum of thiol POSS synthesised in ethanol at 90 °C (1st attempt) (taken on 400 MHz NMR spectrometer in CDCl₃ using TMS as an internal standard)

However, performing (retrialing) the reaction again (refluxing in ethanol at 90 °C) gave a very different result. Instead of a crystalline solid precipitating, a colourless transparent oil formed, and on cooling to room temperature, an oily material precipitated. The ¹H NMR spectrum of the oily material (Figure 4.12) was similar to that of the ¹H NMR spectrum crystalline solid (Figure 4.10). However, the signals were broadened, with signals from un-hydrolysed ethoxy-groups at 1.22 and 3.79 ppm^[30] observed.



Figure 4.12 - ¹H NMR spectrum of thiol POSS synthesised in ethanol at 90 °C (retrial) (taken on 400 MHz NMR spectrometer in CDCl₃)

The ²⁹Si NMR spectrum (Figure 4.13) showed multiple signals in the -65 to -69 ppm region as well as the signal corresponding to thiol POSS at -67.07 ppm, indicating that there was significant contamination from other condensation products produced during the reaction. Why further attempts at synthesising thiol POSS in refluxing ethanol at 90 °C failed to produce the same result is unclear, but it was apparent a more reproducible method was needed if a significant quantity of thiol POSS with good purity could be obtained. Since using ethanol as the solvent for the synthesis of thiol POSS had given the best result, ethanol was continued to be used in further experiments. Further experiments were then carried out in ethanol but varying the concentration of HCl acid, water and MPTMS.



Figure 4.13 - ²⁹Si NMR spectrum of thiol POSS synthesised in ethanol at 90 $^{\circ}$ C (retrial) (taken on 400 MHz NMR spectrometer in CDCl₃ using TMS as an internal standard)

4.4.2 Synthesis of thiol POSS in ethanol – effect of acid concentration (Trials 6-12) Since it has been established that the thiol POSS is a crystalline solid (with the presence of by-products producing noticeably oily compounds), the success of further reactions was assessed solely by the quality of the product produced. The results of the reactions are summarised in Chapter 2, Section 2.3.3.7, Table 2.3. For convenience Table 2.3 is reproduced here as Table 4.1. These trials largely focused on changing the quantity of acid added to the reaction; in order to keep conditions similar across all reactions, any reduction in volume of acid was replaced with deionised water to maintain a similar total volume. This does increase the concentration of water as more acid is substituted out, but this was thought to be a relatively minor issue compared to the concentration of acid changing. As the best results of ar had been using ethanol as a solvent, ethanol was used throughout these trials.

| ethanol. | | | | | | |
|------------|---------------|----------------------|---------------------|-----------------|-------------------------|-----------------------------------|
| Trial # | MPTMS (mL) | Conc. HCl (mL) | DI water (mL) | Ethanol (mL) | Reaction Time (h) | Product |
| 6 | 3 | 8 | 0 | 72 | 24 | Oily material |
| 7 | 3 | 4.5 | 1.5 | 72 | 24 | Mixture of crystalline/waxy solid |
| | | | | | 48 | Mixture of crystalline/waxy solid |
| | | | | | 72 | Mixture of crystalline/waxy solid |
| 8 | 3 | 3 | 3 | 72 | 24 | Crystalline |
| | | | | | 48 | Mixture of crystalline/waxy solid |
| | | | | | 72 | Mixture of crystalline/waxy solid |
| 9 | 3 | 1.5 | 4.5 | 72 | 24 | Crystalline |
| | | | | | 48 | Mixture of crystalline/waxy solid |
| | | | | | 120 | Mixture of crystalline/waxy solid |
| 10 | 3 | 0.75 | 5.25 | 72 | 24 | Crystalline |
| | | | | | 48 | Crystalline |
| | | | | | 72 | Oily material |
| 11 | 3 | 0.5 | 5.5 | 72 | 48 | Crystalline |
| 12 | 3 | 0.25 | 5.75 | 72 | 60 | Crystalline |
| | | | | | 84 | Mixture of crystalline/waxy solid |
| 13 | 3 | 0.75 | 19.4 | 58 | 24 | Oily material |
| 14 | 3 | 0.75 | 0 | 77.25 | 24 | No product |
| | | | | | 48 | No product |
| | | | | | 72 | No product |
| | | | | | 96 | No product |
| | | | | | 264 | No product |
| 15 | 3 | 0 | 6 | 72 | 24 | No product |
| | | | | | 48 | No product |
| | | | | | 72 | No product |
| | | | | | 96 | No product |
| | | | | | 264 | No product |
| 16 | 4.5 | 0.75 | 5.25 | 72 | 24 | Mixture of crystalline/waxy solid |
| | | | | | 48 | Oily material |

Table 4.1 - Volumes of reagents used in different trials to synthesise thiol POSS in ethanol.

Firstly, the volume of acid was increased from 6 mL to 8 mL (Trial # 6, Table 4.1); this seemed to reduce the control of the reaction, causing not only a clear oil to form but also caused the solution to become noticeably opaque. The product that precipitated on cooling was very oily; clearly increasing the acid concentration was not the way to improve control of the reaction.

Next, one quarter of the volume of acid was substituted with deionised water (Trial # 7, Table 4.1). This appeared to improve reaction control, giving a mixture of crystalline and waxy solid after 24 h of refluxing. Refluxing for 48 h and 72 h increased the amount of solid produced, but otherwise did not appear to change the quality.

Following this improvement, one half of the volume of acid was substituted with deionised water (Trial # 8, Table 4.1). After 24 h of refluxing this gave a very small amount of crystalline solid. To try to increase the yield (as the amount after 24 h refluxing was not deemed worthy of recovering), refluxing was continued. However, this caused the resulting product to deteriorate in quality, becoming noticeably waxy the longer the reaction was refluxed. A similar result was obtained when three quarters of the volume of acid was substituted with deionised water (Trial # 9, Table 4.1).

Further decreasing the acid concentration (seven eights of the volume of acid was substituted with deionised water (Trial #10, Table 4.1) gave a similar result after 24 h of reflux, but after 48 h still gave crystalline material albeit more of it. After 72 h of reflux an oily material appeared. However, decreasing the acid concentration any further compared to trial # 10 resulted in little change (Trial # 11- 12, Table 4.1).

4.4.3 Synthesis of thiol POSS in ethanol – other conditions (Trials 13-16)

Having established a good concentration of HCl for synthesising thiol POSS in the ethanol, the next set of experiments dealt with changing the water concentration, to give an understanding of the influence of water on the reaction. The concentration of acid was maintained at approximately the same as trial # 10, as this gave good results. Substituting one quarter of the volume of ethanol with DI water (Trial # 13, Table 4.1) gave a similar result to increasing high acid concentration ((Trial # 6, Table 4.1)), causing both the solution to become opaque as well as producing clear oil, and gave an oily material as product.

On the other hand, if only a small amount of HCl solution was added to the reaction (with no DI water), no thiol POSS was observed to form, even after refluxing the solution for 264 h (Trial # 14, Table 4.1). A similar result was observed for the reaction with only DI water added (no HCl solution) (Trial # 15, Table 4.1). The results of Trials # 14 and # 15 demonstrate that having both HCl solution and DI water was necessary to produce thiol POSS using MPTMS in ethanol. However, adding too much HCl solution and/or DI water causes the condensation of MPTMS to go out of control, producing a multitude of other condensation products other than thiol POSS.

Finally, in the last trial (Trial # 16, Table 4.1), similar conditions to trial # 10 were used, except that the concentration of MPTMS was increased. After 24 h of refluxing this reaction produced a noticeably waxy material, which became increasingly oily after 48 h of refluxing. This indicated that increasing the MPTMS concentration in the current methodology resulted in a more uncontrolled condensation of MPTMS.

Overall, only trials # 10-12 produced purely crystalline material, and so the conditions of trial # 10 were chosen to scale-up for the bulk synthesis of thiol POSS.

4.4.4 Bulk Synthesis of thiol POSS

The previous experiments successfully determined the reaction conditions that were necessary to yield the crystalline thiol POSS from the condensation of MPTMS. However, if thiol POSS is to be used in any significant quantity, the reaction needs to be up-scaled otherwise it would consume too much time to synthesise. The conditions chosen were based on trial # 10, Table 4.1, as this trial gave promising results.

The bulk synthesis of thiol POSS was conducted at approximately four times the scale of previous reactions in refluxing ethanol at 90 °C. After refluxing for 48 h, the reaction solution remained transparent and colourless with no signs of precipitate formation. After cooling in a freezer overnight, a moderate amount of crystalline material precipitated, with a yield of 0.484 g (7.06 %, fraction 1). To see if the reaction solution could yield more thiol POSS, the reaction solution was placed back on the oil bath to reflux for a further 48 h. After this period, cooling in the freezer overnight again produced more crystalline material with a yield of 0.319 g (4.65 %, fraction 2). Repeating this process to the reaction solution of refluxing for 48 h, cooling in the freezer overnight, and recovering the precipitate another 2 times gave more crystalline material, yielding 0.307 g (4.48 %, fraction 3) and 0.206 g (3.01 %, fraction 4). giving a total combined yield 19.20 %. Refluxing for a further 48 h not only gave very small amounts of product (approx. 0.065 g), but the product was also found to be oily, and therefore assumed to be contaminated with other condensation products.

Analysis by ¹H and ²⁹Si NMR spectroscopy were taken of each fraction separately, confirming that the product was in fact thiol POSS of adequate purity. This was shown by the presence of a single peak at -67.09 ppm in the ²⁹Si NMR spectra (Figure 4.14, for fraction 1; ²⁹Si NMR spectra for fractions 2-4 can be found in Appendix A, Figures A 1-A 3)). The ¹H NMR spectra (Figure 4.15 for fraction 1; ¹H NMR spectra for fractions 2-4 can be found in Appendix A, Figures A 2-4 can be found in Appendix A, Figures A 4-A 6) showed the expected result for thiol POSS. The signals for the propyl arm appear at 0.75 ppm (1), 1.70 ppm (2) and 2.54 ppm (3) and for the thiol at 1.36 ppm (4), and have the expected integral ratios of 2:2:2:1 respectively, and also with the expected coupling patterns.







Figure 4.15 - ¹H NMR spectrum of thiol POSS synthesised from the bulk synthesis (fraction 1) (taken on 600 MHz NMR spectrometer in CDCl₃ using TMS as an internal standard)

4.4.4.1 Analysis by ATR-FTIR spectroscopy

Comparison of the ATR-FTIR spectra of thiol POSS synthesised by the literature method^[17-23] in methanol (trial 1) and from the bulk synthesis method (Figure 4.16, black and red lines, respectively) shows that there are very distinct differences in the materials. While the ATR-FTIR spectra of both materials display the expected C-H stretches between 3000-2800 cm⁻¹ and S-H stretch at 2522 cm⁻¹,^[15] there is a notable difference in the 1250-950 cm⁻¹ region of the spectra. The 1250-950 cm⁻¹ region of ATR-FTIR spectra shows signals usually due to Si-O bonds.^[35] The thiol POSS made by the literature method^[17-23] in methanol has four distinct peaks at 1087, 1065, 1038 and 1002 cm⁻¹ (Figure 4.16, black line), whereas the thiol POSS synthesised from the bulk synthesis shows two clear peaks at 1080 and 1002 cm⁻¹ (Figure 4.16, red line). This difference in the ATR-FTIR spectra was attributed to the presence of additional condensation products other than thiol POSS in the material synthesised using the literature method. This was indicated earlier by the presence of multiple peaks in the ²⁹Si NMR spectrum of this material (see Figure 4.5). This point is also backed up by the presence of a signal at 920 cm⁻¹ in the ATR-FTIR spectrum of thiol POSS synthesised by the literature method^[17-23] (Figure 4.16, black line) which was

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attributed to silanol (Si-OH groups)^[35] from incompletely condensed product(s) present in the material.



Figure 4.16 - ATR-FTIR spectra of thiol POSS synthesised by literature method $^{[17-23]}$ (trial 1) and using the bulk synthesis method. Inset – ATR-FTIR spectra of the 1250–850 cm⁻¹ region.

4.5 Results and discussion - thiol-ene addition chemistry with thiol POSS

Having successfully synthesised thiol POSS, the following discusses the results of experiments involving modification of thiol POSS by thiol-ene addition. These reactions were conducted to examine the reactivity of thiol POSS in thiol-ene addition reactions. The results of these reactions would determine if thiol-ene addition would be a viable choice to produce different POSS derivatives using thiol POSS, or use thiol POSS as a potential cross-linking reagent.

Different catalyst systems were trialled, including a thermally induced radical initiator, 2,2'-azobis(2-methylpropionitrile) (AIBN), a base, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and UV-light (with and without benzophenone as a photo-catalyst). The experimental details for these reactions can be found in Chapter 2, Sections 2.3.5, 2.3.6, 2.3.7, and 2.3.8, respectively.

The outcome of these reactions helped to determine which catalyst systems would be best to use to modify thiol POSS by thiol-ene addition. The following discusses the results of the reactions trialled using these different catalyst systems. The general thiol-ene addition reaction of thiol POSS with alkenes, as well as the structures of the alkenes used in these reactions, is presented in Figure 4.17





4.5.1 AIBN-catalysed thiol-ene addition with thiol POSS

Thiol-ene addition reactions with thiol POSS using AIBN as a catalyst were trialled with four different alkenes; allyl alcohol, 2-allyloxyethanol, 6-chloro-1-hexene and 6-bromo-1-hexene, all carried out in toluene at 60 °C. An overview of these reactions is presented in Figure 4.18. AIBN acts as a radical source in this reaction.



Figure 4.18 – Schematic of the thiol-ene addition reactions of thiol POSS with different alkenes, catalysed by AIBN, examined in this work. The structures of the desired product from the reaction is also shown.

The thiol-ene addition reaction of thiol POSS with allyl alcohol was found to produce a two-phase mixture, with toluene solution on top, and a viscous, yellowish oil on the bottom. After precipitating the yellowish oil in hexane and drying, the product of the reaction between allyl alcohol and thiol POSS (a white solid), was analysed by ¹H NMR spectroscopy. As the product was found to be insoluble in CDCl₃, the NMR sample was instead prepared in D₆-DMSO. The ¹H NMR spectrum (Figure 4.19) is significantly different from the starting materials, showing complete consumption of the thiol (absence of triplet at 1.25-1.50 ppm region), as well as loss of the alkene protons of allyl alcohol (signals in the 5-6 ppm region (not shown)). The signals present in the spectrum confirm the presence of all the protons expected for thiol-ene addition across allyl alcohol through an anti-Markovnikoc mechanism. However, the spectrum is complicated by signals from protons adjacent to the

thioether linkage (**3** + **4**) overlapping and signals from protons beta to the thioether linkage (**2**+ **5**) overlapping. Also of note is the presence of a signal at 1.18 ppm, which is indicative of some thiol groups adding by a Markovnikov mechanism across allyl alcohol (approximately 11.8% Markovnikov addition). Although this does cause some structural differences in the final product, the addition reaction has still occurred and was deemed to not be a significant issue. The ¹H NMR spectrum appears to be consistent with thiol POSS successfully adding to allyl alcohol. ¹³C and 2D NMR spectra of this compound can be found in Appendix A, Figures A 8-A 11.



Figure 4.19 - ¹H NMR spectra of the product obtained from reacting thiol POSS with allyl alcohol using AIBN as the catalyst (taken on 400 MHz NMR spectrometer in D_{6} -DMSO)

The thiol-ene addition reaction between 2-allyloxyethanol and thiol POSS, after being heated together with AIBN in toluene at 60 °C overnight, caused a twophase mixture to form, with a toluene layer on top and viscous, reddish oil as the bottom layer. After precipitation of the reaction mixture in hexane and drying, a clear and colourless viscous oil was recovered, and found to be completely soluble in CDCl₃. Analysis by ¹H NMR spectroscopy (Figure 4.20) confirmed successful addition of thiol POSS across the double bond of 2-allyloxyethanol. No signal due to thiol (triplet at 1.25-1.50 ppm region) was observed, or signals due to alkene protons (5-6 ppm region (not shown)). The ¹H NMR spectrum was consistent with the expected

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structure, but as with allyl alcohol, there are additional signals (3.60, 2.92, 2.77, 2.64, 2.04, 1.75 and 1.25 ppm) due to some Markovnikov addition occurring (approximately 8.3 % Markovnikov addition). ¹³C and 2D NMR spectra of this compound can be found in Appendix A, Figures A 12-A 15.



Figure 4.20 - ¹H NMR spectra of the product obtained from reacting thiol POSS with 2-allyloxyethanol using AIBN as the catalyst (taken on 400 MHz NMR spectrometer in CDCl₃)

The thiol-ene addition reaction between 6-chloro-1-hexene and thiol POSS did not produce any real change to the solution after being heated together with AIBN in toluene at 60 °C overnight. After precipitation in methanol and drying, a clear and colourless viscous oil was recovered, and found to be completely soluble in CDCl₃. Analysis by ¹H NMR spectroscopy (Figure 4.21) confirmed successful addition of thiol POSS to 6-chloro-1-hexene, showing no signal due to thiol (triplet at 1.25-1.50 ppm region) or signals to due to alkene protons (5-6 ppm region (not shown)). The ¹H NMR spectrum is consistent with the expected structure, but as with previous thiol-ene addition reactions with thiol POSS, there were additional signals (2.66, 1.87 and 1.26 ppm) due to some Markovnikov addition occurring (approximately 3.2 % Markovnikov addition). ¹³C and 2D NMR spectra of this compound can be found in Appendix A, Figures A 16-A 19.



Figure 4.21 - ¹H NMR spectra of the product obtained from reacting thiol POSS with 6-chloro-1-hexene using AIBN as the catalyst (taken on 400 MHz NMR spectrometer in CDCl₃)

The thiol-ene addition reaction between 6-bromo-1-hexene and thiol POSS caused the solution to become slightly yellowed after being heated together with AIBN in toluene at 60 °C overnight. After precipitation in methanol and drying, a clear and slightly yellowed viscous oil was recovered, and found to be completely soluble in CDCl₃. Analysis by ¹H NMR spectroscopy (Figure 4.22) confirmed successful addition of thiol POSS to 6-bromo-1-hexene, showing no signal due to thiol (triplet at 1.25-1.50 ppm region) or signals to due to alkene protons (5-6 ppm region (not shown)). The ¹H NMR spectrum was consistent with the expected structure, but as with previous thiol-ene addition reactions with thiol POSS, there were additional signals (2.79, 2.66, 1.75 and 1.26 ppm) due to some Markovnikov addition occurring (approximately 3.2 % Markovnikov addition). ¹³C and 2D NMR spectra of this compound can be found in Appendix A, Figures A 20-A 23.



Figure 4.22 - ¹H NMR spectra of the product obtained from reacting thiol POSS with 6-bromo-1-hexene using AIBN as the catalyst (taken on 400 MHz NMR spectrometer in CDCl₃)

All of these reactions were moderate to high yielding (yields ranged from 66-92 %), as to be expected for thiol-ene addition reactions. One significant difference between these reactions is the amount of Markovnikov addition that has occurred. With terminal alkenes, the thiol can add either to the more substituted carbon (Markovnikov addition) or the less substituted carbon (anti-Markovnikov addition) (see Figure 4.23). The product resulting from anti-Markovnikov addition is the major product owing to the higher thermodynamic stability of the intermediate. ^[36] A small amount of Markovnikov addition does still occur however, resulting in additional signals in the ¹H NMR spectrum, the most notable signal being a doublet at 1.18 ppm (relative to D₆-DMSO) or 1.24 ppm (relative to CDCl₃) (as well as other signals). Interestingly, the two alcohol-containing alkenes, allyl alcohol and 2-allyloxyethanol, gave higher amounts of Markovnikov addition (11.8 and 8.3 % respectively, as determined by ¹H NMR spectroscopy) in the thiol-ene addition reaction with thiol POSS as compared to the halogen-containing alkenes (6-chloro- and 6-bromo-1hexene) which only gave 3.2 % Markovnikov addition. This difference was attributed

to the closeness of the alkene to other functional groups, namely the alcohol and ether in allyl alcohol and 2-allyloxyethanol, respectively. It is known that electronwithdrawing substituents on alkenes increase the extent of Markovnikov addition of radicals occurring, by reducing the activation energy for the intermediate formed during Markovnikov addition.^[36] Anti-Markovnikov addition is still more favourable and is still the major product, but the increase in stability of the intermediate formed during Markovnikov addition of the thiol radical across the alkene allows for more Markovnikov addition to occur. On the other hand, as the halogens on 6-chloro- and 6-bromo-1-hexene are too far removed from the alkene, the anti-Markovnikov radical intermediate is relatively more stable (as compared to allyl alcohol and 2-allyloxyethanol) and so anti-Markovnikov addition is more favoured.





4.5.2 DBU-catalysed thiol-ene addition with thiol POSS

Next, the base-catalysed thiol-ene addition reaction of thiol POSS was trialled, using DBU as the catalyst and styrene and eugenyl methacrylate (EgMA) as the alkenes. EgMA was chosen due to having antibacterial properties,^[28, 37] which once attached to POSS could then be used as an antibacterial additive in polymeric systems. However, EgMA has the challenge of having two alkenes on the same molecule, so that reaction conditions will have to be controlled to prevent cross-linked products from forming. It is known that base-catalysed thiol-ene addition proceeds via a

nucleophilic method, giving more selectivity as only activated (or electron-deficient) alkenes show significant activity.^[15, 38] A general overview of these reactions is presented in Figure 4.24.



Figure 4.24 - Schematic of the thiol-ene addition reactions of thiol POSS with styrene or EgMA, catalysed by DBU. The structures of the desired product from the reaction is also shown.

After reacting styrene with thiol POSS for 24 h and then precipitating in methanol, the reaction with styrene produced a white solid precipitate, which was found to be insoluble in common organic solvents, and was not analysed further. Repeating this reaction with styrene but increasing the DBU content ten-fold gave a similar result. As the precipitate was insoluble in chloroform and other organic solvents the product could not be analysed by solution NMR spectroscopy and so was not analysed further. A plausible explanation for the cause of the insoluble precipitate forming is back-biting reactions. It is proposed that in the presence of DBU, the thiols become activated enough to attack the Si atoms of the POSS cage,

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and upon precipitation in methanol, these bonds hydrolyse into silanols, ^[39] which in the presence of DBU condense to form larger particles which are insoluble in organic solvents.

On the other-hand, the reaction of EgMA with thiol POSS produced a light yellow oil, with a moderate yield of 56 %. Analysis by ¹H NMR spectroscopy (Figure 4.25) confirmed the complete reaction between EgMA and thiol POSS. as indicated by the absence of the S-H triplet at 1.36 ppm as well as the loss of the methacrylate alkene singlets at 5.74 ppm and 6.36 ppm from EgMA. The ¹H NMR spectrum also confirmed that the thiol added across the methacrylate alkene exclusively, with the spectrum still displaying signals from the allyl alkene at 5.10 (**16**) and 5.95 ppm (**15**) with the approximate integrals of 2 and 1, respectively. ¹³C and 2D NMR spectra of this compound can be found in Appendix A, Figures A 24-A 27. This selectivity allowed an organic-soluble POSS material to be produced which has strong potential for antibacterial properties, making it a potential antibacterial additive for polymeric systems.

As for why this reaction of thiol POSS with EgMA avoided the back-biting reactions that occurred when reacting thiol POSS with styrene, it is proposed that the reaction of the thiol with the methacrylate alkene is much more rapid and out competes the back-biting reactions.



Figure 4.25 - ¹H NMR spectrum of the product of the reaction of thiol POSS with eugenyl methacrylate catalysed by DBU (taken on 400 MHz NMR spectrometer in $CDCI_3$)

4.5.3 UV-catalysed thiol-ene addition with thiol POSS without benzophenone

The previous experiments have demonstrated that thiol POSS undergoes thiol-ene addition chemistry readily, both using AIBN and DBU (in select cases). However, in order to be able to use thiol POSS as a cross-linker in PVDF water filtration membranes, using UV-light is the most straight forward way to do so. As alkenes are less reactive towards nucleophilic thiol-ene addition (as demonstrated with experiments using DBU as the catalyst), DBU is not the best choice as catalyst for thiol-ene addition, especially if the reactivity of the alkene is unknown (such as alkenes on PVDF produced by dehydrofluorination). On the other hand, heating the cast polymer-solution film (before forming the membrane by NIPS) to use AIBN as a catalyst would lead to the film drying out, which may not give reproducible membranes.

Firstly, thiol POSS was reacted with alkenes under just UV-light to see if a photo-catalyst would be necessary. All the alkenes used were the same as with previous reactions, to keep the analysis simple. A schematic of these reactions is shown in Figure 4.26.



Figure 4.26 - Schematic of the thiol-ene addition reactions of thiol POSS with different alkenes examined in this work, catalysed by UV-light. The structures of the desired product from the reaction is also shown.

The simple alkenes and styrene did not react readily with thiol POSS under UV-light alone for 4 h. Analysis by ¹H NMR spectroscopy indicated that 2allyloxyethanol did not react. The ¹H NMR spectrum (Figure 4.27) only displayed the presence of unreacted thiol POSS and 2-allyloxyethanol.

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Figure 4.27 - ¹H NMR spectrum of the crude product of the reaction of thiol POSS with 2-allyloxyethanol under UV-light without benzophenone. Signals denoted with * are from unreacted 2-allyloxyethanol (taken on 400 MHz NMR spectrometer in CDCl₃)

The reactions using 6-chloro-1-hexene, 6-bromo-1-hexene and styrene did show some functionalisation, giving conversions of ~17 %, ~4 % and ~16 %, respectively, as determined by ¹H NMR spectroscopy (see Figure 4.28, Figure 4.29, and Figure 4.30, respectively). The ¹H NMR spectra are dominated by the signals from thiol POSS, with the S-H triplet at 1.36 ppm clearly present in all of the ¹H NMR spectra. As each sample was unlikely to be exposed to the same intensity of UV radiation, these conversion values may not be reflective of the actual rate of reactions (i.e., rates of reactions cannot be compared). Based on these results, the reaction would likely be too slow (in air) to avoid disulphide formation with just UVlight.











Figure 4.30 - ¹H NMR spectrum of the crude product of the reaction of thiol POSS with styrene under UV-light without benzophenone. Signals denoted with * are from unreacted thiol POSS (taken on 400 MHz NMR spectrometer in CDCl₃, NMR spectral assignments determined using ChemDraw 12.0 ¹H NMR spectrum simulator)

The reaction between thiol POSS and EgMA under UV-light produced a yellow, semi-transparent film on the bottom of the reaction flask, but was found to be insoluble in chloroform. The likely cause of this is either (or a combination of) the formation of cross-links from thiols adding across both alkenes of EgMA, or the alkenes of EgMA (particularly the methacrylate alkene) undergoing addition/polymerisation reactions stimulated by UV-light. As this is unlikely to be avoided when using radical catalysed thiol-ene addition with EgMA, investigations of thiol-ene addition reactions with EgMA were not continued.

These experiments show that the UV-light source used is not intense enough to complete the thiol-ene addition with thiol POSS in 4 h, though UV-light alone does appear to be able to allow the reaction to occur with these particular alkenes.

4.5.4 UV-catalysed thiol-ene addition with thiol POSS with benzophenone

In order to speed up the thiol-ene addition reaction of thiol POSS with alkenes under UV-light, a photo-catalyst, benzophenone was included in the reaction. A general overview of the reactions trialled is presented in Figure 4.31.



Figure 4.31 - Schematic of the thiol-ene addition reactions of thiol POSS with different alkenes examined in this work, catalysed by UV-light and benzophenone. The structures of the desired product from the reaction is also shown.

The addition of benzophenone to the UV-catalysed thiol-ene addition reaction between thiol POSS and the different alkenes produced a very marked change in the reaction. After 4 h of irradiation with UV-light, all of the reactions were found to have gone to completion, as determined by ¹H NMR spectroscopy (see Figures 4.26-4.28),

showing no presence of signal from unreacted thiol POSS, or remaining alkenes (signals between 5–6 ppm (not shown)). The ¹H NMR spectra of the reaction thiol POSS with 2-allyloxyethanol (Figure 4.32), with 6-chloro-1-hexene (Figure 4.33), and with 6-bromo-1-hexene (Figure 4.34) are very similar to those same reactions using AIBN as the catalyst (Section 4.5.1).



Figure 4.32 - ¹H NMR spectrum of the crude product of the reaction of thiol POSS with 2-allyloxyethanol under UV-light with benzophenone (taken on 400 MHz NMR spectrometer in CDCl₃).



Figure 4.33 - ¹H NMR spectrum of the crude product of the reaction of thiol POSS with 6-chloro-1-hexene under UV-light with benzophenone (taken on 400 MHz NMR spectrometer in CDCl₃).



Figure 4.34 - ¹H NMR spectrum of the crude product of the reaction of thiol POSS with 6-bromo-1-hexene under UV-light with benzophenone (taken on 400 MHz NMR spectrometer in CDCl₃).

However, in comparison to using AIBN as the catalyst, there is a difference in the amount of Markovnikov addition occurring when using benzophenone/UV-light catalysis. Previously, it was shown that when using AIBN as the catalyst, the thiol-ene

addition reactions of thiol POSS with 2-allyloxyethanol and 6-bromo-1-hexene gave percentages of Markovnikov addition of ~8.3 % and ~3.2 %, respectively. In comparison, using benzophenone/UV-light catalysis, the thiol-ene addition reactions of thiol POSS with 2-allyloxyethanol and 6-bromo-1-hexene gave percentages of Markovnikov addition of ~5.3 % and ~0 %, respectively. The reaction of thiol POSS with 6-bromo-1-hexene reduced the Markovnikov addition to be immeasurable by ¹H NMR spectroscopy, the doublet at 1.24 ppm cannot be observed in the ¹H NMR spectrum (see Figure 4.34).

The amount of Markovnikov addition from reacting thiol POSS with 6-chloro-1-hexene was similar using either AIBN or benzophenone/UV-light as catalysts (~3.2 vs ~3.8 % respectively). The reason why different catalysts result in a difference in the amount of Markovnikov addition is unknown. It is possible that the difference in the temperature of the reaction causes this effect (AIBN catalysed reactions were run at 60 °C, as compared to room temperature for benzophenone/UV-light catalysed reactions). However, this does not explain why there was no change in the amount of Markovnikov addition in the thiol-ene reaction when 6-chloro-1-hexene was used, and exploring this phenomenon is beyond the scope of this thesis.

The thiol-ene addition between thiol POSS and styrene also proceeded to completion using benzophenone/UV-light catalysis, with the ¹H NMR spectrum (Figure 4.35) indicating that no unreacted thiol remains, as shown by the absence of the triplet at 1.36 ppm corresponding to the S-H of thiol POSS. Although the ¹H NMR spectrum does display the expected signals for thiol POSS adding across styrene in an anti-Markovnikov mechanism (as determined using ChemDraw 12.0 ¹H NMR simulator). There are clearly additional signals at 3.09 ppm and in the range 1.5-2.0 ppm (overlapping with the signal at 1.71 ppm) (Figure 4.35). These signals are potentially due to Markovnikov addition, as the simulated ¹H NMR spectrum using ChemDraw 12.0 does predict a doublet at 1.58 ppm due to the –CH₃ group produced by Markovnikov addition. However, this does not account for all the signals. Contamination from polystyrene formed during the reaction could also be the cause of signals in the range 1.5–2.0 ppm.^[40]

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Figure 4.35 - ¹H NMR spectrum of the crude product of the reaction of thiol POSS with styrene under UV-light with benzophenone (taken on 400 MHz NMR spectrometer in CDCl₃. NMR spectral assignments determined using ChemDraw 12.0 ¹H NMR spectrum simulator).

Overall, the use of benzophenone/UV-light catalysis proceeds to completion regardless of the alkene used, indicating that benzophenone/UV-light catalysis is appropriate to use to form cross-linked PVDF membranes.

4.6 Conclusions

Owing to the difficulty in forming a pure octa(3-mercaptopropyl) POSS (thiol POSS) compound using literature methods, a new method of synthesising thiol POSS was investigated. The method devised in this thesis of synthesising thiol POSS provided a yield of 19.2 %, with the structure confirmed by ¹H, ¹³C, and ²⁹Si NMR spectroscopies.

Following the successful synthesis of thiol POSS, the modification of thiol POSS by thiol-ene addition chemistry was examined using different alkenes and under different conditions. Allyl alcohol, 2-allyloxyethanol, 6-chloro-1-hexene and 6-bromo-1-hexene have been shown to react smoothly with thiol POSS using AIBN as a catalyst, giving isolated yields of 86 %, 92 %, 81 %, and 66 %, respectively. The thiol-ene addition of the latter three alkenes (as well as styrene) under UV/benzophenone also

proceeded smoothly, whereas UV-light alone was unable to complete the reaction within the same irradiation period of 4 h.

Using a base catalyst (DBU), the thiol-ene addition of thiol POSS could be controlled to selectively adding across the methacrylate alkene of EgMA, producing a soluble compound in a yield of 56 %. Using UV-light however, produced an insoluble material, presumably due to cross-linking from thiol POSS adding across both alkenes of EgMA. This EgMA-POSS compound may have use as an antibacterial additive in polymeric systems.

This work demonstrates the ease at which thiol POSS can be chemically modified under thiol-ene addition conditions, opening the way for using thiol POSS as an adaptable additive for polymeric systems, as well as a cross-linker in UV-curing systems. In particular, using the combination of UV-light with benzophenone demonstrates the readiness of which thiol POSS adds to different types of alkenes.

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Chapter 5 Modification of PVDF by dehydrofluorination and thiol-ene addition

5.1 Synopsis

The aim of this Chapter was to develop a method to cross-link PVDF membranes with model thiols. This was achieved through the modification of PVDF by dehydrofluorination (to introduce alkene functionalities) that then underwent thiolene additions with the model thiols. This newly developed system can then be used to cross-link modified PVDF with the thiol-functionalised POSS (synthesised in Chapter 4) as a method of improving the mechanical properties of PVDF membranes to reduce membrane compaction. This chapter discusses the investigation of the dehydrofluorination of PVDF (d-PVDF) by 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) to produce an alkene modified PVDF (d-PVDF). Two different thiols (1-dodecanethiol and 3-mercaptopropionic acid) were used in a thiol-ene addition to modify the dehydrofluorinated PVDF both during, and after DBU treatment. These experiments provided a framework/model system to cross-link PVDF with thiol POSS.

Analysis of the final precipitated d-PVDF polymer, after various treatments, by ATR-FTIR spectroscopy indicated that DBU was an effective reagent for dehydrofluorination of PVDF at room temperature in DMAc. It was found that the maximum quantity of alkenes was generated on the PVDF backbone after a reaction time of 4 h. The two thiols tested were found to be covalently attached to the PVDF backbone, both when included with DBU during the dehydrofluorination reaction in a one-pot procedure, or by UV-irradiation of a solution containing dehydrofluorinated PVDF with the thiol. These results show that cross-linking PVDF with thiols was a viable reaction. Thus, affording the ability to use a multi-thiol containing molecule, such as thiol POSS, in solution, to cross-link with the d-PVDF membranes, which is described in Chapter 6.

5.2 Introduction

Cross-linking polymers with POSS is a well-known strategy for improving the mechanical properties of polymeric materials.^[1-5] Applied to polymeric water filtration membranes, cross-linking should improve the mechanical properties of the membranes, which in turn should reduce the flux decline due to compaction. In order to be able to cross-link PVDF, reactive functional groups need to be introduced onto the backbone of PVDF.

A common method of modifying PVDF is by dehydrofluorination with bases. Dehydrofluorination of PVDF with bases introduces alkenes onto the PVDF backbone with removal of HF. This reaction was chosen as it is simple to perform, only requiring a strong base such as sodium hydroxide.^[6-8] The introduction of alkenes allow PVDF to be further modified by thiol-ene addition, where thiols add across the alkenes, becoming covalently bound.^[9-12] The dehydrofluorination of PVDF combined with thiol-ene addition, in solution, allows for the cross-linking of PVDF with a broad range of thiol containing compounds, including thiol POSS. There are only a few examples of using of thiols to modify PVDF in literature, which are discussed in the following text.

Smith^[13, 14] examined the cross-linking of Viton A, a copolymer of vinylidene difluoride and hexafluoropropylene, using dithiols with tertiary amines. This method was capable of cross-linking the copolymer, using a press cure at 150 °C followed by an oven cure at 204 °C for 18 h. Whilst this method was successful in cross-linking Viton A, it is not useful in the fabrication of water filtration membranes as it produces dense films, rather than porous materials needed for effective water filtration membranes.

Other studies have involved modifying the surface of the solid PVDF, rather than the bulk of PVDF. Yuan *et al.*^[9] first treated PVDF membrane surfaces with NaOH to produce alkenes by dehydrofluorination, which were then used to tether a thiolepoxy hydrogel to the membrane surface via thiol-ene addition, during the hydrogel formation (Figure 5.1). The thiol-epoxy hydrogel was formed using a tetra-thiol (pentaerythritol tetrakis(3-mercaptopropionate)), and a di-epoxy (diethylene glycol diglycidyl ether), using AIBN as a radical source to induce the hydrogel formation. Figure has been removed due to Copyright restrictions

Figure 5.1 – Schematic of the process used to tether a cross-linked thiol-epoxy hydrogel to the surface of a PVDF membrane bearing alkenes from NaOH treatment.^[9]

Sharma *et al.*^[10] also used thiol-ene addition to tether pentaerythritol tetrakis(3-mercaptopropionate) across the alkenes of a d-PVDF, the product of which was then used to cast a PVDF membrane by NIPS (Figure 5.2). The membrane possessed thiols on the surface which were used to tether silver nanoparticles to add antibacterial properties (as demonstrated against *E. coli*) and reduce leaching of the silver from the nanoparticles.

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Figure 5.2 – General processing steps used to form a PVDF membrane with a thiol-functionalised surface.^[10]

While these studies provided promising results in regards to modifying PVDF with thiols, this reaction had never since this thesis been tested for modifying PVDF in solution, which is necessary if the bulk PVDF is to be cross-linked. Cross-linking

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polymers provides a method of improving the mechanical properties of polymeric materials,^[1, 15, 16] which when applied to polymeric membranes, should improve the compaction resistance of the membranes.

5.3 Chapter Aim

The aim of this chapter is to provide an understanding of how readily PVDF can be modified by thiols, using dehydrofluorination by base to produce synthetic alkene footholds for thiols to attach to the polymer backbone.

Based on the mechanism of how hydroxide bases react with PVDF, there are two different mechanisms by which thiols can add to PVDF. The d-PVDF can undergo nucleophilic substitution of activated fluorines^[7, 17, 18] (fluorines attached to carbons adjacent to alkenes) or by the thiol adding across the alkenes (thiol-ene addition)^[11, 19] produced by the dehydrofluorination reaction. The general scheme of this reaction is shown in Figure 5.3.



Figure 5.3 - Chemical modification of PVDF using base to induce dehydrofluorination, producing alkenes on the PVDF backbone, and the two pathways for thiols to covalently attach to PVDF. Thiols can covalently attach to dehydrofluorinated PVDF by thiol-ene addition (addition of the thiol across the double bond), and by nucleophilic substitution (substitution of activated fluorines).

To maximise the number of available reaction sites on d-PVDF for thiols to attach, the amine base, DBU, was used during the dehydrofluorination of PVDF. Unlike hydroxide bases, which have been shown to undergo nucleophilic substitution during the dehydrofluorination of PVDF, ^[7, 17, 18] DBU should not undergo nucleophilic

substitution, as it has been demonstrated to be non-nucleophilic.^[20-22] This leaves more sites on the polymer backbone for thiols to attach by nucleophilic substitution.

The first part of this work investigates the modification of PVDF by addition of DBU with and without co-addition of thiols, first in THF at reflux, then in DMAc at room temperature. This was done to develop a method for producing organic solvent soluble d-PVDF, as well as to examine if the dehydrofluorination and thiol addition steps could be conducted in a one-pot procedure.

Following this, the UV-catalysed thiol-ene addition of dehydrofluorinated PVDF was examined, which allowed for the thiol addition to d-PVDF as a separate step, a preferable method if reagents sensitive to strong bases are to be used. The overarching aim of this research therefore was to provide an understanding of how readily PVDF can be modified by thiols, to identify strategies to produce cross-linked PVDF using thiol POSS.

5.4 Results and Discussion

5.4.1 Dehydrofluorination of PVDF by DBU, with and without nucleophiles

This section discusses the results and analysis by ATR-FTIR spectroscopy of the products of the dehydrofluorination of PVDF with DBU, with and without the co-addition of nucleophiles, as a one-pot procedure. The experimental for this section can be found in Chapter 2, Section 2.3.9.

This section is split into two distinct parts. The first part (Sections 5.4.1.1 and 5.4.1.2) covers the results of experiments conducted in THF, using DBU, with *n*-butylamine or 1-dodecanethiol as the nucleophile. The experimental for this section can be found in Chapter 2, Sections 2.3.9.1-2.3.9.5.

The second part (Section 5.4.1.3) discusses the results of experiments conducted in DMAc, using DBU with 1-dodecanethiol or 3-mercaptopropionic acid as the nucleophiles. The experimental for this section can be found in Chapter 2, Sections 2.3.9.6-2.3.9.9.

A general overview of these reactions is presented in Figure 5.4.



Figure 5.4 – The reaction of PVDF with DBU, w/ and w/o different nucleophiles, conducted in THF at 90 °C, or in DMAc at room temperature.

5.4.1.1 Dehydrofluorination of PVDF in THF with DBU – analysis by ATR-FTIR spectroscopy

After the treatment of PVDF with DBU (1 or 5 %), it was observed that the polymer precipitated during the reaction. The precipitate was black, compared to unmodified PVDF, which is a white powder. These polymers were analysed by ATR-FTIR spectroscopy, to determine what changes had occurred to PVDF after treatment with DBU.

The ATR-FTIR spectra of PVDF after treatment with DBU (1 % or 5 %) is presented in Figure 5.5. It should be noted that in the ATR-FTIR spectra for all the treatments that changes in the <1400 cm⁻¹ region were attributed to changes in the crystallinity of PVDF rather than evidence of functionalisation. The best example of

this is the increase in intensity of the signal at 839 cm⁻¹ in the ATR-FTIR spectra (Figure 5.5), which has been demonstrated to be due to the β and/or γ crystal phases of PVDF.^[23, 24] Changes due to the reaction can reliably be observed within the 4000-1400 cm⁻¹ region, which will be the focus of this discussion.

Analysis of PVDF treated with 1 % DBU did not show any significant changes in the 4000-1400 cm⁻¹ region of the ATR-FTIR spectrum (Figure 5.5, red line) compared to pristine PVDF (Figure 5.5, black line), despite being a black precipitate compared to the pristine PVDF, which is a white powder. This attributed to treatment of PVDF with 1 % DBU introducing too low a quantity of functionalisation to be observed in the ATR-FTIR spectrum of the treated polymer.

In comparison, PVDF treated with 5 % of DBU shows much more dramatic changes in the ATR-FTIR spectrum (Figure 5.5, dark blue line). A very broad absorbance in the 1750-1450 cm⁻¹ region appeared which was attributed to alkenes;^[17, 25] the broadness of the signal is a result of the presence of conjugated alkenes.^[6, 8, 17, 25] Two signals in the C-H stretching region at 2921 cm⁻¹ and 2851 cm⁻¹ were observed, while the ATR-FTIR spectrum still showed the C-H stretches from PVDF at 3027 cm⁻¹ and 2984 cm⁻¹. The exact cause of these new C-H signals in the ATR-FTIR spectrum is not known; in literature, where observed, it is not mentioned.^[17]

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Figure 5.5 - ATR-FTIR spectra of PVDF before and after treatment with DBU (1% or 5%) in refluxing THF. Inset – Close-up of the 3200-2750 cm⁻¹ and the 1850-1400 cm⁻¹ regions of the ATR-FTIR spectra.

A very small signal at 1736 cm⁻¹ in the ATR-FTIR spectrum of PVDF after treatment with 5 % DBU (see the inset of Figure 5.5, dark blue line) was attributed to the presence of ketones, ^[7, 17, 18] which is commonly observed in literature when using hydroxide bases to react with PVDF.^[7, 8, 18] The presence of ketones on PVDF after treatment with DBU is due to residual water in the reaction, which is activated by DBU and undergoes nucleophilic attack on the PVDF, resulting in ketone production. The general scheme of this process is presented in Figure 5.6.

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Figure 5.6 – General scheme of ketone production during dehydrofluorination of PVDF using DBU as the base. Mechanism based on that proposed in by Brewis *et* $al.^{[7]}$

These results indicate that the treatment of PVDF with DBU has resulted in dehydrofluorination of PVDF, introducing alkenes on the polymer backbone. DBU is

preferable to the hydroxide bases commonly used to dehydrofluorinate PVDF, as the hydroxide bases themselves are known to undergo nucleophilic substitution with dehydrofluorinated PVDF,^[20-22]whereas DBU is known to be non-nucleophilic.^[20-22] As this reaction is being examined for the attachment of thiol POSS, treatment with DBU should provide a greater number of sites by which thiol POSS can attach to dehydrofluorinated PVDF by nucleophilic substitution, rather than hydroxide bases, which will compete with thiol POSS. To confirm if dehydrofluorinated PVDF by DBU can be used to attach nucleophiles, further experiments were conducted using DBU to treat PVDF with different nucleophiles, such as amines or thiols, to determine if this method can be used to attach POSS with thiol or amine groups.

5.4.1.2 Dehydrofluorination of PVDF in THF with DBU and nucleophiles – analysis by ATR-FTIR spectroscopy

The reaction of DBU (1%) with PVDF was also examined with the co-addition of two different nucleophiles – namely, *n*-butylamine and 1-dodecanethiol. These experiments were undertaken to determine if thiols or amines can be covalently bound to PVDF during the dehydrofluorination reaction with DBU, and if this method could be used to attach thiol POSS. The ATR-FTIR spectra of PVDF after these treatments is presented in Figure 5.7.

The ATR-FTIR spectrum of the PVDF treated with 1 % DBU and *n*-butylamine (Figure 5.7, red line) shows a distinct peak at 1648 cm⁻¹, which is attributed to the N-H bending mode^[25, 26] of covalently bound *n*-butylamine. Also present is a broad absorbance in the 1750-1450 cm⁻¹ region overlapping with the peak at 1648 cm⁻¹ which was identified to be due to alkene moieties.^[17, 25] In comparison to PVDF treated with 1 % DBU, PVDF treated with 1 % DBU with *n*-butylamine shows new peaks in the ATR-FTIR spectrum (Figure 5.7, black and red lines, respectively) at 2921 cm⁻¹ and 2851 cm⁻¹, attributed to be from the C-H groups of the alkyl chain of *n*-butylamine. This data suggests that *n*-butylamine has been covalently bound to the PVDF backbone, with alkene moieties also present.

In comparison, the analysis of PVDF treated with 1 % of DBU and 1dodecanethiol (Figure 5.7, dark blue line) shows little absorbance in the 1750-1450 cm⁻¹ of the ATR-FTIR spectrum, indicating that the treated polymer shows little alkene functionality. However, the spectrum does show additional signals at 2921 cm⁻¹ and 2851 cm⁻¹, attributed to the C-H stretching from the alkyl chain of 1-dodecanethiol. This indicates that 1-dodecanethiol has become covalently bound to PVDF, and that, in comparison to PVDF treated with 1 % DBU and *n*-butylamine, that PVDF treated with 1 % DBU and 1-dodecanethiol possesses less alkene functionality.



Figure 5.7 - ATR-FTIR spectra of PVDF after treatments with 1 % DBU, with and without different nucleophiles present, in refluxing THF. Inset – Close-up of the 3200-2750 cm⁻¹ and the 1850-1400 cm⁻¹ regions of the ATR-FTIR spectra.

The difference in the ATR-FTIR spectra of PVDF treated with *n*-butylamine and 1dodecanethiol (with 1 % of DBU) was attributed to a difference in the chemical properties of the two nucleophiles. Both amines and thiols are well known to be nucleophilic, and both are known to undergo nucleophilic substitution reactions readily, as well as add across alkenes.^[19] However, thiols more readily add across alkenes than primary amines,^[11, 19] so much so that primary amines have been

successfully used to catalyse the addition of thiols across alkenes.^[11, 27] *N*-butylamine is also known to be able to cause dehydrofluorination of PVDF with heating, ^[28] resulting in more alkene moeities in the d-PVDF, whereas thiols are not known to cause dehydrofluorination. The combination of these factors (greater reactivity of thiols to add across alkenes, and *n*-butylamine causing dehydrofluorination by itself) accounts for the larger amount of alkene moeities on the PVDF treated with 1 % DBU and *n*-butylamine, compared to the reaction of PVDF with 1 % DBU and 1dodecanethiol. This point is significant, as excessive dehydrofluorination of PVDF can lead to insoluble products forming, and also reduces the mechanical properties of PVDF.^[29, 30] This result indicates that a thiol-functionalised POSS is preferable to an amine-functionalised POSS to use to cross-link PVDF using dehydrofluorination, as the amine-functionalised POSS would likely lead to excessive dehydrofluorination in this reaction.

To examine if AIBN, a known catalyst for thiol-ene addition,^[12, 31] could aid in the thiol-ene addition of 1-dodecanethiol across the alkenes of d-PVDF, a reaction with AIBN, 1 % DBU and 1-dodecanethiol was performed. The ATR-FTIR spectrum is presented in Figure 5.7 (magenta line). As there is little difference to the ATR-FTIR spectrum of PVDF treated with 1 % DBU, 1-dodecanethiol and no AIBN (Figure 5.7, dark blue line), it was concluded that the addition of AIBN did not appreciably increase the attachment of 1-dodecanehiol under the conditions examined.

This study indicated that the addition of amine or thiol containing nucleophiles with DBU to treat PVDF leads to covalent attachment of the nucleophile to the backbone of PVDF. However, in THF, PVDF was observed to precipitate from solution during the reaction, limiting the functionalisation of PVDF to the surface rather than the bulk of the polymer. In an effort to avoid the precipitation of PVDF, further reactions were conducted in DMAc. The improved solubility of PVDF in DMAc compared to THF also allowed the reactions to be conducted at room temperature, simplifying the procedure, and also allowed greater concentrations of DBU to be used. This allows more alkene functionality to be introduced on resulting d-PVDF, which provides more sites for thiol POSS to attach.

5.4.1.3 Dehydrofluorination of PVDF in DMAc with DBU only

The dehydrofluorination of PVDF with 10 % of DBU alone was examined in DMAc at room temperature, and was monitored with different reactions times (2 h, 4 h, 6 h, and 16 h). The d-PVDF was recovered by precipitation in ethanol, and the oven-dried polymer analysed by ATR-FTIR spectroscopy. It was noted that after 16 h of treatment, the solution had formed a semi-solid, black, gel-like substance in the reaction flask.

5.4.1.4 Dehydrofluorination of PVDF in DMAc with DBU only – ATR-FTIR analysis

Monitoring the dehydrofluorination of PVDF with 10 % DBU in DMAc by ATR-FTIR spectroscopy (Figure 5.9) shows similar changes in the spectrum as compared to conducting the reaction in THF (Section 5.4.1.1, Figure 5.5). A broad absorbance in the 1750-1450 cm⁻¹ region appeared at ~1650 and ~1530 cm⁻¹, which were attributed to the production of unconjugated and conjugated alkenes, respectively.^[6, 8, 17, 25] Additional signals in the C-H stretching region of the spectrum appeared at 2921 cm⁻¹ and 2851 cm⁻¹.

Comparing different treatment times of PVDF with DBU revealed significant changes in the ATR-FTIR spectra of the d-PVDF. The relative intensity of the absorbance(s) associated with alkene functionality (broad absorbance in the 1750-1450 cm⁻¹ region) increased with time up to 4 h, then significantly decreased at reaction times ≥ 6 h. After treatment of PVDF with DBU for 16 h, the intensity of this absorbance increased again, although notably the absorbance was centred at ~1650 cm⁻¹, rather than a broad absorbance spanning across the whole 1750-1450 cm⁻¹ region. The significance of the absorbance being centred at ~1650 cm⁻¹ (as opposed to a broad absorbance spanning the 1750-1450 cm⁻¹ region) is that this indicates that the alkenes on the polymer are unconjugated, ^[8, 17, 25] as conjugated alkenes show a lower wavenumber of the C=C stretch in IR spectroscopy.^[8, 17, 25] This data also indicates qualitatively that the quantity of alkenes on the polymer increases with DBU treatment up to 4 h, but then significantly decays after 6 h of reaction time. A similar result has been observed in Raman spectroscopy of a PVDF surface treated with hydroxide base.^[32] In that study, it was found that the maximum quantity of polyene/conjugated double bonds was reached after 4 h of treatment, but then decayed with longer treatment times.^[32] No real explanation was given as to why this

was occurring. Possibly this is due to cross-linking reactions, such as those proposed by Smith^[14] involving Diels-Alder cycloaddition of alkenes (see Figure 5.8). The crosslinking of the polymer may also explain why leaving the reaction to run for 16 h produced a gel-like material.

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Figure 5.8 – General scheme of alkene consumption during dehydrofluorination of PVDF by Diels-Alder cycloaddition proposed by Smith.^[14]

Increasing the reaction time from 6 h to 16 h led to an increased amount of alkene moeities in the d-PVDF. However, the alkenes in the final product were more unconjugated, as the main absorbance was centred at ~1650 cm⁻¹ which is associated with the C=C stretch of unconjugated alkenes.^[8, 17, 25] Although the signals at 2921 cm⁻¹ and 2851 cm⁻¹ also vary in intensity in the ATR-FTIR spectrum with DBU treatment time, no real understanding of the significance of this observation can be made as their origin is currently unknown.

This experiment indicated that (qualitatively) a 4 h treatment of PVDF with DBU provides the maximum amount of alkenes on the polymer backbone, while longer reaction times reduced the alkene functionality. If the reaction was left for excessive periods of time, such as 16 h, insoluble products formed due to cross-linking.



Figure 5.9 - ATR-FTIR spectra of PVDF before and after treatments with DBU for different times in DMAc at room temperature. Inset – Close-up of the 3200-2750 cm⁻¹ and the 1850-1400 cm⁻¹ regions of the ATR-FTIR spectra.

5.4.1.5 Dehydrofluorination of PVDF in DMAc with DBU and 1-dodecanethiol

To investigate how thiols react during the dehydrofluorination of PVDF with 10 % DBU in DMAc as a solvent, a 1:5 mol ratio of DBU and 1-dodecanethiol were used to treat PVDF. The DBU concentration was maintained at 10 %. The reaction was monitored again at 2 h, 4 h, 6 h, and 16 h, by precipitating the polymer in ethanol, and analysing the polymer by ATR-FTIR spectroscopy. Unlike the reaction with 10 % DBU alone, the reaction with 10 % DBU and 1-dodecanethiol did not produce insoluble materials after 16 h of reaction time.

5.4.1.6 Dehydrofluorination of PVDF in DMAc with DBU and 1-dodecanethiol – ATR-FTIR analysis

The ATR-FTIR spectrum of PVDF modified by 10 % DBU and 1-dodecanethiol in DMAc is presented in Figure 5.10. It can be observed that the intensity of the signals at 2921

cm⁻¹ and 2851 cm⁻¹ increased with increasing reaction time (see inset of Figure 5.10), showing the largest relative intensity after treatment of 16 h (Figure 5.10, light blue line). Signals in the 1750-1450 cm⁻¹ region of the ATR-FTIR spectrum are slow to appear, with 2 h and 4 h of treatment (Figure 5.10, red and green lines, respectively) showing no signals in the 1750-1450 cm⁻¹ region of the spectrum. With 6 h of treatment (Figure 5.10, dark blue line), only relatively small signals in the 1750-1450 cm⁻¹ region of the spectrum appeared, while after 16 h of treatment (Figure 5.10, light blue line), a broad absorbance in this region appeared with a distinct peak at ~1650 cm⁻¹.

This data indicates that 1-dodecanethiol and 10 % DBU together in the solution with PVDF results in covalent attachment of 1-dodecanethiol to the PVDF backbone. Moreover, the longer the period of the reaction the more 1-dodecanethiol becomes covalently bound, as evidenced by the increase in intensity of the signals at 2921 cm⁻¹ and 2851 cm⁻¹ (attributed to the C-H stretch of the alkyl chain of 1-dodecanethiol). However, the quantity of alkene functionality produced on the polymer is considerably less than with DBU alone (no thiol), due to consumption of the alkenes by thiol-ene addition. As more 1-dodecanethiol becomes covalently bound to the polymer backbone, the rate of alkene formation begins to exceed the rate of thiol-ene addition. This results in alkene functionality appearing in PVDF treated with 1-dodecanethiol and DBU for 6 h and longer.



Figure 5.10 - ATR-FTIR spectra of PVDF before and after treatments with DBU and 1dodecanethiol (1:5 mol ratio) in DMAc at room temperature. Inset – Close-up of the 3200-2750 cm⁻¹ and the 1850-1400 cm⁻¹ regions of the ATR-FTIR spectra.

5.4.1.7 Dehydrofluorination of PVDF in DMAc with DBU and 3-mercaptopropionic acid

To provide further evidence that DBU can be used to covalently attach thiols to PVDF, a similar experiment was conducted using 3-mercaptopropionic acid with DBU (instead of 1-dodecanethiol). The reaction was run with 10 % DBU. The advantage of using 3-mercaptopropionic acid is that it possesses a carbonyl group (from the carboxylic acid), which should appear prominently in IR spectroscopy, making it easier to analyse during the modification.^[25]

Initially, 3-mercaptopropionic acid was added in a 1:1 mol ratio to DBU, and allowed to react for 24 h. To accelerate the reaction, a further 1 mol equivalent of DBU was added, and allowed to react for a further 48 h (72 h total reaction time). Polymer samples were isolated from the reaction at 24 h (1:1 mol ratio of thiol:DBU), 48 h (24 h after adding the extra 1 mol equivalent of DBU, mol ratio of 1:2 of thiol:DBU), and 72 h (48 h after adding the extra 1 mol equivalent of DBU, mol ratio of 1:2 of thiol:DBU). No insoluble materials were produced by this reaction.

5.4.1.8 Dehydrofluorination of PVDF in DMAc with DBU and 3-mercaptopropionic acid – ATR-FTIR analysis

The ATR-FTIR spectra of PVDF treated with DBU and 3-mercaptopropionic acid for different treatment times, and conditions, is presented in Figure 5.11.

After treatment of PVDF for 24 h reaction with a 1:1 mol ratio of 1mercaptopropionic acid and DBU, the ATR-FTIR spectrum (Figure 5.11, red line) shows a broad absorption in the 1750-1450 cm⁻¹ region of the spectrum, with four signals at ~1720, 1648, 1577 and 1540 cm⁻¹. After adding an additional 1 mol equivalent of DBU to the reaction, and leaving to react for an additional 24 h (labelled 48 h (1:2 thiol:DBU), Figure 5.11, green line), the ATR-FTIR spectrum of the resulting polymer was similar. Leaving the reaction for an additional 24 h, for a total of 72 h since starting the reaction (48 h after adding the additional 1 mol equivalent of DBU) the ATR-FTIR spectrum (labelled 72 h, 1:2 thiol:DBU, Figure 5.11, dark blue line) gives a very different result. The ATR-FTIR spectrum (Figure 5.11, dark blue line) showed three prominent signals at 1720, 1648, and 1590 cm⁻¹. The signals at 1720 and 1648 cm⁻¹ were attributed to the C=O stretch of the carboxylic acid of 3-mercaptopropionic acid.^[25, 33, 34] The reason for the dual signals in the ATR-FTIR spectrum for the carbonyl stretch was attributed to the different environments of the carboxylic acid groups. Specifically, coordination with amines,^[35] or due to differences in hydrogen bonding environments.[33, 34]

These results indicate that 3-mercaptopropionic acid has also been covalently attached to the backbone of PVDF. However, the addition of 3-mercaptopropionic acid appears to be slower (in comparison to 1-dodecanethiol), perhaps due to the carboxylic acid functionality neutralising some of the DBU and slowing the dehydrofluorination reaction.





5.4.1.9 Issues with the one-pot method for forming cross-linked PVDF membranes

The one pot method to modify PVDF with thiols, by simultaneous dehydrofluorination with DBU showed promise this was originally investigated as a method of forming cross-linked PVDF membranes. This was to be accomplished by adding the appropriate reagents (DBU and thiol POSS) to the membrane casting solution (PVDF with PVP in DMAc). The cross-linked PVDF membranes could then be formed by one of two methods. The first was to leave the casting solution to react and cross-link for different periods of time before casting the solution onto a glass plate, and forming the membrane by immersion in a coagulation bath. The other method was to, after forming a homogenous casting solution, immediately cast the

solution onto a glass plate, and then leave the as cast film to cross-link before immersion in the coagulation bath.

However, these methods suffered from one major flaw. Attempting to add DBU to a typical casting solution of 20 wt% of PVDF (and 5 wt% PVP) in DMAc resulted in the formation of an insoluble black film on the surface of the casting solution, which prevented DBU from mixing in. While this could potentially be overcome by dissolving DBU in DMAc first, and then adding PVDF, the time taken to dissolve the PVDF would lead to excessive dehydrofluorination, as it usually takes at least 12 h with heating to dissolve all the PVDF at the concentrations typically used for membrane fabrication (typically 10-20 wt% of the casting solution).^[36-39] This would result in the production of insoluble materials, which would be difficult (if not impossible) to cast as a homogenous film, and likely make this method give irreproducible results.

To avoid the difficulty in adding DBU directly to the membrane casting solution, it was devised that PVDF be cross-linked in two distinct steps. First, PVDF is dehydrofluorinated with DBU to introduce the alkenes onto the polymer, and the d-PVDF recovered from solution. The membrane casting solution is then made using d-PVDF with thiol POSS, and UV-catalysed thiol-ene addition applied to cross-link d-PVDF with thiol POSS. The advantage of using UV-catalysed thiol-ene addition is that the reaction is driven by UV-irradiation, which can easily be done on the cast d-PVDF-solution film with UV lamps. This strategy also avoids the issue of cross-linking PVDF before casting the casting solution, as the cross-linking reaction would likely form insoluble materials that cannot be cast homogenously.

To model if the UV-catalysed thiol-ene addition is a viable option for crosslinking d-PVDF in solution, experiments were carried out using d-PVDF solutions in DMAc with model thiols. These solutions of d-PVDF were treated with UV-irradiation, with and without benzophenone (a well-known photocatalyst for thiol-ene addition),^[31, 40, 41] as well as with 1-dodecanethiol or 3-mercaptopropionic acid as the model thiols.

5.4.2 Post-modification of dehydrofluorinated PVDF with UV-catalysed thiol-ene addition

This section investigated the covalent attachment of 1-dodecanethiol and 3mercaptopropionic to d-PVDF in solution, using UV-catalysed thiol-ene addition. The experimental methods can be found in Chapter 2, Section 2.3.10. The d-PVDF used in the following experiments was synthesised by reacting PVDF with 10 % DBU in DMAc for 4 h, followed by precipitating in ethanol and washing with ethan ol, and drying in an oven at 60 °C (see Chapter 2, Section 2.3.9.9 for full details). A schematic of the thiol-ene reaction of d-PVDF with the different thiols is presented in Figure 5.12.





5.4.2.1 Post-modification of dehydrofluorinated PVDF with UV-irradiation, with and without benzophenone

To investigate the effect of UV-irradiation, as well as the presence of benzophenone (a photocatalyst) on d-PVDF dissolved in DMAc, experiments were conducted using the same UV source with irradiation times of 1 h, with and without benzophenone. An additional experiment was conducted using 4 h of UV-irradiation with double the amount of benzophenone. After recovering the polymer from the solution by

precipitation in ethanol (and oven-drying at 60 °C), the resulting polymers (which were dark brown in colouration, compared to the black d-PVDF before UV-irradiation) were then analysed by ATR-FTIR spectroscopy.

5.4.2.2 Post-modification of dehydrofluorinated PVDF with UV-irradiation, with and without benzophenone – ATR-FTIR spectroscopy

The ATR-FTIR spectra of d-PVDF, before and after treatment with UV-irradiation with or without benzophenone, are presented in Figure 5.13. As with the previous section (Section 5.4.1), any changes in the 1450-500 cm⁻¹ region of the FTIR spectra cannot be reliably used, as changes in the crystallinity of PVDF caused changes in this region of the ATR-FTIR spectrum.^[23, 24]

The treatment of d-PVDF with UV-irradiation resulted in similar changes in the ATR-FTIR spectra of the treated polymers, with or without benzophenone. After treatment, the ATR-FTIR spectra shows a disappearance of the signals at 2921 cm⁻¹ and 2851 cm⁻¹, as well as a loss of the intensity of the absorbance(s) in the ~1600-1480 cm⁻¹ region. The signal at 1650 cm⁻¹ does not change significantly after the treatments. This data indicated that UV-irradiation resulted in the elimination of the conjugated alkenes, while either producing isolated alkenes or leaving the isolated alkenes unreacted. This is indicated by the signal at 1650 cm⁻¹ in the ATR-FTIR spectra of the treated polymers (inset of Figure 5.13, red, purple, and dark blue lines) not being removed after UV-irradiation with or without benzophenone, as this signal is associated with isolated alkenes.^[8, 17, 25] The removal of the conjugated alkenes from the UV-treated d-PVDF can be observed by the removal of the absorbance in the ~1600-1480 cm⁻¹ region of the ATR-FTIR spectra (inset of Figure 5.13, red, purple, 5.13, red, purple, and dark blue lines) compared to d-PVDF before UV-irradiation (inset of Figure 5.13, black line). The inclusion of benzophenone does not seem to effect the reaction.





5.4.2.3 Post-modification of dehydrofluorinated PVDF with UV-irradiation and 1dodecanethiol

1-dodecanethiol was dissolved together with d-PVDF, with and without benzophenone, and the solutions were then irradiated with UV-light for 1 h. The resulting polymer was recovered by precipitation in ethanol, and after drying in an oven at 60 °C, were then analysed by ATR-FTIR spectroscopy.

5.4.2.4 Post-modification of dehydrofluorinated PVDF with UV-irradiation and 1dodecanethiol – ATR-FTIR analysis

The ATR-FTIR spectra of d-PVDF after treatment with UV-irradiation and 1dodecanethiol with or without benzophenone is presented in in Figure 5.14. For

reference, the ATR-FTIR spectrum of d-PVDF treated with UV-irradiation for 1 h with benzophenone (with no 1-dodecanethiol) is also included (Figure 5.14, black line).

Focusing on the 3200-2750 cm⁻¹ and the 1850-1400 cm⁻¹ regions of the ATR-FTIR spectra (see inset of Figure 5.14), UV-irradiation for 1 h with 1-dodecanethiol (with or without benzophenone) reduces the relative intensity of the signal associated with isolated alkenes (signal at 1650 cm⁻¹).^[6, 8, 17, 25] Bands at 2921 cm⁻¹ and 2851 cm⁻¹ are also present in the ATR-FTIR spectra with the inclusion 1-dodecanethiol, which is from the C-H stretch of the alkyl chain of 1-dodecanethiol. The inclusion of benzophenone as a photocatalyst during the UV-treatment with 1-dodecanethiol resulted in a greater relative intensity reduction of the band at 1650 cm⁻¹, and a relatively larger increase in the bands at 2921 cm⁻¹ and 2851 cm⁻¹. These results indicated that 1-dodecanethiol has been successfully grafted to d-PVDF, and that the inclusion of benzophenone in the reaction results in a greater quantity of 1dodecanethiol becoming attached. This data indicates that d-PVDF can be successfully modified by thiol-ene addition in solution with UV-irradiation with 1dodecanethiol.



Figure 5.14 - ATR-FTIR spectra of d-PVDF after treatment with 1 h UV irradiation and; benzophenone (black line); 1-dodecanethiol (red line); and 1-dodecanethiol and benzophenone (blue line). Inset – Close-up of the 3200-2750 cm⁻¹ and the 1850-1400 cm⁻¹ regions of the ATR-FTIR spectra.

5.4.2.5 Post-modification of dehydrofluorinated PVDF with UV-irradiation with 3mercaptopropionic acid – ATR-FTIR analysis

To provide further evidence that thiols can be attached to d-PVDF with UVirradiation, experiments were conducted with 3-mercaptopropionic acid. Solutions of d-PVDF and 3-mercaptopropionic acid in DMAc, with or without benzophenone, were treated with 1 h of UV irradiation. The ATR-FTIR spectra of the isolated polymers are presented in Figure 5.15. Focusing on the 3200-2750 cm⁻¹ and the 1850-1400 cm⁻¹ ¹ regions of the ATR-FTIR spectra (see inset of Figure 5.15), UV-irradiation for 1 h with 3-mercaptopropionic acid (without benzophenone, red line) greatly reduces the relative intensity of the signal at 1650 cm⁻¹ (corresponding to the C=C vibration of isolated alkenes),^[6, 8, 17, 25] as well as showing weak bands at 2921 cm⁻¹ and 2851 cm⁻¹. The inclusion of benzophenone in the reaction (Figure 5.15, dark blue line) resulted in an increase in the intensity of the signal at 1650 cm⁻¹, as well as two additional bands at 1722 and 1577 cm⁻¹. These bands are attributed to the carbonyl group of 3-mercaptopropionic acid.^[25, 33, 34] These results can be explained by the inclusion of benzophenone resulting in greater quantities of thiol -ene addition of 3-mercaptopropionic acid to d-PVDF, compared to the similar reaction without benzophenone. Due to overlap of the alkene signals (C=C vibration) with the C=O vibrations, the intensity of the signal at 1650 cm⁻¹ increased due to the attachment of 3-mercaptopropionic acid to d-PVDF. As the attachment of 3-mercaptopropionic acid to d-PVDF was previously shown to result in multiple peaks due to C=O vibrations (see Section 5.4.1.8, Figure 5.11), the additional bands at 1722 cm⁻¹ and 1577 cm⁻¹ were attributed to C=O vibrations of grafted 3-mercaptopropionic acid.^[25, 33, 34]



Figure 5.15 - ATR-FTIR spectra of d-PVDF after treatment by 1 h UV irradiation and; benzophenone (black line); 3-mercaptopropionic acid (red line); 3mercaptopropionic acid with benzophenone (blue line). Inset – Close-up of the 3200-2750 cm⁻¹ and the 1850-1400 cm⁻¹ regions of the ATR-FTIR spectra. This data indicates that 3-mercaptopropionic acid has been successfully grafted to d-PVDF, by UV-catalysed thiol-ene addition. The 3-mercaptopropionic acid covalently attached to d-PVDF is increased with the inclusion of benzophenone in the reaction solution during the UV-irradiation for 1 h.

5.4.2.6 Post-modification of dehydrofluorinated PVDF with UV-irradiation with double the quantity of 3-mercaptopropionic acid – ATR-FTIR analysis

To provide further evidence of successful attachment of thiols by UV-irradiation, the reaction of d-PVDF with 3-mercaptopropionic acid was performed again. The time of UV-irradiation was increased to 4 h, and the quantities of benzophenone and 3-mercaptopropionic acid added to the solutions were doubled, as compared to the previously described experiments involving UV-catalysed thiol-ene addition of 3-mercaptopropionic acid with d-PVDF (Section 5.4.2.5). The quantities of d-PVDF and DMAc added to the solutions were kept the same, as compared to the previous experiments (Section 5.4.2.5).

The ATR-FTIR spectra of d-PVDF after treatment with UV-irradiation for 4 h and double the quantity of 3-mercaptopropionic acid used in previous experiments (with and without benzophenone) are presented in Figure 5.16 (red and dark blue lines, respectively).

Focusing on the 1850-1400 cm⁻¹ region of the ATR-FTIR spectra (see inset of Figure 5.16), the ATR-FTIR spectrum of d-PVDF treated of d-PVDF with UV-light and benzophenone without 3-mercaptopropionic acid (Figure 5.16, black line) shows only a signal at 1650 cm⁻¹. In the ATR-FTIR spectrum of d-PVDF treated with 3-mercaptopropionic acid and UV-irradiation (both with and without benzophenone, Figure 5.16, red and dark blue lines, respectively), two broad bands at 1720 cm⁻¹ and 1620 cm⁻¹ can be observed in the 1700-1500 cm⁻¹ region of the ATR-FTIR spectra can be observed, with no peak at 1650 cm⁻¹. These bands at 1720 cm⁻¹ and 1620 cm⁻¹ are associated with the C=O vibrations of 3-mercaptopropionic acid, ^[25, 33, 34] whereas the band at 1650 cm⁻¹ in the ATR-FTIR spectrum of d-PVDF treated with UV-irradiation and benzophenone (without 3-mercaptopropionic acid) is associated with unconjugated alkenes, as discussed in Section 5.4.2.2. This confirms that d-PVDF has been successfully grafted with 3-mercaptopropionic acid. In these experiments, there is little difference between the ATR-FTIR spectra of d-PVDF treated with 3-

mercaptopropionic acid with (Figure 5.16, dark blue line) and without benzophenone (Figure 5.16, red line). This was attributed to saturation of 3-mercaptopropionic acid on d-PVDF with 4 h of UV-irradiation alone, and as such, the addition of benzophenone did not increase the amount of 3-mercaptopropionic acid grafted to the d-PVDF.





This method of modifying d-PVDF with thiols in solution by UV-irradiation will provide a way to form cross-linked PVDF membranes using octa(3-mercaptopropyl) POSS.

5.5 Conclusions

This chapter discusses the dehydrofluorination of PVDF using DBU as the base, alone. This was then followed by a discussion on the dehydrofluorination of PVDF using DBU

(at 1 %, 5% and 10%) with different thiols, and the resulting polymers isolated from the reaction analysed by ATR-FTIR spectroscopy. Treating PVDF in solution (in THF or DMAc) with DBU led to the production of conjugated and unconjugated (isolated) alkenes onto the polymer backbone by dehydrofluorination, producing broad absorbance(s) in the 1750-1450 cm⁻¹ region. Inclusion of 1-dodecanethiol in the reaction with DBU resulted in attachment of 1-dodecanethiol, increasing the relative intensity of the C-H bands 2921 cm⁻¹ and 2851 cm⁻¹ from the alkyl chain of 1dodecanethiol. The alkene content in the final polymer was greatly reduced by inclusion of 1-dodecanethiol in solution (compared to the reaction with DBU only), indicating that the thiol was added to PVDF by a combination of nucleophilic substitution and DBU catalysed thiol-ene addition, the latter reaction consuming the alkenes as they were produced. For further evidence, a similar reaction was conducted with 1-mercaptopropionic acid instead of 1-dodecanethiol, and the final polymers showed carbonyl vibrations from the carboxylic acid of 3mercaptopropionic acid. This confirms that thiols can be covalently bound to dehydrofluorinated PVDF using DBU in a one-pot reaction.

Furthermore, the UV-catalysed thiol-ene addition of dehydrofluorinated PVDF (dehydrofluorinated prior to thiol-ene addition) with either 1-dodecanethiol or 3-mercaptopropionic acid was performed, by UV-irradiation of solutions in DMAc. Analysis of the polymers isolated from the solution after the treatments by ATR-FTIR spectroscopy confirmed the successful grafting of both thiols, with the inclusion of benzophenone as photocatalyst increasing the amount of thiol-ene addition.

Overall, these experiments demonstrate that thiols can be covalently bound to PVDF, either by using a one-pot method (DBU and thiols added together with PVDF in solution) or a two-step method, by dehydrofluorination of PVDF first with DBU, followed by UV-catalysed thiol-ene addition. For forming cross-linked PVDF membranes with thiol POSS, the two-step method of modifying PVDF with thiols is preferable. The main reason being is that the latter method (dehydrofluorination followed by UV-catalysed thiol-ene addition) avoids the issue of trying to incorporate DBU into the casting solution, which showed issues with mixing with highly concentrated PVDF solutions typically used to form PVDF membranes.

5.6 References

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Chapter 6 Cross-linked and EgMA-POSS modified PVDF membranes

6.1 Synopsis

This chapter discusses the analysis of cross-linked PVDF membranes, and EgMA-POSS modified PVDF membranes, which were produced by chemical modification of PVDF homopolymer. Both of these types of membranes were produced using thiol-ene addition of octa(3-mercpatopropyl) POSS (thiol POSS), catalysed by UV-irradiation with benzophenone. Cross-linked PVDF membranes were produced by thiol POSS adding across the alkenes of dehydrofluorinated PVDF (d-PVDF) alone. EgMA-POSS modified PVDF membranes were produced by thiol POSS modified PVDF membranes were produced by thiol POSS adding across the alkenes of dehydrofluorinated PVDF (d-PVDF) alone. EgMA-POSS modified PVDF membranes were produced by thiol POSS adding across the alkenes of both d-PVDF and eugenyl methacrylate (EgMA).

Analysis of the cross-linked PVDF membranes (using thiol POSS only (0-10 wt%), no EgMA) indicated that the Young's modulus of the membranes typically increased with thiol POSS loading. The cross-linked membranes showed improved compaction resistance, showing less flux decline during filtrations of pure water, with the membrane with 10 wt% of thiol POSS giving the least flux decline.

Bacterial adhesion tests on the EgMA-POSS modified PVDF membranes (membranes with 10 wt% of thiol POSS with varying loadings of EgMA (0-20 wt%)) showed that inclusion of thiol POSS promoted bacterial adhesion. While inclusion of EgMA could reduce bacterial adhesion with loadings of 10 and 20 wt% in the casting solution, the membrane without thiol POSS or EgMA showed the least amount of bacterial adhesion.

6.2 Introduction

Two common issues that cause flux decline during water filtration with polymeric membranes are compaction and biofouling. Compaction results from physical compression of the membrane due to the pressure applied to drive the filtration, which restricts the pores/pore channels, decreasing the water flux.^[1-4] Biofouling, on the other hand, occurs when microorganisms form biofilms on the membrane surface. This reduces the water flux by blocking the pores of the membrane, as well

as by adding another layer that the water has to penetrate to be able to pass through.^[5-7] To reduce the effect of membrane compaction, cross-linking PVDF was chosen as a strategy to increase the mechanical properties, which is discussed in Section 6.2.1. To improve the biofouling resistance of PVDF membranes, incorporation of antibacterial compounds is examined in Section 6.2.2.

6.2.1 Reducing membrane compaction – cross-linking PVDF

Compaction of polymeric membranes leads to flux decline during filtration, which reduces the efficiency of the filtration process.^[2, 3, 8-10] Improving the mechanical properties of the membranes provides a way to reduce the flux decline due to compaction.^[11-13] One method of improving the mechanical properties of polymeric materials is through cross-linking.^[14-17] So far, the chemical cross-linking of PVDF is limited in literature, and there are few examples. The methods typically involve either forming copolymers of PVDF with reactive pendant or end-groups, or chemically modifying the PVDF homopolymer to add cross-linkable moieties. Both of these methods are discussed in the following.

6.2.1.1 Cross-linking PVDF using reactive copolymers

The following discusses methods found in literature to produce cross-linked PVDF, by forming PVDF with polymerisable end-groups, or by forming a copolymer of PVDF with a reactive pendant group.

Guerre et al.^[18] synthesised short PVDF chains using reversible additionfragmentation chain transfer (RAFT) polymerisation. A very simplified explanation of RAFT polymerisation is given here, however a more detailed explanation can be found in literature.^[19-22] During RAFT polymerisation, radical species (either from a radical initiator or growing polymer chains) adds to a RAFT agent, such as a dithiocarbonate compound. This addition reaction is reversible, reforming the RAFT agent and the radical species, the latter which can polymerise (more) monomer. The reversible addition of the radical species to the RAFT agent limits the concentration of radicals at any given time, which reduces termination reactions. At the end of the polymerisation, the RAFT agent remains on the end of the polymer chain, which can be lysed to form thiols.^[19-22] Back to the work of Guerre et al.^[18], after forming short PVDF chains by RAFT polymerisation, the RAFT end groups were lysed to form thiols. These thiols were used to attach 3-(acryloyloxy)-2-hydroxypropyl methacrylate by thiol-ene addition, producing a linear methacrylate terminated PVDF species (Figure 6.1, top image), which was shown to be co-polymerisable with methyl methacrylate under RAFT polymerisation. In a similar method, Lopez et al.^[23] used a tetra-functional RAFT agent to polymerise vinylidene difluoride to form a 4-arm branched PVDF species. Lysis of the RAFT groups at the polymer chain ends yielded thiols which was used to form a tetra-methacylate terminated PVDF species (Figure 6.1, bottom image) by thiol-ene addition with 3-(acryloyloxy)-2-hydroxypropyl methacrylate. The resulting tetramethacrylate species could be cross-linked by UV-light, offering a simple method to form semi-fluorinated films for coating purposes.

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Figure 6.1 – Methacrylate terminated PVDF species. TOP – the linear methacrylate terminated PVDF species synthesised by Guerre at al.^[18] BOTTOM – tetramethacrylate terminated PVDF species synthesised by Lopez et al.^[23]

In a different method, Amérduri et al.^[24] copolymerised vinylidene difluoride with trifluorovinyl ω -thioacetate monomer, which after treatment with KCN converted the thioacetate groups of the resulting copolymer to thiols. The pendant thiols groups could then be use to cross-link the PVDF copolymer with hex-1,5-diene by thiol-ene addition with a radical source (Figure 6.2).

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Figure 6.2 – Synthesis and cross-linking of a PVDF copolymer with thiol functionality, as performed by Amérduri et al.^[24]

Although these are effective methods to produce cross-linked PVDF films, they require that either the PVDF be synthesised by RAFT polymerisation (in order to possess the RAFT agent as an end group to then produce the thiol), or that a copolymer of PVDF be synthesised. Neither of these methods can be applied to the PVDF homopolymer. The monomer used to produce PVDF, vinylidene difluoride (a.k.a. 1,1-difluoroethylene), is a gas at room temperature,^[25] and the polymerisation is typically performed under pressure,^[18, 23, 24] which requires specialist equipment. This makes these methods of forming cross-linked PVDF less attractive to use. A method of cross-linking PVDF which uses the PVDF homopolymer would be ideal, as the PVDF homopolymer is much easier and safer^[26] to handle compared to vinylidene difluoride.

6.2.1.2 Cross-linked PVDF by chemical modification of PVDF homopolymer

The following discusses chemical methods in literature used to cross-link PVDF homopolymer.

Liu et al.^[27] modified PVDF over a series of steps to introduce benzoxamine pendant groups on the PVDF backbone (PVDF-Bz), which underwent ring-opening polymerisation at 160 °C to yield cross-linked PVDF (see Figure 6.3 for the full reaction scheme). Stress-strain experiments demonstrated that cross-linking PVDF-Bz
increased the Young's modulus to 240 MPa, compared to 53 MPa before crosslinking.

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Figure 6.3 – Modification of PVDF to produce PVDF with benzoxamine pendant groups (PVDF-Bz), which then is cross-linked by ring opening of the benzoxamine at 160 °C. Image taken from ref.^[27]

Chen et al.^[28] grafted a silane containing polymer, poly(3-propyl methacrylate trimethoxysilane), onto the PVDF backbone with ATRP, and after forming a membrane by NIPS, treated the membrane with aqueous ammonia to drive hydrolysis and condensation of the silane. The resulting membrane formed Si-O-Si bridge cross-links, and was shown to increase the PWF and membrane pore size, but the mechanical properties of the membranes were not assessed. While these methods succeeded in cross-linking PVDF, the former method (using benzoxamine side groups) requires multiple steps and high temperatures, whereas the latter method (grafting poly(3-propyl methacrylate trimethoxysilane)) requires ATRP conditions, which requires multiple reagents (catalyst and ligands) as well as an oxygen-free environment.

Cai et al.^[29] used ozone treatment to add initiating sites to the PVDF backbone to then polymerise allyl methacrylate, and then used the modified PVDF to form a membrane by NIPS. This membrane (PVDF-*g*-PAMA membrane) possessed –CH=CH₂ groups on the surface, which were used to graft 3-mercaptopropionic acid or 1,6hexanedithiol using heat or UV-light, respectively. Using 1,6-hexanedithiol yielded a thiol functionalised membrane surface, which was then used to graft *N*,*N'*-dimethyl-(methylmethacryloyl ethyl) ammonium propane sulfonate by further thiol-ene addition (Figure 6.4). This treatment produced a membrane that showed improved resistance to bacterial adhesion from *S. epidermidis* on the membrane surface. Although this method has not been used to cross-link PVDF, it does offer a method of doing so (for example, by thiol-ene addition of 1,6-hexanedithiol across the alkenes of PVDF-*g*-PAMA in solution) but does require multiple steps in order to do so. Figure has been removed due to Copyright restrictions

Figure 6.4 – Full process to form a PVDF membrane with surface –CH=CH₂ groups, and subsequent modification by thiol-ene addition, as performed by Cai et al.^[29] Image taken from ref.^[29]

While these methods provide ways to cross-link PVDF using the PVDF homopolymer, they require multiple steps or strict reaction conditions (such as ATRP) to achieve the cross-linking. A simpler, and more robust method of cross-linking PVDF in solution would be preferred, so as to be easily applied for the production of PVDF water filtration membranes.

6.2.2 Reducing biofouling – incorporating silver-based compounds

Another issue with polymeric water filtration membranes is biofouling, which reduces the water flux due to the formation of biofilms on the membrane surface. A common strategy to increase the biofouling resistance of PVDF membranes is to

incorporate silver-based compounds. Silver is well known to provide antibacterial properties to PVDF membranes when incorporated, ^[30-38] disrupting the biofilm formation on the membrane surface. ^[30, 35] Ag(0) nanoparticles, ^[30] Ag(0) nanowires, ^[31] Ag⁺-lactate nanoparticles, ^[32] Ag-GO hybrids, ^[33, 34] and Ag-loaded zeolites ^[35-38] are some of the examples of silver-based compounds incorporated into PVDF membranes which have been demonstrated to impart antibacterial properties. However, an issue with using silver-based compounds in membranes is that the silver leaches from the membrane over time, ^[30, 34] which diminishes the performance of the membranes. ^[30, 35]

To avoid the issue of leaching, but still provide antibacterial properties to the membranes, covalently attaching an antibacterial organic compound is a potential strategy. Covalently attaching the antibacterial compound should prevent the compound from leaching from the membrane, and should therefore impart effectively permanent antibacterial properties to the membrane. Work by Rojo et al.^[39, 40] has identified that eugenyl methacrylate (EgMA), a derivative of eugenol, possesses antibacterial activity when incorporated into polymers. Therefore, EgMA was chosen as the compound to be covalently bound to PVDF membranes, as it possess antibacterial activity as well as reactive functional groups (alkenes) which can be used to covalently bind EgMA.

6.3 Chapter Aim

This chapter reports on the analysis of PVDF membranes that have either been chemically cross-linked, or have incorporated an antibacterial alkene-containing molecule, EgMA. Cross-linking PVDF with thiol POSS should provide membranes with improved mechanical properties (as demonstrated with other polymers)^[14-17] to better resist membrane compaction, while the membranes incorporating EgMA should be antibacterial,^[39, 40] and better resist biofouling. The advantage of incorporating EgMA, over using for example silver, is that once EgMA is covalently bound the antibacterial properties of the membrane should be effectively permanent, as EgMA will not leach from the membrane, which is known to occur with silver materials.^[30, 34]

The membranes were formed using a combination of dehydrofluorinated PVDF (d-PVDF) (which was discussed in Chapter 5) with thiol POSS (synthesis and

thiol-ene reactivity discussed in Chapter 4). Both the PVDF membranes (cross-linked or EgMA-POSS modified, respectively) were produced via UV-catalysed thiol-ene addition using the thiol POSS, with benzophenone as a photocatalyst (see Chapter 2, Sections 2.3.11 and 2.3.12, respectively, for full experimental details).

The method used to produce these membranes is presented in Figure 6.5. To summarise, cross-linked PVDF membranes were produced by adding a thiol POSS and benzophenone solution (in THF) to a solution of d-PVDF and PVP in DMAc. This then constituted a casting solution for membrane production. After casting the casting solution onto a glass plate, the cast film was irradiated with UV-light for 1 h, followed by immersion in a coagulation bath to form a membrane. EgMA-POSS modified PVDF membranes were produced in an identical manner, except that EgMA was also added to the casting solution. Thiol POSS was expected to add across the alkenes of both d-PVDF and EgMA, leading to EgMA becoming covalently bound within the membrane.



Figure 6.5 - Process of forming cross-linked PVDF membranes using UV-catalysed thiol-ene addition of thiol POSS across the alkenes of d-PVDF. EgMA-POSS modified PVDF were produced in an identical manner, except eugenyl methacrylate (EgMA) was added to the membrane casting solution as well.

This method of membrane formation was chosen as it only requires two steps (first dehydrofluorination of PVDF with DBU, followed by UV-catalysed thiol-ene addition with thiol POSS). UV-irradiation can then be performed on the cast d-PVDF-DMAc film, which avoids the issue of using casting solutions containing cross-linked PVDF. Had PVDF been cross-linked before casting the casting solution, it would likely have formed insoluble materials, which would make inhomogeneous water filtration membranes.

6.4 Results and Discussion – Cross-linked PVDF membranes

The cross-linked PVDF membranes were produced by UV-catalysed thiol-ene addition between thiol POSS and d-PVDF. This was accomplished by adding a solution of thiol POSS and benzophenone in THF to a solution of d-PVDF and PVP in DMAc, forming the casting solution. This casting solution was then hand-cast with a Doctor's blade onto a glass plate, the solution-polymer film (on the glass plate) was then irradiated with UV-light for 1 h. After UV-irradiation was complete, the membrane was formed by adding the irradiated solution-polymer film to a coagulation bath of water.

As thiol POSS possesses multiple thiol groups, and d-PVDF possesses multiple alkenes, this should lead to the material becoming cross-linked. The full method used to form the cross-linked PVDF membranes can be found in Chapter 2, Section 2.3.11.

1.1.1 ATR-FTIR spectroscopy studies

The ATR-FTIR spectra of the cross-linked PVDF membranes with different loadings of thiol POSS in the casting solution is shown in Figure 6.6. The ATR-FTIR spectra of the cross-linked PVDF membranes indicate that all the spectra are largely dominated by the IR signals due to PVDF. The intense signals at 1402 cm⁻¹, 1275 cm⁻¹, 1175 cm⁻¹, 1072 cm⁻¹, 876 cm⁻¹, and 840 cm⁻¹ are all attributed to PVDF, specifically the C-H bending mode,^[41] the C-F out of plane deformation (β -phase),^[42] the CF₂ symmetric stretch,^[41] amorphous polymer,^[41] and the CH₂ rocking (β or α -phase),^[42] of PVDF, respectively. The strong signal at 1665 cm⁻¹ was attributed to the carbonyl stretch of residual PVP in the membrane.^[43, 44]

Without any thiol POSS in the membrane casting solution, only the weak C-H stretch bands of PVDF was observed at approximately 3020 cm⁻¹ and 2978 cm⁻¹ in the 3200-2800 cm⁻¹ region of the ATR-FTIR spectrum of the membrane (inset (a) of Figure

6.6, black line). As the quantity of thiol POSS in the membrane casting solution is increased, additional weak bands at around 2924 cm⁻¹ and 2854 cm⁻¹ appear in the ATR-FTIR spectra of the membranes (see inset (a) of Figure 6.6, red, green and dark blue lines), and grow more intense as the loading of thiol POSS is increased in the casting solution. These additional bands are attributed to the C-H stretch of thiol POSS.

Furthermore, a shoulder in the ATR-FTIR spectra of the cross-linked PVDF membranes with thiol POSS appears in the 1125-1075 cm⁻¹ region of the spectra (see inset (b) of Figure 6.6), and increases in intensity with thiol POSS loading in the membrane casting solution. This shoulder was attributed to the Si-O-Si vibration of thiol POSS. Although the Si-O-Si band of pristine thiol POSS, which appears at 1080 cm⁻¹ in the ATR-FTIR spectrum (see Chapter 4, Section 4.4.4.1, Figure 4.16) is the most intense IR band of thiol POSS, due to overlap with the IR bands from PVDF, it only appears as a shoulder in the ATR-FTIR spectra of the cross-linked PVDF membranes (see inset (b) of Figure 6.6).

Overall, the ATR-FTIR spectral analysis of the cross-linked PVDF membranes indicates that increasing the thiol POSS loading in the membrane casting solution results in more thiol POSS in the final membranes. However, this analysis does not provide proof of whether the thiol POSS has successfully cross-linked the PVDF during the UV-irradiation for 1 h, as the signals relating to thiols and thioethers (thiols that have undergone thiol-ene addition successfully) are too weak in IR spectroscopy.^[45, 46] It was assumed that thiol POSS would have grafted to the d-PVDF, based on the combined results of Chapters 4 and 5.

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Figure 6.6 – Normalised ATR-FTIR spectra of cross-linked PVDF membranes using different loadings of thiol POSS (0-10 wt%) in the casting solution, after treatment with UV-irradiation and benzophenone for 1 h. Inset (a) 3150-2750 cm⁻¹ region of the ATR-FTIR spectra. Inset (b) 1250-1050 cm⁻¹ region of the ATR-FTIR spectra.

6.4.1 Stress-strain experiments

The tensile properties of the cross-linked PVDF membranes were assayed by stressstrain experiments, the results of which are presented in Figure 6.7. Starting with the Young's modulus of the membranes (Figure 6.7, top left) it can be seen that incorporation and cross-linking with thiol POSS increases the Young's modulus of the membranes. On increasing the thiol POSS loading from 0 to 1 wt%, the Young's modulus increases from 36.60 \pm 1.85 MPa to 47.40 \pm 1.70 MPa, respectively. While increasing the thiol POSS loading from 1 wt% to 5 wt% does not change the Young's modulus significantly, with an average value of 44.50 \pm 3.10 MPa with 5 wt% of thiol POSS, increasing the thiol POSS loading to 10 wt% increases the Young's modulus to 54.6 \pm 1.97 MPa. This result indicates that the membranes have become stronger, requiring more force to induce the same amount of strain.

As expected with using POSS as a cross-linking agent in a polymeric matrix, ^[16, 47, 48] the membranes became more brittle, the % strain at break (Figure 6.7, top right)

almost halving with just 1 wt% of thiol POSS from 44.00 \pm 6.56 % to 24.10 \pm 2.47 %. While increasing the thiol POSS loading from 1 wt% to 5 wt% does not change the % strain at break a great deal compared to 1 wt% (giving a value of 31.00 \pm 5.47 %). Increasing the loading of thiol POSS to 10 wt% decreases the % strain at break to 12.90 \pm 0.90 %.

The stress at break of the cross-linked PVDF membranes (Figure 6.7, bottom) does not show much of change with the inclusion and cross-linking with thiol POSS, giving values of 1.170 ± 0.057 MPa, 1.060 ± 0.103 MPa, 1.020 ± 0.048 MPa, and 1.210 ± 0.082 MPa, for thiol POSS loadings of 0 wt%, 1 wt%, 5 wt%, and 10 wt%, respectively.

The results of the tensile tests on the cross-linked PVDF membranes indicated that cross-linking PVDF with thiol POSS results in stronger membranes, increasing the Young's modulus with thiol POSS loading. However, the membranes became more brittle, showing reduced % strain at break. These results indicate that increasing the loading of thiol POSS in the membranes would likely result in very brittle membranes, which may break under high pressures.^[49] Brittle membranes would need to be handled and transported carefully to avoid breakage of the membrane. As the stress at break of the membranes were not changed significantly with thiol POSS loadings from 1-10 wt%, the inclusion of thiol POSS to the membranes does not make the membranes easier to break.

Overall, the improvement in Young's modulus of the membranes cross-linked with thiol POSS shows promise as improvements in membrane tensile properties often also result in improved compaction resistance.^[11, 12, 50]

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Figure 6.7 – Young's modulus, % strain at break, and stress at break of cross-linked PVDF membranes with varying loadings of thiol POSS.

6.4.2 SEM of membrane cross-section

The cross-sectional morphology of a water filtration membrane plays an important role in the compaction behaviour of the membrane.^[2, 51, 52] Therefore, the cross-sectional morphology of the cross-linked PVDF membranes were observed using SEM (Figure 6.8). All of the membranes examined displayed the asymmetric structure of membrane cross-sections, having a combination of large macrovoids separated by more dense, sponge-like material.

With 0 wt% of thiol POSS in the casting solution, the membrane cross-section (Figure 6.8, (a)) shows larger, irregularly shaped macrovoids near the bottom surface, with a layer of smaller, tear-shaped macrovoids sitting above the larger macrovoids.

While the cross sections of membranes with 0 and 1 wt% of thiol POSS in the casting are similar (Figure 6.8, (a) and (b) respectively), increasing the thiol POSS loading to 5 wt% led to the formation of larger macrovoids (Figure 6.8, (c)). The macrovoids in the membrane with 5 wt% of thiol POSS are wider and longer (compared to the membranes with 0 or 1 wt% of thiol POSS), almost extending the full length of the membrane cross-section, with a layer of much smaller macrovoids sitting just below the membrane top surface.

With increasing the thiol POSS loading to 10 wt% in the casting solution, the cross-section of the resulting membrane (Figure 6.8, (d)) shows larger, irregularly shaped macrovoids towards the bottom surface of the membrane, with a layer of smaller macrovoids extending to the top membrane surface. This cross-sectional morphology of the membrane with 10 wt% of thiol POSS is similar to the cross-sectional morphology of the membrane with 0 wt% of thiol POSS (Figure 6.8, (a) and (d), respectively). However, with membrane with 10 wt% of thiol POSS showed smaller macrovoids near the bottom surface, with larger macrovoids near the top surface, when compared to the membrane with 0 wt% of thiol POSS.



Figure 6.8 – SEM images of the cross-sections of cross-linked PVDF membranes with different loadings of thiol POSS (a) 0 wt%, (b) 1 wt%, (c) 5 wt%, and (d) 10 wt%.

The thicknesses of the cross-linked PVDF membrane also changed with the incorporation of thiol POSS, presented in Figure 6.9. It can be seen that the inclusion of 1 wt% thiol POSS in the membrane casting solution does not change the thickness of the final membrane when compared to the membrane with 0 wt% thiol POSS, showing membrane thicknesses of 163.0 \pm 1.3 µm and 155.0 \pm 1.8 µm, respectively. Increasing the thiol POSS loading to 5 wt% in the casting solution led to a large increase in the membrane thickness, increasing to 272.0 \pm 1.7 µm, but then the membrane thickness decreased to 204.0 \pm 2.0 µm with a loading of 10 wt% of thiol POSS.

The morphology of polymeric membranes formed by NIPS is known to be affected by the composition of the casting solution, as it effects the rate of demixing of the polymer from solution (precipitation of the polymer).^[53-56] With inclusion and cross-linking with thiol POSS, the solubility of PVDF in DMAc is reduced (based on literature that cross-linking polymers leads gel/insoluble materials),^[57-59] which is known to increase the rate of demixing.^[60] However, the solution viscosity is known to be increased by cross-linking the polymers in solution,^[57-59] as well as by the addition of fillers.^[60-63] Increasing the solution viscosity is known to inhibit the exchange of the solvent with the non-solvent during the coagulation step of the membrane formation,^[60-63] which slows the demixing process.^[60-63]

For the cross-linked PVDF membranes, the two effects (increasing the rate of demixing by reducing the solubility of PVDF, as compared to decreasing the rate of demixing by increasing the solution viscosity) compete during the membrane formation. Based on the morphologies of the membranes observed by SEM, for the casting solutions containing thiol POSS loading of 5 wt%, the reduction of PVDF solubility due to the inclusion of thiol POSS with cross-linking dominates. This causes the rate of demixing to increase (compared to the casting solution with 0 wt% of thiol POSS), and hence increasing the macrovoid size in the membrane cross-sections (compare (a) and (c), Figure 6.8).^[60-63] With 10 wt% of thiol POSS with cross-linking dominates, causing the rate of demixing to be reduced compared to the casting solution with 5 wt% of thiol POSS. This leads to a suppression of the macrovoid size in the membrane with 10 wt% of thiol POSS in the casting solution (compare (c) and (d), Figure 6.8).^[60-63]



Figure 6.9 – Thicknesses of cross-linked PVDF membranes with different loadings of thiol POSS in the membrane casting solution

6.4.3 SEM of membrane surfaces

As the surface morphology of a water filtration membrane greatly affects the filtration properties (particularly the pore size, which determines the flux and rejection of the membrane),^[60-63] the surfaces of the cross-linked PVDF membranes were imaged with SEM (Figure 6.10). With no thiol POSS in the casting solution (0 wt%), the surface of the membrane was covered in small pores, which appear uniform in size (Figure 6.10, (a)). With 1 wt% of thiol POSS in the membrane casting solution, the surface of the membrane showed a bimodal dispersion of pore sizes, featuring a combination of very large pores with much smaller pores (Figure 6.10, (b)). Increasing the thiol POSS loading to 5 wt% and 10 wt% in the casting solution resulted in a reduction of the surface pore size of the membranes with increasing thiol POSS loading. Further, the pore sizes became more uniform (Figure 6.10, (c) and (d), respectively).



Figure 6.10 - SEM images of the surfaces of cross-linked PVDF membranes with different loadings of thiol POSS (a) 0 wt%, (b) 1 wt%, (c) 5 wt%, and (d) 10 wt%

The changes in the surface morphologies was attributed to the effect of cross-linking of PVDF with thiol POSS. In literature, it has been found that increasing the cross-linking density of polymers typically leads to a reduction in the pore size of the resulting material, as demonstrated with Psf membranes with a UV-cross-linkable coating,^[64] as well as with polymeric microgels/beads.^[65-67] This correlates with the observation by SEM (Figure 6.10) that the surface pore size of the cross-linked PVDF membranes with thiol POSS typically decreases with increasing thiol POSS loading.

The cause of the bimodal distribution of pore sizes on the cross-linked PVDF membrane with 1 wt% of thiol POSS is not easily explained. It was hypothesised that the cause was due to the concentration of cross-linker (thiol POSS) being too low. This led to the membrane surface forming cross-linked and uncross-linked regions after UV-irradiation, with the d-PVDF in the cross-linked regions being denser than

the uncross-linked regions. Upon immersion in the coagulation water bath, the crosslinked regions precipitate first, forming more dense (less porous regions), while the regions of uncross-linked d-PVDF precipitate more slowly, forming larger pores. With 5 wt% and 10 wt% of thiol POSS, the number of cross-linked regions increases and is more homogenously distributed, which prevents the formation of larger pores, and generally decreased the pore size.

No large aggregates of thiol POSS were observed on the surface of the crosslinked PVDF membranes, even with the highest loading of thiol POSS (10 wt%) in the casting solution. This was due to a combination of the covalent attachment of thiol POSS to the d-PVDF aiding in the dispersion of thiol POSS throughout the polymer matrix of the membrane, ^[17, 68-70] as well as the membrane formation process by NIPS suppressing the aggregation of POSS.^[71, 72]

6.4.4 Pore size distributions

The pore size distributions of the cross-linked PVDF membranes with thiol POSS are presented in Figure 6.11. The pore sizes were calculated using ImageJ software on the SEM images of the surfaces of the membranes. It should be noted that the image resolution obtained using SEM means the proportion of pores in the < 100 nm range are likely to be underestimated. However, the pore size distribution shown in Figure 6.11 does give a basic understanding of how the pore size varies with thiol POSS loading.

For the membrane with a 0 wt% loading of thiol POSS, a large proportion of the pores are found in the 80-180 nm pore size radius, with a large portion of pore radii (~50 %) in the 80-120 nm range. With the addition of 1 wt% of thiol POSS, the membrane pore sizes become much more spread out, the distribution showing a tailing effect due to the production of larger (> 200 nm) sized pores. It should be noted that ~2 % of the proportion of pores have radii greater than 600 nm, however the spread of the pore sizes and the low numbers of pores with these pore sizes means that their relative frequency is too low to seen on the chart. As the thiol POSS loading is increased to 5 wt% and then 10 wt%, the proportion of larger sized pores (> 200 nm) is reduced, with the membrane with 10 wt% of thiol POSS having almost all the pores having pores sizes between 70-250 nm.



Figure 6.11 – Pore size distributions of cross-linked PVDF membranes with different loadings of thiol POSS, as calculated from the SEM images of the membrane surfaces using ImageJ.

6.4.5 Pure water flux (PWF) measurements

The method used to perform the pure water flux (PWF) experiments can be found in Chapter 2, Section 2.4.4. Briefly, the membranes tested were initially soaked in IPA for 30 min, and then MilliQ water for 30 min to fully wet the membrane. Following this, the membrane PWF was measured for 1 h under 100 kPa of pressure (referred to as Phase 1), then the pressure was released and the membrane allowed to recover for 1 h (referred to as the Recovery Phase). The membrane was then rinsed with MilliQ water before again being tested at 100 kPa for a further hour (referred to as Phase 2).

6.4.5.1 Initial and final PWFs

The initial and final PWF values of both Phases 1 and 2 of the cross-linked PVDF membranes are presented in Figure 6.12. In Phase 1 of the PWF measurements, the addition of thiol POSS at 1 wt% loading increases the initial PWF from 1750 \pm 416 L.m⁻².h⁻¹ to 3102 \pm 251 L.m⁻².h⁻¹. The initial PWF values then decreased with increasing thiol POSS loading, to 2295 \pm 503 and 1910 \pm 262 L.m⁻².h⁻¹ for thiol POSS loadings of 5 wt% and 10 wt%, respectively. This decline in PWF values is due to compaction of the membranes.

The final PWF values of the membranes of Phase 1 (also in Figure 6.12) showed a similar trend as to the initial PWF values. With the addition of 1 wt% of thiol POSS, the final PWF of Phase 1 increased from 1263 \pm 287 L.m⁻².h⁻¹ to 2385 \pm 292 L.m⁻².h⁻¹. The final PWF values then decreased with thiol POSS loading to 1911 \pm 324 L.m⁻².h⁻¹ and 1764 \pm 265 L.m⁻².h⁻¹ for 5 and 10 wt% loading of thiol POSS, respectively.

After releasing the pressure at the end of the Phase 1 of the PWF experiments (1 h), the membrane was allowed to recover for 1 h (recovery phase) without any applied pressure. After the recovery phase, the PWF of the membranes was then remeasured for 1 h again at 100 kPa (Phase 2). The initial PWF of Phase 2 of the PWF measurements (Figure 6.12) show the same trend as with Phase 1. When the thiol POSS loading was increased to 1 wt%, the initial PWF (Phase 2) increases from 1352 \pm 297 L.m⁻².h⁻¹ to 2557 \pm 387 L.m⁻².h⁻¹, which then decrease with thiol POSS loading to 2047 \pm 386 L.m⁻².h⁻¹ and 1765 \pm 271 L.m⁻².h⁻¹, with 5 and 10 wt% of thiol POSS, respectively. As with Phase 1 of the PWF measurements, the PWF declines over the

1 h due to compaction, the final PWF (Phase 2) reaching 1182 \pm 267 L.m⁻².h⁻¹, 2105 \pm 219 L.m⁻².h⁻¹, 1746 \pm 268 L.m⁻².h⁻¹, and 1657 \pm 268 L.m⁻².h⁻¹, for membranes with thiol POSS loadings of 0, 1, 5, and 10 wt%, respectively.



Figure 6.12 - PWF of cross-linked PVDF membranes, containing different loadings of thiol POSS, from the PWF measurements of Phases 1 and 2 (run at 100 kPa at room temperature)

Overall, the PWF of the cross-linked PVDF membranes follows the order (from highest PWF to lowest) of 1 wt% > 5 wt% > 10 wt% > 0 wt%, based on the thiol POSS loading in the casting solution used to form the membrane. This order arises largely from the changes in the surface morphologies of the membranes, as imaged by SEM and discussed in section 6.4.3. The PWF of the membranes also agrees with the pore size distributions determined from the SEM images (Figure 6.11), as the the proportion of larger-sized pores on the membrane surfaces followed the order (based on thiol POSS loading) of 1 wt% > 5 wt% > 10 wt% > 0 wt%. As the size of the pores on the membrane surface directly effects the PWF of water filtration

membranes,^[73-75] the changes in PWF in the membranes with inclusion of thiol POSS is attributed to changes in the membrane pore size distribution, as observed by SEM.

6.4.5.2 Compaction

The effect of compaction during Phase 1 and Phase 2 of the PWF measurements can be observed by comparing the initial and final PWF values of the same Phase of measurement. This value is calculated as the % flux change, which represents the decline in the PWF during the measurement due to compaction. This data is presented in Figure 6.13.

Starting with Phase 1, the % flux change values are -26.3 ± 2.6 %, -23.5 ± 5.2 %, -12.5 ± 4.1 %, and -8.3 ± 2.0 %, for cross-linked PVDF membranes with thiol POSS loadings of 0, 1, 5, and 10 wt% respectively. This indicates that the decrease in the PWF value over the 1 h becomes less with increased thiol POSS loading in the casting solution of the membrane, though this effect only becomes significant with at least 5 wt% of thiol POSS. This indicates that the inclusion and cross-linking with thiol POSS with PVDF has produced membranes that are better able to resist compaction, and that the improvement in compaction resistance is greater the higher the loading of thiol POSS in the casting solution.



Figure 6.13 - % Flux change between the initial and final PWF of cross-linked PVDF membranes, containing different loadings of thiol POSS, during Phase 1 and 2 of the PWF measurements (run at 100 kPa at room temperature)

After the 1 h recovery phase, the membranes underwent further compaction during the Phase 2 of the PWF measurements (Figure 6.13). The % flux change for the membranes with thiol POSS loading of 0, 1, 5, and 10 wt% were -12.8 ± 1.7 %, -15.7 ± 3.6 %, -12.1 ± 3.3 %, and -6.3 ± 2.4 %, respectively. This indicates the relative effect of compaction was only significantly reduced for the membrane with 10 wt% of thiol POSS. This improvement in the compaction resistance is attributed to the crosslinking of PVDF by thiol POSS. This fits with the results of the stress-strain experiments (see section 6.4.1) which indicated that cross-linking the membranes with thiol POSS improved the membranes resistance to tensile strain (increased the Young's modulus).

As the cross-section morphologies of the cross-linked PVDF membranes did not vary too significantly with changes in the thiol POSS loading, the changes in the

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cross-sectional morphologies do not account for the changes in compaction resistance of the membranes. All membranes possess the asymmetric cross-sectional morphologies, and all possess large macrovoids, as discussed in Section 6.4.2. Thus, the compaction resistance of the membranes is attributed to the inclusion and cross-linking with thiol POSS.

6.4.5.3 Flux recovery

To measure the extent of how reversible the compaction is, the percentage difference in the final PWF of phase 1 and the initial PWF of phase 2 was calculated. The resulting value (% flux recovery) was used to compare how the incorporation and cross-linking with different loadings of thiol POSS changed how reversible the compaction of the membrane was. The % flux recoveries of the cross-linked PVDF membranes are presented in Figure 6.14. As it can be observed, the % flux recoveries of the membranes produced with 0, 1, and 5 wt% loading of thiol POSS in the casting solution are similar, having % flux recoveries of 7.8 \pm 3.0 %, 5.9 \pm 4.0 % and 6.0 \pm 3.7 %, respectively. On increasing the thiol POSS loading to 10 wt%, the flux recovery of the membrane was reduced to 0.7 \pm 3.9 %. This reduction in flux recovery with 10 wt% of thiol POSS loading is attributed to the thiol POSS showed the least overall compaction during the filtration, and the flux recoveries for the other membranes is small, the reduction in flux recovery for the membrane with 10 wt% of thiol POSS is considered to be a minor issue.



Figure 6.14 – The flux recovery of cross-linked PVDF membranes with varying loadings of thiol POSS.

6.4.6 BSA rejection

To examine the separation properties of the cross-linked PVDF membranes, rejection tests of BSA were performed, the results of which can be found in Figure 6.15. As it can observed in Figure 6.15, the membranes formed by this casting procedure possess very low rejections of BSA. With 0 wt% of thiol POSS, the BSA rejection starts at 9.6 \pm 3.2 %, which decreases to 2.5 \pm 2.6 % with 1 wt% of thiol POSS in the membrane casting solution. The BSA rejection then increases slightly with increasing thiol POSS loading, increasing to 7.2 \pm 2.8 % then 16.0 \pm 12.2 %, with thiol POSS loadings of 5 and 10 wt%, respectively. Although there are large variations in the BSA rejection data, the trend in the BSA rejection follows the trends in the PWF values, with BSA rejection decreasing as the PWF increases. This is commonly observed with the changes in the membranes pore size, as increasing the pore size increases the PWF, and decreases the rejection, and vice versa.^[53, 76, 77]

This data also indicates that the cross-linked PVDF membranes, with the method of casting used in this work, are more suited to microfiltration purposes, as

the low rejection of BSA limits the usefulness of these membranes for ultrafiltration purposes.^[78]



Figure 6.15 – BSA rejection of cross-linked PVDF membranes with different loadings of thiol POSS

6.5 Results and Discussion – EgMA-POSS modified PVDF membranes

The EgMA-POSS modified PVDF membranes discussed in the following were produced by UV-catalysed thiol-ene addition of thiol POSS across the alkenes of both d-PVDF and EgMA. This was accomplished by adding a solution of thiol POSS and benzophenone in THF to a solution of d-PVDF and PVP in DMAc, forming the casting solution, with EgMA. For EgMA loadings of 1 and 5 wt%, EgMA was co-dissolved in the THF solution of thiol POSS and benzophenone. For EgMA loadings of 10 and 20 wt%, EgMA was added to the d-PVDF and PVP solution in DMAc. The casting solution was then hand-cast with a Doctor's blade onto a glass plate, the solution-polymer film (on the glass plate) was then irradiated with UV-light for 1 h. After UV-irradiation was complete, the membrane was formed by adding the irradiated solution-polymer film to a coagulation bath of water.

Under these conditions, thiol POSS, which possesses multiple thiol groups, adds across the C=C bonds of d-PVDF as well as EgMA, resulting in EgMA becoming covalently tethered to d-PVDF. As both the EgMA and the polymers of EgMA have been demonstrated to possess EgMA-POSS modified properties,^[39, 40] the resulting membranes should possess antibacterial properties. This will help resist bacterial adhesion, and disrupt biofilm formation. The full method for the formation of the EgMA-POSS modified PVDF membranes can be found in Chapter 2, Section 2.3.12. The following discusses the analysis of these EgMA-POSS modified PVDF membranes.

6.5.1 ATR-FTIR spectroscopy studies

Analysis by ATR-FTIR spectroscopy of the EgMA-POSS modified PVDF membranes produced using 10 wt% of thiol POSS with differing quantities of EgMA in the casting solution can be found in Figure 6.16. The ATR-FTIR spectrum of EgMA is also shown for comparison (Figure 6.16, black line). It was found that no significant changes in the ATR-FTIR spectra of the EgMA-POSS modified membranes was observed until the EgMA content in the casting solution reached 10 wt%. With 10 wt% of EgMA in the casting solution, new bands in the ATR-FTIR spectrum of the membrane (Figure 6.16, light blue line) were observed at 1758 cm-1, 1606 cm-1, and 1508 cm-1 (see inset of Figure 6.16). The band at 1758 cm-1 corresponded to the C=O strectch of the ester of EgMA, and the bands at 1606 cm-1, and 1508 cm-1 corresponded to the C=C stretching of the aromatic ring of EgMA.^[40] A very small signal at 1121 cm-1 in the ATR-FTIR spectra of the EgMA-POSS modified PVDF membranes produced with 10 wt% of thiol POSS and 10 and 20 wt% of EgMA in the casting solution (Figure 6.16, light blue and purple lines, respectively), were attributed to the C-O stretch of EgMA.[40] The presence of these bands indicated that increasing the EgMA in the membrane casting solution increased the EgMA content in the membranes, up to 10 wt%.

However, in comparing the ATR-FTIR spectra of the EgMA-POSS modified PVDF membranes made from the casting solutions containing 10 and 20 wt% of EgMA (Figure 6.16, light blue and purple lines, respectively), there was not a continued increase in the intensity of the bands associated with EgMA (1758 cm⁻¹, 1606 cm⁻¹, 1508 cm⁻¹, and 1121 cm⁻¹) with increasing EgMA content in the membrane casting solution. This indicated that a loss of EgMA must occur during the membrane formation, most likely during the membrane precipitation step when placed in the water coagulation bath, which is known to occur when adding particles to the casting solution.^[32, 79, 80]



Figure 6.16 – Normalised ATR-FTIR spectra of EgMA-POSS modified PVDF membranes produced using 10 wt% of thiol POSS and different loadings of eugenyl methacrylate (EgMA) in the membrane casting solution. The ATR-FTIR spectrum of EgMA at ½ the normalised absorbance is included for reference. Inset – Close-up of the 3200-2750 cm⁻¹ and the 1850-1450 cm⁻¹ regions of the ATR-FTIR spectra.

Other changes observed in the ATR-FTIR spectra of the EgMA-POSS modified PVDF membranes, with increasing the EgMA content from 10 to 20 wt% in the casting

solution, were the increase in the intensities of the bands at 975 cm⁻¹, 796 cm⁻¹, 763 cm⁻¹, and 614 cm⁻¹ (Figure 6.16, light blue and purple lines, respectively). These were attributed to changes in the crystallinity of PVDF. Specifically, the bands at 975 cm⁻¹, 763 cm⁻¹, and 614 cm⁻¹ are associated with the α -phase of the crystal phases of PVDF, while the band at 796 cm⁻¹ is associated with the γ -phase of the crystal phases of PVDF. ^[42] This indicates that while increasing the EgMA content in the casting solution from 10 to 20 wt% did not increase the EgMA content in the final membrane, the increase in EgMA content in the casting solution increase the formation of the α - and γ -phases of PVDF crystallinity.

The reason as to why increasing the EgMA content in the membrane casting solution from 10 to 20 wt% did not increase the EgMA content in the resulting membranes is unclear. One possibility is that the EgMA content is too high relative to the content of thiol POSS, leading to the EgMA not becoming covalently bound, and is extracted from the membrane in the coagulation bath. To test the necessity of having thiol POSS in the casting solution to covalently attach EgMA, membranes were formed using the UV-cross-linking procedure with different amounts of EgMA in the casting solution (5-20 wt%), however, no thiol POSS was included. The resulting membranes were also analysed by ATR-FTIR spectroscopy.

The ATR-FTIR spectra of the membranes treated by the UV-irradiation procedure containing varying amounts of EgMA without any thiol POSS in the casting solution are presented in Figure 6.17. Unlike the ATR-FTIR spectra of the EgMA-POSS modified PVDF membranes with both thiol POSS and EgMA in the casting solution (Figure 6.16), the ATR-FTIR spectra of the membranes treated by the UV-irradiation procedure without thiol POSS did not show any bands due to EgMA. Even with 20 wt% of EgMA in the casting solution, the C=O stretch at 1758 cm⁻¹ and the C=C stretch at 1606 cm⁻¹ and 1508 cm⁻¹ of EgMA do not appear in the ATR-FTIR spectra of the membrane (see inset of Figure 6.17, light blue line). However, it is noted that the increasing EgMA content in the casting solution increases the crystallinity of PVDF in the resulting membranes, as indicated by the increase of the signal intensity of the peaks at 975, 763 and 614 cm⁻¹ (due to the α -phase of PVDF) and 796 cm⁻¹ (due to the γ -phase of PVDF).^[42]



Figure 6.17 – Normalised ATR-FTIR spectra of PVDF membranes produced using 0 wt% of thiol POSS and different loadings of eugenyl methacrylate (EgMA) in the membrane casting solution. The ATR-FTIR spectrum of EgMA at ½ the normalised absorbance is included for reference. Inset – Close-up of the 3200-2750 cm⁻¹ and the 1850-1450 cm⁻¹ regions of the ATR-FTIR spectra.

The combination of the results of the ATR-FTIR analysis of PVDF membranes treated with the UV-irradiation procedure with EgMA, with and without thiol POSS, indicates that without thiol POSS, EgMA is not retained in the final membrane. This is potentially due to EgMA leaching from the membrane in the coagulation bath during the membrane formation, whereas with thiol POSS present, it becomes covalently bound to the membrane and therefore does not leach. However, if there is not enough thiol POSS present to react with all the EgMA, any excess EgMA is removed by the coagulation bath. This explains why even with thiol POSS, increasing the EgMA content in the casting solution from 10 to 20 wt% did not increase the EgMA content in the final membranes (Figure 6.16, light blue and purple lines, respectively, and the associated text). Having confirmed the presence of EgMA in the membranes, the membranes were then subjected to bacterial adhesion tests, to observe whether the presence of EgMA can reduce the adhesion of bacterial cells to the membrane surface, as EgMA is known to possess anti-bacterial properties.^[39, 40]

6.5.2 Bacteria adhesion tests – cell counts

To determine the antibacterial performance of the EgMA-POSS modified PVDF membranes towards bacterial adhesion and biofilm formation, bacterial adhesion tests to the membrane top surface were performed. The full procedure and method of analysis of the bacterial adhesion tests can be found in Chapter 2, Section 2.4.6. Briefly summarised, the bacterial adhesion tests on the membranes were performed by immersing small pieces of membrane in a nutrient solution for different periods of time (1, 2, 4 or 6 days) to promote growth of bacteria in the solution. After the immersion time in the nutrient solution was complete, the membrane piece was removed, the bacteria fixed with formaldehyde and glutaraldehyde, and then the number of bacterial cells on the membrane top surface were counted using SEM. The aim of the bacterial adhesion tests was to provide an indication of the biofouling resistance of the membranes tested. It was proposed that the EgMA, with its antibacterial properties, [39, 40] would reduce the extent of bacterial adhesion and delay biofilm formation. The membranes compared in the bacteria adhesion tests included membranes containing thiol POSS with varying loadings of EgMA in the casting solution, as well as a membrane containing no thiol POSS or EgMA in the membrane casting solution. The results of the bacteria adhesion tests on all of these PVDF membranes are presented in Figure 6.18.

6.5.2.1 Immersion time

First, the effect of different immersion times on the extent of bacterial adhesion to the membrane surfaces is discussed. As can be seen in Figure 6.18, the number of bacterial cells per area on the membrane surface slowly increased from day 1 to day 2 of immersion in the nutrient solution. They then increased dramatically on day 4 of immersion in the nutrient solution, and then decreased substantially on day 6 for all the membranes examined. This sudden growth and decline in bacterial cells adhered to the membrane surface follows the behaviour previously observed with biofilms in literature.^[81-83] A simplistic model of biofilm formation involves four

stages. First, bacteria adhere to the membrane surface, which then excrete Extracellular Polymeric Substances (EPS) to promote adhesion of other bacteria cells and also grow the biofilm. The bacteria then undergo further growth (while continuing to excrete EPS) until the biofilm reaches maturation, where upon bacteria are released back into solution.^[83, 84] Comparing the extent of bacterial adhesion to the membrane surfaces at the different days of immersion in the nutrient solution provided an insight into how the properties of the membranes alter the biofilm formation.

6.5.2.2 Membrane composition

Examination of the data presented in Figure 6.18 indicated that, after 1 day of immersion in the nutrient solution, the membrane incorporating no thiol POSS or EgMA (0 thiol POSS – 0 EgMA) showed a higher bacterial cell count (677 \pm 162 cells.mm⁻²) compared to the membranes with 10 wt% of thiol POSS (counts ranged from 96-368 cells.mm⁻²). The membranes with 10 wt% of thiol POSS have similar quantities of bacterial adhesion after 1 day of immersion in the nutrient solution, regardless of EgMA content in the membranes.

After day 2 of immersion, the bacterial cell count decreased, based on EgMA loading in the casting solution of the membrane, of 1 wt% (4992 ± 984 cell.mm⁻²) > 0 wt% (2374 ± 410 cell.mm⁻²) \approx 10 wt% (1691 ± 468 cell.mm⁻²) > 5 wt% (1253 ± 103 cell.mm⁻²) \approx 20 wt% (1305 ± 324 cell.mm⁻²). However, the membrane with no thiol POSS or EgMA had the least amount of bacterial adhesion to the membrane surface, having a cell count of 610 ± 132 cells.mm⁻².

After day 4 of immersion, the order (again based on EgMA content) shifted to 5 wt% (331465 ± 13357 cells.mm⁻²) \approx 1 wt% (320226 ± 4381 cells.mm⁻²) > 0 wt% (253806 ± 5797 cells.mm⁻²) > 10 wt% (230147 ± 10867 cells.mm⁻²) >> 20 wt% (44401 ± 4375 cells.mm⁻²). However, the 0 thiol POSS – 0 EgMA showed the lowest levels of bacterial adhesion, with a cell count of 15061 ± 1631 cells.mm⁻².

Finally, after day 6 of immersion, the extent of bacterial adhesion showed the order (based on the wt% of EgMA used in the membrane casting solution) of 10 wt% (43358 ± 3962 cells.mm⁻²) > 0 wt% (28214 ± 4249 cells.mm⁻²) > 1 wt% (17623 ± 1691 cells.mm⁻²) \approx 20 wt% (15801 ± 892 cells.mm⁻²) > 5 wt% (11027 ± 1683 cells.mm⁻²).

Again, the control membrane (0 thiol POSS - 0 EgMA membrane) showed the lowest levels of bacterial adhesion with 7157 \pm 1081 cells.mm⁻².

The combination of results show several important features. The first is that incorporation of 10 wt% of thiol POSS greatly increased the levels of bacterial adhesion from days 2 through to day 6 of immersion of the membranes in the nutrient solution, compared to the membrane with no thiol POSS or EgMA in the casting solution. The incorporation of EgMA in the membranes does not completely mitigate the effect of the thiol POSS, leading to the membrane without thiol POSS or EgMA showing the least bacterial adhesion.

Secondly, the incorporation of 1 wt% of EgMA into the membranes does not reduce the extent of bacterial cells adhered to the membrane surface, and can in fact result in greater extents of bacterial adhesion (compare the day 2 and day 4 data of Figure 6.18).

Thirdly, higher loadings of EgMA (5-20 wt%) in the membrane casting solution does initially reduce the extent of bacterial adhesion to the membrane surface (see the day 2 data of Figure 6.18), and typically reduces the extent of bacterial adhesion after the bacteria are released from the membrane surface (see day 6 data, Figure 6.18), except for the membrane with 10 wt% of EgMA. However, after day 4 of immersion in the nutrient solution, the membranes with 1-10 wt% of EgMA showed greater or equivalent amounts of bacterial adhesion to the membrane without EgMA (10 thiol POSS – 0 EgMA membrane), indicating that the bacteria are able to overcome the antibacterial effect of EgMA.

Finally, the membrane with 20 wt% of EgMA in the casting solution typically performed the best in terms of bacterial adhesion to the membranes that contain thiol POSS, for all the immersion times examined, the effect being particularly noticeable for day 4 of immersion in the nutrient solution (see Figure 6.18).

These observations are unusual, especially as it would not be expected that the inclusion of EgMA would increase the extent of bacterial adhesion on the membranes. The large difference in the extent of bacterial adhesion to the membranes with 10 and 20 wt% of EgMA in the casting solution is also unexpected. However, this was assuming that the content of EgMA in the membranes is the most

significant factor affecting bacterial adhesion, which is clearly not the case. To better understand these results, the surface morphology of the membranes and the behaviour of the bacteria that adhere to the membrane surface also need to be examined.



Figure 6.18 – The cell count (average number of bacterial cells adhered to the membrane surface per mm²) of EgMA-POSS modified PVDF membranes incorporating 10 wt% of thiol POSS and varying loadings of EgMA, after immersion in nutrient solution for 1 and 2 days (left graph), and after immersion in nutrient solution for 4 and 6 days (right graph).

6.5.3 Bacteria adhesion tests – SEM images

Representative SEM images of the surfaces of the EgMA-POSS modified PVDF membranes, after different immersion times in the nutrient solution, are shown in Table 6.1 (all the SEM images with individual bacterial counts can be found in Appendix B). In comparing the membrane surfaces, the membrane surfaces appeared rough, except for the membrane with 20 wt% of EgMA in the casting solution, which appeared to have a flat surface with larger-sized pores. Inclusion of 1 wt% of EgMA has formed larger sized pores on the membrane surface while creating a more heterogeneous surface, while with 5 wt% of EgMA the surface remains rough but with smaller surface pores. Increasing the EgMA loading in the casting solution to 10 wt% increases the pore size, but noticeably, produced a membrane surface dominated with 'wrinkles'. It is well known that surface morphology plays a large role in bacterial adhesion and biofilm formation,^[85, 86] with more heterogeneously rough surfaces promoting biofilm growth and protein adsorption on surfaces.^[85, 86] The differences in bacterial adhesion tests seen in this work can therefore be largely attributed to the changes in the surface morphology of the membranes, which had a much larger effect than the antibacterial properties of the incorporated EgMA. This is due to the surfaces of the membranes becoming rougher (or are just as rough as the 0 wt% EgMA membrane) with inclusion of EgMA of 1-10 wt% in the membrane casting solution, which resulted in a greater bacterial adhesion.

The antibacterial properties of EgMA appear to alter the behaviour of the bacteria on the membrane surface. It is observed that there is a change in the way the bacteria adhere to the membrane surface, particularly on day 4 of immersion of the membranes in nutrient solution, for the membrane with 10 wt% of EgMA in the casting solution. While membranes with 0-5 wt% of EgMA content in the casting solution showed an even coverage of bacterial cells across the membrane surface, the membrane with 10 wt% of EgMA in the casting solution is very heterogeneous in terms of bacterial coverage. The bacteria appear to have formed dense clumps of bacteria, perhaps in an effort to minimise contact with the membrane surface. This effect has been observed when examining the growth and adhesion of *E. coli* onto blended chitosan/cellulose acetate membranes incorporating either antibacterial Ag⁺ ions, heparin (an anti-adhesion agent), or both. In the study, it was indicated that despite the incorporation of the antibacterial Ag⁺, a large amount of bacterial

adhesion still occurred. This was proposed to be due to the production of a layer of dead cells on the surface, that acted as a buffer between the bacterial cells and the Ag⁺ ions, allowing the bacteria and the biofilm to proliferate unhindered.^[87]

A similar effect was observed in a study involving PES membranes, where it was shown that incorporating Ag(0) nanoparticles with 2,4,6-triaminopyrimidine as a co-additive into the membranes produced superior anti-adhesion properties (as well as a more hydrophilic and smoother membrane surface) to *E. coli* cells, as compared to a PES membrane incorporating only Ag(0) nanoparticles.^[88] Another study also demonstrated that a commercial RO membrane coated with a polyelectrolyte multilayer embedded with Ag(0) nanoparticles and then coated with a zwitterionic copolymer (anti-adhesion agent) had superior anti-adhesion properties to *P. putida*, as compared to a RO membrane only coated with a polyelectrolyte multilayer embedded with Ag(0) nanoparticles (without anti-adhesion agent).^[89] These studies indicate that having a bactericidal agent alone is not enough to prevent biofouling, and that having an anti-adhesion agent with a bactericidal agent more effectively reduces bacterial adhesion.^[87-89]

It is well established that the monomer EgMA possess bactericidal properties to S. mutans and E. coli by zone inhibition tests, and polymers and copolymers of EgMA inhibit the growth of these bacteria when in contact with the material.^[39, 40] In combination with the results seen in this work, it is proposed that inclusion of EgMA does produce an antibacterial effect to bacteria in direct contact with the membrane surface, if the content of EgMA in the membrane is high enough. This results in the bacteria forming dense colonies on the membrane to minimise contact with the membrane surface, as seen in the behaviour of the bacteria on the membrane with 10 wt% of EgMA in the casting solution. However, as with the example involving Ag⁺ ions incorporated into chitosan-cellulose acetate blended membranes,[87] the antibacterial effect of EgMA alone is not enough to prevent bacterial adhesion, as EgMA is not expected to be an effective anti-adhesion agent (on the basis of lacking hydrophilic groups). This is proposed to be due to the formation of either, a layer of dead cells on the membrane surface, or due to excessive contamination of the surface with EPS materials, acting as a buffer between the living cells and the membrane surface.^[87]
Overall, this indicates that incorporation of EgMA alone is not an effective method to reduce bacterial adhesion or disrupt biofilm formation for water filtration membranes.

Table 6.1 – SEM images of the top surface of EgMA-POSS modified PVDF membranes incorporating 10 wt% of thiol POSS with varying quantities of EgMA, as well as a membrane without thiol POSS or EgMA as a control, after immersion in nutrient solution for 1, 2, 4, or 6 days. Scale bar is 50 μm on all images.







6.6 Conclusions

Cross-linked or EgMA-POSS modified PVDF membranes have been successfully formed using a combination of dehydrofluorinationed PVDF (d-PVDF) and UV-light/benzophenone catalysed thiol-ene addition of thiol POSS. Cross-linked PVDF membranes were formed by adding thiol POSS (no eugenyl methacrylate (EgMA)) to the casting solution, while EgMA-POSS modified PVDF membranes were formed by adding both thiol POSS and EgMA to the casting solution.

Analysis of the cross-linked PVDF membranes indicated that with the highest loading of thiol POSS examined, 10 wt%, the Young's modulus of the membrane increased from 36.60 \pm 1.85 to 54.60 \pm 1.97 MPa. However, the membrane also became more brittle with thiol POSS loading and the % strain at break decreased from 44.00 \pm 6.56 to 12.90 \pm 0.90 %. The improvement in tensile properties was found to correlate with the compaction resistance of the membranes, with the membrane with 10 wt% of thiol POSS showing the least flux decline during PWF measurements.

Preliminary results of the EgMA-POSS modified PVDF membranes indicated, by ATR-FTIR spectroscopy, that EgMA was not incorporated into the resulting membranes if no thiol POSS was used as a cross-linking agent. For membranes with thiol POSS, the EgMA content of the membranes increased with EgMA loading in the membrane casting solution up to 10 wt%, but did not increase EgMA content in the membrane when 20 wt% of EgMA was used. Bacterial adhesion tests performed on these membranes found that the surface morphology of the membranes had a far larger effect on bacterial adhesion than the presence of EgMA, resulting in the membrane with neither thiol POSS or EgMA showing the least extent of bacterial adhesion.

6.7 References

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Chapter 7 Conclusions and Future Work

7.1 General overview

The use of polymeric water filtration membranes for the purification of water is a widely adopted technology primarily because it is a highly efficient technique.^[1-4] However, during the pressure-driven filtration of water, the flux of the membranes declines, due to fouling, biofouling, and compaction. In order to improve the properties of the membranes to resist flux decline, this work has focused on the incorporation of a class of materials known as polyhedral oligomeric silsesquioxane (POSS). The incorporation of POSS has been shown to be able to improve the mechanical properties of polymeric materials.^[5-14] However, there are limited studies involving the incorporation of POSS into water filtration membranes.

In order to provide improvements to PVDF water filtration membranes, two different strategies to incorporate POSS were used. Firstly, a commercial POSS, 3,3,3trifluropropyl POSS (TFP POSS), was blended into PVDF by simply dissolving TFP POSS in the casting solution. The tensile and filtration properties of the resulting PVDF-TFP POSS membrane were then examined.

The second strategy of incorporating POSS into PVDF membranes was to cross-link PVDF with POSS, using octa(3-mercaptopropyl) POSS (thiol POSS) through a benzophenone/UV catalysed thiol-ene addition. This was accomplished by using PVDF modified to possess alkenes by dehydrofluorination. The reactions of thiol POSS, as well as dehydrofluorinated PVDF, were modelled separately in order to determine the feasibility of cross-linking PVDF with thiol POSS.

The following sections outline the overall conclusions from each chapter of the thesis.

7.1.1 Blending TFP POSS into PVDF membranes

In Chapter 3, the properties of PVDF membranes incorporating TFP POSS were examined. TFP POSS has been shown to be improve the mechanical properties of other PVDF materials when incorporated as a filler,^[15] but so far has not been used in PVDF water filtration membranes. TFP POSS was incorporated into PVDF

membranes by dissolution into the casting solution, and then using the casting solution to form the membrane. The loadings of TFP POSS, relative to PVDF, were varied from 1-20 wt%.

Analysis of the membranes by ATR-FTIR spectroscopy indicated that increasing the TFP POSS loading in the membrane casting solution increased the TFP POSS content in the membranes. Scanning electron microscopy showed that the incorporation of TFP POSS altered the morphology of the PVDF membranes. In the membrane cross-sectional morphology, the inclusion of TFP POSS suppressed the size of the macrovoids. In addition, the surface morphology of the membranes was also changed, with 1-10 wt% of TFP POSS producing a 'zig-zag' valley of pores on the membrane surface, which became a straight-line of pores with 20 wt% of TFP POSS. Overall, the inclusion of TFP POSS did not alter the tensile properties of the membranes significantly.

In terms of filtration properties of the membranes, inclusion of TFP POSS did not affect the BSA rejection of the membranes significantly, and reduced the average PWF of the membranes. The compaction of the membranes was assessed, and found that the inclusion of TFP POSS did not reduce the flux decline due to compaction during the filtration of pure water. However, the inclusion of TFP POSS did increase the flux recovery of the membranes with 10 wt% and 20 wt% of TFP POSS after compaction.

These results indicated that TFP POSS did not provide significant improvements to the mechanical properties or the compaction resistance of the PVDF water filtration membranes. Following these results, alternative functionalised POSS' were investigated.

7.1.2 Synthesis and thiol-ene addition of thiol POSS

In Chapter 4, the synthesis and thiol-ene addition reactions of octa(3mercaptopropyl) POSS (thiol POSS) were discussed. Thiol POSS possesses 8 thiol groups, which allows thiol POSS to be readily modified by thiol-ene addition with different alkenes. This allows thiol POSS to be modified to maximise compatibility of POSS with PVDF, by reaction with alkenes with fluoroalkyl groups, or to us e thiol POSS as a cross-linker for PVDF.

To synthesise thiol POSS, a literature method was adapted. Initially, the hydrolysis and condensation of 3-mercaptopropyltrimethoxysilane (MPTMS) was conducted in methanol with high concentrations of HCl and water. This was found to produce an oily material, which by ²⁹Si NMR spectroscopy, was determined to be a mixture of different condensation products of MPTMS, as well as the desired thiol POSS. The method of synthesising thiol POSS was then further refined, which yielded the desired thiol POSS as a crystalline material in an overall yield of 19.2 %. Analysis by ¹H, ¹³C, and ²⁹Si NMR spectroscopies, as well as ATR-FTIR spectroscopy, confirmed that the crystalline product obtained was thiol POSS.

Following the successful synthesis of thiol POSS, a series of experiments were performed using thiol POSS in thiol-ene addition reactions. Different alkenes and different catalysts were examined. Using AIBN as the catalyst, thiol POSS was found to react readily with allyl alcohol, 2-allyloxyethanol, 6-chloro-1-hexene, and 6-bromo-1-hexene, in yields of 66-92 %. Using a combination of benzophenone and UV-light as catalysts, the above alkenes, as well as styrene, were found to readily undergo thiol-ene addition with thiol POSS in solution, while eugenyl methacrylate (EgMA) formed an insoluble product. Using DBU as the catalyst, EgMA selectively underwent thiol-ene addition with thiol POSS across the methacrylate alkene, while leaving the allyl alkene unreacted, yielding a soluble product in a yield of 56 %.

These results confirmed that a thiol POSS could be selectively obtained from the condensation and hydrolysis of MPTMS, and that thiol POSS readily undergoes thiol-ene addition with different alkenes under different catalytic conditions.

7.1.3 Dehydrofluorination and thiol addition to PVDF

In Chapter 5, the dehydrofluorination of PVDF with DBU was examined, as well as the addition of thiols to PVDF, either as co-additives with DBU, or by post treatment of dehydrofluorinated PVDF (d-PVDF). This reaction was examined as a means of cross-linking PVDF with thiol POSS.

First, the dehydrofluorination of PVDF with DBU alone was examined, with analysis conducted by ATR-FTIR spectroscopy of the treated PVDF after recovery of the polymer by precipitation. With DBU alone, the maximum quantity of alkenes on the polymer was reached after 4 h, with longer reaction times leading to a loss of the

alkenes. With the inclusion of model thiols (1-dodecanethiol or 3-mercaptopropionic acid) with DBU, it was found that the thiols became covalently bound to PVDF.

A 2-step method of attaching thiols to PVDF was investigated. This provides a more suitable method for forming water filtration membranes. This first involved dehydrofluorination of PVDF with DBU, followed by thiol-ene addition of the thiol with benzophenone/UV catalysis in DMAc solution. In these experiments, it was demonstrated by ATR-FTIR spectroscopy that the use of benzophenone/UV catalysis led to the attachment of the model thiols to PVDF. This 2-step method of attaching thiols to PVDF was then applied to produce cross-linked, or EgMA-POSS modified PVDF membranes, using thiol POSS.

7.1.4 Fabrication of cross-linked and EgMA-POSS modified PVDF membranes

Finally, in Chapter 6, thiol POSS was attached to PVDF using the 2-step method. This comprised of modifying PVDF by dehydrofluorination to produce alkenes, followed by benzophenone/UV catalysis with thiol POSS. Chapter 6 largely focused on the analysis of cross-linked PVDF membranes using this method, with some preliminary studies on antibacterial performance of the PVDF membranes produced with a similar method of fabrication.

Using a casting solution of d-PVDF, thiol POSS, PVP, and benzophenone in the casting solution, cross-linked PVDF membranes were UV-irradiated to induce thiolene addition. Thiol POSS loadings were varied between 1-10 wt% (relative to d-PVDF) in the casting solution. Analysis of these cross-linked PVDF membranes showed that the Young's modulus of the membranes increased with increasing loading of thiol POSS. Moreover, the compaction resistance of the cross-linked PVDF membranes with 10 wt% of thiol POSS showed improved compaction resistance, reducing the flux decline during the filtration of pure water.

Using a casting solution of d-PVDF, thiol POSS, PVP, benzopheone, and EgMA (an antibacterial compound with alkenes), EgMA-POSS modified PVDF membranes were produced by benzophenone/UV-catalysed thiol-ene addition. The thiol-ene addition of thiol POSS across the alkenes of both EgMA and d-PVDF led to EgMA being retained in the final membrane. EgMA was not retained in the membranes when the thiol POSS was not included in the casting solution. Bacterial adhesion tests

performed on these EgMA-POSS modified PVDF membranes indicated that the surface morphology of the membranes played a larger role on the extent of bacterial adhesion than the incorporation of EgMA. This was attributed to either extracellular polymeric substances secreted by the bacteria, or dead bacterial cells, acting as a buffer layer to prevent EgMA exhibiting an antibacterial effect.

7.2 Future work

7.2.1 Incorporation of TFP POSS into PVDF water filtration membranes

As discussed in Chapter 3, TFP POSS was incorporated into PVDF water filtration membranes. However, TFP POSS was found to have no significant effect on the mechanical properties of the PVDF water filtration membranes formed by NIPS, and did not reduce compaction during filtration. The reason for this is currently unknown. One possibility is the difference in the methods of preparation of the PVDF materials compared to the PVDF membranes formed in this work.

In the literature involving incorporating TFP POSS into PVDF materials, the materials were prepared by solvent evaporation. This method of preparing the PVDF-TFP POSS materials was observed to lead to aggregation of TFP POSS.^[16, 17] Although excessive aggregation leads to a reduction in mechanical properties of PVDF materials,^[16] nano-sized aggregates were found to reinforce the polymeric material.^[16] For the PVDF membranes formed by NIPS in this work, even with 20 wt% of TFP POSS, no large aggregates of TFP POSS were observed. Solvent precipitation (which is similar to the NIPS process, as it involves precipitating polymeric solutions with a non-solvent) of polymeric materials with POSS is known to suppress aggregation of POSS.^[18] It could be that the combination of high compatibility of TFP POSS with PVDF,^[15, 19] and the suppression of POSS aggregates do not form, which in turn provides no mechanical improvement to the PVDF membranes. It should be noted that current data obtained in this work (done by SEM) is not sensitive enough to observe the nano-sized aggregates, so this is only a hypothesis.

Future work in incorporating TFP POSS in PVDF water filtration membranes formed by NIPS should first focus on analysing the membranes with more sensitive techniques, such as transmission electron microscopy and wide-angle x-ray

spectroscopy. This should be done to determine how the TFP POSS has aggregated in the PVDF membranes formed by NIPS, and the size of the aggregates. Then studies should focus on altering the aggregation behaviour of TFP POSS in the PVDF membranes, by changing the NIPS conditions, such as adding additives such as LiCl to the casting solution, or changing the coagulation bath composition or temperature. The focus would be to control the aggregation of TFP POSS, and how that impacts the PVDF membrane properties. This should allow a method to form nano-aggregates of TFP POSS which are homogenously dispersed throughout the PVDF matrix, and then the resulting membrane analysed to determine if the mechanical properties, and the compaction properties of the membranes, are improved.

7.2.2 Dehydrofluorination of PVDF and thiol attachment

In Chapter 5, the dehydrofluorination of PVDF and attachment of thiols was examined. However, the analysis conducted was limited to ATR-FTIR spectroscopy, which only provides limited information regarding the chemical changes occurring to PVDF.

Currently, there is little information regarding how rapidly the dehydrofluorination reaction of PVDF leads to cross-linking and/or the production of insoluble materials. This could be investigated using techniques that are able to measure molecular weight of the polymers, such as gel permeation chromatography. This would allow the change in molecular weight of PVDF during the dehydrofluorination reaction to be determined. The effect of different bases, presence of thiols or amines, solvents, temperature, etc, could then be examined. In conjunction with mechanical tests of the materials this would provide a better understanding of how rapidly cross-linking occurs during the reaction, and how the mechanical properties of PVDF are changed. The effect of including thiols in the reaction would be particularly interesting, as the information obtained from this work indicates that the thiols consume the alkenes as they are produced by the base. This could mean that the amount of cross-linking is reduced, as side reactions involving the alkenes would be less likely to occur.

The method of attaching thiols to PVDF by adding thiols with DBU could also be expanded. Other strong bases could be investigated for the dehydrofluorination step, such as the standard hydroxide bases, to see whether the attachment of thiols

still readily occurs with these bases. This would allow the less expensive hydroxide bases to be used rather than DBU. Moreover, this method of attaching thiols to PVDF could also be used to attach thiols to the surface of PVDF materials. This would allow a simple surface modification of PVDF materials to be used, which (potentially) only requires a strong base and a thiol. This would allow thiols to be attached such as to provide antifouling, antimicrobial, or other desired surface properties to PVDF materials.

7.2.3 Cross-linking PVDF with thiol POSS

The success of improving the mechanical properties by cross-linking PVDF with thiol POSS is a promising avenue to reduce the compaction of PVDF membranes, as discussed in Chapter 6 of this thesis. However, the methodology used in this thesis does have several issues that would have to be addressed in order for it to be commercially viable, as well as further research to improve membrane properties further.

Currently, the efficiency of the cross-linking process of thiol POSS with d-PVDF (how many thiol groups per POSS cage have reacted, whether it has definitely crosslinked PVDF or not) using the method investigated needs to be assessed. This information would be useful in regards to how well the current method of crosslinking of PDVF using thiols actually works, and what changes could be undertaken to improve the efficiency of the cross-linking process. For example, using multi-thiol molecules with longer alkyl chains connecting the thiols may provide better crosslinking, as it will be able to reach other alkenes in solution more easily. Using a commercially available multi-thiol molecule would also be more preferable, such as pentaerythritol tetrakis(3-mercaptopropionate), as this would avoid having to synthesise thiol POSS.

One issue is that the current process has not been optimised. Optimisation of the process could be done in several ways. One way would be to determine the optimal amount of dehydrofluorination of PVDF needed for the optimal membrane properties from cross-linking, as excessive dehydrofluorination has been shown to weaken PVDF membranes.^[20, 21]

Another way to optimise the process includes determining the optimal amount of photointiator needed to drive the thiol-ene addition reaction (which crosslinks the membrane), as well as different photoinitators other than benzophenone could be examined. This could result in significantly less photoinitiator needed to result in effective cross-linking of PVDF, as well as potentially reduce the UVirradiation time required.

Furthermore, the effect of UV-irradiation time on the membrane properties should be examined, to ensure the optimal membrane properties are achieved in the shortest time possible. Using a UV-source with greater intensity should be able to reduce the UV-irradiation required. Performing the UV-irradiation step under a controlled atmosphere, which limits the exposure of the polymer film to water, may provide improvements as well. This is because long exposure times of the cast polymer-solution film to the atmosphere, as well as a higher humidity, has been implicated in reducing the mechanical properties of PVDF membranes.^[22]

7.2.4 EgMA-POSS modified PVDF membranes

In Chapter 6, EgMA was incorporated into PVDF membranes to provide antibacterial properties, so that the membrane would be more resistant to biofouling. Although the membranes were not investigated in-depth, the bacteria adhesion tests performed on the membranes indicated that EgMA was ineffective at reducing bacterial adhesion. This was attributed to the presence of extra cellular polymeric substances, or dead bacterial cells, preventing the EgMA from coming into contact with the bacteria.^[27] Since this was not confirmed experimentally, future work could further investigate how to make EgMA an effective antibacterial agent for use in water filtration membranes.

One method to improve the antibacterial performance of the membranes would be to prevent the accumulation of foulants and dead cells that protect the adhering bacteria from the antibacterial properties of EgMA. This could be done by including an antifouling agent along with EgMA.^[27] Further improvements could also be made by forming a copolymer on the membrane surface, which includes both the antifouling agent as well as EgMA. This way, the amount of EgMA/antifouling agent needed to be effective would be minimised, as they these agents would be

concentrated at the membrane surface, rather than dispersed throughout the bulk of the membrane.

Another approach to improving the antibacterial properties of the EgMA-POSS modified PVDF membranes might be to incorporate a different antibacterial agent. A different derivative of eugenol, ethoxyeugenyl methacrylate, has been demonstrated to possess greater antibacterial properties than eugenyl methacrylate.^[28, 29] Moreover, materials incorporating ethoxyeugenyl methacrylate showed greater antibacterial performance than EgMA,^[28, 29] and therefore incorporating ethoxyeugenyl methacrylate may impart biofouling resistance to polymeric membranes.

7.3 References

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Figure A 1 - ²⁹Si NMR spectrum of thiol POSS synthesised in the bulk synthesis method (fraction 2) (taken on 400 MHz NMR spectrometer in CDCl₃ using TMS as an internal standard)



Figure A 2 - ²⁹Si NMR spectrum of thiol POSS synthesised in the bulk synthesis method (fraction 3) (taken on 400 MHz NMR spectrometer in CDCl₃ using TMS as an internal standard)











Figure A 5 - ¹H NMR spectrum of thiol POSS synthesised in the bulk synthesis method (fraction 3) (taken on 400 MHz NMR spectrometer in CDCl₃)







Figure A 7 - ATR-FTIR spectra of thiol POSS synthesised by the bulk synthesis method (fractions 2-4)

-39.51 Exp 45.14 allyl alcohol.006.001.1r.esp R 1.0 0.9 0.8 R 0.7 R Normalized Intensity 0.6 R= ΟH 0.5 -32.49 5 59.39<mark>0</mark> 0.4 4 -22.62 **C** 27.57 0.3 -33.56 🖌 10.48 0.2 18.09 41.39 -23.18 86 -10.57 36.05 0.1 65. 0 40 35 30 25 65 20 15 10 60 55 50 45 Chemical Shift (ppm)

A2. ¹³C and 2D NMR of the products of thiol-ene addition reactions of

thiol POSS

Figure A 8 - ¹³C NMR spectrum of the product obtained from reacting thiol POSS with allyl alcohol using AIBN as the catalyst (taken on 400 MHz NMR spectrometer in D₆-DMSO)



Figure A 9 - ¹H-¹H COSY NMR spectrum of the product obtained from reacting thiol POSS with allyl alcohol using A IBN as the catalyst (taken on 400 MHz NMR spectrometer in D₆-DMSO)



Figure A 10 - ¹H-¹³C HMQC NMR spectrum of the product obtained from reacting thiol POSS with allyl alcohol using AIBN as the catalyst (taken on 400 MHz NMR spectrometer in D₆-DMSO)



Figure A 11 - ¹H-¹³C HMBC NMR spectrum of the product obtained from reacting thiol POSS with allyl alcohol using AIBN as the catalyst (taken on 400 MHz NMR spectrometer in D₆-DMSO)



Figure A 12 - ¹³C NMR spectrum of the product obtained from reacting thiol POSS with 2-allyloxyethanol using AIBN as the catalyst (taken on 400 MHz NMR spectrometer in CDCl₃)



Figure A 13 - ¹H-¹H COSY NMR spectrum of the product obtained from reacting thiol POSS with 2-allyloxyethanol using AIBN as the catalyst (taken on 400 MHz NMR spectrometer in CDCl₃)



Figure A 14 - ¹H-¹³C HMQC NMR spectrum of the product obtained from reacting thiol POSS with 2-allyloxyethanol using AIBN as the catalyst (taken on 400 MHz NMR spectrometer in CDCl₃)



Figure A 15 - ¹H-¹³C HMBC NMR spectrum of the product obtained from reacting thiol POSS with 2-allyloxyethanol using AIBN as the catalyst (taken on 400 MHz NMR spectrometer in CDCl₃)



Figure A 16 - ¹³C NMR spectrum of the product obtained from reacting thiol POSS with 6-chloro-1-hexene using AIBN as the catalyst (taken on 400 MHz NMR spectrometer in CDCl₃)


Figure A 17 - ¹H-¹H COSY NMR spectrum of the product obtained from reacting thiol POSS with 6-chloro-1-hexene using AIBN as the catalyst (taken on 400 MHz NMR spectrometer in CDCl₃)



Figure A 18 - ¹H-¹³C HMQC NMR spectrum of the product obtained from reacting thiol POSS with 6-chloro-1-hexene using AIBN as the catalyst (taken on 400 MHz NMR spectrometer in CDCl₃)



Figure A 19 - ¹H-¹³C HMBC NMR spectrum of the product obtained from reacting thiol POSS with 6-chloro-1-hexene using AIBN as the catalyst (taken on 400 MHz NMR spectrometer in CDCl₃)

Appendix A



Figure A 20 - ¹³C NMR spectrum of the product obtained from reacting thiol POSS with 6-bromo-1-hexene using AIBN as the catalyst (taken on 400 MHz NMR spectrometer in CDCl₃)



Figure A 21 - ¹H-¹H COSY NMR spectrum of the product obtained from reacting thiol POSS with 6-bromo-1-hexene using AIBN as the catalyst (taken on 400 MHz NMR spectrometer in CDCl₃)



Figure A 22 - ¹H-¹³C HMQC NMR spectrum of the product obtained from reacting thiol POSS with 6-bromo-1-hexene using AIBN as the catalyst (taken on 400 MHz NMR spectrometer in CDCl₃)



Figure A 23 - ¹H-¹³C HMBC NMR spectrum of the product obtained from reacting thiol POSS with 6-bromo-1-hexene using AIBN as the catalyst (taken on 400 MHz NMR spectrometer in CDCl₃)

Appendix A



Figure A 24 - ¹³C NMR spectrum of the product obtained from reacting thiol POSS with eugenyl methacrylate using DBU as the catalyst (taken on 400 MHz NMR spectrometer in CDCl₃)



Figure A 25 - ¹H-¹H COSY NMR spectrum of the product obtained from reacting thiol POSS with eugenyl methacrylate using DBU as the catalyst (taken on 400 MHz NMR spectrometer in CDCl₃)



Figure A 26 - ¹H-¹³C HMQC NMR spectrum of the product obtained from reacting thiol POSS with eugenyl methacrylate using DBU as the catalyst (taken on 400 MHz NMR spectrometer in CDCl₃)



Figure A 27 - ¹H-¹³C HMBC NMR spectrum of the product obtained from reacting thiol POSS with eugenyl methacrylate using DBU as the catalyst (taken on 400 MHz NMR spectrometer in CDCl₃)

B1. Bacterial Adhesion Tests (SEM images and bacteria cell counts) – Day

1 of immersion in nutrient solution

Table B 1 - SEM images with bacterial cell counts for the 0 wt% thiol POSS – 0 wt%EgMA PVDF membrane, after immersion in nutrient solution for 1 day













Table B 3 - SEM images with bacterial cell counts for the 10 wt% thiol POSS – 1 wt%EgMA PVDF membrane, after immersion in nutrient solution for 1 day





Table B 4 - SEM images with bacterial cell counts for the 10 wt% thiol POSS – 5 wt%EgMA PVDF membrane, after immersion in nutrient solution for 1 day





Table B 5 - SEM images with bacterial cell counts for the 10 wt% Thiol POSS – 10 wt% EgMA PVDF membrane, after immersion in nutrient solution for 1 day





Table B 6 - SEM images with bacterial cell counts for the 10 wt% thiol POSS – 20wt% EgMA PVDF membrane, after immersion in nutrient solution for 1 day



B2. Bacterial Adhesion Tests (SEM images and bacteria cell counts) – Day

2 of immersion in nutrient solution

Table B 7 - SEM images with bacterial cell counts for the 0 wt% thiol POSS – 0 wt%EgMA PVDF membrane, after immersion in nutrient solution for 2 days



















Table B 10 - SEM images with bacterial cell counts for the 10 wt% thiol POSS – 5 wt% EgMA PVDF membrane, after immersion in nutrient solution for 2 days











Table B 12 - SEM images with bacterial cell counts for the 10 wt% thiol POSS – 20wt% EgMA PVDF membrane, after immersion in nutrient solution for 2 days



4 of immersion in nutrient solution

Table B 13 - SEM images with bacterial cell counts for the 0 wt% thiol POSS - 0 wt%EgMA PVDF membrane, after immersion in nutrient solution for 4 days



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*Cells counted using ImageJ software with the 'Analyze Particles' function







*Cells counted using ImageJ software with the 'Analyze Particles' function



Table B 16 - SEM images with bacterial cell counts for the 10 wt% thiol POSS – 5wt% EgMA PVDF membrane, after immersion in nutrient solution for 4 days



*Cells counted using ImageJ software with the 'Analyze Particles' function







*Cells counted using ImageJ software with the 'Analyze Particles' function

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6 of immersion in nutrient solution

Table B 19 - SEM images with bacterial cell counts for the 0 wt% thiol POSS – 0 wt%EgMA PVDF membrane, after immersion in nutrient solution for 6 days



Appendix B







Appendix B





Table B 21 - SEM images with bacterial cell counts for the 10 wt% thiol POSS – 1wt% EgMA PVDF membrane, after immersion in nutrient solution for 6 days

Appendix B











Table B 23 - SEM images with bacterial cell counts for the 10 Thiol POSS – 10 EgMAPVDF membrane, after immersion in nutrient solution for 6 days

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