NANOFILTRATION MEMBRANES MODIFIED WITH AROMATIC POLYAMIDE DENDRIMERS ACTIVE LAYERS

BY

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THESIS

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This thesis describes the modification of the commercial TFC-S nanofiltration membrane with shape-persistent dendritic architectures. Amphiphilic aromatic polyamide dendrimers (G1-G3) are synthesized via a divergent approach and used for membrane modification by direct percolation. The permeate samples collected from the percolation experiments are analyzed by UV-Vis spectroscopy to instantly monitor the influence of dendrimer generations on percolation behaviors and new active layer formation. The membrane structures are further characterized by Rutherford backscattering spectrometry (RBS) and atomic force microscopy (AFM) techniques, suggesting a low-level accumulation of dendrimers inside the TFC-S NF membranes and subsequent formation of an additional aramide dendrimer active layer. Thus, all the modified TFC-S membranes have a double active layer structure. A PES-PVA film is used as a control membrane showing that structural compatibility between the dendrimer and supports plays an important role in the membrane modification process. The performance of modified TFC-S membrane is evaluated on the basis of rejection abilities of a variety of water contaminants having a range of sizes and chemistry. As the water flux is inversely proportional to the thickness of the active layer, we optimize the amount of dendrimers deposited for specific contaminants to improve the solute rejection while maintaining high water flux.
To my family
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CHAPTER 1

INTRODUCTION

1.1 Advanced Membrane Techniques for Water Purification

One of the most severe problems worldwide is inadequate access to sufficient clean water: 1.2 billion people lack access to safe drinking water, 2.6 billion have little or no sanitation, and millions of people die annually from diseases transmitted through unsafe water or human excreta.\(^1\) Meanwhile, in both developing and industrialized nations, a growing number of contaminants are entering water supplies from human activity: from traditional compounds such as heavy metals and distillates to emerging micropollutants such as endocrine disrupters and nitrosoamines.\(^2,3\) Addressing these problems calls out for a tremendous amount of research on efficient methods and novel materials for water purification and regeneration.\(^4-6\)

Compared to traditional evaporation technologies, membrane filtration is emerging as an efficient and economical drinking water treatment process, because of its ability to remove various contaminants from water in a single treatment step with much lower consumption of energy (up to 10 times less electricity consumption).\(^7\) In the filtration process, external pressure is applied to overcome osmotic pressure, and force water to pass through a semi-permeable membrane, resulting in the removal of contaminants (Figure 1.1).
1.1.1 Membrane Categories

Based on the pore size difference, the membranes for industrial water treatment are characterized into the following categories: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). All these processes are pressure-driven membrane separation processes. Microfiltration and ultrafiltration are basically similar, in which the mode of separation is molecular sieving through increasingly fine pores. MF membranes filter colloidal particles and bacteria from 0.1 to 10 μm in diameter. UF membranes can be used to filter dissolved macromolecules, such as proteins, from solutions. The mechanism of separation by RO membranes is quite different. In RO membranes, the membrane pores are so small, from 3 to 5 Å in diameter, which are within the range of thermal motion of the polymer chains that form the membrane. The accepted mechanism of transport through these membranes is called the solution-diffusion model. According to this model, solutes permeate the membrane by dissolving in the membrane material and diffusing down a concentration gradient. Separation occurs because of the difference in solubilities and mobilities of different solutes in the membrane. The principal application of reverse osmosis is desalination of brackish groundwater or seawater. Finally, NF membranes have transient pores on the order of
one nanometer or less, and therefore fall into the intermediate region between RO and UF membranes. They have a lower sodium chloride rejection (20 - 80%) than RO (over 98%), but with higher retention capacity for multivalent ions (e.g. Ca\(^{2+}\), Mg\(^{2+}\), and SO\(_4\)^{2-}\)). The pressure required by NF is usually much lower than RO process (typically 0.3 - 3 MPa), therefore NF membranes are sometimes regarded as “loose” or “low-pressure” RO membranes.\(^8\)

![Diagram of Membrane Pore Sizes](image)

**Figure 1.2.** Reverse osmosis, nanofiltration, ultrafiltration, and microfiltration are related processes differing principally in the average pore size of the various membranes. The relative size of different solutes removed by each class of membrane is illustrated in this schematic diagram.

1.1.2 RO/NF Membrane Configurations

In terms of providing purified water for drinking and industrial purpose, two major approaches are commonly used, including: (1) seawater desalination, and (2) municipal water (brackish and drinking water) treatment. Both approaches involve the application of RO and NF processes in order to remove the dissolved salts and minerals by filtration.\(^9\) Therefore, the discussion in this thesis is mainly focused on the RO and NF membranes.
Currently, commercially available RO and NF membranes are mainly derived from two basic types of polymers: cellulose acetate (CA) and aromatic polyamides (PA).\textsuperscript{10,11} The CA membranes are usually prepared by casting a film from a CA solution and subsequently immersing the film in a nonsolvent for the polymer, such as water. Upon contact with water, the CA polymer precipitates out to form the membrane with an integrally asymmetric structure shown in Figure 1.3. On the contrary, the PA membranes show a composite structure with a thin aromatic polyamide layer on the top of a reinforced microporous support made by a polymer different from the top layer.

![Figure 1.3. Schematic diagrams of two major type of RO/NF membranes](image)

1.1.3 Cellulose Acetate (CA) Membranes

The first CA membrane was developed from cellulose diacetate polymer in the late 1950’s, and commercially applied for seawater desalination in 1960’s.\textsuperscript{8} The current cellulose acetate membrane is usually made from either cellulose acetate (acetylation degree from 1 to 3) or their blend, in form of asymmetric configuration (Figure 1.4).\textsuperscript{12} Specifically, the full acetyl substitution (acetylation degree of 3) renders high salt rejection but low water fluxes. Lower yet moderate degree of acetylation can provide a
better trade-off between rejection and permeability. For example, most commercial CA membranes have an acetylation degree of 2.7.

![Figure 1.4](image)

**Figure 1.4.** Structure of cellulose acetate with full acetyl substitution

Because of the neutral surface and tolerance to limited free chlorine, cellulose acetate membranes usually have stable performance in applications where the feed water has high fouling potential (e.g. with municipal effluent and surface water supplies). Furthermore, CA are of relatively low cost as they derive from abundant naturally occurring cellulose. However, the widespread development of cellulose acetate membranes has met some disadvantages, such as a narrow operating pH range (4.5 - 7.5), susceptibility to biological attack, structural compaction under high pressure and low upper temperature limit. The CA membranes were the industry standard through the 1960s to the mid-1970s, until Cadotte, at North Star Research, developed the interfacial polymerization method of producing polyamide thin film composite (TFC) membranes.

### 1.1.4 Polyamide (PA) Membranes

The PA TFC membranes (RO and NF) are typically a composite structure with a *ca.* 50 μm asymmetric porous support layer and a *ca.* 50-250 nm thin active layer that serves as a barrier to water contaminants. The materials used for the mechanical support layer
are usually polysulfone or polyethersulfone, while the active layers are usually made by the
method of interfacial polymerization resulting in a negatively charged thin film of
crosslinked polyamide.\textsuperscript{10,15,16} As compared with CA membranes, the PA membranes
exhibit superior water flux, salt and organic rejections, and pressure compaction resistance,
wider operating temperature range (0 - 45 °C) and pH range (from 1 to 11), and higher
stability to biological attack.\textsuperscript{10} Therefore, they are now widely used in commercial single
pass seawater desalination plants around the world offering a combination of high flux and
high selectivity unmatched by other types of RO/NF membranes.\textsuperscript{17}

![Figure 1.5. Representative structure of aromatic polyamide active layer of RO/NF membranes](image)

However, commercial PA membranes still have some drawbacks in the
desalination processes, such as a propensity to undergo fouling\textsuperscript{18-20} and low tolerance to
free chlorine\textsuperscript{21-23}, which may affect the membrane performance, e.g. by shortening
membrane lifetime, and reducing flux or salt rejection. Specifically, in terms of the NF
membranes, the disadvantage also includes inability to adequately reject certain common
water contaminants, e.g. sodium chloride, barium chloride and arsenic(III), predominantly
arsenious acid (H\textsubscript{3}AsO\textsubscript{3}).\textsuperscript{24-27} Therefore, there is a need to develop a new generation of
RO/NF membranes having active layers with adjustable chemistry and structure to achieve
optimal water/solute selectivity for the broad range of conditions encountered in water quality control applications.

1.2 Membrane Modification

In order to overcome the above disadvantages and improve the performance of the commercial RO/NF membranes, it is important to perform surface modification for the membranes. As the properties of polyamide active layers determine the performance of the TFC membranes, the modification of PA layers could exhibit decisive affects on the performance of RO/NF membranes. To date, many approaches to membrane modification have been tried, including coating, plasma treatment, chemical treatment, graft polymerizations, and UV irradiation.28,29

1.2.1 Coating

The coating is commonly applied to modify RO/NF membranes by physical adsorption with fouling-resistant and highly water-permeable polymers or surfactants. In such physical modification process, the coating layer is physically attached to the membrane surface without interfering with the chemistry of selective layer. Polyvinyl alcohol, polyethyleneimine and polyether-polyamide block copolymers have been used in recent studies.30-32 The modified membranes normally exhibited similar or improved rejection, but usually accompanied with significantly decreased water flux. The observation of significant drop of water flux indicates that the coating materials not only
covered the membrane surface, but also penetrated into the open pore structures. Fortunately, such water flux loss could be compensated by the significantly improved fouling behavior. Among those studies, the modification with polyethylenimine is an attractive approach, as the polymer can reverse surface charges on the polyamide active layers and thus increase the membrane fouling resistance to cationic foulants by the enhanced electrostatic repulsion. Furthermore, the increased surface hydrophilicity could minimize the flux reduction. This modification method tends to increase salt rejection of membranes, and the increase in the rejection rate was more significant for divalent cations (Mg\(^{2+}\)) than monovalent cations (Na\(^{+}\)).

### 1.2.2 Plasma Treatment

Plasma treatment is a convenient technique for the surface modification of polymer materials for improving the surface properties, such as adhesion and wettability. These properties result from introducing functional groups or making crosslinking in the molecule’s surface. The plasma treatment has also been applied to the modification of PA TFC membranes in form of oxygen and argon plasma. The water permeability of oxygen-plasma modified membrane increases and the chlorine resistance of argon-plasma modified membrane increases. The modified membranes were characterized by the attenuated total reflection-Fourier transform infrared (ATR-FTIR), X-ray photoelectron spectroscopy (XPS), and the contact angle measurement in order to explain the different improvement between the two treatment. It showed that the carboxyl groups were
introduced to the surface of the TFC membranes by oxygen plasma modification and made the permeability increase, while argon plasma caused cross-linking at the nitrogen site of the PA membranes enhancing the chlorine resistance.\textsuperscript{33}

1.2.3 Chemical Treatment

Chemical modification can usually be achieved by reacting hydrophilic molecules with activated PA membranes. The resulting membranes generally demonstrate increased hydrophilicity as well as improved water permeability and antifouling ability.\textsuperscript{34,35} For example, hydrophilic poly(ethylene glycol) was grafted onto the surface of nascent PA membrane before the hydrolysis of acyl chloride groups in the interfacial polymerization. Modified with aminopolyethylene glycol monomethylether (MPEG-NH\textsubscript{2}), the resulting membranes showed improved antifouling property owing to the enhanced hydrophilicity and steric repulsion effect.\textsuperscript{34} However, the significance of improved antifouling property was not as much as expected. More recently, a hydantoin derivative, 3-monomethylol-5,5-dimethylhydantoin, was grafted onto the PA membrane surfaces by reacting with acyl chloride.\textsuperscript{35} After exposure to microbial cells, less permeability loss verified a substantial improvement against biofouling for the modified membranes. This was a significant finding as these membranes are superior to the other modified membranes in terms of antifouling properties. However, decreased salt rejection was observed for certain modified polyamide membranes due to the fewer numbers of negative charges on the membrane surface.\textsuperscript{35}
1.2.4 Graft Polymerization

A special case of chemical modification is the graft polymerization, which attaches hydrophilic monomers covalently to the primary radical site on the membrane surfaces. The primary radical can be formed either directly using radiation techniques such as ion beam, plasma, \( \gamma \)-irradiation, and ozone treatment or by electron transfer from a free radical initiator.\textsuperscript{36,37} The free radical can be generated by hemolytic decomposition of compounds like photoinitiators or peroxide using heat or light or by a redox reaction between a suitable oxidizer and reductant.\textsuperscript{38-40} Specifically, the redox method has shown advantages in membrane modification as it is facile and can be used in aqueous media at room temperature without an external activation. The grafted commercial PA membranes exhibited improved hydrophilicity. Furthermore, the surface modification of the membranes resulted in a drastic decrease in contaminant adsorption for some polymer grafts and increased ease in rinsing the contaminated surface.\textsuperscript{41,42} The modified membranes showed slower flux reduction with unchanged or increased salt rejection compared to the untreated membranes.\textsuperscript{42}

1.3 Thesis Organization

The overall objective of this collaborative interdisciplinary research is the development of novel NF/RO membrane active layer materials with adjustable chemistry and structure. The research presented in this thesis focuses on the synthesis and characterization of amphiphilic aromatic polyamide dendrimers with well-defined
branched structures for the modification of polyamide active layers of commercial NF membranes.

As the structural mimics for the molecules in polyamide NF membranes, the aromatic polyamide dendrimers were synthesized in stepwise growth and functionalized for sufficient solubility and hydrophilicity (Chapter 2). Their structures were characterized by $^1$H NMR, $^{13}$C NMR, and MALDI-TOF mass spectrometry. Chapter 3 describes the utilization of the aromatic polyamide dendrimers for membrane modification. A commercial polyamide NF membrane (TFC-S) was chosen as the representative membrane, while the PES membrane was used in a control experiment. The quality of the aramide dendrimer modified active layers was characterized by UV-Vis spectroscopy, atomic force microscopy (AFM) and Rutherford backscattering spectrometry (RBS). Membrane performance was evaluated on the basis of rejection capabilities of Rhodamine WT (R-WT), sodium chloride, barium chloride and arsenic(III). Conclusions and suggestion on future work are discussed in Chapter 4.
CHAPTER 2
SYNTHESIS AND CHARACTERIZATION OF AROMATIC POLYAMIDE DENDRIMERS

2.1 Introduction

It is widely recognized that there is a need to develop a new generation of RO/NF membranes having active layers with adjustable chemistry and structure to achieve optimal water/solute selectivity for the broad range of conditions encountered in water quality control applications. The utilization of dendrimers as building blocks for membrane active layer preparation tends to be an attractive approach as the high degree of control over the physical and chemical properties of the dendrimers’ structure provides the oppotunity to meet the above goal.

Dendrimers are regularly branched, three dimensional macromolecules. Many of their characteristics, for example the size and shape of the molecule and the position of functional groups, can be well controlled by systematic changes in their synthesis. Thus, they usually exhibit unique properties, such as good solubility, low viscosity, multivalence, and encapsulation effects, leading to a variety of applications.43

As a specific category, aromatic polyamide (aramide) dendrimers have been prepared by both convergent and divergent synthetic approaches in recent years.44,45 They maintain the good thermal, chemical, and mechanical properties of linear aromatic polyamides, but with improved solubility, functionality and processability. From a
structural view, there is high similarity between these aramide dendrimers and the interfacial polymerized polyamides in RO/NF membrane active layers. However, unlike the highly crosslinked and cyclized polyamides in active layers, aramide dendrimers have sufficient solubility in organic solvents. Therefore, they have the potential to be deposited on the support membrane by percolation, making them good candidates for polyamide membrane modification. By increasing the dendrimer generation and tailoring the peripheral group chemistry, it is possible to use these structurally well-defined aramide dendrimers to systematically investigate the membrane-performance relationships.

A series of bidendron aramide dendrimers were chosen as target compounds (Figure 2.1). Since the repeating unit has all substitutes in the $m$-position, the aramide dendrimers are good mimics to the polyamide networks used in commercial membranes, but with a perfectly defined molecular structure. $p$-Phenylenediamine (PDA) as the core structural unit reduces the steric hindrance between the two dendritic segments. To overcome the dendrimer’s limited solubility in methanol, oligoethylene glycol (OEG) side chains were attached to the dendrimer’s periphery through amide bond linkages.
2.2 Synthesis and Characterization

The synthesis of aramide dendrimers G1-G3 followed a facile divergent approach recently reported by Ueda and coworkers (Scheme 2.1). Amine-terminated NH$_2$-Gn (n = 1-3) were synthesized by performing stepwise growth from the p-phenylenediamine core using 3,5-bis(trifluoroacetamido)benzoyl chloride as an AB$_2$ building block. 2-[2-(2-Methoxyethoxy)ethoxy]acetyl chloride, which was obtained by reacting 2-[2-(2-methoxyethoxy)ethoxy]acetic acid with thionyl chloride, was used to functionalize the amine-terminated NH$_2$-Gn (n = 1-3) by amide bond formation.$^{48}$ Aramide dendrimers G1-G3 were then obtained in moderate yield after column chromatography.
The structures of dendrimers G1-G3 have been characterized by $^1$H NMR, $^{13}$C NMR, MALDI-TOF mass spectrometry and gel permeation chromatography (GPC). The $^1$H NMR spectrum of the dendrimers showed signals in three chemical shift regions corresponding to the amide protons, the aromatic protons, and the ethylene glycol side chain protons, respectively. As shown in Figure 2.2, the MALDI-TOF mass spectra of dendrimers G1-G3 gave m/z values of 1039.0, 2215.8, and 4567.5 Da, which are within experimental error of the calculated m/z values of 1039.5, 2215.9, and 4568.9 Da, respectively.
Furthermore, the GPC traces of all three dendrimers were unimodal and had narrow distributions (Figure 2.3). These results indicated the formation of the desired dendrimers.

<table>
<thead>
<tr>
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<th>$M_n$</th>
<th>$M_w/M_n$</th>
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<tbody>
<tr>
<td>G1</td>
<td>1800</td>
<td>1.03</td>
</tr>
<tr>
<td>G2</td>
<td>4000</td>
<td>1.03</td>
</tr>
<tr>
<td>G3</td>
<td>6200</td>
<td>1.03</td>
</tr>
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In order to quantify the amount of polyamide dendrimers within a molecular thin film (i.e., using the Rutherford backscattering technique), heavy elements, such as iodine, are incorporated into dendrimer molecules. Due to the divergent feature of synthesis approach, the synthesis is facilitated by incorporating iodine atoms into the dendrimer core. Thus, 2,6-diodobenzene-1,4-diamine was synthesized by reduction of diiodonitroaniline.
and used for dendrimer preparation in the same way as for dendrimers G1-G3.\textsuperscript{50} Dendrimers 2I-Gn (n = 1-3) were obtained in the yield of 43\%, 72\%, 56\%, respectively. Their structures have been characterized by $^1$H NMR, $^{13}$C NMR, and MALDI-TOF mass spectrometry. For example, the $^1$H NMR spectrum of dendrimer 2I-G1 showed peaks corresponding to the amide protons at chemical shifts of 10.46, 10.28, 9.87 ppm, and peaks corresponding to the aromatic protons at 8.38, 8.25, 7.90, 7.84 ppm, indicating the asymmetric nature of the diiodo-substituted compounds. The MALDI-TOF mass spectra showed signals corresponding to the dendrimer molecular weight peaks with m/z values at 1271.0, 2467.1, and 4818.9 Da, while the calculated m/z values are 1268.9, 2467.7, and 4820.7, respectively. According the $^1$H NMR spectra, the purity of these dendrimers is over 95\%.

\textbf{2.3 Experimental section}

\textbf{2.3.1 Materials}

Unless otherwise stated, all starting materials were obtained from commercial suppliers and used without purification. Tetrahydrofuran (THF) was dried over sodium and benzophenone and distilled before use under nitrogen. Anhydrous $N$-methyl-2-pyrrolidinone (NMP) was purchased in a Sure/Seal bottle from Aldrich and stored under nitrogen. 3,5-bis(trifluoroacetamido)benzoyl chloride was synthesized following literature procedure.\textsuperscript{46}
2.3.2. General Methods

All glassware was oven- or flame-dried before use. All reactions were performed under N₂ unless otherwise specified. Reactions were monitored by thin layer chromatography (Merck silica gel F254, 0.25 mm) and visualized under UV irradiation at 254 nm or by iodine stain. Flash column chromatography was performed with silica gel 60 (230-400 mesh) from EM science.

2.3.3. Measurements

The \(^1\)H and \(^1^3\)C NMR spectra were recorded on Varian Unity 400, Varian Unity 500, or Varian VXR 500 spectrometers. Proton chemical shifts are expressed in parts per million (δ) using the residual solvent protons as an internal standard. Carbon-13 chemical shifts are also expressed in parts per million (δ) using the solvent’s \(^1^3\)C resonance as an internal standard. Coupling constants (J) are reported in Hertz (Hz), and splitting patterns are designated as s (singlet), d (doublet), t (triplet), m (multiplet), and br (broad). Low-resolution matrix-assisted laser desorption ionization (MALDI) mass spectra were obtained using a Voyager-DE STR spectrometer using 1,8-dihydroxy-9,10-dihydroanthracen-9-one (dithranol) as matrix. Other mass spectrometric methods were performed by the Mass Spectrometry Center at School of Chemical Science, University of Illinois at Urbana-Champaign. Gel permeation chromatography (GPC) measurements were performed using DMF containing 0.05 M LiBr as eluent on a Waters Sytrigel HR3 triple column coupled with a Viscotek TDA model 300 triple detector array. Molecular
weights were calibrated with polystyrene standards. Melting points were obtained using an electrothermal melting temperature apparatus (Mel-Temp, Model 1001).

2.3.4. Synthesis and Characterization

Synthesis of 3,5-Bis(trifluoroacetamido)benzoyl Chloride (AB₂ monomer)

This AB₂ monomer was prepared following a reported procedure. mp 145-146 °C; \(^{1}H\) NMR (500 MHz, CDCl₃, \(\delta\)): 8.44 (t, \(J = 2.0\) Hz, 1H; Ar H), 8.19 (d, \(J = 2.0\) Hz, 2H; Ar H), 8.10 (s, 2H, NH); FDMS (m/z): 362.1 [M⁺]; Anal. calcd for C₁₁H₅ClF₆N₂O₃: C 36.43, H 1.39, N 7.73; Found: C 36.69, H 1.42, N 7.92.

Synthesis of NH₂-G1 Dendrimer

NH₂-G1 Dendrimer was prepared following a modified reported procedure.\(^{46}\) p-Phenylenediamine (54.1 mg, 0.50 mmol) was dissolved in NMP (1 mL). 3,5-Bis(trifluoroacetamido)benzoyl chloride (398.9 mg, 1.10 mmol) was added to this solution at 0 °C under nitrogen. The solution was stirred at the temperature for 5 min, followed by 25 °C for 1 h. Then, water (0.1 mL) was added and the solution was heated at 50 °C for 1 h. The reaction mixture was treated with hydrazine monohydrate (300 mg,
6.00 mmol) for 2 h at the same temperature and then poured into 2% NaHCO₃ solution (50 mL). The resultant white precipitate was filtered, washed with water, and dried at 120 °C under vacuum to give NH₂-G₁ as a white solid (178.8 mg, 95% yield). mp (DSC) 313 °C; ¹H NMR (500 MHz, DMSO-­d₆, δ): 9.87 (s, 2H, NH), 7.64 (s, 4H, Ar H), 6.27 (d, J = 1.5 Hz, 4H; Ar H), 5.97 (s, 2H, Ar H), 4.93 (s, 8H, NH₂); ¹³C NMR (125 MHz, DMSO-­d₆, δ): 166.7, 148.8, 136.7, 134.8, 120.1, 102.3 ppm.

### Synthesis of NH₂-G₂ Dendrimer

NH₂-G₂ Dendrimer was prepared following a modified reported procedure.⁴⁶ NH₂-G₁ dendrimer (94.1 mg, 0.25 mmol) was dissolved in NMP (2 mL). 3,5-Bis(trifluoroacetamido)benzoyl chloride (398.9 mg, 1.10 mmol) was added to this solution at 0 °C under nitrogen. The solution was stirred at the temperature for 5 min, followed by 25 °C for 2 h. Then, water (0.1 mL) was added and the solution was heated at 50 °C for 1 h. The reaction mixture was treated with hydrazine monohydrate (300 mg, 6.00 mmol) for 2 h at the same temperature and then poured into 2% NaHCO₃ solution (50 mL). The resultant brown precipitate was filtered, washed with water, and dried at 120 °C under vacuum to give NH₂-G₂ as a brown solid (208.9 mg, 92% yield). ¹H NMR
(500 MHz, DMSO-$d_6$, $\delta$): 10.26 (s, 2H, NH), 10.10 (s, 4H, NH), 8.36 (s, 2H, Ar H), 7.90 (d, $J$ = 2.0 Hz, 4H; Ar H), 7.73 (s, 4H, Ar H), 6.37 (d, $J$ = 2.0 Hz, 8H; Ar H), 6.00 (s, 4H, Ar H), 4.93 (s, 16H, NH$_2$); $^{13}$C NMR (125 MHz, DMSO-$d_6$, $\delta$): 167.0, 165.7, 148.9, 139.4, 136.4, 135.9, 134.9, 120.3, 115.3, 114.8, 102.4 ppm.

**Synthesis of NH$_2$-G3 Dendrimer**

NH$_2$-G3 Dendrimer was prepared following a modified reported procedure.

NH$_2$-G2 dendrimer (114.1 mg, 0.125 mmol) was dissolved in NMP (2 mL). 3,5-Bis(trifluoroacetamido)benzoyl chloride (398.9 mg, 1.10 mmol) was added to this solution at 0 ºC under nitrogen. The solution was stirred at the temperature for 5 min, followed by 25 ºC for 2 h. Then, water (0.1 mL) was added and the solution was heated at 50 ºC for 1 h. The reaction mixture was treated with hydrazine monohydrate (300 mg, 6.00 mmol) for 2 h at the same temperature and then poured into 2% NaHCO$_3$ solution (50 mL). The resultant brown precipitate was filtered, washed with water, and dried at 120 ºC under vacuum to give NH$_2$-G3 as a brown solid (213.7 mg, 92% yield). $^1$H NMR
(500 MHz, DMSO-$d_6$, $\delta$): 10.57 (s, 4H, NH), 10.39 (s, 2H, NH), 10.16 (s, 8H, NH), 8.51 (s, 2H, Ar H), 8.38 (s, 4H, Ar H), 8.00 (s, 4H, Ar H), 7.96 (s, 8H, Ar H), 7.76 (s, 4H, Ar H), 6.34 (s, 16H, Ar H), 6.00 (s, 8H, Ar H), 4.97 (s, 32H, NH$_2$); $^{13}$C NMR (125 MHz, DMSO-$d_6$, $\delta$): 167.3, 166.3, 165.7, 149.1, 139.6, 139.5, 136.6, 136.3, 135.8, 135.0, 120.5, 115.4, 115.0, 102.4 ppm.

**Synthesis of 2-[2-(2-Methoxyethoxy)ethoxy]acetyl Chloride**

\[
\text{O} - \text{O} - \text{O} - \text{CO}_2\text{H} \xrightarrow{\text{SOCl}_2} \text{O} - \text{O} - \text{O} - \text{COCl}
\]

2-[2-(2-Methoxyethoxy)ethoxy]acetic acid (8.91 g, 50 mmol), and thionyl chloride (18.2 mL, 0.25 mol) were dissolved in CH$_2$Cl$_2$ (50 mL) and heated at 80 ºC for 6 h. Then, the mixture solution was evaporated to remove CH$_2$Cl$_2$ and unreacted thionyl chloride. The residual liquid was used for the next reaction without further purification.

$^1$H NMR (500 MHz, CDCl$_3$, $\delta$): 4.49 (s, 2H, CH$_2$), 3.76-3.77 (m, 2H, CH$_2$), 3.66-3.67 (m, 2H, CH$_2$), 3.59-3.60 (m, 2H, CH$_2$), 3.53-3.54 (m, 2H, CH$_2$), 3.36 (s, 3H, CH$_3$); $^{13}$C NMR (125 MHz, CDCl$_3$, $\delta$): 172.0, 76.6, 71.7, 71.2, 70.6, 70.5, 58.9 ppm.

**Synthesis of G1 Dendrimer**

\[
\text{NH}_2\text{-G1 dendrimer} (23.1 mg, 0.06 mmol) was dissolved in NMP (2 mL). 2-[2-(2-Methoxyethoxy)ethoxy]acetyl chloride (72.4 mg, 0.37 mmol) was added to this solution at 0 ºC under nitrogen. The solution was stirred at the temperature for 5 min,
followed by 25 °C for overnight. The reaction mixture was poured into 2% NaHCO₃ solution (20 mL) and extracted with CH₂Cl₂. The organic phase was washed with water, dried over anhydrous Na₂SO₄, and concentrated in vacuo. The residue solution was then placed on a Kugelrohr apparatus to remove remaining NMP solvent. The crude product was purified by column chromatography (CH₂Cl₂/MeOH, 15/1, v/v) to afford G1 as a light brown solid (62.3 mg, 84%). mp (DSC): 121 °C; ¹H NMR (500 MHz, DMSO-d₆, δ): 10.29 (s, 2H, NH), 9.84 (s, 2H, NH), 8.24 (s, 2H, Ar H), 7.81 (d, J = 1.5 Hz, 4H; Ar H), 7.71 (s, 4H, Ar H), 4.10 (s, 8H, CH₂), 3.66-3.68 (m, 8H, CH₂), 3.60-3.61 (m, 8H, CH₂), 3.56-3.57 (m, 8H, CH₂), 3.44-3.46 (m, 8H, CH₂), 3.21 (s, 12H, CH₃); ¹³C NMR (125 MHz, DMSO-d₆, δ): 171.2, 167.8, 139.6, 137.7, 136.3, 122.3, 116.7, 72.8, 72.0, 71.4, 71.3, 71.2, 59.1 ppm; MALDI-MS (dithranol, m/z): [M⁺] calcd 1016.5, found 1017.0; [M⁺Na⁺] calcd 1039.5, found 1039.0. GPC: 1800 (Mₙ), 1.03 (Mₖ/Mₙ).

**Synthesis of G2 Dendrimer**

NH₂-G2 dendrimer (18.2 mg, 0.02 mmol) was dissolved in NMP (2 mL). 2-[2-(2-Methoxyethoxy)ethoxy]acetyl chloride (47.2 mg, 0.24 mmol) was added to this
solution at 0 ºC under nitrogen. The solution was stirred at the temperature for 5 min, followed by 25 ºC for overnight. The reaction mixture was poured into 2% NaHCO₃ solution (20 mL) and extracted with CH₂Cl₂. The organic phase was washed with water, dried over anhydrous Na₂SO₄, and concentrated in vacuo. The residue solution was then placed on a Kugelrohr apparatus to remove remaining NMP solvent. The crude product was purified by column chromatography (CH₂Cl₂/MeOH, 15/1, v/v) to afford G2 as a light brown solid (39.8 mg, 91 %). mp (DSC): 180 ºC; ¹H NMR (500 MHz, DMSO-ᴅ₆, δ): 10.56 (s, 4H, NH), 10.39 (s, 2H, NH), 9.88 (s, 8H, NH), 8.48 (s, 2H, Ar H), 8.23 (s, 4H, Ar H), 7.98 (d, J = 1.5 Hz, 4H; Ar H), 7.88 (d, J = 2.0 Hz, 8H; Ar H), 7.75 (s, 4H, Ar H), 4.12 (s, 16H, CH₂), 3.67-3.69 (m, 16H, CH₂), 3.60-3.62 (m, 16H, CH₂), 3.57-3.58 (m, 16H, CH₂), 3.45-3.46 (m, 16H, CH₂), 3.22 (s, 24H, CH₃); ¹³C NMR (125 MHz, DMSO-ᴅ₆, δ): 168.7, 166.2, 166.0, 139.5, 138.8, 136.2, 135.0, 120.6, 115.6, 114.7, 114.2, 71.4, 70.6, 70.3, 69.7, 58.2, 58.1 ppm; MALDI-MS (dithranol, m/z): [M+Na]+ calcd 2215.9, found 2215.8; GPC: 4000 (Mₙ), 1.03 (Mₙ/Mₘ).
NH₂-G₃ dendrimer (24.7 mg, 0.012 mmol) was dissolved in NMP (3 mL). 2-[2-(2-Methoxyethoxy)ethoxy]acetyl chloride (58.7 mg, 0.30 mmol) was added to this solution at 0 ºC under nitrogen. The solution was stirred at the temperature for 5 min, followed by 25 ºC for overnight. The reaction mixture was poured into 2% NaHCO₃ solution (20 mL) and extracted with CH₂Cl₂. The organic phase was washed with water, dried over anhydrous Na₂SO₄, and concentrated in vacuo. The residue solution was then placed on a Kugelrohr apparatus to remove remaining NMP solvent. The crude product was purified by column chromatography (CH₂Cl₂/MeOH, 10/1-5/1, v/v) to afford G₃ as a light brown solid (29.8 mg, 40 %). $^1$H NMR (500 MHz, DMSO-$d₆$, δ): 10.65 (s, 4H, NH), 10.58 (s, 8H, NH), 10.39 (s, 2H,NH), 9.86 (s, 16H, NH), 8.52 (s, 2H, Ar H), 8.47 (s, 4H, Ar H), 8.23 (s, 8H, Ar H), 8.03 (s, 8H, Ar H), 8.02 (s, 4H, Ar H), 7.87 (s, 16H, Ar H), 7.71 (s, 4H, Ar H), 4.10 (s, 32H, CH₂), 3.66-3.68 (m, 32H, CH₂), 3.59-3.61 (m, 32H,
CH₂), 3.55-3.56 (m, 32H, CH₂), 3.44-3.45 (m, 32H, CH₂), 3.19 (s, 48H, CH₃); ¹³C NMR (125 MHz, DMSO-d₆, δ): 168.6, 165.9, 165.9, 141.1, 139.4, 139.0, 138.6, 136.2, 136.1, 135.3, 127.4, 120.5, 115.3, 114.6, 114.1, 71.2, 70.4, 70.2, 69.6, 58.0 ppm; MALDI-MS (dithranol, m/z): [M+Na]⁺ calcld 4568.9, found 4567.5; GPC: 6200 (Mₙ), 1.03 (Mₘ/Mₙ).

**Synthesis of 2,6-Diiodobenzene-1,4-diamine**

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2,6-Diiodo-4-nitroaniline (3.90 g, 10.0 mmol) was dispersed in ethanol (20 mL) and heated to 60 °C. Hydrazine monohydrate (5.0 mL, 100 mmol) and ruthenium (5% on carbon, 200 mg, 0.10 mmol Ru) was then added to this solution. The reaction mixture was refluxed at 80 °C for 2 h. After evaporation of the solvent, the residue was dissolved in THF (20 mL). The resulting yellow solution was filtered through celite 545. Evaporation of the solvent, followed by recrystallization from ethanol yielded 2,6-diiodobenzene-1,4-diamine as a yellow needle-like crystal (1.87 g, 52%). ¹H NMR (500 MHz, CDCl₃, δ): 7.14 (s, 2H, Ar H). LRMS (FD, m/z): [M]⁺ calcld for C₆H₆I₂N₂, 359.9; found 359.9. HRMS (ESI, m/z): [M + H]⁺ calcld for C₆H₇I₂N₂, 360.8699; found, 360.8700. Anal. calcld for C₆H₇I₂N₂: C 20.02, H 1.68, N 7.78; Found: C 19.95, H 1.42, N 7.50.
Synthesis of 2I-NH$_2$-G1 Dendrimer

2,6-Diiodobenzene-1,4-diamine (359.9 mg, 1.00 mmol) was dissolved in NMP (1.5 mL). 3,5-Bis(trifluoroacetamido)benzoyl chloride (797.7 mg, 2.20 mmol) was added to this solution at 0 ºC under nitrogen. The solution was stirred at the temperature for 5 min, followed by 25 ºC for 1 h. Then, water (0.1 mL) was added and the solution was heated at 50 ºC for 1 h. The reaction mixture was treated with hydrazine monohydrate (600 mg, 12.00 mmol) for 2 h at the same temperature and then poured into 2% NaHCO$_3$ solution (50 mL). The resultant light brown precipitate was filtered, washed with hot methanol to remove the mono-substituted product, subsequently washed with water, and finally dried at 120 ºC under vacuum to give 2I-NH$_2$-G1 as a light brown solid (267.8 mg, 43% yield). $^1$H NMR (d$_6$-DMSO, 500 MHz): $\delta = 10.08$ (s, 1H), 9.82 (s, 1H), 8.35 (s, 2H), 6.38 (d, $J = 1.5$ Hz, 2H), 6.27 (d, $J = 2.0$ Hz, 2H), 6.00 (s, 1H), 5.99 (s, 1H), 4.97 (s, 4H), 4.91 (s, 4H). $^{13}$C NMR (d$_6$-DMSO, 125 MHz): $\delta = 167.4$, 166.5, 149.2, 149.0, 137.3, 135.9, 129.4, 113.8, 102.4, 102.2, 100.2 ppm.
Synthesis of 2I-NH₂-G₂ Dendrimer

2I-NH₂-G₁ dendrimer (188.5 mg, 0.30 mmol) was dissolved in NMP (2 ml). 3,5-Bis(trifluoroacetamido)benzoyl chloride (478.6 mg, 1.32 mmol) was added to this solution at 0 °C under nitrogen. The solution was stirred at the temperature for 5 min, followed by 25 °C for 2 h. Then, water (0.1 mL) was added and the solution was heated at 50 °C for 1 h. The reaction mixture was treated with hydrazine monohydrate (360 mg, 7.20 mmol) for 2 h at the same temperature and then poured into 2% NaHCO₃ solution (50 mL). The resultant light brown precipitate was filtered, washed with water, and dried at 120 °C under vacuum to give 2I-NH₂-G₂ as a light brown solid (298.4 mg, 85% yield).

¹H NMR (d⁶-DMSO, 500 MHz): δ = 10.48 (s, 1H), 10.26, (s, 1H), 10.16 (s, 2H), 10.14 (s, 2H), 8.40 (s, 2H), 8.38 (s, 1H), 8.33 (s, 1H), 8.01 (s, 2H), 6.33 (m, 8H), 5.99 (s, 4H), 4.95 (s, 8H), 4.94 (s, 8H). ¹³C NMR (d⁶-DMSO, 125 MHz): δ = 167.4, 167.3, 165.6, 149.2, 139.8, 139.6, 137.5, 136.5, 135.2, 129.8, 115.8, 115.3, 114.9, 102.4 100.1 ppm.
2I-NH$_2$-G2 dendrimer (174.7 mg, 0.15 mmol) was dissolved in NMP (2 mL). 3,5-Bis(trifluoroacetamido)benzoyl chloride (418.6 mg, 1.32 mmol) was added to this solution at 0 °C under nitrogen. The solution was stirred at the temperature for 5 min, followed by 25 °C for 2 h. Then, water (0.1 mL) was added and the solution was heated at 50 °C for 1 h. The reaction mixture was treated with hydrazine monohydrate (360 mg, 7.20 mmol) for 2 h at the same temperature and then poured into 2% NaHCO$_3$ solution (50 mL). The resultant brown precipitate was filtered, washed with water, and dried at 120 °C under vacuum to give 2I-NH$_2$-G3 as a brown solid (318.5 mg, 95% yield). $^1$H NMR (d$_6$-DMSO, 500 MHz): $\delta = 10.61$ (s, 4H), 10.39 (s, 2H), 10.17 (s, 8H), 8.51 (s, 2H), 8.43 (s, 4H), 8.38 (s, 4H), 8.11 (s, 4H), 7.98 (s, 8H), 6.34 (s, 16H), 6.00 (s, 8H), 4.96 (s, 32H). $^{13}$C NMR (d$_6$-DMSO, 125 MHz): $\delta = 167.4$, 166.4, 149.2, 148.9, 139.7, 136.6, 135.8, 129.86, 115.6, 115.1, 114.5, 109.3, 102.4, 100.2 ppm.
Synthesis of 2I-G1 Dendrimer

2I-NH₂-G1 dendrimer (47.1 mg, 0.075 mmol) was dissolved in NMP (1 mL). 2-[2-(2-Methoxyethoxy)ethoxy]acetyl chloride (88.5 mg, 0.45 mmol) was added to this solution at 0 °C under nitrogen. The solution was stirred at the temperature for 5 min, followed by 25 °C for overnight. The reaction mixture was poured into 2% NaHCO₃ solution (20 mL) and extracted with CH₂Cl₂. The organic phase was washed with water, dried over anhydrous Na₂SO₄, and concentrated in vacuo. The residue solution was then placed on a Kugelrohr apparatus to remove remaining NMP solvent. The crude product was purified by column chromatography (CH₂Cl₂/MeOH, 15/1, v/v) to afford G1 as a light brown solid (62.3 mg, 84 %). ¹H NMR (d⁶-DMSO, 500 MHz): δ = 10.46 (s, 1H), 10.28 (s, 1H), 9.87 (s, 4H), 8.38 (s, 2H), 8.25 (s, 2H), 7.90 (s, 2H), 7.84 (s, 2H), 4.11 (s, 8H), 3.66-3.68 (m, 8H), 3.60-3.62 (m, 8H), 3.57-3.58 (m, 8H), 3.44-3.46 (m, 8H), 3.22 (s, 6H), 3.21 (s, 6H). MALDI-MS (dithranol): [M]⁻ calcd 1268.9, found 1271.0.
2I-NH₂-G2 dendrimer (58.2 mg, 0.05 mmol) was dissolved in NMP (1 mL). 2-[2-(2-Methoxyethoxy)ethoxy]acetyl chloride (117.9 mg, 0.60 mmol) was added to this solution at 0 ºC under nitrogen. The solution was stirred at the temperature for 5 min, followed by 25 ºC for overnight. The reaction mixture was poured into 2% NaHCO₃ solution (20 mL) and extracted with CH₂Cl₂. The organic phase was washed with water, dried over anhydrous Na₂SO₄, and concentrated in vacuo. The residue solution was then placed on a Kugelrohr apparatus to remove remaining NMP solvent. The crude product was purified by column chromatography (CH₂Cl₂/MeOH, 15/1, v/v) to afford G1 as a light brown solid (88.3 mg, 72 %). \(^1\)H NMR (d⁶-DMSO, 500 MHz): \(\delta = 10.58\) (s, 2H), 10.58 (s, 2H), 10.55 (s, 1H), 10.37 (s, 1H), 9.87 (s, 4H), 9.86 (s, 4H), 8.48 (s, 2H), 8.24 (s, 2H), 8.22 (s, 2H), 8.08 (s, 2H), 8.01 (s, 2H), 7.88-7.89 (m, 8H), 4.11 (s, 24H). MALDI-MS (dithranol): [M+Na]⁺ calcd 2467.7, found 2467.1.
**Synthesis of 2I-G3 Dendrimer**

2I-NH$_2$-G3 dendrimer (67.1 mg, 0.03 mmol) was dissolved in NMP (1.5 mL). 2-[2-(2-Methoxyethoxy)ethoxy]acetyl chloride (176.9 mg, 0.9 mmol) was added to this solution at 0 ºC under nitrogen. The solution was stirred at the temperature for 5 min, followed by 25 ºC for overnight. The reaction mixture was poured into 2% NaHCO$_3$ solution (20 mL) and extracted with CH$_2$Cl$_2$. The organic phase was washed with water, dried over anhydrous Na$_2$SO$_4$, and concentrated in vacuo. The residue solution was then placed on a Kugelrohr apparatus to remove remaining NMP solvent. The crude product was purified by column chromatography (CH$_2$Cl$_2$/MeOH, 10/1-5/1, v/v) to afford G1 as a light brown solid (80.5 mg, 56 %). $^1$H NMR (d$_6$-DMSO, 500 MHz): δ = 10.67 (s, 4H), 10.60 (s, 8H), 10.38 (s, 2H), 9.85 (s, 16H), 8.53 (s, 2H), 8.48 (s, 2H), 8.46 (s, 2H), 8.43 (s, 2H), 8.23 (s, 8H), 8.11 (s, 2H), 8.04 (m, 10H), 7.87 (s, 16H), 4.10 (s, 32H), 3.66-3.68 (m,
3.59-3.61 (m, 32H), 3.55-3.57 (m, 16H), 3.43-3.465 (m, 32H), 3.20 (s, 48H).

MALDI-MS (dithranol): [M+Na]^+ calcd 4820.7, found 4818.9.
CHAPTER 3
MEMBRANE MODIFICATION WITH AMPHIPHILIC AROMATIC POLYAMIDE DENDRIMERS

3.1 Introduction

A versatile approach to membrane modification that utilizes well-defined macromolecular architectures was described recently. In this approach, shape-persistent macromolecules are synthesized and directly percolated through a support film to fabricate a new generation of NF membranes. For example, rigid star amphiphiles (RSAs) with 1-2 nm hydrophobic cores and hydrophilic side chains were coated onto polyethersulfone (PES) ultrafiltration (UF) membranes to create NF membranes. Characterization of these membranes revealed that the RSAs produced a uniform, active layer atop the PES support, but also that some of the macromolecules penetrated deeper into the support, blocking pores and reducing the water flux. The rejection of arsenic(III) achieved with the RSA membranes was comparable to the rejection obtained by other NF membranes. These findings encourage us to extend this molecular deposition method to the modification of commercial polyamide NF membranes. The small pore size distribution of NF membranes prevents building block molecules breaking through, minimizing pore blocking and water flux decrease during membrane modification.

Here we survey the use of aromatic polyamide dendrimers with varied compositions and structures for NF membrane modification. We believe that by increasing
the dendrimer generation and tailoring the peripheral group chemistry, and by studying the influence of pore size distribution of the PA membranes on dendrimer deposition, it is possible to use these structurally well-defined aramide dendrimers to tune the membrane properties for optimum performance. The quality of the aramide dendrimer modified active layers was characterized by UV-Vis spectroscopy, atomic force microscopy (AFM) and Rutherford backscattering spectrometry (RBS). Membrane performance was evaluated on the basis of rejection capabilities of Rhodamine WT (R-WT), sodium chloride, barium chloride and arsenic(III). In addition, a PES-PVA film is used as a control membrane showing that structural compatibility between the dendrimer and supports plays an important role in the membrane modification process.

3.2 Percolation of Aramide Dendrimers for the PES UF Support

As for the control experiments, aramide dendrimers G1-G3 were deposited on a previously described polyvinyl alcohol (PVA) modified PES UF membrane by percolation. The PVA plugged the largest pores of the support eliminating possible advective permeation. With such support membranes, we are able to compare the aramide dendrimers with our previous results on RSAs and to survey the influence of dendrimer size on the interaction between dendrimers and support membranes.

Dendrimers G1-G3 were dissolved in methanol at approximately 6 mg/L, and percolated through the above support film. Percolated samples were collected as a function of time, and the product flux of methanol (Figure 3.1a) was measured gravimetrically with
an analytical balance.\textsuperscript{49} In the blank experiment with pure methanol solvent, an approximately constant flow rate was maintained over the whole percolation time. In great contrast, all of the aramide dendrimer solutions underwent a decrease in percolation flow to various degrees. Dendrimer G1 had the smallest effect on the percolation flow, as the flow rate slightly decreased to about 67\% of the initial value. On the other hand, both dendrimers G2 and G3 caused more dramatic reduction in the percolation flow, leading to only 20\% and 28\% of the initial value, respectively. These flow rate changes are consistent with G1 having less interaction with the membrane meaning that it likely gets washed through the support. In contrast, G2 and G3 resulted in greater permeate flux resistance, consistent with higher pore blockage of the support and/or the formation of a thin layer.\textsuperscript{53} The flow rate decreased by G2 was even larger than that by G3, possibly because the size of G2 may be better matched to the size of the support’s pores. Therefore, more G2 molecules would go inside the membrane pores than the G3 molecules leading to more blockage in the case of G2.\textsuperscript{53}
Figure 3.1. a) Permeate flow of various dendrimer methanol solutions and a blank versus sampling time for the modified PES membrane. b), c) and d) are UV/Vis spectra of permeate versus time for G1, G2, and G3 dendrimer solutions, respectively. The presence of the dendrimers in the permeate solutions is evident by absorption in the wavelength range of 295 to 350 nm. For all the three plots the line Gi+MeOH in the legend indicates the feed solution of the dendrimer in methanol.

The permeate samples collected from the percolation experiments were analyzed by UV-Vis spectroscopy to provide direct information about the amount of dendrimers in the permeate solutions versus the percolation time (Figure 3.1b-d). For dendrimer G1, the UV-Vis spectra for all samples, including feed solution and permeates, showed the same absorption intensity at 300 nm, the band associated with the $\pi-\pi^*$ transition of the aramide dendrimers. These observations indicate that G1 broke through the support at a constant
rate with little retention. In contrast, the absorption intensity for dendrimer G2 at 300 nm continuously increased over time until reaching a value close to that of the feed solution. Thus, dendrimer G2, which diffused into the support membrane pores, slowly permeated, and eventually fully broke through the support film. Finally, the absorption spectra for G3 showed intensity at 300 nm decreasing to a value close to zero. This observation suggested that most G3 dendrimers stayed within or on top of the support film after the initial penetration of a few G3 molecules in the permeate solutions. These findings show the importance of dendrimer size on membrane modification and they are consistent with the flow rate data (Figure 3.1a).

In order to identify the spatial distribution of aramide dendrimers on and within the PES-PVA support, RBS experiments were carried out to provide a depth profile of the elemental concentration using methods similar to those previously reported. Following the same procedures to prepare the membranes mentioned before, target membranes were prepared with aramide dendrimers of three generations, each of which contained two iodo groups (2I-G1, 2I-G2, and 2I-G3). Approximately one mg of the dendrimer molecules was applied to the supports during the percolation. The amount of deposited aramide dendrimers on PES-PVA membranes varied with dendrimer generations similar to the non-iodinated dendrimers noted above. Once the filtration was finished, the membrane coupons were air dried and subjected to RBS analysis, in which a 2-MeV He\(^+\) beam was directed onto the membrane surfaces with the backscattering particles providing information on elemental composition as a function of sample depth.
Figure 3.2 shows a comparison of three membranes fabricated with each dendrimer generation on the PES-PVA support. The iodine signals are identified as diagnostic peaks for the presence of iodinated aramide dendrimers on the membrane. The position and intensity of these peaks provide direct information on the status of the dendrimers. In all three cases, the dendrimer molecules impregnated the UF support, with little or no dendrimers on top. This can be inferred by the broad peaks at 1550-1800 keV, consistent with the wide distribution of dendrimer molecules inside the support. A mass balance simulation was performed to the RBS spectrum of the G3 dendrimer modified membrane using the computer program SIMNRA, and the results suggested that less than 1% of the macromolecules stayed on top of the support.

The contaminant rejection performance of the new generated membranes was studied using R-WT as a surrogate for trace organic contaminants. Fluorescence analysis indicated R-WT rejection was constant at approximately 80%, much lower than
that of 98-99% for a RSA deposited PES-PVA membrane, for the feed pressure range tested of 0.21 to 0.41 Mpa (data not shown). Analysis of the permeate samples also revealed that the smaller G1 and G2 dendrimers were breaking through the support during the rejection test. Such results were consistent with the RBS conclusions that the aramide dendrimers did not form a thin active layer on top of the UF support. Therefore, only limited rejection was obtained for the dendrimer deposited membranes with PES-PVA support.

The above findings were compared with the previous results on RSAs deposited PES-PVA membranes to obtain further understanding of the interactions between dendrimers and support membranes. The RBS spectra for all three dendrimer deposited membranes are similar to those RSA membranes of high water permeability, whereby RSAs only adsorbed inside the support without forming a detectable thin layer of pure RSA. Such high water permeability \( A_D = 5.2 \text{ m/(MPa·d)} \) was comparable to that of the G3 membrane \( A_D = 5.5 \text{ m/(MPa·d)} \) and slightly larger than that of the G2 membrane \( A_D = 4.3 \text{ m/(MPa·d)} \) (Figure 3.3). However, continuing percolation did not result in the formation of a dendrimer layer onto the support which was observed for RSAs. The possible reason for such difference is that the aramide cores of the dendrimers are more hydrophilic than the hydrophobic oligophenylene cores of the RSAs.
Figure 3.3. Experimental water flux of dendrimer-modified (G2-G3) PES-PVA membranes. Water permeability coefficients was calculated from the slope of fitted flux data and compared with the value of the RSA membranes with high water permeability ($A_D = 5.2 \text{ m/(MPa·d)}$).

At this point we reasoned that the high hydrophilicity of the aramide dendrimers could be advantageous for the modification of a commercial polyamide NF membrane. As the pore size distribution is small for the NF membranes, the aramide dendrimers can still be stabilized with a low hydrophobic interaction. The relatively high hydrophilicity might help maintain good water flux and also improve rejection to potential hydrophilic contaminants.

3.3 Percolation of Aramide Dendrimers for the Modification of TFC-S NF Membrane

The TFC-S membrane was chosen as the representative commercial polyamide NF membrane for the dendrimer modification. Compared to other NF membranes, the TFC-S membrane exhibits relatively low rejection performance for our prototype
contaminants, arsenious acid, sodium chloride, and barium chloride, etc.\textsuperscript{49,57} Improvement in contaminant rejection by the dendrimer modification should thus be discernable. Unlike the PES support, PVA modification was not used in case of the TFC-S membrane simplifying the membrane preparation process.

The modification for the TFC-S support was performed in the same manner as for the PES-PVA control support, in which the membrane was exposed to approximately one mg of the dendrimer. Permeate was again collected as a function of time, and the flux of the methanol was measured gravimetrically (Figure 3.4a). Dendrimer G1 caused a decrease in the percolation flow to about 76\% of the initial value, while dendrimers G2 and G3 caused higher flux decreases, as to 30\% and 59\% of the initial flux, respectively. In each case, the percent decrease in permeate flow was smaller for the TFC-S membrane than for the PES-PVA membrane. The result was consistent with the high ratio of macromolecule size to pore size for the TFC-S membrane, favoring a lower level pore blockage and higher flux. Absorption measurement showed that dendrimer G3 did not break through the TFC-S after initial stage of the entire percolation period (Figure 3.4d). In contrast both G1 and G2 broke through, although the quantity of G2 was less than G1 (Figure 3.4b-c). Since the absorbance intensity for permeates never reached the level for feed solutions in all three cases, it is expected that aramide dendrimer molecules accumulated and a thin layer built up on top of the TFC-S membranes. More convincing evidence of this behavior is provided by RBS measurements of iodo-labeled dendrimers.
Figure 3.4. a) Permeate flow of various dendrimer methanol solutions versus sampling time for the NF membrane TFC-S. b), c) and d) are UV/Vis spectra of permeate versus time for G1, G2, and G3 dendrimer solution respectively. The presence of the dendrimers in the permeate solutions is evident by absorption in the wavelength range of 295 to 350 nm. For all the three plots the line G\textsubscript{i}+MeOH in the legend indicates the feed solution of the dendrimer in methanol.

The RBS spectra of iodinated aramide dendrimers (2I-G\textsubscript{n}, n = 1-3) modified TFC-S membranes are shown in Figure 3.5. For all three dendrimer generations, the relatively narrow and isolated iodine peaks at ca. 1750-1800 keV indicate that the iodinated dendrimers had a narrow spatial distribution along the membrane.\textsuperscript{49} SIMNRA was then used to fit the experimental spectra in order to simulate the location of iodine atoms contained in dendrimers.\textsuperscript{55} For all three dendrimers, the best fit for these iodine peaks was
obtained by assuming that the dendrimers filled ridge-and-valley of the TFC-S polyamide active layer, and further formed a layer on top of the original active layer, which revealed that all the modified NF membranes have a “double active layer” structure.

Figure 3.5. RBS spectra of the TFC-S membranes that have been treated with iodinated aramide dendrimers. The simulation of the experimental data was performed with the program SIMNRA.55

The average thickness of the dendrimer layer atop the polyamide was calculated with the expression reported by Mi et al.14 Considering a commercial polyamide has a density ranged between 1.09 and 1.24 g/cm³, the density of the aramide dendrimers was assumed to have an average value of 1.1 g/cm³, due to the structural similarity between dendrimers and such linear polymers.58,59 Increased thickness was observed for the dendrimer layer with higher generation. The fit for the iodine peaks in the range 1750-1800 keV revealed that the dendrimers’ layer thickness was around 14 nm for G1, 25 nm for G2, and 41 nm for G3. These findings indicate that larger dendrimer molecules accumulated better on the TFC-S membranes, thus forming thicker active layers.
The aramide dendrimers that broke through the membrane absorbed preferentially in a defined region of the support, as shown by the broad RBS peaks between 1400 and 1600 keV. The low peak intensity suggested that the amount of those dendrimer molecules was relatively small. The occurrence of a gap between the deposited dendrimer active layer and the layer of dendrimer absorbed inside the support was also observed by Lu et al. for the RSA membranes.\textsuperscript{49} In the case of the RSA, RBS data were best modeled as having a thin vacant layer next to the support interface with a thickness of approximately 40 nm and RSAs being absorbed in subsequent sublayers each with a thickness of about 185 nm at a constant concentration within each sublayer. However, the separation between the dendrimer active layer peak (\textit{ca.} 1750-1800 keV) and the membrane adsorption peak (\textit{ca.} 1400-1600 keV) was more pronounce for the dendrimer modified TFC-S membranes. Furthermore, instead of forming subsequent sublayers, the single peak between 1400 and 1600 keV revealed that only one sublayer existed in the PS support. The three RBS spectra are thus analyzed as low-level accumulation of dendrimers inside the TFC-S NF membranes and subsequent formation of an additional aramide dendrimer active layer.

The double active layer structured TFC-S membranes were further characterized by AFM to study the surface morphology and roughness.\textsuperscript{60} Generally, the surface roughness increased as the dendrimer generation increased. The roughness change was especially prevalent from the membrane with dendrimer G1 active layer to the one with G2 layer. There were more irregularities and protuberances on the membrane surface with G2 or G3 active layer than other ones (see Figure 3.6 for representative AFM images).
Figure 3.6. Representative AFM topography comparison of membrane surface roughness: a) commercial TFC-S membrane; b) TFC-S membrane with 1 mg dendrimer G1 active layer; c) TFC-S membrane with 1 mg dendrimer G2 active layer; d) TFC-S membrane with 1 mg dendrimer G3 active layer; e) TFC-S membrane with 0.05 mg dendrimer G2 active layer; f) TFC-S membrane with 0.05 mg dendrimer G3 active layer.

A more accurate evaluation of the surface roughness is provided by the root-mean-square (RMS) roughness, which was obtained by scanning an area of 10×10 μm² with an AFM in tapping mode (Table 3.1). The RMS roughness for the commercial TFC-S membrane was 25.9 nm, and was 32.0 nm for the membrane with G1 active layer.
The values increased significantly for the membrane with G2 and G3 active layers, being measured as 41.3 and 44.4 nm respectively. The AFM analysis revealed an uneven distribution of dendrimers in the active layer, probably due to the agglomeration with each other.

**Table 3.1:** Root-mean-square roughness values for unmodified and aramide dendrimer-modified (1 mg to 0.05 mg) TFC-S membranes collected from AFM measurements

<table>
<thead>
<tr>
<th>Membrane</th>
<th>RMS Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmodified TFC-S</td>
<td>25.9 ± 1.0</td>
</tr>
<tr>
<td>TFC-S modified with 1mg G1</td>
<td>32.0</td>
</tr>
<tr>
<td>TFC-S modified with 1mg G2</td>
<td>41.3</td>
</tr>
<tr>
<td>TFC-S modified with 1mg G3</td>
<td>44.4</td>
</tr>
<tr>
<td>TFC-S modified with 0.05 mg G2</td>
<td>31.1 ± 4.8</td>
</tr>
<tr>
<td>TFC-S modified with 0.05 mg G3</td>
<td>34.0 ± 1.6</td>
</tr>
</tbody>
</table>

The modified TFC-S membranes’ performance was evaluated by measuring their transport properties including water flux and rejection of arsenious acid, a representative small, neutral contaminant (full details reported elsewhere\(^6\)). It was found that dendrimer G1 modified membrane was not stable during the rejection test, as small size G1
broke though the pores of the NF active layer. However, for both G2 and G3 modified membranes, significantly increased rejection to arsenic(III) was measured. Rejection up to 70% was observed compared to the original membrane rejection of ca. 20%. Considering that only one mg dendrimer molecules was deposited on a 14 cm² membrane coupon, the density of dendrimer on TFC-S membrane could be estimated as 71 μg/cm². Although a significant improvement in rejection performance was observed for dendrimer-modified membranes, the water flux dropped 80% from the original TFC-S membrane. Because the water flux is inversely proportional to the thickness of the active layer, we optimized the amount of dendrimers deposited for specific contaminants to improve the solute rejection while maintaining high water flux.

In a systematic study, dendrimers G2 and G3 with amounts 0.1 mg, 0.05 mg, 0.03 mg, 0.01 mg were deposited on the TFC-S membrane by percolation, respectively. The densities of dendrimer on TFC-S membrane were then estimated as 7.1 μg/cm², 3.6 μg/cm², 2.1 μg/cm², 0.71 μg/cm², respectively. AFM images were collected for the TFC-S membranes modified with 0.05 mg dendrimers of these two generations (Supporting Information). The RMS roughness for these membranes was measured as 31.1 nm, 34.0 nm, respectively (Table 3.1). These values were slightly larger than that of the original membrane and relatively close to the value of one mg G1 modified membrane. Such result suggested that the tiny amount of dendrimer deposited mainly filled the ridge-and-valley of the TFC-S polyamide active layer, which was confirmed by RBS measurement (Figure 3.7).
Figure 3.7. RBS Spectra of the TFC-S membranes modified with dendrimer G3. The green curve corresponds to modification with 1 mg G3, the pink curve corresponds to modification with 0.1 mg G3. The simulation of the experimental data was performed with the program SIMNRA.  

Figure 3.8 shows the rejection of modified TFC-S membranes for prototypical water contaminants. Membrane performance was measured for each of the solutes with the TFC-S membrane without modification (blank sample) and for the same NF membrane modified with different amount and different type of dendrimers. In order to compare the membrane rejection between various contaminants, all data were acquired with a permeate flow of 0.4 m/d. As for R-WT, even 0.71 μg/cm² dendrimer deposition on the TFC-S membrane increased the rejection from ca. 98.3% to over 99.4%, which means the contaminant concentration in the permeate was almost one order smaller than the unmodified membranes. Specifically, G2 membrane showed improved rejection as the dendrimer amount increased, while G3 membrane showed maxima rejection at 99.8% as low as the 0.71 μg/cm² deposition. Figure 8b-c shows the improvement for the modified
membranes on salt rejection. With a 7.1 \( \mu \text{g/cm}^2 \) dendrimer deposition, both NaCl and BaCl\(_2\) could be rejected to about 90\%, which is not common for a low pressure NF membrane. Interestingly, dendrimer G2 showed a higher rejection to NaCl than G3, while the opposite trend was found for the BaCl\(_2\) rejection. Finally, the rejection of arsenic(III) by the membrane with either G2 or G3 modification was not significantly increased at the low modification level (0.71 \( \mu \text{g/cm}^2 \)), each of which increased from \textit{ca.} 20\% to 30\%. 
Figure 3.8. Rejection performance of G2 or G3 modified TFC-S membranes to prototypical contaminants. All data were acquired with a permeate flow of 0.4 m/d.
3.4 Experimental Section

3.4.1 Materials and Methods

PES UF membrane (model HFK-328) and TFC-S NF membrane were purchased from Koch Membrane Systems Inc., Wilmington, MA. Circular coupons with effective surface area of approximately 14 cm² were cut and installed in the dead-end filtration reactor. PES UF membrane with nominal molecular weight cutoff of 900-2300 Da was pretreated with PVA using a slightly modified procedure previously reported. TFC-S membrane was rinsed with distilled deionized (DDI) water (MP-11A, Barnstead, Boston MA) and stored in DDI water until needed for use. Rhodamine WT (R-WT, received as 35% (w/v) solution, Turner Designs, Sunnyvale, CA), As (III) (H₃AsO₃, received as NaAsO₂ (99%), Sigma-Aldrich), sodium chloride (99.5% NaCl, Sigma-Aldrich) and barium chloride (99% BaCl₂·2H₂O, Sigma-Aldrich) were selected as solutes to test membrane performance. The UV-Vis spectra were recorded on a Shimadzu (model UV-2401PC) spectrophotometer using a 1-cm quartz cell. Fluorescence analysis was performed with a Shimadzu (RF-5301 PC, Shimadzu Scientific Instruments Inc.) spectrofluorophotometer using a 1-cm quartz cell with excitation and emission wavelengths at 550 and 580 nm, respectively.

3.4.2 PES-PVA Support Membrane Preparation

PES-PVA support membrane was prepared by a slightly modified method described previously. The PES membrane was installed in the cell of the membrane
filtration system and preconditioned by filtering DDI water (MP-11A, Barnstead, Boston MA) at a pressure of 0.41 MPa (60 psi) for an hour, during which the product water flux was recorded. Afterward, 50 mL of methanol were filtered also at 0.41 MPa through the PES membrane. Then, an aqueous PVA solution at a concentration of 1 mg/L was prepared by dissolving the polymer (Sigma-Aldrich, 99%+ hydrolyzed, 85 000-124 000 Daltons) in a sealed glass bottle with distilled water and magnetically stirred at 80 °C for 12 h. The last step in the support modification was a filtration of the PVA solution at 0.41 MPa. The PVA addition was stopped when the fluxed reached a level of approximately 6 m/d. Excess PVA on the surface was then removed by rinsing the membrane with DDI water. Subsequently the PVA was cross-linked by filtering an aqueous solution containing 300 mg/L of glutaraldehyde and 2.5 mg/L of acetic acid at 0.41 MPa for 30 seconds and then the membrane was dipped and left overnight in the same solution.

3.4.3 Membrane Modification by Aramide Dendrimers

All membranes were modified and tested using a bench-scale dead-end membrane filtration system (M8400, Millipore Co, Bedford, MA). Circular coupons of support membrane (PES-PVA film or TFC-S film) were cut and installed in such filtration reactor. The transmembrane pressure was set at 0.41 MPa (60 psi). The active layers were prepared by filtering the methanol solutions containing approximately 6 mg/L of each aramide dendrimer (G1-G3) through the above support film at room temperature. The target mass of dendrimers deposited on TFC-S support was 1 mg. WINWEDGE software
(TAL Technologies Inc., Philadelphia, PA) was used for real-time data collection of permeate flux of the methanol solution, which was measured gravimetrically with an analytical balance (BP211S, Sartorius Co., Edgewood, NY) connected to a computer. The amounts of dendrimers in permeate samples over time were monitored using a UV-Vis spectrophotometer (UV-2401 PC, Shimadzu, Japan).

3.4.4 Membrane Characterization

Membranes modified with iodinated aramide dendrimers based on either PES-PVA or TFC-S supports were characterized by RBS. The double active layer structured NF membranes based on the TFC-S support were further characterized by AFM.

(1) RBS. RBS analysis were performed at room temperature with a 2-MeV \( \text{He}^+ \) beam generated by a Van de Graaff accelerator. The incident, scattering and exit angles of the beam were 22.5°, 52.5°, and 150° respectively; the beam current was ca. 80 nA, and the beam diameter was 3 mm. The sample was scanned with the ion beam to limit the fluence of \( \text{He}^+ \) ions at any given area of the sample surface to a threshold value of \( 3 \times 10^{14} \text{ cm}^2 \). The RBS detector resolution was measured by testing a standard sample (5 Å thick gold film, and 2 nm cupper atop a layer of silicon). RBS data analyses were carried out with SIMNRA software.

(2) AFM. Membranes were examined using an atomic force microscope (model Dimension 3100, Digital Instruments/Veeco). The instrument was operated in a tapping
mode using silicon tips with nanometer scale resolution in air. The tip used for surface roughness analysis had a radius of 10 nm (BS-Tap300, Al coating, Nanoscience Instruments). For detection of ultrafine features, a 2 nm tip was used. Wet samples were dried at room temperature overnight and further irradiated with IR light for 20 min prior to testing. AFM images were obtained for the commercial TFC-S membrane and TFC-S membrane with dendrimer active layers (G1-G3).

3.4.5 Membrane Performance Analysis

The performance of prepared NF membranes was evaluated by measuring their rejection of R-WT, NaCl, BaCl₂, and arsenic(III) at a constant permeate flow of 0.4 m/d at room temperature. Feed solutions of R-WT were prepared by dissolving this organic molecule in DDI to a concentration of 2.5 mg/L and adjusting the pH to 7.5. Feed solutions of NaCl and BaCl₂ were prepared by dissolving the each salt in DDI to a concentration of 400 mg/L. Feed solutions of arsenic(III) were prepared by dissolving NaAsO₂ (99% purity, Sigma-Aldrich) in DDI water. The pH was adjusted to 6 to ensure that all the arsenic was in the neutral arsenious acid (H₃AsO₃) form. The feed solution concentration was 4 mg/L as As. Magnetic stirring was used for minimizing solute concentration polarization during rejection testing. The concentration of R-WT in the feed and product water was measured by fluorescence (excitation/emission wavelengths 550/580 nm). Arsenious acid was analyzed by a colorimetric method using the UV-Vis spectrophotometer (UV-2401PC, Shimadzu, Japan). The concentration of NaCl and
BaCl$_2$ in the feed and permeate was analyzed by ion chromatography (Dionex IC S-2000; Dionex ion Pac As 18 column, 36 mM KOH as eluent, 1 mL/min eluent flow rate, 25 mL injection loop). Solute rejection was calculated with the expression $SR = (1 - c_p/c_f) \times 100\%$ where $c_f$ and $c_p$ are the solute concentrations in the feed and product water, respectively. The rejection performance data were analyzed by parameter fitting method using MATLAB software.
CHAPTER 4
CONCLUSIONS AND FUTURE WORK

4.1 Conclusions

In conclusion, our present research effort focused on utilizing shape-persistent dendritic architectures to modify a commercial NF membrane. Amphiphilic aromatic polyamide dendrimers (G1-G3) have been synthesized via a divergent approach and used for NF membrane modification by direct percolation. A PES-PVA film as control membrane and a commercial TFC-S NF membrane were used showing that structural compatibility between the dendrimer and supports plays an important role in the membrane modification process. All dendrimers broke through the PES-PVA UF support due to their hydrophilicity; however, they all formed additional active layers on top of the TFC-S NF membrane in varying thickness. The dendrimer size had determinative effects in the formation of the new active layer, as increasing the dendrimer generation resulted in changes of percolation behaviors, such as breakthrough of permeates and percolation flux. The membrane structures were further investigated by RBS and AFM techniques, suggesting a double active layer structure for the modified TFC-S membranes. Membrane performance was evaluated on the basis of rejection abilities of a variety of water contaminants having a range of sizes and chemistry. The amount of deposited dendrimers was optimized to improve the solute rejection while minimizing water flux losses. The next research phase will focus on stabilizing the dendrimers on the support.
4.2 Future Work

Based on the promising results shown above, a key goal of next research stage will be to increase the stability of physically adsorbed aramide dendrimers on TFC-S membrane, since the current major stabilization factor comes from the hydrophobic interaction between the dendrimer and the support. Thus, in order to obtain a membrane with high contaminant rejection in a long operating period while maintaining comparable water permeability, it is important to immobilize minimal amount of aramide dendrimers on the polyamide NF membrane by strong interactions, such as electrostatic interaction and covalent bonding.

The research in Mariñas group showed that most commercially available polyamide NF membrane has unreacted carboxyl groups in the active layer. The oxygen-to-nitrogen (O/N) ratio obtained from RBS measured the degree of polyamide cross-linking, as a high O/N value indicates greater presence of carboxyl groups. Specifically, the O/N ratio for the ESNA membrane was 1.1 which was close to that of fully cross-linked polyamide, while the value 1.4 was obtained for the TFC-S membranes, which would be consistent with incomplete polyamide cross-linking. Therefore, the TFC-S membrane will be used in the following research as it has more carboxyl groups as the reacting units for membrane modification.

Under normal operating pH conditions, TFC-S membranes are negatively charged due to the excess carboxyl groups on the surface. It is expected that positively charged dendrimers would have strong electrostatic interaction with the membranes. Recently,
Aida and coworkers showed dendritic molecules carrying multiple guanidinium (Gu⁺) ion pendants served as molecular glues because of the salt-bridge formation between the Gu⁺ ions and certain oxyanions. This concept inspires us to prepare aramide dendrimers with multiple sticky Gu⁺ pendants. As the dendrimer generation grows, more Gu⁺ pendants exist, and thus stronger interaction between the dendrimer and the TFC-S membranes. High stability and long operating time are expected for the new membrane with such modification.

Scheme 4.1. Aramide dendrimer G₁-Gu⁺ with positive charged pendants
Another strategy for dendrimer stabilization is the amide bond formation, which includes the activation of the carboxyl group with a coupling reagent followed by the aminolysis with corresponding amine. Among all potential methods for amide bonding, the EDC coupling attracts our interests due to the high efficiency, solvent compatibility and easy work-up. To couple with the NF membranes, amine functionality will be introduced on the dendrimers first. These amine terminated dendrimers will then react with activated TFC-S membrane for modification. The modified NF membranes are planned to be characterized by ATR-FTIR, contact angle measurement, AFM, elemental analysis and RBS.
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