

**ENGINEERING OF RECYCLABLE 6FDA-BASED POLYIMIDE
MEMBRANES FOR DESALINATION IN
MEMBRANE DISTILLATION**

BY

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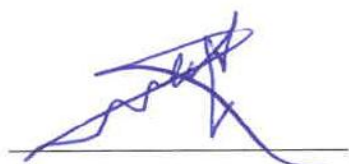
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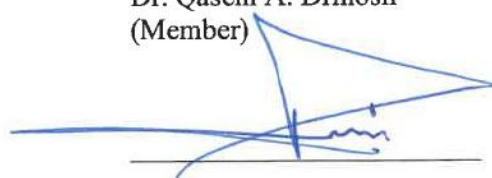
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DEDICATION

I wish to dedicate this work to my mother, who has taught me the value of dedication and hard work and has been a source of motivation and inspiration in my life endeavors.

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First and foremost, I am grateful to Almighty Allah (S.W.A) for giving me the patience and resilience to conduct this research successfully and overcome the challenges I encountered.

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May 2025 |

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LIST OF ABBREVIATIONS

MD: Membrane Distillation

6FDA: 4,4'-(Hexafluoroisopropylidene) diphtalic anhydride

*m*PDA: *m*-phenylenediamine

AGMD: Air Gap Membrane Distillation

SEM: Scanning Electron Microscopy

NIPS: Non-solvent Induced Phase Separation

VIPS: Vapor-induced Phase Separation

AFM: Atomic Force Microscopy

TGA: Thermogravimetric Analysis

WXRD: Wide-angle X-ray Diffraction

NMR: Nuclear Magnetic Resonance

FTIR: Fourier Transform Infrared spectroscopy

DABA: Diamino benzoic acid

DMF: Dimethyl formamide

DI: Deionized water

PVDF: Polyvinylidene fluoride

PTFE: Polytetrafluoroethylene

PP: Polypropylene

PE: Polyethylene

rGO: reduced graphene oxide

PES: Polyethersulfone

GO: Graphene oxide

ODA: Octadecylamine

CNTs: Carbon nanotubes

RO: Reverse osmosis

UF: Ultrafiltration

NF: Nanofiltration |

ABSTRACT

Full Name : Ameenu Yakubu

Thesis Title : Engineering of Recyclable 6FDA-Based Polyimide Membranes for Desalination in Membrane Distillation

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Desalination and water recycling have long been identified as an ideal cornerstone to handle the major challenge of water scarcity by providing safe and clean water, especially in places where seawater is the major source of fresh water. Membrane distillation (MD) is a membrane-based process that has attracted huge research interest. However, despite growing research interest in developing membrane materials for MD applications, efforts remain focused on modifying existing membranes, which increases costs and raises concerns about the toxicity of modifying agents, particularly long-chain fluoroalkyl substances and nanoparticles. Surface engineering offers significant potential for enhancing the properties and performance of polymeric membranes. For this purpose, numerous methods of modification have been investigated. However, the complexity of these approaches has limited their practical application in membrane development. In this study, we developed polyimide membranes from 4,4'-(hexafluoroisopropylidene) diphthalic anhydride and *m*-phenylenediamine (6FDA-*m*PDA) for desalinating highly saline water (70,000 ppm), achieving enhanced properties and performance for MD

applications. Due to its relatively quick demixing process, NIPS generated membranes with a sponge-like cross-section (known to contribute to mass transfer resistance), smooth surfaces, and low surface porosity. Among the NIPS-based membranes, N_13 ultimately demonstrated the best performance, with a maximum flux of $13.03 \text{ kg m}^{-2} \text{ h}^{-1}$ and a consistent salt rejection of 99.98%. Additionally, to induce a slower and more uniform phase inversion and enhance the performance of the polyimide-based membranes, we introduced a straightforward surface engineering process employing vapor-induced phase separation (VIPS). Moreover, we investigated the influence of polymer concentrations and vapor type on membrane structure and performance. A prolonged exposure period produced the ideal membrane porosity with water vapor. In contrast, membranes with a higher porosity and a shorter exposure period were obtained by adding ethanol to form a binary non-solvent vapor, and this motivated the use of ethanol as the non-solvent. Interestingly, membrane hydrophobicity and permeability were improved, and membrane porosity was further increased in addition to changing the surface and cross-sectional structure from finger to sponge-like. Notably, membranes prepared using ethanol vapor exhibited exceptional characteristics, with the highest water contact angle (WCA) reaching 150° with a flux of $26.26 \text{ kg m}^{-2} \text{ h}^{-1}$ and a salt rejection of 99.98% in air gap membrane distillation. The resulting membrane morphologies were characterized using various surface analysis techniques, including scanning electron microscopy (SEM), energy-dispersive X-ray (EDX), and atomic force microscopy (AFM). The combination of VIPS with advanced polyimides holds promise for developing high-performance membranes for desalination applications.

ملخص الرسالة

الاسم الكامل: أمينو يعقوب

عنوان الرسالة: هندسة أغشية بوليميد قابلة لإعادة التدوير قائمة على FDA 6 لتحلية المياه باستخدام التقطير الغشائي

التخصص: علوم وهندسة المواد

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تُعد تحلية المياه وإعادة تدويرها حجر الزاوية المثالي منذ زمن بعيد لمواجهة التحدي الكبير المتمثل في ندرة المياه، من خلال توفير مياه آمنة ونظيفة، خاصة في المناطق التي يُعتبر فيها ماء البحر المصدر الرئيسي للمياه العذبة. يُعد التقطير الغشائي عملية تعتمد على الأغشية وقد حظيت باهتمام بحثي كبير. ومع ذلك، وعلى الرغم من تزايد الجهود البحثية لتطوير مواد أغشية مخصصة لتطبيقات التقطير الغشائي، لا تزال الجهود تتركز على تعديل الأغشية الحالية، مما يؤدي إلى ارتفاع التكاليف ويثير القلق بشأن سمية عوامل التعديل، وخصوصاً المواد الفلوروكربونية السلسلة والجسيمات النانوية. توفر هندسة السطح إمكانيات كبيرة لتحسين خصائص وأداء الأغشية البوليمرية، وقد تم استكشاف العديد من طرق التعديل لهذا الغرض. ومع ذلك، فإن تعقيد هذه الطرق حدّ من تطبيقها العملي في تطوير الأغشية. في هذه الدراسة، قمنا بتطوير الأغشية بوليميد باستخدام 4,4'- (هكسافلوروأيزوبروبيلدين) أنهيدريد دي فتاليك وميتا-فينيلين دي أمين (6FDA-mpDA) لتحلية مياه عالية الملوحة (70,000 جزء في المليون)، محققين خصائص محسنة وأداءً عالياً لتطبيقات التقطير الغشائي. ونظراً لأن عملية الفصل الطوري غير المحفز (NIPS) تتسم بسرعة الخلط النسبي، فقد نتج عنها أغشية ذات مقطع عرضي إسفنجي (والذي يُعرف بمساهمته في مقاومة انتقال الكتلة)، بالإضافة إلى أسطح ناعمة ومسامية سطحية منخفضة. من بين أغشية NIPS، أظهر الغشاء N_13 أفضل أداء، حيث بلغ التدفق الأقصى له 13.03 كجم/م²/ساعة مع معدل رفض للأملاح ثابت بنسبة 99.98%. وبهدف تحفيز انقلاب طوري أبطأ وأكثر تجانساً وتحسين أداء أغشية البوليميد، قمنا بإدخال عملية بسيطة لهندسة السطح باستخدام فصل الطور المحفز بالبخار. كما درسنا تأثير تركيزات البوليمر ونوع البخار على بنية الغشاء وأدائه. وقد أدى التعريض لفترة طويلة لبخار الماء إلى إنتاج بنية مسامية مثالية. وعلى النقيض، فإن استخدام الإيثانول لتكوين بخار مزدوج (مع الماء) نتج عنه أغشية ذات مسامية أعلى ووقت تعريض أقصر.

وقد تم اختيار الإيثانول كمذيب غير محبب نظراً لهذا التأثير. ومن المثير للاهتمام أن قابلية الغشاء للماء وزاوية التلامس قد تحسنت، كما ازدادت المسامية، وتحول التركيب السطحي والمقطعي من الشكل الإصبعي إلى الشكل الإسفنجي. ومن الجدير بالذكر أن الأغشية المحضرة باستخدام بخار الإيثانول أظهرت خصائص استثنائية، حيث بلغت زاوية التلامس مع الماء (WCA) أقصاها عند 150°، مع تدفق قدره 26.26 كجم/م²/ساعة ونسبة رفض للأملاح بلغت 99.98% في نظام التقطير الغشائي بالهواء الفاصل. وقد تم توصيف البنى الناتجة للأغشية باستخدام تقنيات تحليل سطحية متعددة، بما في ذلك المجهر الإلكتروني الماسح، والتحليل الطيفي بالأشعة السينية المشتتة للطاقة، والمجهر القوة الذرية. إن الجمع بين تقنية الطور المحفز بالبخر والبوليميدات المتقدمة يُظهر وعداً كبيراً في تطوير أغشية عالية الأداء لتطبيقات تحلية المياه.

CHAPTER 1

INTRODUCTION

1.1 Background and motivation

Although water accounts for about $\frac{3}{4}$ of the Earth, its scarcity still poses a major threat to survival [1], especially in rural and dry areas. Nevertheless, this is not surprising because out of the 2.5% of the portable water, only 1% is easily accessible [2]. The sustainability of clean and portable water supply is, therefore, among the major problems the world is currently experiencing, especially with the increase in demand because of population expansion [2–4]. Desalination and water recycling have long been recognized as a practical cornerstone to handling this major challenge by providing safe and clean water in many dry places where seawater is the major source of freshwater [5]. Desalination may be the most practical method for supplying fresh water, allowing for sustainable development, and supporting population expansion in this contemporary civilization, especially for water-scarce areas like the Middle East and North Africa [6].

1.2 Membrane technology

Chemical separations are thought to be responsible for almost half of the energy used in the US industry and 10–15% of the country's overall energy consumption. Interestingly, 80% of these separation methods might become ten times more energy-efficient if

alternative heat-free technologies are developed. In recent decades, membrane science has gained significant attention due to the increasing competitiveness of membrane processes compared to traditional methods for separation. These methods offer prospective solutions for desalination and water treatment while addressing pollution and water scarcity [7]. Moreover, they are one of the most significant and well-known methods for desalination and wastewater treatment. In addition to the energy efficiency associated with membrane separation, it offers other advantages like low cost and eco-friendliness compared to the conventional methods [8], making it a promising technology [9,10]. A membrane is defined as a thin barrier (as thin as 10 nm) that selectively allows something to pass through it while preventing another, as depicted in **Figure 1a**. This can be based on the size or chemical interaction of the separating species and the membrane. Porous polymeric membranes have a track record in numerous fields, including chemical separation [11], water desalination [12], food processing/manufacturing [13], chemical catalysis [14], and energy storage [15] (Some examples are summarized in **Figure 1b**. Despite their wide range of applications, they still face challenges due to the need to balance selectivity and permeability, issues with fouling, and limited adaptability to handle variable and harsh environments [16]. The most common techniques employing polymer membranes for desalination are reverse osmosis, ultrafiltration, and nanofiltration, amongst others. In all these processes, the membrane is the crucial element, especially in a reverse osmosis desalination plant, as its performance in separation is primarily dictated by it [17]. While pressure-driven processes such as nanofiltration and reverse osmosis have shown effectiveness for desalination [18] [19], their energy demand and maintenance cost have hindered their widespread application in practice [20,21]. Moreover, the chemicals

required to clean and restore the membrane, as well as membrane fouling in RO, lead to increased detrimental costs. Although thermal separation is considered to be the best option in terms of salt removal efficiency, the large quantity of fuel that is required to heat the system to evaporate the salty water leads to a high desalination cost [9].

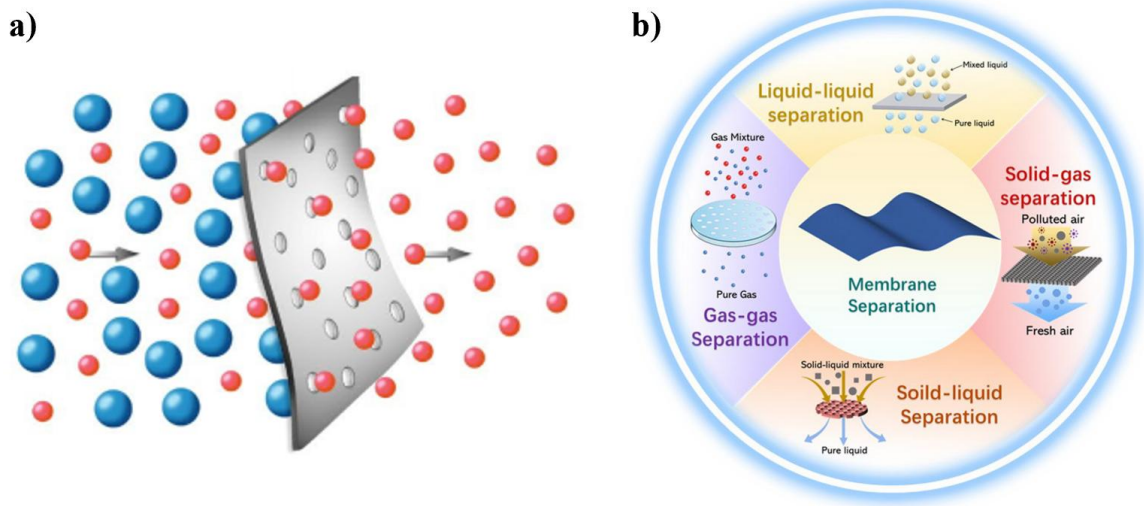


Figure 1. Membrane separation: **a)** schematic of a membrane, **b)** different types of membrane separation [22,23].

1.3 Membrane distillation for desalination

As an alternative method, a non-isothermal membrane process that has gained a lot of attention recently is membrane distillation (MD) [22,23], particularly for the desalination of saline water [24–26]. The investigations of air flux through a porous medium through a non-isothermal process started in 1873, while liquid transport was first established in 1907. Initially, this process was carried out through hydrophilic and dense membranes and did not include liquid/vapor phase transition, and was referred to as

thermo-osmosis. About half a decade later, porous hydrophobic membranes were employed, and the non-isothermal vapor transport was investigated through dry pores, and the phenomenon was known as MD [27]. In an MD process, vapor molecules are the only components permitted to flow across the membrane [22,28–31]. Separation thus occurs when the hydrophobic membrane's surfaces are subjected to pressure differences brought on by temperature differences [32]. When compared to other processes, the MD method offers special benefits. For example, operating pressure is lower, which increases process safety and lowers operational costs. Also, the temperature of the feed does not need to get to the point of boiling, and it has a low-temperature requirement [33,34]. Despite its advantages, several obstacles and constraints have hindered the development of industrial-scale MD systems. This includes its low flux compared to other desalination processes, concentration polarization, fouling, and wetting, which reduce the reliability and long-term performance of the process [35]. Therefore, industrialization of the process has become limited [26]. In the conventional MD processes, direct contact membrane distillation (DCMD), air-gap membrane distillation (AGMD), sweeping gas membrane distillation (SGMD), and vacuum membrane distillation (VMD) are the four primary configurations that are widely employed [36–39]. The AGMD configuration creates an air gap between the membrane and the coolant side. Membranes tested with this setup have low flux associated with low thermal efficiency [42]. More about different MD configurations will be discussed in Chapter 2.

1.4 Introduction to 6FDA-Based Polyimides

Polyimides are a class of high-performance polymers that were first developed in 1955 and commercialized in the 1960s [43]. Over the past two decades, the polyimide family has grown in significance for gas separation and subsequent pervaporation, and they have proven to be ideal materials for producing asymmetric membranes [44]. The inherent microporosity, thermal, mechanical, and chemical reliability of polyimide membranes, particularly the 6FDA-based polyimides, allow them to have outstanding intrinsic separation capabilities [45,46]. They belong to high-temperature polymers with exceptional film-forming abilities and balanced chemical and mechanical properties [47]. The flexibility of polyimide chemistry, its straightforward synthesis, and uncomplicated customization offer polymer and membrane researchers the effective means to adjust the molecular structure of polyimides, achieving desired physical and chemical characteristics and high separation efficiency [47]. Because of their unique benefits, ease of processing, and ideal gas separation performance, polymeric membranes, particularly the aromatic polyimide (PI) ones, have been thoroughly studied for molecular separation, especially gas separation [48–50].

1.5 Research problem and purpose

1.5.1 Challenges with conventional membranes in MD

Membrane fouling and wetting are among the critical issues that diminish the performance of membranes in MD. The loss in membrane hydrophobicity usually results in wetting, which allows foulants to pass through the membrane alongside the permeate.

The feed solution penetrates the membrane pores when the hydrostatic pressure of the transmembrane is greater than the liquid entry pressure or when solutions containing organic or inorganic pollutants absorb or deposit on the surface of the membrane. Following membrane wetting, fouling and scaling occur due to the accumulation of microorganisms and organic species on the surface of the membrane. Depending upon the nature of the pore wetting, it can result in either a decrease in permeate flux in the case of partial wetting or a decline in permeate quality when the membrane is fully wetted. Another critical challenge is the thermal stability of the membranes over a long period of exposure to a harsh environment of chemicals and pollutants, resulting in the degradation of membrane properties and subsequently diminishing their separation efficiency. Overcoming these challenges will pave the way for MD to compete with the current membrane separation process and contribute to providing environmental solutions.

1.5.2 Research purpose

While MD continues to attract interest owing to its theoretical 100 % salt rejection and low energy requirement compared to other membrane separation processes, the issues discussed in the problem statement still hinder the process's scalability for industrial applications. After a comprehensive literature review, our study discovered that research to address these critical issues mainly centered around modifying the existing polymeric membranes, as shown in **Figure 2**. Although this method has yielded membranes with enhanced characteristics and performance, its practicality in membrane development, particularly for industrial applications, has been constrained by its intricacy. Furthermore, the cost, toxicity, and long-term stability of the chemicals employed for the modification are seldom considered. Therefore, creating high-performance, sustainable membranes will

enable MD to compete with existing separation technologies. Hence, the current research revolves around straightforward membrane engineering of advanced recyclable polyimide membranes for enhanced desalination in membrane distillation. This research aims to contribute to providing solutions in addressing the current challenges in MD without the need for additional chemical modification, aiming to reduce cost and the toxicity concern of long-chain fluoroalkyl substances and nanomaterials, making the technology sustainable and practically viable for large-scale industrial applications.

1.6 Importance of materials development for MD applications

Being a thermally driven process dependent on hydrophobic membranes to achieve desalination or water purification, the separation efficiency of MD and the viability of scaling up the process largely depend on the properties and performance of the membrane materials themselves. Innovative advances in membrane materials are critical to the progress of MD since they profoundly affect the process's efficiency, stability, and versatility. Advanced materials with improved characteristics, including surface hydrophobicity, pore size, and high thermal stability, contribute towards better water vapor transport and consistent protection against fouling or scaling over the long term. The most promising thematic areas contributing to developing selective membranes, energy-efficient material processing, and recyclable materials include engineered fibers, surface-engineered polymers, and green materials. The number of publications from the most common polymers utilized for MD applications over the past 20 years is summarized in **Figure 2**. It can be observed that among these polymers with a total publication of 1781, PVDF and PTFE have the highest number of publications, with 1104 and 473, respectively. It is worth

noting that the research efforts of membrane scientists towards developing ideal membranes for MD have been focused on the modification of these few polymers, while very minimal attention has been given to new materials.

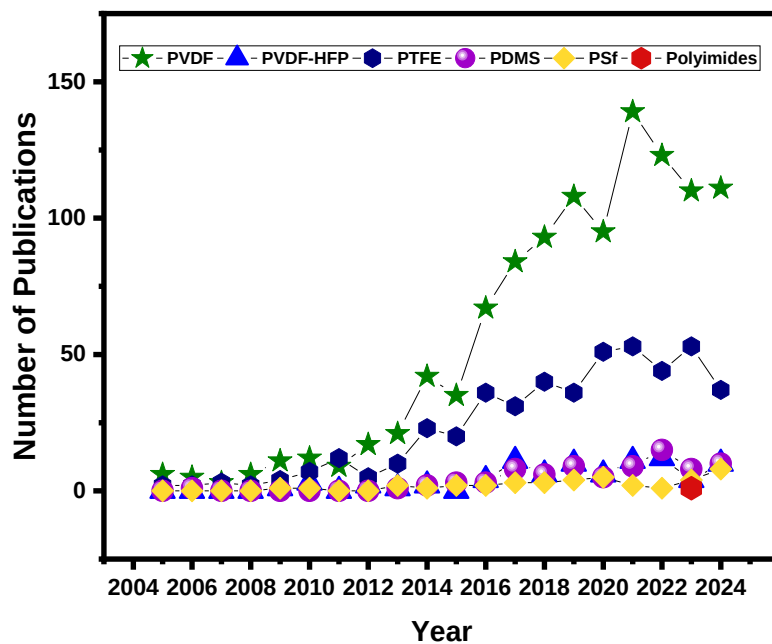


Figure 2. Number of published articles from the most reported polymer materials applied in membrane distillation from the past two decades in Web of Science (obtained by searching the keywords “polymer name” and “membrane distillation”). Total articles (1781).

While these materials have been used to fabricate membranes with outstanding properties and reasonable performance, most of these fabrication methods are complex, time, and energy-consuming. Of more concern is the modification utilizing toxic materials. As a result, this not only increases the cost of the membrane fabrication process and challenges its viability for large-scale applications, but also poses the risk of leaching the modifying material. To this end, developing new materials with intrinsic properties required for MD applications without the need for extensive use of chemicals and intricate steps will make

the technology ubiquitous and sustainable for industrial applications. In addition, developing green materials will ensure the sustainability of the process of producing clean water. By overcoming the limitations of prior materials, these innovations bring MD closer to achieving advanced, cost-effective, and scalable solutions to worldwide water purification and desalination problems.

1.7 Objectives and research questions

1.7.1 Thesis goals

This thesis has been designed to achieve the following objectives and answer the subsequent research questions.

1. To synthesize a recyclable polyimide derived from 4,4'-(Hexafluoroisopropylidene) diphtalic anhydride (6FDA) and *m*-phenylenediamine (mPDA).
2. To engineer membranes from the synthesized polymer and optimize properties such as hydrophobicity, controlled porosity, thickness, surface morphology, and mechanical strength suitable for MD applications
3. To evaluate the efficiency and performance of the membranes in membrane distillation and test their potential in real-world desalination applications.
4. To benchmark the performance of the advanced polyimide membranes against existing commercial membranes used in MD or other separation processes.

This thesis intends to answer some research questions: Can polyimide-based membranes be engineered to achieve optimal properties without additional chemical modification?

What is the influence of fabrication methods and conditions on the final properties of the polyimide membranes? Could the developed polyimide membranes be applied in MD? How do developed membranes compare to commercial MD membranes and previously developed membranes from literature? Can the developed membranes perform in real-world desalination applications? Fouling and Scaling Resistance: How do advanced polyimide membranes resist fouling caused by scaling due to salts in high-concentration feed solutions?

1.7.2 Scope and limitations of the research

This research is limited to the introduction of 6FDA-*m*PDA membranes as a new class of membrane materials for MD applications. It includes the synthesis of the polymer and optimization of fabrication conditions and parameters to achieve desired properties for enhanced desalination applications in MD. This study does not investigate the theoretical aspects, that is, the thermodynamics and kinetics of phase separation of the newly developed systems. Moreover, all membranes were tested in AGMD.

1.7.3 Thesis outline

This thesis has been designed to introduce a new class of polymer materials for MD applications. The thesis has been organized into four chapters to understand the mechanism underlying the performance of these polymer materials in this application.

Chapter one of the thesis discusses the background and motivation behind conducting this research and how it will contribute to providing sustainable solutions to the problems of water scarcity and other environmental issues. In addition, this chapter discusses the

research gaps, the significance of materials development, the need for sustainability in MD, and the research objectives and questions the research intends to address.

Chapter two discusses the principles and operation mechanisms of MD. Moreover, it presents different membrane engineering techniques summarized from the literature and different phase inversion techniques.

Chapter three discusses the main approaches followed to address the research questions. Firstly, the potential of the 6FDA-mPDA membranes was evaluated using the conventional non-solvent-induced phase inversion method. Following that, a modified vapor-induced phase inversion was employed to optimize the properties and performance of the developed membranes. Ultimately, the performance of the developed membranes was evaluated.

Chapter four entails a conclusion of the thesis and recommendations.

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CHAPTER 2

LITERATURE REVIEW

2.1 Membrane distillation overview

Franken and Smolders first documented the phenomenon of MD to describe the characteristics and requirements of the process. This came from a defined nomenclature by a committee formed to standardize the terminologies used in describing the processes during a workshop on MD in Rome (1986) [51]. According to this documentary, the membrane to be used in MD should be porous, should not be wetted by the feed solution (i.e., should be highly hydrophobic), and no capillary condensation should occur within the membrane pores. In addition, at least one side of the membrane must be in direct contact with the feed, and the membrane should not change the equilibrium of the vapor-liquid of different components in the feed solution. Ultimately, the driving force of the process is the partial pressure gradient in the vapor phase induced by the temperature gradient [52]. The term ‘membrane distillation’ was coined because the process is like conventional distillation. Both the traditional and MD processes rely on the equilibrium of vapor-liquid as the driving force for separation and require the latent heat of vaporization to be supplied to achieve the behavioral phase change [51]. Bodell was the first to describe an early version of MD in 1963 in a United States patent granted in 1966. In his patent work, Bodell developed and built a device that included a tank with a parallel array of silicone tube membranes that circulated a brine solution through silicone rubber membranes (0.64 mm

outside diameter and 0.30 mm inner diameter). An external condenser was used for condensing and collecting the permeate vapor after ambient air was forced through the silicone membranes' pores [53]. In another patent in 1967, Weyl proposed another process for improving the desalination of feed solution by MD. In his work, he discovered that a hydrophobic porous membrane can be utilized as a membrane in a vapor pressure-driving system to recover pure water from saline sources by placing the membrane between the feed and cold permeate in a direct contact mode [54]. The interest in employing MD for desalination diminishes because it could only achieve a water flux of $1 \text{ kg m}^{-2} \text{ h}^{-1}$ with PTFE membranes, a value far below that of reverse osmosis systems [51]. The unavailability of ideal membranes for the MD process also contributed to the loss of interest in the process. The interest in MD was revived when Findley published his findings after performing experiments with different membranes in the direct contact mode described by Weyl. Despite his relatively unsophisticated experimental setup and methods, Findley accounted for the impacts of air trapped in the membrane pores, membrane thickness, heat loss by conduction, and porosity on the process efficiency. He concluded that this method might become an economical means of evaporation and an important option in treating saline water if cost-effective, high-temperature, long-term stable membranes with desirable features can be produced [55].

Interest in MD was rekindled in the early 1980s when new membrane fabrication methods were introduced, resulting in membranes with thicknesses as low as $50 \text{ }\mu\text{m}$ and porosities up to 80%. Compared to the membranes employed by Wyle and Findley in the 1960s, this results in a membrane permeability that is more than 100 times higher. The resurgence of interest in MD and the emergence of a more competitive process were also facilitated by

advancements in module design and a more comprehensive understanding of the effects of temperature and concentration polarization on MD performance. The timeline of MD development and the number of published articles in MD are shown in **Figure 3** and **Figure 4**, respectively.

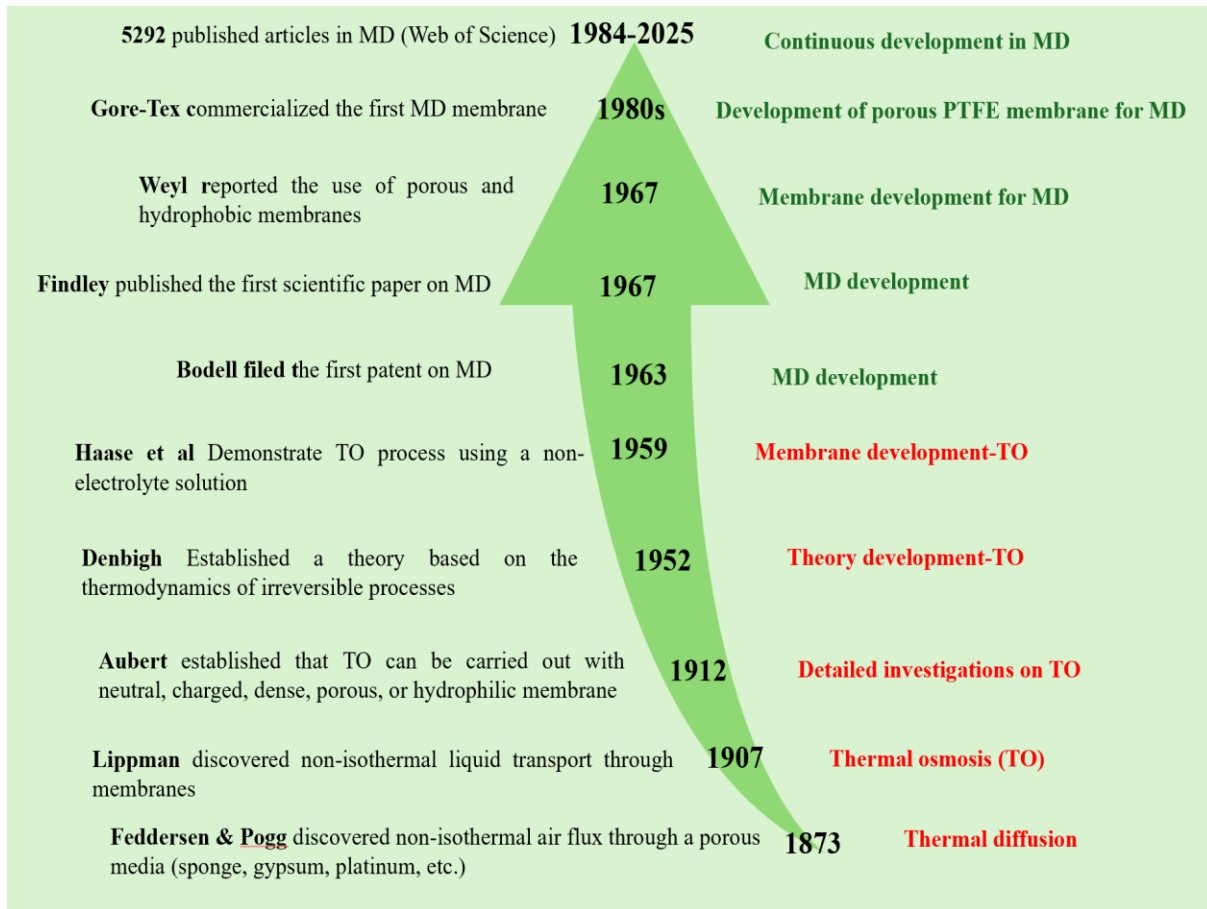


Figure 3. Timeline in MD development (Data generated from [30,56]).

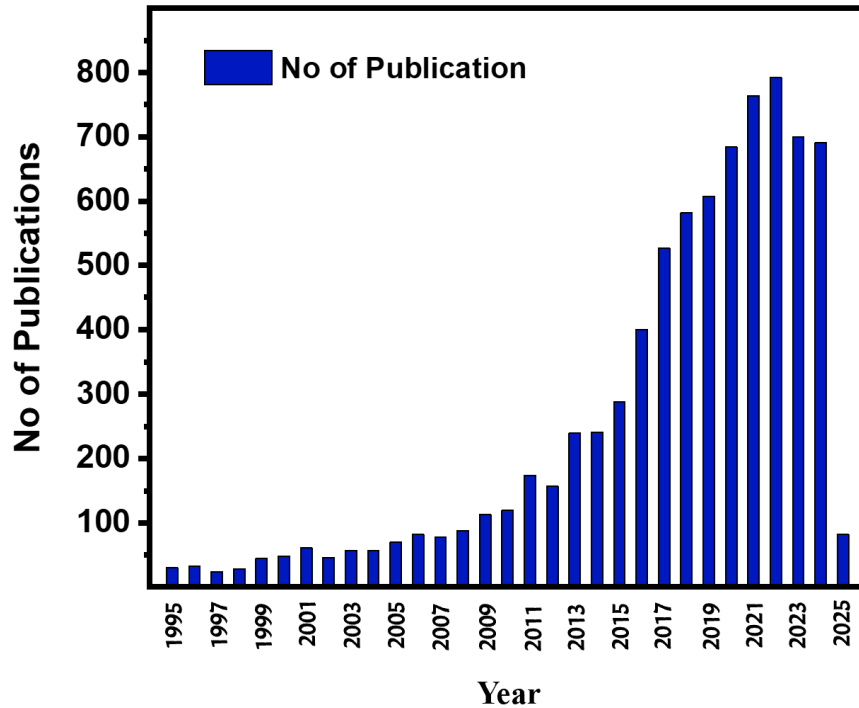


Figure 4. A plot of the number of publications on membrane distillation over the last three decades from the Web of Science was searched using the keywords “membrane distillation,” with each bar representing a year.

2.2 Principles and operation mechanisms

The transport phenomenon of energy or matter through any membrane, whether porous or dense, is caused by a thermodynamic imbalance. In general, a difference in the chemical potential of substances between the membrane's feed and permeate sides can cause this difference, as can variations in pressure, temperature, concentration, electrical potential, and other factors. Membrane processes are typically analyzed from the perspective of irreversible thermodynamic processes, which have been shown to offer no

molecular-level explanation of the phenomenon. For instance, Fourier's theory states that when a temperature differential is applied between two sides of a membrane, a conjugate heat flux is created in the direction of the temperature drop from high to low. The mechanism of crossflow of mass through the membrane depends on whether it is hydrophobic, dense, porous, or electrically charged.

The description of an MD process is relatively non-complex. The feed side of a microporous, hydrophobic membrane is exposed to a hot aqueous feed solution. Because the membrane's hydrophobic properties restrict any liquid solution from entering the pores, there is a vapor-liquid interface at each pore entrance. A cross-sectional schematic of a hydrophobic membrane with regular cylindrical pores interacting with a liquid solution is depicted in **Figure 5** to demonstrate how the vapor-liquid interfaces are stabilized at the pore openings.

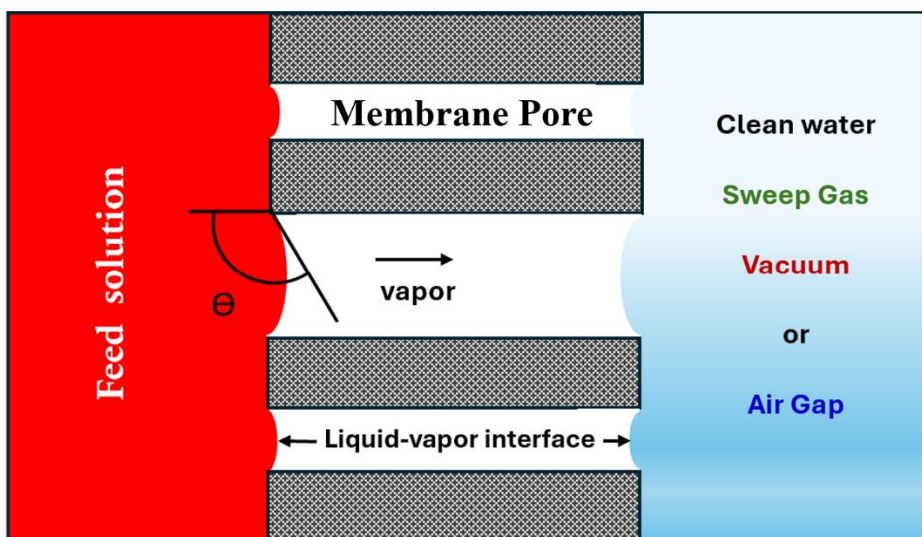


Figure 5. A typical Vapor-liquid interface with a hydrophobic membrane in MD.

2.3 Types of MD configurations

Several techniques can induce flux by imposing a vapor pressure differential across the membrane. In all these MD variations, the feed solution to be treated is kept in direct contact with the membrane and cycled tangentially to the feed side. Only the permeate side of the membrane differs from the other suggested arrangements. Air gap membrane distillation (AGMD) is the MD configuration that occurs when a cold surface is positioned inside the permeate side of the membrane to perform the condensation phenomenon. In this instance, the evaporated water and volatile molecules pass through the dry pores and the stagnant air gap to condense on the cold surface. It should be noted that no liquid is in touch with the membrane's permeate surface; instead, the generated liquid permeate is collected at the membrane module's lowest end. DCMD is the configuration that occurs when a solution cooler than the feed solution is kept in direct contact with the membrane and cycled tangentially to the permeate side. The given transmembrane temperature gradient induces the required vapor pressure difference. As a result, water and volatile molecules condense in the cold liquid/vapor interface within the membrane module after evaporating at the hot liquid/vapor interface and passing through the membrane pores in the vapor state. Sweeping gas membrane distillation (SGMD) is the MD design in which a cold inert gas, rather than a cold liquid solution, passes the permeate side of the membrane, conveying the volatile molecules and evaporated water. The condensation process in this instance occurs beyond the membrane cell. The MD arrangement is called vacuum membrane distillation (VMD) when a vacuum is introduced to the permeate side of the membrane to lower the pressure below the point of saturation of water and volatile molecules contained within the feed solution. In this instance, the condensation event

occurs outside the membrane module as well. In general, AGMD and DCMD are best suited for applications where water is permeating flux. SGMD and VMD are typically used to remove volatile organic or dissolved gases from an aqueous solution. **Figure 6** shows several typical MD process configurations that can be used to achieve the necessary driving force, with the advantages and drawbacks of each configuration presented in **Table 1**.

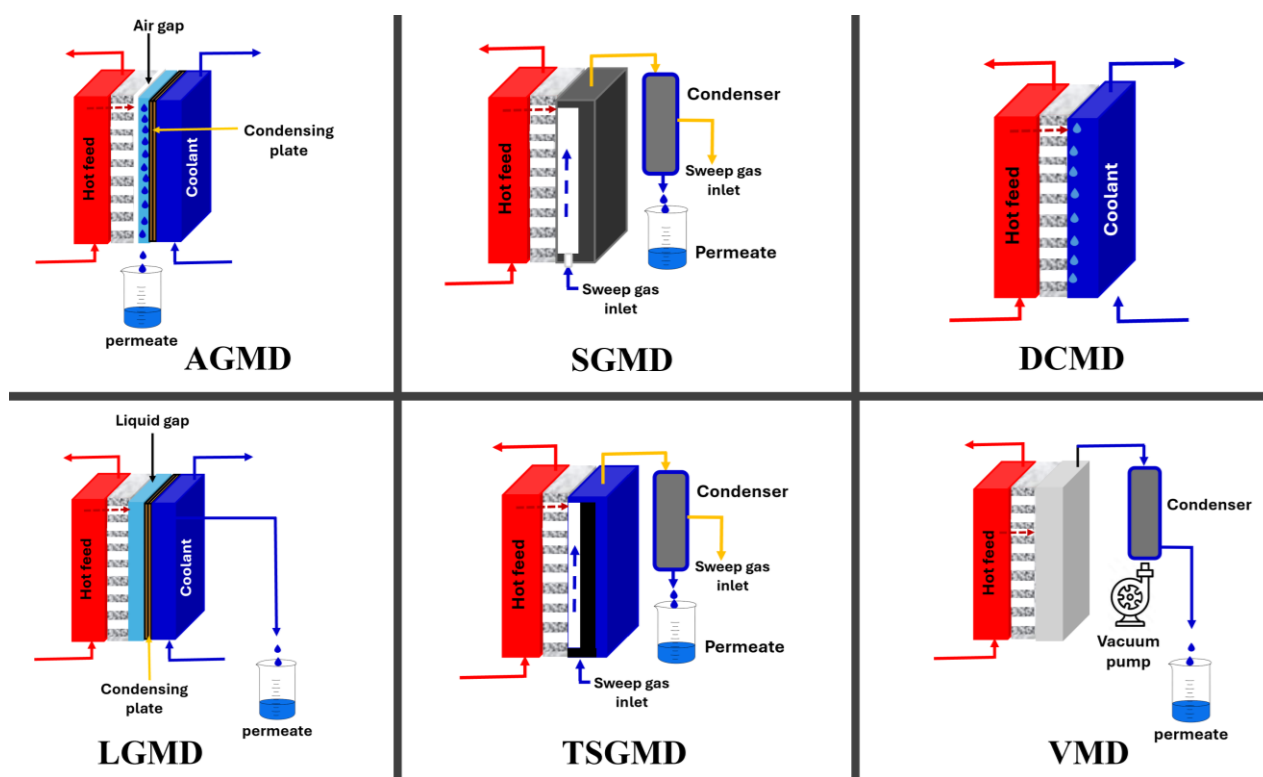


Figure 6. Common configurations used in MD.

Table 1. Comparisons between various categories of MD configurations

MD Configurations	Advantages	Drawbacks
DCMD	Simplicity, i.e., the ease of operation High water recovery.	High conductive heat loss due to direct contact between hot and cold streams
AGMD	Improvement in thermal efficiency due to the presence of an air gap	Increase in mass and energy transfer resistance. Low permeate flux compared to DCMD.
VMD	High permeate flux due to the vacuum applied on the permeate side	Operational complexity. Increase in Energy consumption Risk of membrane wetting.
SGMD	High permeate flux due to improvement in mass transfer at the permeate side. Low conductive heat loss	Complex module design. Risk of membrane wetting, like VMD.

2.4 Key parameters in MD

Being a process that works based on the vapor-liquid equilibrium, membranes for MD must prevent wetting and fouling. Thus, membranes must be hydrophobic [57]. The most commonly used polymer membrane materials in MD have been depicted in **Figure 2**. These materials have continuously been explored due to their intrinsic hydrophobicity. Several characteristics are necessary for membranes to perform well in the MD process

[58]. Apart from low mass transfer resistance, strong thermal stability with low thermal conductivity at high temperatures, and great resistance to chemicals, these membranes need to have the following characteristics [28,59].

2.4.1 Liquid entry pressure (LEP)

According to Smolder and Franklin [56], LEP is the pressure at which water permeates the membrane pores, causing droplets to appear on the membrane surface. LEP depends on the maximum pore size and membrane hydrophobicity. This means that to obtain a high LEP, the materials to be used for membranes must have high hydrophobicity, low energy levels, and small maximum pore size [60]. However, it should be noted that a smaller maximum pore size leads to a reduction in the permeability of the membrane [61]. LEP must be as high as possible to prevent the occurrence of pore wetting. Therefore, optimizing these parameters must be carefully controlled to achieve optimum performance. By optimizing the LEP of a membrane, the membrane-wetting resistance could be enhanced. The presence of organic species such as alcohol [62] and the temperature of the feed solution could lead to a reduction in membrane LEP [63].

2.4.2 Membrane porosity, pore size, and distribution

It has been noted that increased pore sizes in the membrane result in higher permeate flux and are proportionally related [64]. However, the LEP decreases with an increase in pore size. This implies that the larger the pore sizes are, the more likely the membranes are prone to wetting. Assume that the feed pressure exceeds the liquid entering pressure. In that scenario, the liquid passes through the membrane's pores, and the membrane's hydrophobicity diminishes [65] based on the relationship in Equation 1. The

pore size range for an ideal MD membrane is between 0.1 and 0.6 [66] or 1 μm [67], with a narrow pore size distribution. A lower pore size can lessen the likelihood of liquid penetration, eventually resulting in pore wetting, even if a bigger pore size is preferred to obtain higher permeate fluxes. Therefore, it is necessary to identify the ideal pore size for various feed solution types and operating circumstances.

$$LEP = \frac{-\beta\gamma_i\cos\theta}{r_{max}} \quad 1$$

where β is a geometrical pore coefficient = 1, γ_i = liquid surface tension, r_{max} = max. pore size, and $\cos\theta$ = contact angle of the water droplet

The MD process occurs in a specific mass transfer mechanism as a function of pore size, which determines the type of mechanism. Knudsen diffusion, for instance, is a mass transfer mechanism when the pore size is small, while the Knudsen-viscose mechanism becomes apparent when the pore size is large [28]. Estimating the vapor flux is done using the mean pore size. The pore diameters of MD membranes are often distributed across a range of sizes rather than being homogeneous. This leads to the simultaneous occurrence of many heat and mass transfer mechanisms. It is worth mentioning that PSD will not significantly impact MD performance. Although Martinez et al. [68] discovered that the heat transfer coefficient can be calculated by considering an evenly distributed pore size that is very approximate to the heat transfer coefficient, Khayet et al. [69], pointed out that the mean pore size might be used rather than PSD in determining the heat transfer coefficient.

Irrespective of the MD type, high porosity membranes have higher fluxes because a greater proportion of the area can be used for evaporation [70]. Regarding energy efficiency, increased porosities reduce the conductive heat transfer through the membrane solid material since the gas heat transfer coefficient is lower than in the polymer. Generally, MD designs typically use membrane porosities within a range of 60 to 85% [71].

2.4.3 Membrane thickness

The effectiveness of heat and mass transfer in MD is greatly influenced by membrane thickness, which is a crucial membrane performance metric. Like similar membrane processes, it has an inverse relationship with the permeate flux in the MD process [28]. The lower the membrane thickness, the higher the fluxes obtained [72]. Consequently, a thin membrane is required to achieve a high MD permeability. On the other hand, a thicker membrane has a lower permeate flux because of the increased time the vapor travels through the membrane before condensing (increase in mass transfer resistance) [28,30]. Nevertheless, improved heat efficiency is often achieved with thicker membranes due to decreased heat loss [73]. In AGMD, the air gap has a greater influence than the membrane thickness [70]. In general, the thickness of a single-layer membrane must be carefully optimized to achieve a higher flux and an ideal mass transfer resistance. According to Lagana et al.[74], the ideal range is between 30 and 60 μm . On the other hand, the hydrophobic layer in a double-layer membrane with a hydrophilic layer must be as thin as possible to lower the resistance to mass transfer. Moreover, the membrane's overall thickness should be as thick as practicable to prevent heat loss [75].

2.5 Phase inversion

2.5.1 Phase inversion of polymeric materials

Porous polymeric membranes can be made using different methods such as electrospinning, phase inversion, stretching, template leaching, and sintering. However, membranes fabricated using the last three methods exhibit low porosity, making them unsuitable for fabricating membranes for MD applications [76]. The phase inversion method was initially reported in 1963 by Loeb and Sourirajan [3], settling the basics for synthesizing most commercialized membranes [78]. This procedure involves several ways of generating a phase separation process, which converts the initially homogenous polymeric dope solution into a solid matrix state by a controlled process of transformation from a liquid state [5,6]. Phase inversion is one of the best and most well-known techniques for creating different morphologies of polymeric membranes in flat shapes and hollow fibers. In this method, the polymeric or dope solution is transformed into a solid membrane by changing the dope solution's equilibrium states by temperature [81] or by using a separate liquid phase, also known as the non-solvent [82]. It is worth mentioning that liquid-liquid demixing occurs before this solidification. The phase with the highest concentration of polymers will begin solidifying via vitrification, gelation, or crystallization at a specific point after the demixing into a polymer-rich and a polymer-lean phase has begun. The solid membrane matrix will result from the polymer-rich phase, whereas the pores in the solidified material will result from the polymer-lean phase. The main fabrication techniques employed in the fabrication of MD membranes are non-solvent-induced phase inversion (NIPS) where the cast film is immersed in a nonsolvent coagulation bath, vapor-induced phase inversion (VIPS) where the membrane is formed by

exposing the polymer solution in the nonsolvent vapor environment, thermal-induced phase inversion (TIPS) where the phase separation is induced by lowering the temperature, evaporation-induced separation in which the volatile solvent is slowly evaporated in a matrix containing nonsolvent and solvent mixture, and electrospinning.

2.6 NIPS: Factors influencing membrane morphology

2.6.1 Non-solvent composition and temperature

The demixing process between the polymer and the solvent is largely influenced by the nature of the precipitation bath, the components in the system, and their concentrations because they can alter mass transfer during the membrane formation process. It is important to highlight that the mass transfer rate will determine the final morphology and hence, the final properties of the membranes [83–86]. Water is the most common non-solvent phase because it is a strong non-solvent that exhibits economic and environmental advantages compared to other substances. However, it also causes a quick demixing process that leaves the membrane's surface covered with a thick skin layer, decreasing the water flux properties of the membrane. Therefore, some researchers have used organic solvents, such as methanol, ethanol, and propanol [86], to avoid the formation of this structure. However, employing these solvents has environmental and economic disadvantages [87]. Similarly, the mass transfer and, ultimately, the final properties of the membranes will be influenced by the thermodynamic affinity between the constituents. For the phase inversion to occur, the non-solvent must have a strong affinity for the solvent but not the polymer. Generally speaking, precipitants with a high affinity for the solvent facilitate a rapid phase separation process; conversely, when the affinity is low, the process is slowed down, resulting in

reduced exchange rates [85,88]. Pagliero *et al.* [83] have studied the effect of non-solvent bath composition by employing different ethanol concentrations in the coagulation bath (25, 50, 75, and 96% ethanol). They discovered that introducing ethanol decreased non-solvent strength, delaying the liquid phase separation and enhancing the hydrophobicity of the membrane (from 84° in the water bath to 150° for 96% ethanol). This phenomenon was explained by considering that crystallization occurs before liquid-liquid demixing at a higher ethanol concentration, forming a bicontinuous structure. Thus, the addition of ethanol to the coagulation bath delays the rate at which solvents and non-solvents exchange, resulting in the creation of more symmetric structures and preventing the production of macrovoids.

The temperature of the coagulation bath is another factor that might affect mass transfer since it can quicken the rate at which mass transfers between solvent and non-solvent occur [89]. Kahrs *et al.* [85] have synthesized PES-based membranes using two kinds of solvents, NMP and 2-pyrrolidone, setting the temperature of the coagulation bath to either 20°C or 40°C. The morphology of the membrane was found to be temperature-dependent, meaning that a rise in temperature causes an increase in the number of voids across the membrane's volume for both solvents. This describes how raising the temperature will improve solvent uptake and lead to an increase in the formation of the polymer-poor phase nuclei by reducing the viscosity of the dope solution and boosting the rate exchange between the solvent and the non-solvent. Meanwhile, at low temperatures, the formation of the macrovoids was suppressed since new nuclei could not form below the existing ones. Fang *et al* [90] have studied the effect of the coagulant bath temperature employing both computational and experimental approaches. The system was PVDF/ DMF/ H₂O, with an

18 wt.% PVDF concentration, considering temperatures from 273.15 K (0 °C) to 353.15 K (80 °C). The phase-field computational model, which is based on the Ginzburg-Landau theory, was used. They conclude that the pore structure of the membrane loosens with rising coagulation bath temperature, increasing the water flux because larger pores are created at higher temperatures due to faster liquid-liquid phase separation. Ultimately, for this system, they suggest employing a temperature range of 35 to 45°C as an optimal value to balance the membrane performance and energy efficiency.

2.6.2 Polymer concentration and additives

It has been found that increasing the concentration of polymer in the solution increases the volume fraction occupied by the polymer molecules, raising the solution viscosity, and affecting the pore size and the mass transfer rates, which leads to different final properties and morphology of the membranes [91]. Kahrs *et al.* [85], observed a final membrane with fewer macrovoids in the morphology by increasing the concentration of PES in the dope solution, producing a denser membrane. In the same way, the mechanical stability of the membranes increased when the PES concentration in the dope solution was raised. The increment of the viscosity will influence the kinetics aspect of phase inversion, delaying the solvent-non-solvent exchange rate, and decreasing the membrane pore size. Subsequently, this will lower the membrane flux. On the other hand, low concentrations will lead to membranes with larger pore sizes and higher permeate flux with low mechanical properties and low integrity, or defective membranes if the solution's viscosity is very low. Therefore, polymer dope concentration must be carefully controlled to generate a membrane with ideal characteristics and performance for MD applications.

The polymer solution's kinetic and thermodynamic characteristics, as well as the membrane generation process, are modified by the additives. Polyvinylpyrrolidone (PVP) and Polyethylene glycol (PEG) are commonly used; they enhance the hydrophilicity of the membrane surface and modify the viscosity of the solution, impacting the mass transfer rate exchange, hence, the pore size and the formation of macrovoids in the membrane structure can be altered by introducing an additive. These types of additives are often called pore-forming agents. In addition, these additives can influence properties such as permeability, rejection properties, stability, and morphology [92]. Lubis *et al.* [93] prepared NIPS PES-based membranes, adding different concentrations of PVP (0%, 1%, 3%, and 5% wt) to study their influence on the final membrane properties and water permeability. They demonstrated that adding PVP to the formulation resulted in bigger pore sizes and macrovoids than the pristine PES membrane. According to their studies, the membrane with 3% PVP showed better performance with a flux of $87.5 \text{ kg m}^{-2} \cdot \text{h}^{-1}$, showing the effectiveness of adding PVP to the solution. Chakrabarty *et al* [94] studied the effect of employing different molecular weight PEG (400 Da, 6000 Da, and 20000 Da) as additives to fabricate polysulfone (PSf) membranes. According to their findings, membranes with higher molecular weights of PEG had more pores overall and more pore area.

Lithium chloride (LiCl) is a salt pore former that strongly interacts to form complexes with the solvents. Lopatina *et al.* [95] studied the effects of LiCl concentrations (0- 2 wt%) in cellulose-based membranes. Thus, lower concentrations of LiCl (up to 0.4%wt) increase linearly the viscosity of the dope solution, creating smoother surfaces. However, when the concentration is increased to more than 0.4 wt.%, the viscosity decreases, exhibiting

openings in the top layer. This phenomenon is due to the initial strong interactions between Li^+ cations within the solvent mixture, forming clusters of polymer chains. When the 0.4 wt.% is exceeded, salt destroys the entanglement networks within molecular chains. *Zheng et al* [96] reported increased pore connectivity with increasing LiCl dosage as an additive for PVDF-CTFE membranes.

2.7 Vapor-induced phase separation (VIPS) and key parameters

The concept of vapor-induced phase separation (VIPS) was initially developed in 1918. The method involves exposing an initial membrane to a non-solvent vapor environment for a period before solidifying the polymer into a membrane by immersing it in a non-solvent coagulation bath. During the VIPS membrane manufacturing process, phase separation occurs primarily due to the infiltration of non-solvent, not the outflow of solvent. By significantly reducing the mass transfer rate (non-solvent absorption and solvent extraction), the VIPS procedure efficiently prevents significant pore defects as compared to the NIPS approach. Furthermore, the VIPS method has a more stable phase separation [97].

2.7.1 Exposure time

Amin et al [98] studied the mechanism and influence of exposure time on pore formation in VIPS and established the following: first, the VIPS approach refers to nucleation and growth as the mechanism for membrane creation. Once the exposure duration in the VIPS method increases, so does the number of nuclei that form at the membrane surface. The growth stage modifies the size of the pores, and these nuclei

become the membrane pore sites at the final step of the phase inversion process. With shorter exposure durations, there are fewer nucleation sites, and the nucleus begins to expand and form big pores when immersed in the coagulation medium. At this point, an increase in exposure duration results in a maximum number of nucleation spots. This is the point where most pores have formed at this time, and they are also the smallest in size. A minor phase separation occurs at this point, and the membrane causes tiny pores with a limited distribution of pore sizes to form. Then, as the exposure period is further increased, the water droplets (nucleation sites) enlarge and combine to produce larger pores, increasing the membrane's mean pore size. The porosity and interconnectivity of pores will change depending on how long they are exposed to vapors. As a result, the pore size increases with exposure time [99]. AlMarzooqui *et al* [100] have evaluated the effect of exposure time of PVDF/DMAc membranes at 60% RH, finding that more time exposure means enlarged mean pore size, due to the formation of spherulitic-like morphology. Using the VIPS approach, Fan [101] developed a hydrophobic PVDF membrane. The hydrophobic membrane generated by prolonged vapor induction has a contact angle of up to 145°. Additionally, the membrane prepared with a longer exposure duration has a higher flux in VMD. The optimal membrane demonstrated a flux of 22.4 LMH at 73 °C feed temperature and 99.9% NaCl rejection for a feed solution with a 3.5 weight percent concentration. Toheeb *et al* [102] discovered that increasing exposure time with ethanol and water vapor in preparing 6FDA-TMPD polyimide membranes resulted in interconnected pores, surface roughness, and AGMD performance.

2.7.2 Relative humidity

In a study conducted by Yip et al [103], the dynamics of phase separation in the polymer film were determined to be significantly influenced by the non-solvent's relative humidity. In general, a higher relative humidity increases the driving force for a net diffusion and buildup of the non-solvent in the film, which causes phase separation in the VIPS process. Consequently, the phase inversion kinetics and ultimate membrane structure in VIPS are significantly impacted by relative humidity. They discovered that phase separation in VIPS is viable at relative humidities above 68 %. In a water vapor system, a higher chemical potential for water absorption on the cast film is provided by an increased relative humidity level; hence, for a given amount of time, a higher relative humidity is projected to result in a higher amount of water uptake [100]. The phase separation is therefore delayed by low relative humidity since the non-solvent penetration rate is low. Meanwhile, when it is high, matrix formation is promoted. For low levels of RH, solvent evaporation will drive the separation process [104].

2.7.3 Vapor temperature

Because the system becomes more thermodynamically unstable at higher vapor temperatures, liquid-liquid demixing was chosen over solid-liquid demixing to favor the formation of cellular structures on the membranes [91]. Bouyer *et al* [105] have shown that the cell size gradient of cellular-like structures was diminished from the top to the bottom of the membrane by lowering the temperature from 40°C to 25°C, explaining that this was due to the temperature-induced slowdown of the mass transfer rate, leading to an increment in the demixing time.

2.8 Polyimide membranes for separation

Compared to most polyimide materials, the 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA)-based polyimides have gathered huge research interest because of increased permeability and selectivity from these polyimides due to the $-C(CF_3)_2-$ bonds preventing the rotation of the phenyl rings [106,107]. Furthermore, because the polymer backbone contains fluorine atoms, the compounds are soluble in most organic solvents, facilitating their processing [108]. Once the dianhydride is fixed, choosing and adjusting the proper chemical structure of diamines offers a practical method of achieving the desired size-sieving capability [107,109]. Subsequently, their gas permeation and separation performance are influenced by the inherent significance of the diamine's functional groups, such as the carboxyl and hydroxyl groups, on the structure of the micropore of the produced polyimide [110,111]. Commercially, several reasonably priced polyimide polymers are on the market [112]. Nevertheless, customized polymers are unavoidably required to satisfy the requirements of certain applications, including gas separation and pervaporation in membrane technologies [113].

Research techniques to accelerate the performance of membranes from these materials, particularly for gas separation and pervaporation, have included the preparation of novel polyimides and the insertion of bulky side groups and functional groups in the fully aromatic polyimides [114]. Al-Masri et al [115] conducted research in which they fabricated membranes from polyimide using methyl-substituted diamine monomers. Their findings suggested that adding methyl groups to the main chain of the polymer resulted in a significant free volume for the gas permeation. Pinel et al, [116] prepared polyimide containing methoxy and trifluoromethyl groups. Their investigations revealed that the

trifluoromethyl substituents reduced the chain cohesion attributes and increased the free space for gas molecules to diffuse; however, the methoxy substituents do not exhibit any reasonable size effects on the gas permeation. Kang et al. [117] hydrophilically modified pyromellitic dianhydride (PMDA) along with 4,4'-oxydianiline (ODA) polyimides with 3,5-diaminobenzoic acid (DABA), and they found that improved permeance and good selectivity of water/ethanol were obtained using membranes prepared from the modified polyimides. This performance was due to the establishment of hydrogen-bonding between carboxylic groups in DABA and water molecules. Despite the vast application of polyimide membranes for separations, their application for desalination using membrane distillation was only employed by Obidara et al [118]. The fabricated membranes from 6FDA-TMPD demonstrated excellent MD performances, with the best membrane reaching a flux of $18.2 \text{ kg m}^{-2} \text{ h}^{-1}$ with a salt rejection of 99.96%.

CHAPTER 3

FINE-TUNING MORPHOLOGICAL PROPERTIES OF 6FDA-*m*PDA POLYIMIDE-BASED MEMBRANES FOR ENHANCED PERFORMANCE IN MD

3.1 Introduction

The surface architecture of membranes has been a key area of research focus in membrane technology since the beginning of membrane research [119]. The surface engineering technique, which involves modifying membrane surfaces, is useful for improving and maximizing the performance of polymeric materials, especially in applications involving membrane-based separation [120]. Yet, surface modifications involve several intricate stages and techniques used to create different surface patterns that could enhance the overall characteristics of the membrane, rendering the process practically not viable [120,121]. Several approaches have been developed to create ordered patterns in porous polymeric films. These techniques include colloidal crystals, emulsions, self-assembled rod-coil copolymers, lithography, or soft lithography [121]. The discovery of a straightforward, cost-efficient process for generating highly ordered honeycomb-structured porous polymer films was reported by Widawski and Francois 20 years ago [122]. In humid conditions, a solution of polymer is left to evaporate in a volatile solvent. As the solvent evaporates quickly, water vapor condenses on the cooling surface. At the

interface of water-solution, the polymer precipitates, stabilizing the droplets and preventing them from merging. The temperature difference within the solution generates convection currents and lateral capillary forces, which work together to create a well-organized structure in the stabilized droplets. Recent reports have highlighted molecular engineering and the control of synthesis parameters of membrane materials as key surface modification strategies. For instance, by controlling the synthesis parameters, Abdulhamid et al. [120] prepared porous and ordered honeycomb membranes from poly(ether-ether-ketone) for application in organic solvent nanofiltration. Adjusting the molecular weight polymer resulted in tuning the morphologies of the membranes from flat to a honeycomb structure. Their other investigations [123,124] revealed that molecular engineering, incorporating specific moieties and crosslinking within the polymer backbone, led to an engineered surface with enhanced membrane porosity and filtration performances.

The NIPS method is the most commonly used method to prepare porous membranes, even at an industrial level. The fundamental idea is that a polymer solution is cast onto a support and then submerged in a non-solvent bath. Phase separation occurs under the bi-directional dynamic diffusion theory in the coagulation bath because of the solvent in the polymer solution dispersing into the non-solvent and the non-solvent diffusing into the polymer solution [125] (**Figure 7**). Ultimately, solid polymer gels precipitate out in solid form [126].

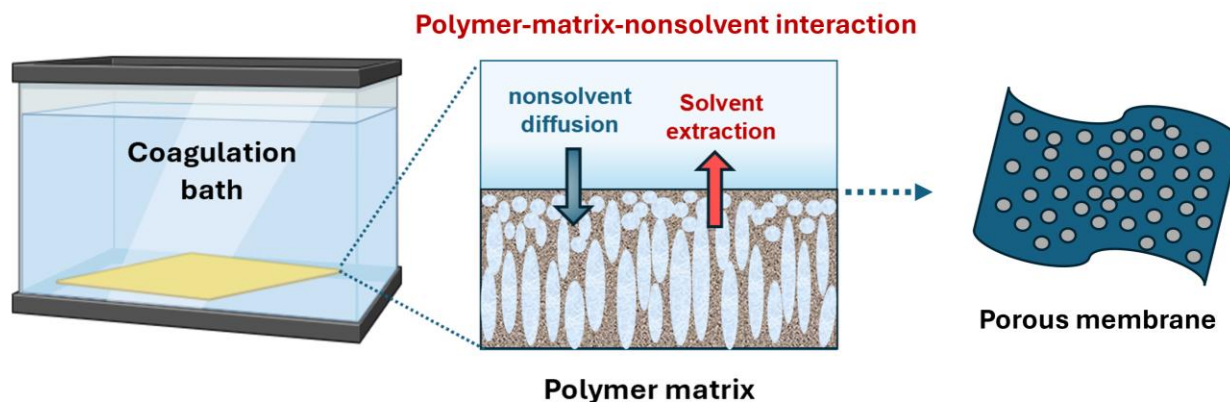


Figure 7. Schematic diagram of the NIPS membrane formation method.

The membrane pore structure for the NIPS method is determined mainly by phase separation, which alters the system's phase composition. Therefore, the driving force for pore formation in NIPS is phase separation [125]. Otitoju et. al., [127], Hou et. al., [128], Wang et. al., [129], etc., all employed the NIPS technique to prepare asymmetric porous membranes for application in membrane distillation.

Although the NIPS method has largely been employed in membrane fabrication, producing an ideal MD membrane directly from the process is still difficult. Ultimately, the NIPS method is followed by post-modifications to achieve the desired membrane. The most common surface modification techniques are coating (including dip coating), grafting, plasma, and interface polymerization. In recent work, fluoroalkyl silanes (FASs) were grafted onto a virgin membrane surface to create hydrophobic hollow fiber membranes stabilized with yttria-zirconia [37]. The modified membrane shows remarkable properties and performance. In a different study, ZnO NPs were added to a polyamide membrane surface via grafting caused by radiation by El-Arnaoty et al. to improve the membrane's anti-biofouling characteristics [38]. Furthermore, the surface coating was used to develop

a chemically stable, superhydrophobic membrane by hydrophobically modifying commercially available polyester (PET) membranes using PDMS-coated SiO₂ NPs [40]. Ray et al. [130] coated TiO₂ nanoparticles to create a membrane from PVDF, the surface was then fluorosilanized to create a superhydrophobic MD membrane. TiO₂ NPs were added to the surface to give it a hierarchical structure and introduce -OH functional groups, which ensured that perfluoro dodecyl trichlorosilane (FTCS) was functionalized effectively. All post-fabrication surface engineering techniques require several steps to achieve the desired result, making the fabrication process costly, requiring high energy, and time-consuming. In addition, the introduction of foreign materials, especially fluoroalkyl substances for surface modification, poses the risk of leaching, leading to environmental concerns. Therefore, developing cost-effective, energy-efficient, and environmentally friendly surface engineering techniques is necessary.

In recent studies, NIPS is followed by pre-modification steps to improve the membrane properties. In a recent study by Yang *et. al.*, they developed PVDF membranes employing the NIPS technique. They later modified the method by first spraying some liquid, followed by the NIPS, and named it spray-assisted non-solvent induced phase separation (SANIPS). The resulting membrane exhibited self-cleaning properties and a water contact angle (WCA) of 154°, indicating its superhydrophobic nature. In comparison to the pristine NIPS membrane, the SANIPS membrane performed better, based on its MD performance. In another modified NIPS technique, Nuaimi *et. al.* prepared uniformly porous PVDF-HFP membranes using the mixed solvent phase separation. They pre-heated the glass substrate to about 80 °C before inserting it in a cold chamber of around 11 °C to induce a phase

separation between the solvent and the desolvent. Subsequently, this was followed by the conventional NIPS technique to obtain porous hydrophobic membranes.

In most VIPS processes, the cast solution is exposed to an atmosphere of the non-solvent vapor for a predetermined amount of time before being submerged in a nonsolvent bath to complete the polymer's inversion into a membrane. Phase separation is mostly caused by the influx of non-solvent rather than solvent outflow (**Figure 8**).

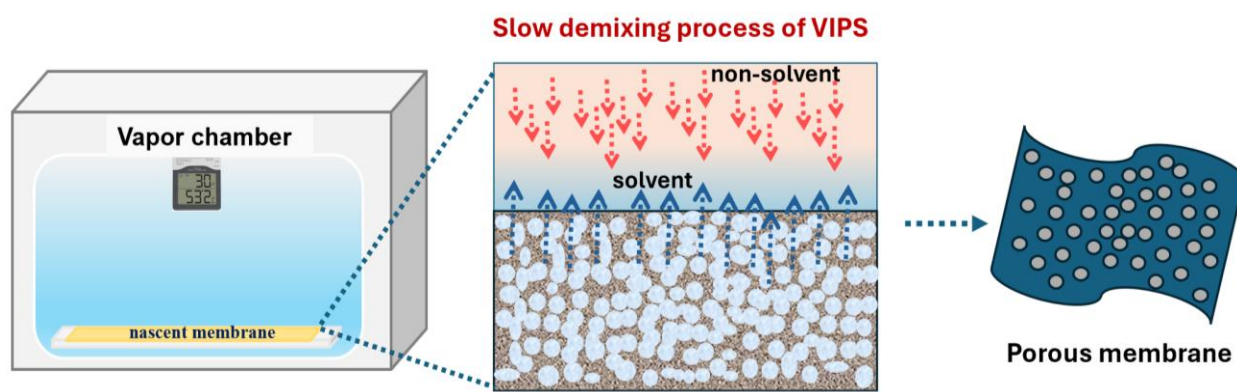


Figure 8. Schematic presentation of the mechanism of the VIPS process.

Large pore defects can be avoided because of the stable phase separation and a significantly lower mass transfer (i.e., non-solvent diffusion and solvent extraction) compared to the NIPS approach. In the VIPS process, slower and more controlled absorption occurs because the non-solvent infiltrates the casting solution as a gas [131]. The vapor exposure time and the miscibility between the solvent and the non-solvent are important factors that affect the kinetics and thermodynamics of the VIPS method. If the Hansen solubility parameter difference between the solvent and the non-solvent is large, a longer exposure time is required to achieve complete precipitation and form a porous membrane. Conversely, complete precipitation and the formation of a porous membrane can be

achieved when there is good miscibility between the solvent and non-solvent, indicated by a close solubility parameter difference.

This process, combined with the slow evaporation of low-volatile solvents, reduces polymer concentration near the membrane's surface [132], making the VIPS process more advantageous because of its capability of controlling and tailoring the morphology of the membrane more accurately than other phase inversion techniques [133]. Consequently, VIPS is particularly effective in producing membranes with porous surfaces, making it unique for fabricating MD membranes.

Currently, only a few vapors are known to be used in VIPS as non-solvent phases due to technological challenges in controlling the state of the gas during the membrane preparation process. Water, acetone, and ammonia vapor are most employed, with humid air being the most prevalent. VIPS phase separation is highly dependent on external conditions because it mostly happens in the environment via a non-solvent. The ultimate membrane structure is significantly influenced by temperature and humidity levels. The membrane preparation process for VIPS is usually performed in enclosures or closed isothermal glass chambers to control the ambient temperature and humidity [134,135].

In this chapter, a series of novel polyimide-based membranes were fabricated from 4,4'-(hexafluoroisopropylidene) diphtalic anhydride-*m*-phenylenediamine (6FDA-*m*PDA) polymer. As a new membrane material for MD, NIPS was first employed to fabricate membranes, and its potential was investigated in air gap membrane distillation. VIPS was then used as a surface engineering method to create a porous structure on the polyimide-based membrane surfaces without incorporating additives or fillers, mimicking the Breath

Figure method [17,27-30]. The surface morphologies, roughness, and other characteristics, such as pore sizes, WCA, porosity, and liquid entry pressure (LEP), were determined to understand the mechanisms of membrane fabrication and performance. It is worth mentioning that all membranes used in this work were recycled and used as fresh material, proving the sustainability and energy efficiency of 6FDA-*m*PDA as a membrane material for MD applications.

3.2 Experimental

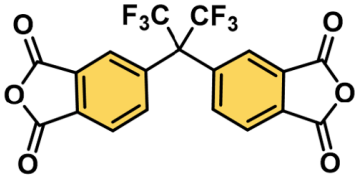
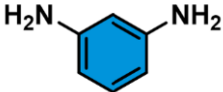
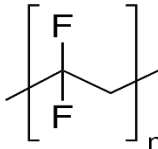
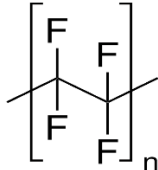
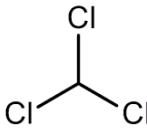
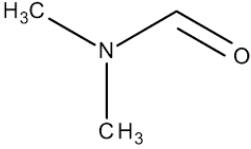
3.2.1 Materials and Chemicals

The materials and chemicals used in this work are 4,4'-(Hexafluoroisopropylidene) diphtalic anhydride (6FDA, 99 %), *m*-phenylenediamine (*m*PDA, 99 %), isoquinoline (97%), *m*-cresol (99 %), *N,N*-dimethylformamide (DMF, 99.9 %), and chloroform (CHCl₃, 99 %) purchased from Merck Sigma-Aldrich. Ethanol (99.8 %) and 2-propanol (IPA, 99.8 %) were obtained from Honeywell (Germany). Sodium chloride (NaCl, 99.5%) was obtained from Fisher Chemical (UK). Deionized (DI) water with a resistivity of 18.2 MΩ-cm was collected from the Millipore system (Milli-Q®). Commercial hydrophobic Polytetrafluoroethylene (PTFE) and PVDF membranes from TISCH Scientific were used. The properties of the commercial membranes used are presented in **Table 2**. The names and chemical structures of some materials and chemicals used in this work are presented in **Table 3**.

Table 2. Properties of the commercial membranes (TISCH Scientific) used.

Membrane	WCA (°)	Pore size (μm)	Thickness (μm)	Porosity (ε%)
PTFE	82 ± 4	0.22	200	62.35
PVDF	74 ± 3	0.22	120.8	54.59

Table 3. Chemical names and structures of materials and some chemicals used in this work.

Chemical	Structure
4,4'-(Hexafluoroisopropylidene) diphtalic anhydride (6FDA)	
<i>m</i> -phenylenediamine (<i>m</i> PDA)	
Polyvinylidene fluoride (PVDF)	
Polytetrafluoroethylene (PTFE)	
Chloroform	
Dimethylformamide (DMF)	

3.2.2 Synthesis of 6FDA-mPDA polymer

The synthesis of the polymer was carried out through a polycondensation reaction, as reported previously, as schematically presented in **Figure 9** [137]. An equimolar amount of 6FDA and *m*PDA was placed in a round-bottom flask equipped with an oil bubbler, an inlet for nitrogen, and a magnetic stirrer. Subsequently, *m*-cresol was added as a solvent. The mixture was initially heated to 80 °C, after which 0.1 mL of isoquinoline was introduced. The temperature was then gradually raised to 200 °C to ensure that the imidization and conversion of poly(amic acid) to polyimide had been accomplished. Finally, the solution was precipitated in methanol, followed by stirring for 4 hours, and the polymer was obtained through filtration. The synthesized polymer was further purified by re-precipitating the polymer solution in methanol. The chemical structure of the resulting polymer was subsequently confirmed by ¹H NMR and FTIR.

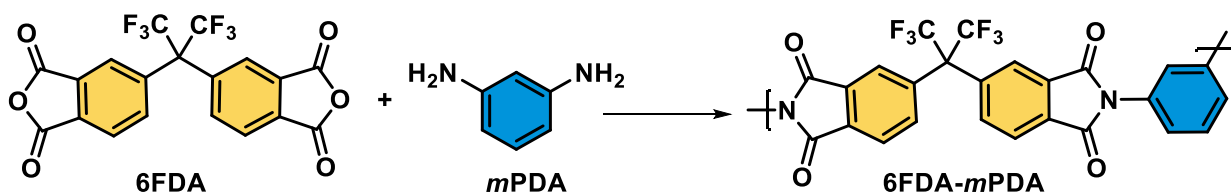


Figure 9. Scheme of the synthesis of 6FDA-mPDA polyimide at 200 °C in *m*-cresol.

3.2.3 Fabrication of membranes

6FDA-*m*PDA polymer was dissolved in the desired solvent with the desired concentrations to prepare membranes through the NIPS method. The mixture was kept

under stirring using an IKA™ RCT 5 Digital Magnetic Hotplate Stirrer at 30 °C until all the polymers had fully dissolved. The prepared dope solution was kept at room temperature for 12 hours to eliminate air bubbles and avoid membrane defects. As presented in **Figure 10**, the NIPS process involved pouring a polymer solution onto a glass substrate using an automatic casting machine (Compact Tape Casting Coater and Film Applicator - MSK-AFA-III) spaced to a gap of 300 µm and the speed was set at 30 mm/sec at a temperature of 24 °C, while the humidity was approximately 50%. This was followed by phase inversion in ethanol for two minutes before storing in DI water for 24 hours. The immersion in ethanol before water was based on our previous work, which showed a higher potential to create a highly porous structure, relative to direct immersion in water, relative to direct immersion in water [26]. The membranes were collected, rinsed, and dried before use. For the VIPS process, the cast solution was quickly transferred to an environment saturated with non-solvent vapor (ethanol, at approximately 68 °C) with relative humidity exceeding 95% and kept for 3 minutes. The developed membranes were then dried using the same technique as for NIPS after being rinsed with water. Membranes with varying polymer concentrations were prepared using both methods (NIPS and VIPS) to determine the influence of polymer concentration on the membrane's properties and performance.

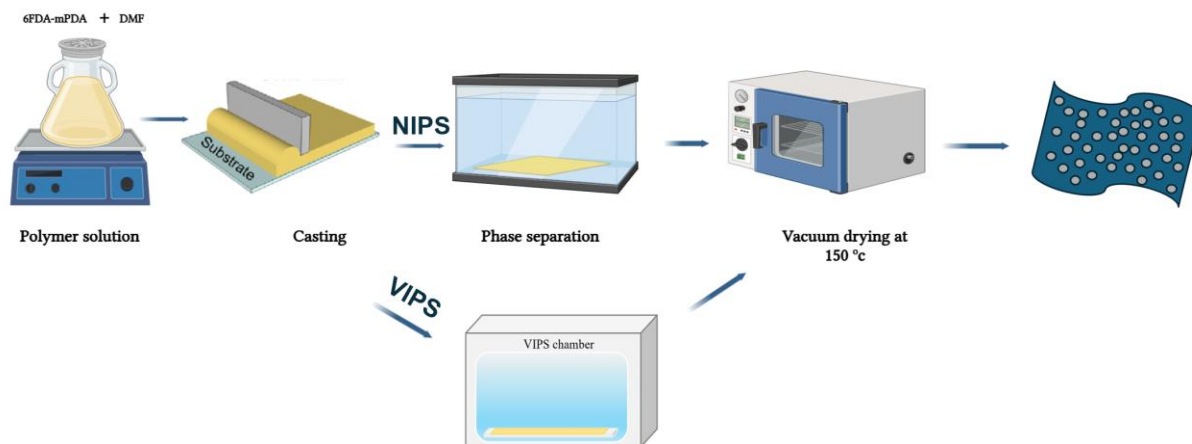


Figure 10. Schematic presentation of the NIPS and VIPS membrane fabrication.

Membranes generated through NIPS are labeled with the designation 'N' and those from VIPS with 'VX_L', with X and L representing polymer concentration and vapor type, respectively. Further details on membrane designations and fabrication conditions have been presented in **Table 4**, **Table 5**, and **Table 6**.

Table 4. Fabrication parameters and designation of 6FDA-*m*PDA-based membranes with a casting knife thickness of 300 μm prepared using NIPS.

Membrane designation	Dope solution concentration (wt. %)	Coagulation Bath
N_13	13	Ethanol ^a
N_15	15	Ethanol ^a
N_17	17	Ethanol ^a

^a Membranes were immersed first in ethanol for 2 minutes, followed by DI for 24 hours

Table 5. Fabrication parameters and designation of 6FDA-*m*PDA membranes with 15 wt.% polymer concentration and a casting thickness of 300 μm .

Membrane	Exposure time (mins)	Vapor
V_W3	3	Water
V_W5	5	Water
V_W8	8	Water
V_W/E_3	3	W: E*
V_W/E_5	5	W: E
V_W/E_8	8	W: E

W: E* = water + ethanol (50:50)

Table 6. Fabrication parameters and designation of 6FDA-*m*PDA-based VIPS membranes with a casting knife thickness of 300 μm and exposure time of 3 minutes.

Membrane designation	Dope solution concentration (wt.%)	Vapor
V13_E	13	Ethanol
V15_E	15	Ethanol
V17_E	17	Ethanol
V13_P	13	Propanol
V15_P	15	Propanol
V15_P	17	Propanol

3.3 Polymer and membrane characterizations

The chemical structure of 6FDA-*m*PDA was confirmed using the proton nuclear magnetic resonance (^1H NMR) spectrum, which was conducted on a Bruker AVANCE-III spectrometer (400 MHz) in CDCl_3 . While Fourier transform infrared (FTIR) spectroscopy conducted with a Bruker INVENIO Series FTIR spectrometer over the range of 400–4000 cm^{-1} was used to identify the functional groups. The thermal properties of 6FDA-*m*PDA were measured using thermal gravimetric analysis (TGA) with a TA Instruments Q600 SDT, at a heating rate of 5 $^{\circ}\text{C min}^{-1}$ up to 800 $^{\circ}\text{C}$. Wide-angle X-ray diffraction (WXR) analysis was conducted on a MiniFlex 600, with a 5° – 40° 2θ range.

The cross-sectional and surface morphologies were analyzed with scanning electron microscopy (SEM, JEOL JSM-6610LV). To enhance image quality and reduce charging, each sample had a thin coating of gold applied to it, using the 108auto Cressington coater. The same SEM instrument was used to measure membrane thickness by examining the cross-sections. For examining the cross-sections, the membranes were initially fractured after being frozen in liquid nitrogen.

The WCA was measured with the contact angle goniometer (DM-501, Kyowa Interface Science Co. Ltd., Japan) via the sessile drop method. This involved placing 5 μL droplets of DI water on different points and taking the average. Surface roughness was assessed with an atomic force microscope (AFM; Agilent Technologies 5500), and the average roughness was calculated from five scans.

The membrane-wetting resistance was evaluated in the laboratory with an in-house LEP set up by applying pressure to a small water chamber positioned against the membranes,

following the method reported by Smolder and Franklin [32]. This approach enabled the determination of the LEP of the produced membranes. The following equation shows how the LEP, maximum pore size, and contact angle are related:

$$LEP = \frac{-\beta\gamma_i\cos\theta}{r_{max}} \quad 2$$

β is a geometrical pore coefficient = 1

γ_i = liquid surface tension

r_{max} = max. pore size

$\cos\theta$ = contact angle of the water droplet.

Using a standard capillary flow porometer (3Gzh, Quantachrome Instrument, USA), the membrane pores' sizes were measured by the liquid expulsion (ethanol) through gas pressure. The instrument made wet and dry measurements, and the membranes' minimum and maximum pore sizes were determined. The gravimetric technique, as previously mentioned, was used to assess the membranes' porosity according to Equation 2 [138]. The membranes were weighed both before and after being submerged in ethanol. Once the membrane surface was fully wet, the remaining ethanol was removed.

$$\varepsilon (\%) = \frac{(W_w - W_d)/d_e}{\left[\frac{W_w - W_d}{d_e}\right] + (W_d/d_m)} \times 100 \quad 3$$

ε represents the porosity of the membrane in %, W_d and W_w are the masses of the dry and wet membranes, respectively, while d_e and d_m represents the densities of ethanol (0.789 g/cm³) and 6FDA-*m*PDA (1.42 g/cm³), respectively.

A discovery hybrid rheometer HR30 from TA Instrument, fixed with a tensile deformation module, was used to assess the mechanical stability of the developed membranes. Membrane samples were clamped meticulously with a 20mm length between grips and stretched at a constant rate of 50 microns/sec.

3.4 Membrane distillation performance

A laboratory-scale AGMD setup was employed to evaluate the performance behavior of the prepared membranes. The system includes a heater tank where the feed solution is heated to approximately 70 °C, connected to an MD cell, housing the membrane. On the opposite side, a chiller condenses the permeated vapor that passes across the porous membrane. To simulate real seawater, a 70,000-ppm feed solution was prepared by dissolving 70 grams of NaCl in 1 L of DI water, which served as the feed solution. The weight of the water condensed across the membrane per unit area and time was used to calculate the flux (J) of pure water. The permeate flux was calculated using Equation 4:

$$J = \frac{m}{A.t} \quad 4$$

Here, the mass of pure water collected over the membranes is represented by m in kilograms, A represents the effective area in m^2 , t is the testing time in hours, and J represents the permeate flux in $(kg/m^2 h)$. The salt rejection was calculated using Equation 5:

$$S.R (\%) = \frac{c_f - c_p}{c_f} \times 100 \quad 5$$

where S.R. stands for salt rejection (%), C_f and C_p are the salt concentrations in ppm for the feed and permeate, respectively. The laboratory-scale AGMD setup is illustrated in **Figure 11**. All the prepared membranes were characterized and tested using the same procedure, and the conditions for the laboratory-scale AGMD setup are presented in **Table 7**.

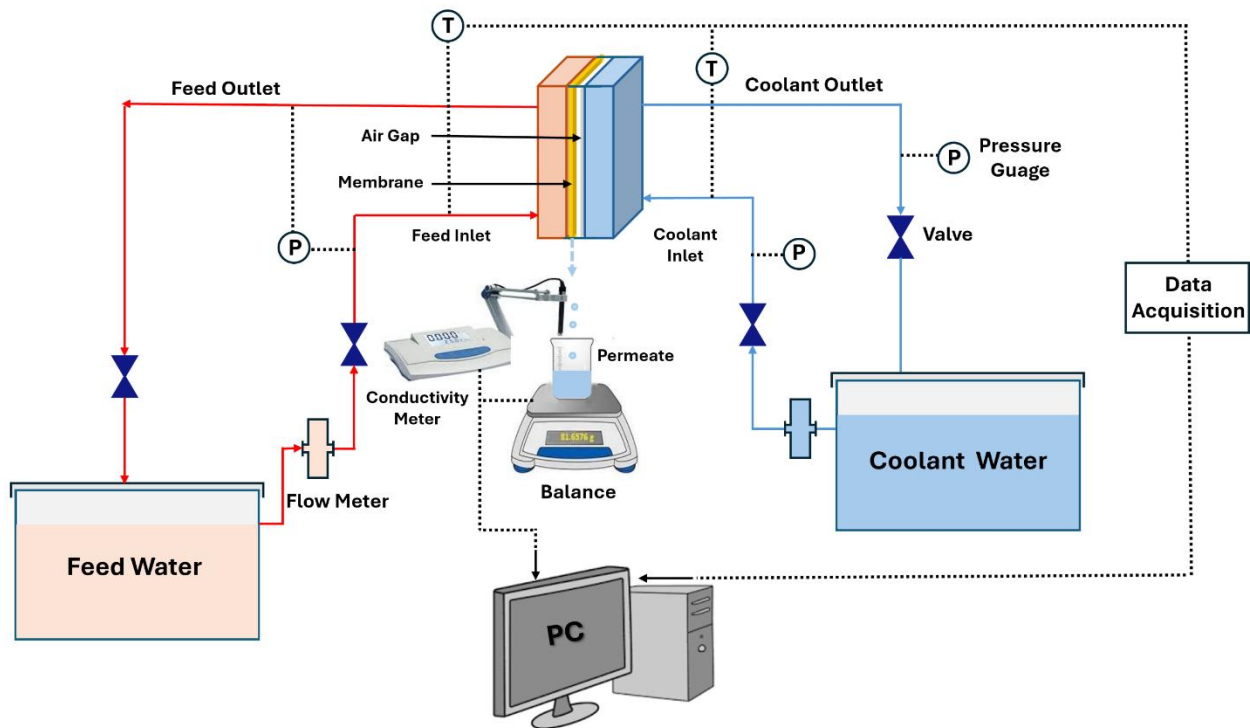


Figure 11. Schematic diagram of the laboratory scale AGMD Set-up.

Table 7. Process conditions for the laboratory-scale AGMD setup.

Parameters	Values	Units
Feed salinity	70000	ppm
Feed flow rate	0.8	L min ⁻¹
Feed temperature	70 ± 0.6	°C
Coolant flow rate	2.0	L min ⁻¹
Coolant temperature	20 ± 0.3	°C
Effective membrane area	7.316 × 10 ⁻⁴	m ²
Air-gap width	3-5	mm

3.5 Results and discussions

3.5.1 Synthesis and characterization of 6FDA-mPDA polymer

6FDA-*m*PDA was prepared by a one-step polycondensation reaction at elevated temperature in *m*-cresol and in the presence of a catalytic amount of isoquinoline. The resulting polymer was washed a few times using methanol.

3.5.1.1 Fourier transform infrared (FTIR) spectroscopy

Fourier transform infrared (FTIR) spectroscopy is an important technique for confirming the complete imidization of polyimides. The information obtained from the analysis is crucial for membrane applications, as it reveals the functional groups responsible for the chemical stability and hydrophobicity of the polymer. The FTIR

spectrum (**Figure 12**) demonstrated the polyimide functional group, with a C–H absorption band observed at 2800–3000 cm^{-1} , symmetric and asymmetric absorption bands of the carbonyl (C=O) group at 1780 and 1718 cm^{-1} , respectively, whereas the C–N absorption band was observed at 1348 cm^{-1} . Imide ring deformation was responsible for the absorption peak at 716 cm^{-1} . The appearance of these peaks in the FTIR results confirms the complete imidization of the polymer, which is an important performance parameter of the developed membranes from the polyimide polymer.

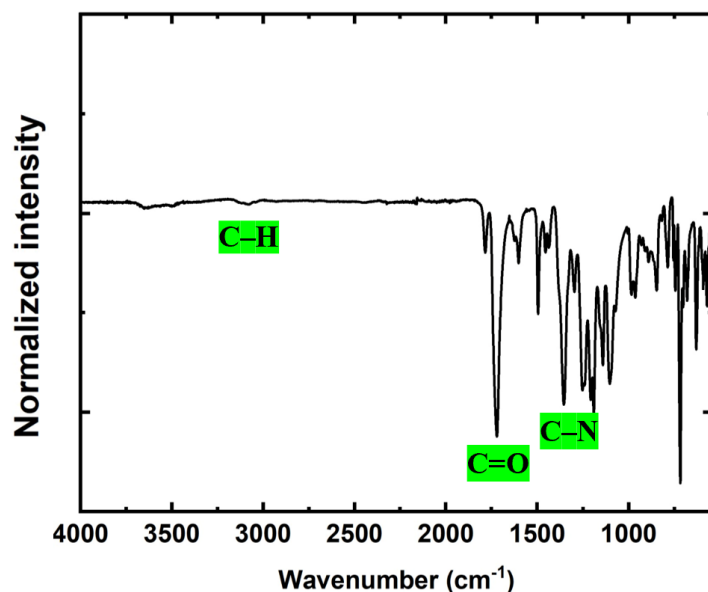


Figure 12. FTIR spectrum of 6FDA-*m*PDA polymer.

The absorption peak at 2800–3000 cm^{-1} assigned to the C–H aromatic stretching confirms that the polymer backbone contains an aromatic ring. The fluorinated 6FDA groups are responsible for the absorption at 1140–1200 cm^{-1} and are important functional groups for the hydrophobicity and separation efficiency of 6FDA-based polyimide membranes. Moreover, their presence in the polymer backbone increases the solubility and processability of this class of polymer family.

These findings follow other similar results from the literature. For instance, Zhang et al. [139] and Mahmoud et al. [140] found similar results for the carbonyl (C=O) groups stretching at 1780 and 1718 cm^{-1} , respectively, confirming a complete imidization. Moreover, another study by Zhen et al. [141] explained that the C–F stretching at 1140–1200 cm^{-1} indicates the hydrophobic groups of the fluorinated polymers, which contribute to the hydrophobicity of the developed membranes. The characteristic functional groups possessed by 6FDA-*m*PDA, such as the fluorinated groups and imide linkages as confirmed by the FTIR analysis, are important for the thermal and chemical stability that are necessary for any high-performance separation, and showed that this polymer is a suitable membrane material for membrane distillation.

3.5.1.2 ^1H NMR analysis

The ^1H NMR of the 6FDA-*m*PDA is presented in **Figure 13**. The successful preparation of 6FDA-*m*PDA was confirmed by the absence of peaks above 10 ppm in the ^1H NMR spectrum and the absence of hydroxyl stretching bands in the FTIR, confirming the complete conversion of poly(amic) acid to polyimide. The ^1H NMR (400 MHz, $\text{DMSO}-d_6$) at δ 7.54 (m, 3H), 7.72 (m, 1H), 7.80 (s, 2H), 7.94 (d, 2H), 8.22 (d, 2H) further confirm that only aromatic protons are present and confirms the complete conversion of polyamic acid.

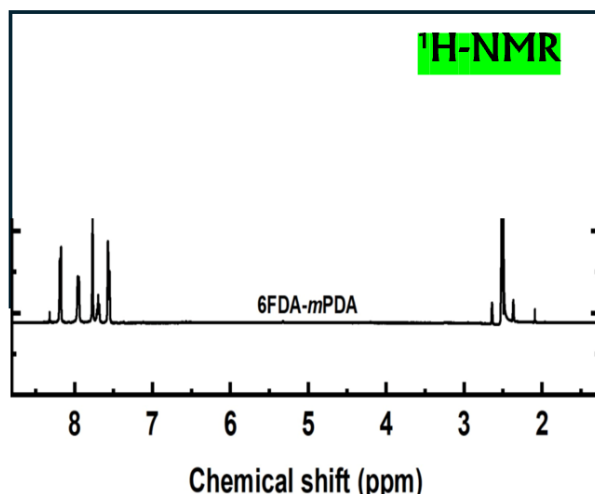


Figure 13. ^1H NMR spectrum of 6FDA-*m*PDA polymer.

3.5.1.3 Thermogravimetric analysis (TGA)

It is important to note that most polymers undergo degradation or melt before 200 °C. On the other hand, a few classes of thermally stable polymers can tolerate temperatures of at least 300 °C in air and 500 °C in inert gases without losing their strength or structural integrity in TGA analysis [142,143]. According to the TGA analysis, 6FDA-*m*PDA demonstrated outstanding thermal stability, with $T_{d,5\%}$ exceeding 500 °C (Figure 14), confirming its great potential to be used under harsh conditions (including high temperature and pressure) without leaching or shedding the 6FDA part. The findings indicate that 6FDA-*m*PDA is more stable than other fluorinated polymers, such as PVDF and PTFE, which are thermally stable because of their robust carbon-fluorine (C–F) linkages. For instance, the semi-crystalline nature of PVDF allows it to maintain a balance between stiffness and flexibility at temperatures between -35°C and 160 °C. However, PVDF undergoes dehydrofluorination when heated over 316 °C, which may result in structural alterations or discoloration [144].

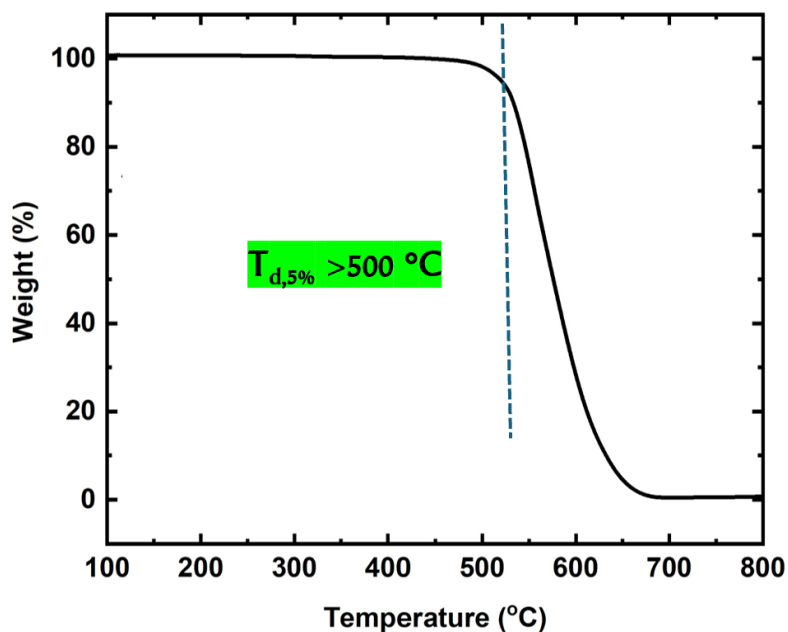


Figure 14. Thermogravimetric analysis of 6FDA-*m*PDA polymer.

3.5.1.4 Wide-angle X-ray diffraction (WXR) analysis

X-ray diffraction (XRD) analysis was employed to ascertain the crystallinity or amorphous nature of the 6FDA-*m*PDA. The amorphous properties of polymers are important, especially in membrane-based applications. While crystalline polymers pack efficiently when crystallized from melt or solution, amorphous polymers tend to possess space due to inefficient packing in their solid state. This can be particularly important in this work, where no pore-forming agent was added for membrane fabrication. The regular arrangement of atoms and molecules in a typical XRD examination will result in a clear diffraction peak, while amorphous regions yield broad halos. Polymers typically exhibit a blend of both in their diffraction pattern [145]. The XRD analysis result of 6FDA-*m*PDA is presented in **Figure 15**, which depicts a broad halo rather than sharp peaks between 10-20° 2 θ , confirms the amorphous properties of 6FDA-*m*PDA.

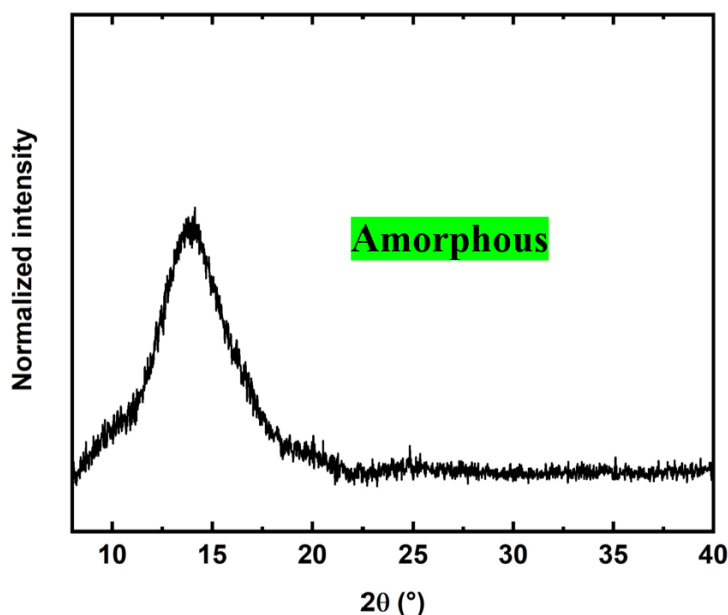


Figure 15. XRD spectrum of 6FDA-*m*PDA polymer.

This result agrees with the findings of Zhang et al. [18], who discovered that fluorinated polyimides have lower crystallinity due to the presence of the bulky CF_3 groups, which prevent complete molecular packing. Additionally, Lim et al. [146] showed that the presence of CF_3 in 6FDA-based polyimides decreases their crystallinity and favors disordered polymer chains. These findings correspond to the XRD spectrum of 6FDA-*m*PDA in this study, where the absence of sharp peaks indicates a highly disordered arrangement, further demonstrating its suitability and potential application in membrane-based applications. The lower crystallinity of 6FDA-*m*PDA might be due to the bulky dianhydride (6FDA) units and the planar (*m*PDA) diamine. This amorphous property of 6FDA-*m*PDA is important in MD applications in enhancing polymer free volume and improving mass transfer properties. Ultimately, selecting 6FDA-based polymers is a one-step process toward addressing the issue of mass transfer resistance and membrane

performance due to the enhanced mechanical, thermal, and hydrophobicity of the membranes.

3.5.2 Membrane morphology and characterization

The surface and cross-sectional morphologies of the NIPS membranes were analyzed using scanning electron microscopy (SEM). **Figure 16** represents the cross-section and surface morphologies of the 6FDA-mPDA-based membranes prepared through the NIPS method with 13, 15, and 17 wt. % representing N_13, N_15, and N_17 respectively. From the images, it is obvious and worth mentioning that the membranes prepared from NIPS (i.e., N_13-N_17) depict finger-like cross-sectional morphologies and a selective skin layer on the membrane surfaces comprising pores, indicating their porosity without the need to add porogen materials.

3.5.2.1 Influence of polymer concentration on NIPS membranes

The surface morphologies in **Figure 16 (a-c)** illustrate how polymer concentration affects the kinetics and thermodynamics of phase separation, two parameters that ultimately determine the final membrane morphology. The membrane prepared with a lower polymer concentration (i.e., N_13 with 13 wt.% %) depicted a surface morphology with many connected pores. This higher porosity is attributable to the lower polymer concentration, which favors a faster demixing process and a larger portion of the polymer-lean phase in the system due to a fast solvent and non-solvent exchange.

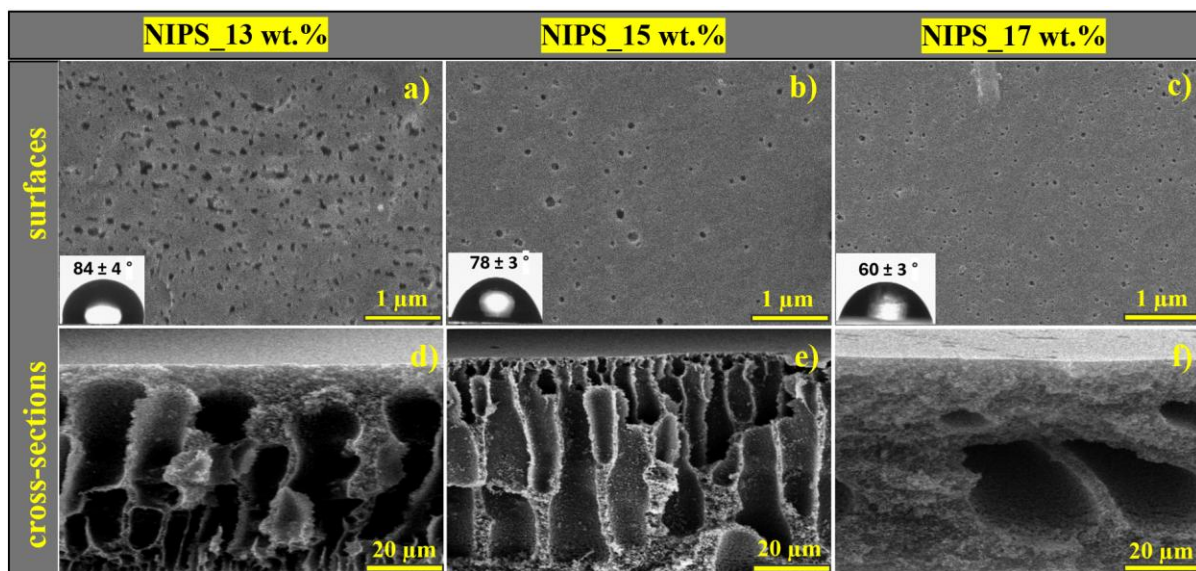


Figure 16. Surface and cross-sectional SEM images of the polyimide membranes prepared using the NIPS method, panel (a–c) show the surface morphologies, and (d–f) present the corresponding cross-sectional morphologies of N_13, N_15, and N_17 membranes, respectively. Insets indicate the measured water contact angles (WCA) for each sample.

The increase in dope solution concentration from 13 to 15 wt.% greatly influenced the thermodynamic stability of the system. As a result, a relatively slower solvent and non-solvent exchange occurred. Moreover, the polymer-rich phase is higher relative to the NI system with a lower polymer concentration. These effects directly impact the membrane surface morphology shown in **Figure 16 (a-c)**, where the membrane porosity decreases, and pore connectivity is reduced. This is due to the increase in viscosity of the solution, which decreases the entropy, as well as the rate of the separation process, i.e., the liquid-liquid demixing process, and subsequently promotes the formation of a denser structure with reduced pore size due to controlled and uniform nucleation [147]. The influence of

polymer concentration on the membrane surface and cross-sectional morphology is more pronounced as the polymer concentration increases to 17 wt. %. Here, the solution viscosity is much higher than in N1 and N2 systems. Ultimately, the entropy of the polymer chains is restricted and favors a much slower demixing and solvent and non-solvent exchange. This results in a more polymer-rich phase during the phase separation, and subsequently, a final membrane with lower porosity and fewer interconnected pores as depicted in SEM images.

The cross-sectional morphologies of the NIPS membranes prepared with an ethanol bath in **Figure 16 (d-f)**, dominated finger-like morphologies for N1 and N2 are the typical morphologies observed for NIPS membranes prepared with water as the non-solvent. For instance, Basko et al. [148] reported similar finger-like cross-sections for PVDF membranes developed using the NIPS method. In another study, Tao He [149], also observed similar membrane cross-sectional morphologies for both polysulfone and polyethersulfone prepared using a water coagulation bath. In agreement with our findings, Toheeb et al. [118] found similar cross-sectional morphologies from 6FDA-TMPD polyimide-based membranes developed using an ethanol coagulation bath at higher casting thickness. However, a spongy-like morphology was observed with a lower casting thickness in the ethanol bath.

Generally speaking, the development of a finger-like macrovoid structure is associated with instantaneous demixing. In contrast, the finger-like structure can be avoided by promoting delayed demixing, as this delays the onset of the nuclei and densifies the top layer of the skin [149]. This may explain why the N3 membrane, prepared with a higher

concentration of 17 wt. %, showed a reduced finger-like cross-section (**Figure 16f**) due to a slower demixing rate.

The SEM analysis of the developed membranes through the NIPS method confirms that polymer concentration greatly influences the morphology and membrane performance. Thus, it is important to optimize the polymer concentration, casting thickness, and non-solvent type to obtain a membrane with ideal properties suitable for the application.

3.5.2.2 Effect of surface modification with VIPS

Because slight variations in the phase separation process can lead to significant changes in surface architecture and modify the membrane properties and performance, VIPS was used to surface-modify 6FDA-*m*PDA-based membranes and alter their porosity. Being the most common non-solvent, water was first employed for the vapor-assisted phase inversion. Later, various non-solvent vapors were used to examine the effect of vapor type and polymer affinity on the membrane properties and performance. Additionally, since ethanol was used in the coagulation bath for preparing membranes by NIPS, ethanol vapor was also used as the non-solvent for membrane preparation using VIPS to systematically study the difference between both methods and their effects on membrane properties and performance. The surface morphologies of the membranes prepared using water vapor at different exposure times are shown in **Figure 17 (a-c)**. Moreover, the impact of vapor type on membrane morphologies has been addressed in a later section. These morphologies could be attributed to crystallization occurring before the liquid-liquid demixing process, making the precipitation process primarily driven by crystallization or nucleation, rather than the demixing process. In this case, the crystallization and the binodal barrier are

separated even more, allowing all the individually formed crystalline granules to develop and combine to create a bi-continuous architecture [150].

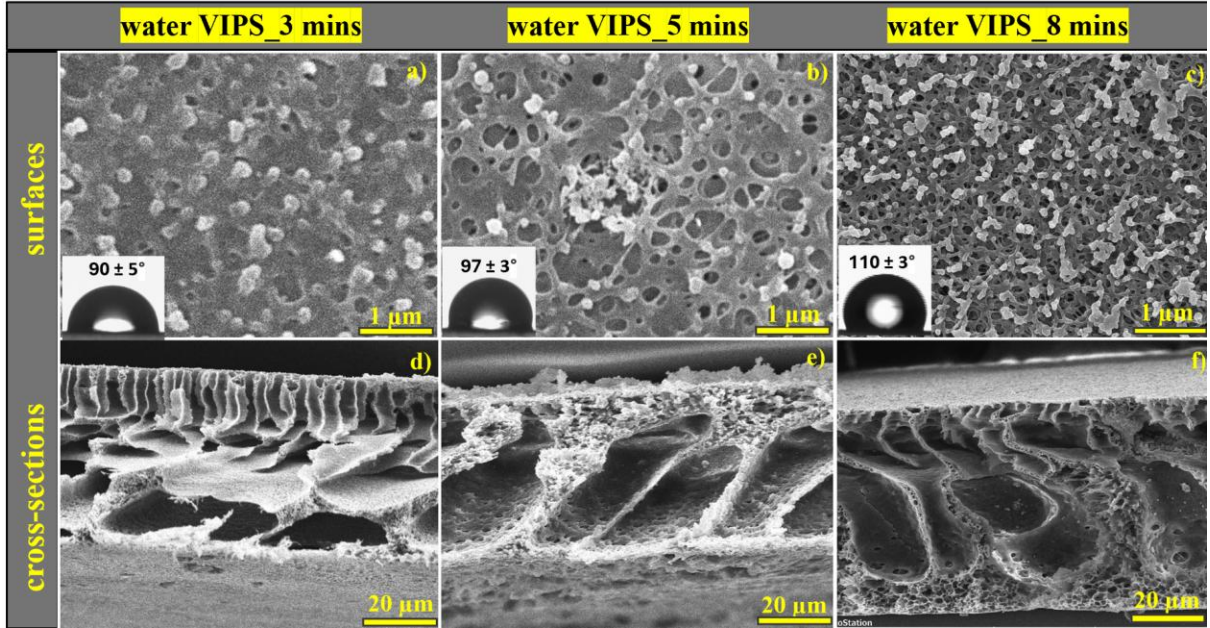


Figure 17. Surface and cross-sectional SEM images of the polyimide membranes prepared through VIPS with water vapor. Panels (a–c) show the surface morphologies, and (d–f) present the corresponding cross-sectional morphologies of V_W3, V_W5, and V_W8 membranes, respectively. Insets indicate the measured water contact angles (WCA) for each sample.

3.5.2.3 Influence of exposure time on water-VIPS membrane morphology

From the SEM images in **Figure 17**, the nature of the surface morphology started with a relatively dense layer at the top of V_W3, depicting that the exposure time of 3 minutes in the water vapor environment was not enough to complete the phase separation and produce a porous membrane due to the limited nucleation. As a result, this

membrane had a pore size of 0.26 μm with low surface porosity. As the exposure time increased to 5 minutes for V_W5, the pore size can be seen to increase to 0.32 μm as the surface becomes more open at the top layer. Yet, the membrane pores remained tightly packed beneath the thin, porous layer. This implies that as the phase separation begins, a thin layer forms. If vapor penetration stops sooner, the inner layer becomes dense rather than porous. When the exposure time increases to 8 minutes in the case of V_W8, the thickness of the porous layer increases deep inside the membrane cross-section. This is evidenced by the interconnected pores observed from the SEM image of this membrane. Moreover, the extended exposure time enhances the nucleation and growth of the non-solvent-rich domains. In addition, this implied a change in the phase separation mechanism from a liquid-liquid demixing to an instantaneous process due to the saturation of water vapor in the polymer matrix. Ultimately, while water vapor produces a separation and a final membrane, a longer exposure time is required to form an interconnected and porous membrane with optimum porosity. This phenomenon is attributed to density and, ultimately, slow penetration (affecting the kinetics) and lower affinity of water vapor towards the cast polymer film, which influences the thermodynamics of the system.

It is worth mentioning that, in the VIPS process, factors such as relative humidity, non-solvent vapor exposure time, and solvent-non-solvent interactions play critical roles in governing pore formation and surface morphology. The high relative humidity ($\geq 95\%$) in the VIPS chamber encourages vapor condensation on the membrane surface, allowing gradual solvent exchange and delayed demixing, which aids in the formation of sponge-like, interconnected pores. Additionally, the controlled exposure time allows crystallization to precede liquid-liquid demixing, leading to uniform and open pore structures that are less

dependent on polymer concentration compared to NIPS membranes. This results in a hierarchical, rough surface and interconnected pore network, which significantly enhances membrane wettability and performance. These findings demonstrate the ability of the VIPS method to tailor membrane porosity and morphology through precise control of process parameters, making it a versatile approach for developing high-performance membranes [38,39].

3.5.2.4 Effects of binary non-solvent (water-ethanol) vapor

To further investigate the influence of vapor on the mechanism of phase separation, a binary non-solvent system of ethanol and water was employed to minimize saturation rates and control the kinetics of the process. The SEM images of the membranes prepared with this vapor system, shown in **Figure 18** indicate that altering the composition of the non-solvent vapor can directly influence the morphological properties of the membranes. For instance, at the same exposure time, V_W/E_3 depicted a porous and interconnected open surface morphology with crystalline granules relative to V_W3.

In contrast to a delayed demixing with water vapor, resulting in a less porous membrane at 3 minutes, the binary water-ethanol system phase separates the cast polymer film through the nucleation and growth mechanism through an instantaneous process. This quicker phase separation mechanism is attributable to the presence of ethanol in the system, which enhances the kinetics and allows the vapor to penetrate the polymer film, evidenced by the sponge-like cross-sectional property of this membrane. Moreover, the membrane showed a unique mixture of symmetric nodular and sponge-like bi-continuous structures [30,36], as previously reported for the VIPS process. As the exposure time increases to 5 minutes

in the case of V_W/E_5, the surface morphology of the membrane becomes less open with a compacted cross-section, as observed from **Figure 18**.

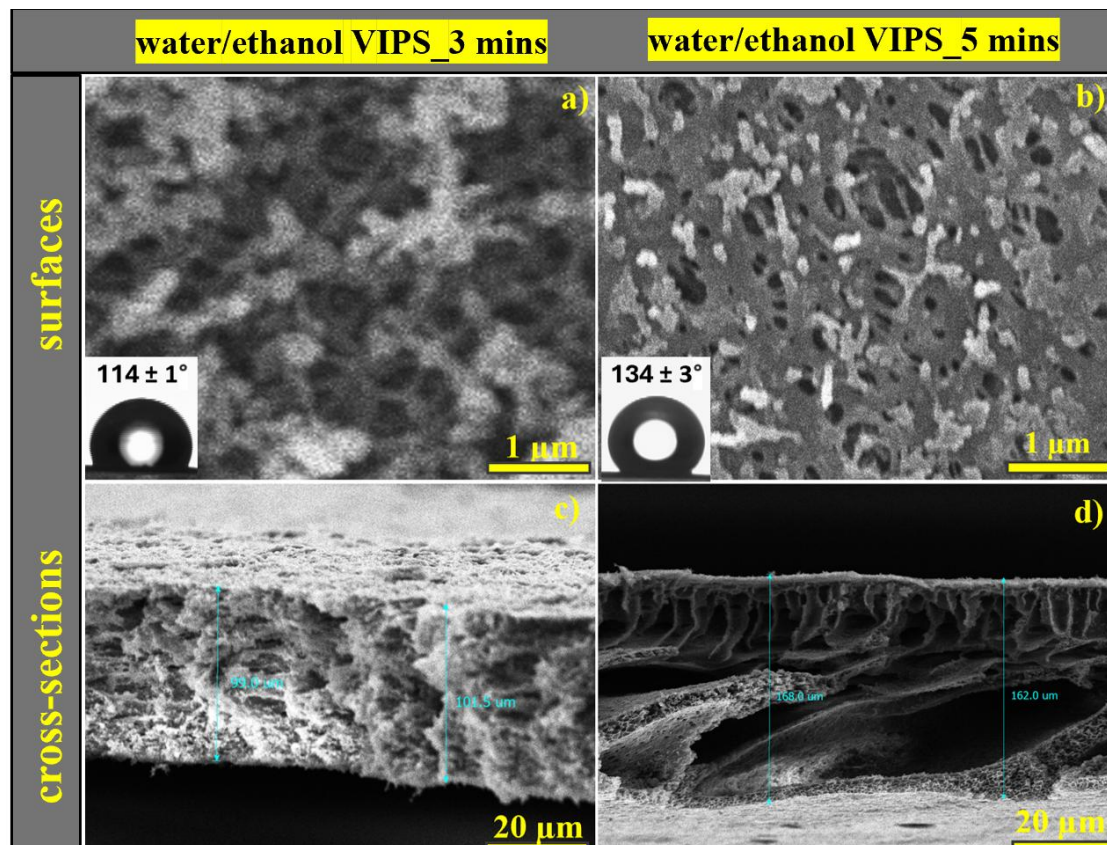


Figure 18. Surface and cross-sectional SEM images of the polyimide membranes prepared through VIPS with water/ethanol vapor. Panels (a–b) show the surface morphologies, and (c–d) present the corresponding cross-sectional morphologies of V_W/E_3 and V_W/E_5 membranes, respectively. Insets indicate the measured water contact angles (WCA) for each sample.

This implies that the extended exposure time causes polymer chains to rearrange and a delayed phase separation. Moreover, as the exposure time increases, the already formed granules prevent non-solvent penetration and cause densification and shrinkage. It is worth

mentioning that a membrane with a longer exposure time of 8 minutes was prepared; however, a physical shrinkage was observed for this membrane, which could not be tested.

Interestingly, membranes prepared by the VIPS displayed unique interconnected porous structures on the surface. In the case of the membrane prepared with the binary non-solvent (i.e., V_W/E_3, a sponge-like morphology in the cross-section was observed. This indicated that the presence of ethanol vapor changed the phase separation mechanism and might be explored further in tuning the cross-sectional morphology of the 6FDA-*m*PDA membranes. Subsequently, membranes were prepared using only ethanol vapor, with varying polymer concentrations discussed in the following section.

3.5.2.5 Influence of ethanol vapor and polymer concentration

While both water and water-ethanol vapors produced membranes with porous and interconnected surface morphologies, several distinctions can be made from the SEM characterizations in **Figure 19**. For instance, the membrane prepared with water vapor tends to be smoother with less exposure time than that prepared with water-ethanol, despite its porous nature. Moreover, the porous structure of the membranes remains nearly on the top surface due to a thick, dense layer near the surface. Conversely, the membrane, V_W/E_3, prepared with water-ethanol vapor, maintained this porous morphology through the membrane cross-section, as seen in the cross-sectional morphology. For this reason, different polymer concentrations were investigated to understand ethanol VIPS further.

Polymer concentration has two main impacts on membrane development in VIPS. First, the pore size is directly affected by variations in the volume fraction occupied by the polymer molecules. Second, the mass transfer rates, along with subsequent mechanisms

and structures of membrane development, are influenced by changes in viscosity. Increasing the concentration of polymers causes the solution to become more viscous, which has a major impact on the kinetics of phase inversion. Raising the viscosity gives the polymer-lean phase more resistance to coarsening because it reduces the polymer chain's mobility and the rate of non-solvent diffusion [153].

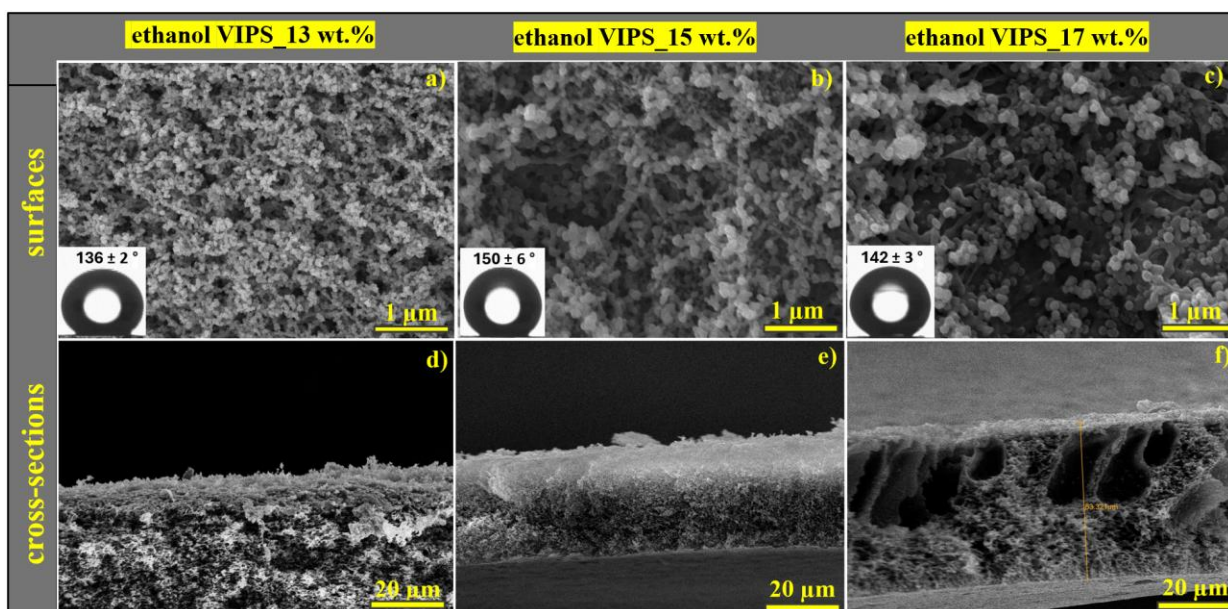


Figure 19. Surface and cross-sectional SEM images of the polyimide membranes prepared through VIPS with ethanol vapor. Panels (a–c) show the surface morphologies, and (d–f) present the corresponding cross-sectional morphologies of V13_E, V15_E, and V17_E membranes, respectively. Insets indicate the measured water contact angles (WCA) for each sample.

The influence of polymer concentration on the morphological analysis of the 6FDA-*m*PDPA membranes prepared using ethanol vapor was analyzed and presented in **Figure 19a-f**. As

described above, the choice of polymer concentration directly influences the microstructure and membrane hydrophobicity. It is noteworthy that the change in polymer concentration in this study does not significantly alter the surface morphology of the membranes, as shown in the images. However, the size of the polymer granules increases with concentration. This could be explained from different points, first, a higher polymer concentration decreases the number of nucleation sites. For instance, the smaller granules of V13_E in **Figure 19a** are attributable to the fast solvent-non-solvent exchange, leading to a fast-demixing rate and a larger number of small granules due to the lower polymer concentration. Conversely, when the polymer concentration increases for V15_E and V17_E, the solution becomes more viscous and slows the non-solvent diffusion, decreasing the number of nucleation sites. This, however, allows the already-formed granules to grow further, leading to a growth-dominated mechanism rather than a nucleation-dominated. Secondly, since VIPS relies on the absorption of non-solvent from the vapor environment, higher polymer concentrations decrease the quick ethanol penetration through the casted film (slower phase separation). This delay in the demixing process permits the smaller formed granules to agglomerate into larger ones. For the cross-sectional morphologies in **Figure 19 (d-f)**, the lower polymer concentrations of V1 and V2 relative to V3 produce membranes with a more open and porous structure and microvoids due to rapid ethanol penetration, leading to quick phase separation and less ordered crystallization. Unlike the rapid solvent removal in NIPS, the crystallization-driven phase separation in VIPS ensures a more gradual structural evolution, with V3 displaying partial finger-like morphology due to increased polymer viscosity and chain entanglement at higher concentrations. Moreover, the cross-section of this membrane is due to the delayed separation process, due to higher

polymer concentration and a narrower demixing front, which favors elongation and nucleation of microvoids. The formation of the skin layer was likely due to the shrinkage and coarsening of the polymer-rich phase near the surface of the cast film. This may have delayed the spinodal decomposition process, preventing it from extending deeper into the film [37]. Consequently, two distinct morphologies were observed.

3.5.2.6 Influence of propanol vapor and polymer concentration

To further understand the influence of the non-solvent on the morphological properties of the membranes, we employed propanol vapor, having a higher molecular weight and size, to investigate the kinetics and the polymer and non-solvent interaction. The resulting morphologies of these membranes are depicted in **Figure 20 (a-f)**.

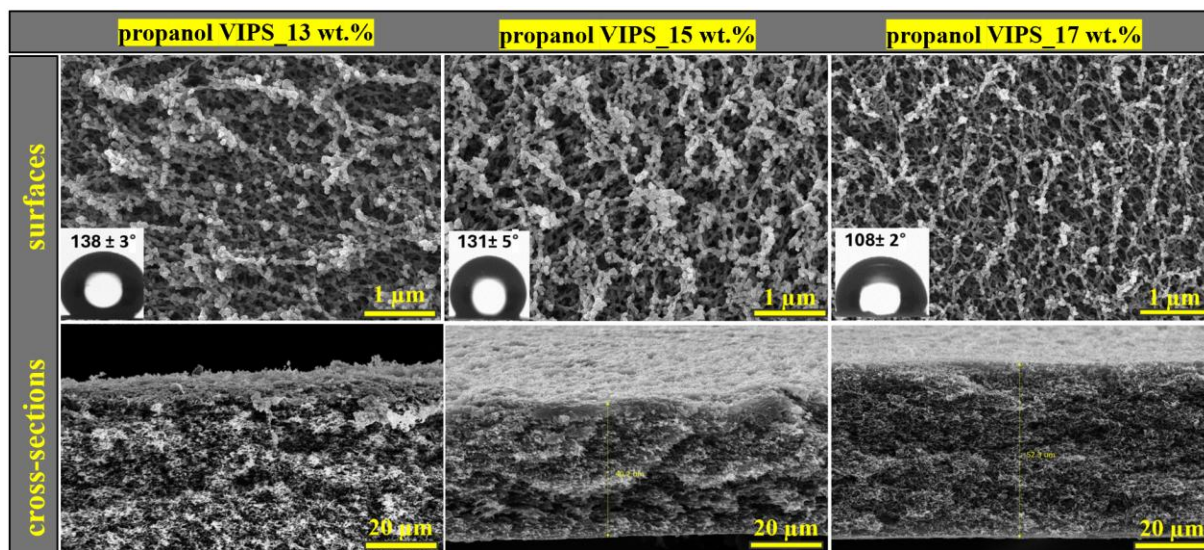


Figure 20. Surface and cross-sectional SEM images of the polyimide membranes prepared through VIPS with propanol vapor. Panels (a–c) show the surface morphologies, and (d–f) present the corresponding cross-sectional morphologies of V13_P, V15_E, and V17_E

membranes, respectively. Insets indicate the measured water contact angles (WCA) for each sample.

To make a better comparison, membranes were prepared with the same concentrations as those prepared with ethanol. While these membranes showed similar morphologies of symmetric nodular and sponge-like bi-continuous structures like those prepared with ethanol vapor, there are distinctions between them brought by changes in separation kinetics. For instance, the structure becomes less open as the polymer concentration increases, contrasting the trend observed from VIPS-ethanol membranes. The porous structure of the membranes follows the trend observed from the NIPS with changing polymer concentration. As expected, **V13_P** prepared with the lowest polymer concentration depicted more open interconnected granules with larger microvoids, with a relatively rough texture. This, as previously explained, is attributable to the rapid phase separation due to the low viscosity of the casting solution and larger area of the polymer-lean phase. It can also be observed that, as the polymer concentration increases, the polymer-rich phase and polymer chains per unit volume increase. This, in turn, makes the solution more viscous, slowing down the non-solvent vapor penetration and ultimately leading to a more uniform but slower demixing process. As a result, **V15_P** is relatively smoother despite maintaining the interconnected surface morphology. As the solution becomes even more viscous in the case of **V17_P**, the surface granules become more compact and denser, making the membrane less porous among the propanol-VIPS membranes

Similar to the ethanol-VIPS membranes, the membranes prepared with propanol also exhibited sponge-like cross-sectional morphologies, as seen in **Figure 20 (d-f)**. The only

noticeable difference is found between **V17_E** and **V17_P**. This variation is primarily due to the solubility and volatility of propanol and ethanol, which influence the phase separation process. The high volatility of ethanol (BP $\approx 78^{\circ}\text{C}$), compared to that of propanol (BP $\approx 97^{\circ}\text{C}$), enables ethanol vapor to rapidly penetrate the cast film, leading to instantaneous demixing and finger-like cross-sectional morphology. Moreover, the mass transfer and diffusion rate of ethanol vapor is higher than propanol vapor due to its molecular size relative to propanol, further facilitating the fast separation process. Conversely, the uniform sponge-like morphology of **V17_P** is due to the delayed demixing as a result of the slow diffusion rate of the vapor.

3.5.2.7 Influence of vapor type

The type of non-solvent vapor can influence the kinetics and thermodynamics of phase separation of membranes prepared using VIPS. The top surface morphologies from the SEM images in **Figure 21 (a-d)** revealed that, at the same exposure time of 3 minutes, the membrane prepared using water vapor has relatively very minimal porosity among the VIPS membranes. This surface structure suggests that, at this exposure time, the amount of water vapor was insufficient to produce a porous membrane. This can be attributed to the high surface tension of water, low volatility, and its low affinity due to the solubility parameter difference with DMF, leading to slow diffusion, which allows the polymer to precipitate as the solvent evaporates, and subsequently, leading to a membrane that lacks porous structure as seen in **Figure 21a**. As ethanol is introduced to the vapor to create a binary vapor, the surface tension of the vapor decreases. On the other hand, the volatility of the vapor increases.

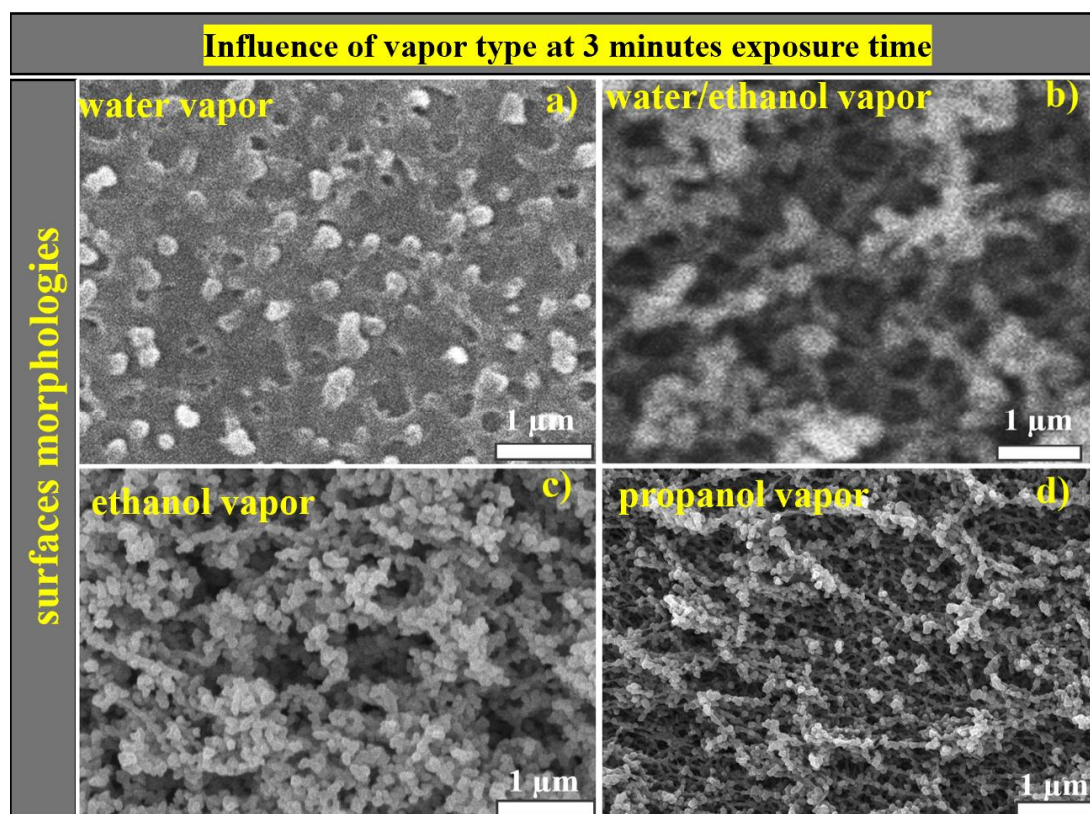


Figure 21. SEM images of the polyimide membranes prepared through VIPS with different vapors (a-d) influence of vapor type on surface morphology; for V15_W_3, V15_W/E_3, V15_P_3, and V15_P_3 membranes, respectively.

As a result, the driving force of the phase separation is decreased, leading to a slower nucleation with less ordered growth (due to differences between water and ethanol) of granules that connect to form a porous network (**Figure 21b**). When pure ethanol was used, the morphology changed to a more porous surface and larger interconnected granules as seen in **Figure 21c**. This is due to the low surface tension and high volatility, leading to higher mass transfer and vapor diffusion into the polymer solution, and ultimately, the formation of uniformly sized crystalline granules that create a network of a uniform porous structure. Because propanol is relatively more viscous and denser than ethanol due to its

high molecular weight, its penetration into the polymer film is relatively slow, resulting in a delayed demixing process. This phenomenon favors a more progressive phase separation that produces sponge-like but denser surfaces or semi-networked morphology.

Thermodynamically, the affinity and solubility parameters affect the phase separation mechanism. The larger the difference in solubility parameter, the less interaction between the polymer matrix and vapor occurs, and rapid phase separation occurs through spinodal decomposition. For instance, the difference in solubility parameter between DMF and water is large ($\Delta\delta = 23.0$), leading to poor miscibility and less interaction, and subsequently, asymmetric membranes are formed. On the other hand, $\Delta\delta$ for DMF and ethanol is relatively very low (1.7). Therefore, a good miscibility leads to a slower solvent-nonsolvent exchange through nucleation and growth, and subsequently, membranes with larger microvoids are formed. This also applies to isopropanol with a $\Delta\delta$ of 1.3 with water. kinetically, water has the highest diffusion coefficient, implying a faster mass transfer rate and a faster demixing process. However, its high surface tension, combined with the above thermodynamic parameters, produces asymmetric membranes. Alternatively, the combined affinity towards the polymer matrix, low surface tension, and moderate diffusion coefficient of alcohols generated membranes with porous networks.

3.5.3 Surface roughness of the 6FDA-*m*PDA

The NIPS membrane's surface roughness was evaluated using Atomic Force Microscopy (AFM) as depicted in **Figure 22** and **Table 8**. From the results of this analysis (3-D presentation), it is clear that the surface roughness of the membranes decreases from N_13 to N_15. Furthermore, as the dope solution concentration increases, the surface

roughness decreases. For instance, the R_q value decreased from 12.3 to 3.3 nm upon increasing the dope solution concentration from 13 to 17 wt%, respectively. These changes in surface roughness were also reflected by the reduction in the WCA, which was reduced from 84 to 60° for N_13 and N_17, respectively. The decrease in surface roughness upon increasing dope solution concentration could be attributed to the smoother membrane surface observed with fewer pores.

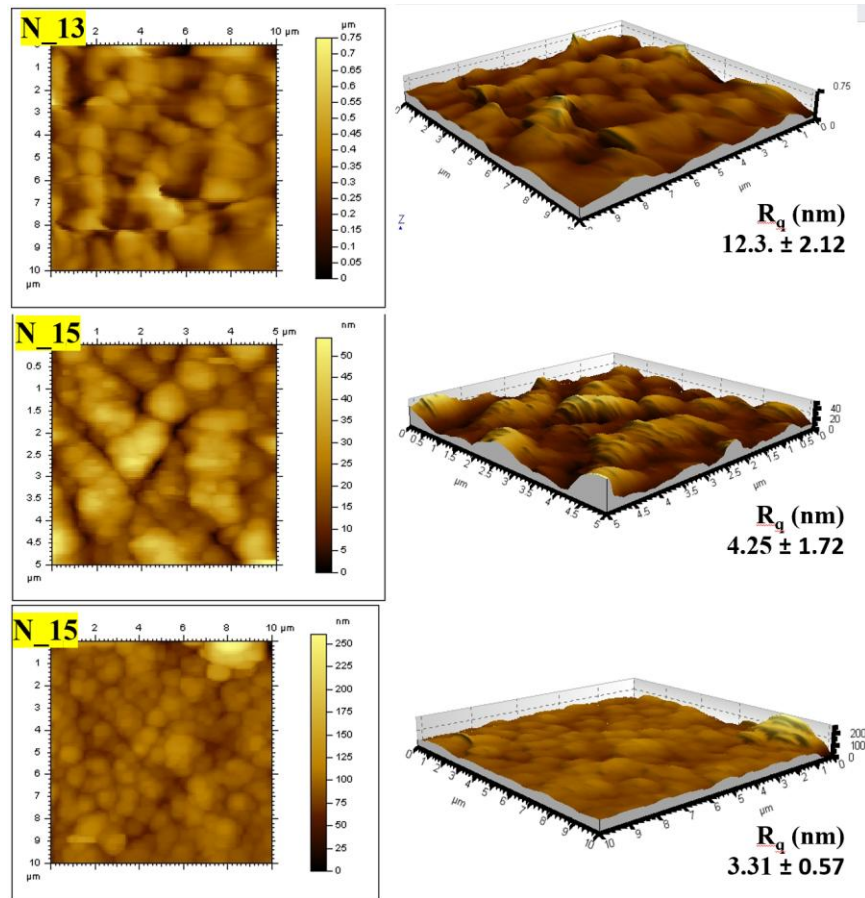


Figure 22. AFM analysis showing surface characteristics of the NIPS membranes with polymer concentrations of 13, 15, and 17 wt.% for N_13, N_15, and N_17, respectively.

The surface roughness is also attributable to the nature of polymer phase separation and the thermodynamic stability of the system. For instance, N_13 with higher system entropy will have a more random polymer arrangement during crystallization than systems with lower entropy (N_15 and N_17). Moreover, the relatively faster demixing rate in a system with a lower polymer concentration will favor a rougher surface due to interconnected pores. For the membrane with a higher concentration, for instance, N3, the slow demixing rate allows the polymer chains to arrange themselves into a more regular and smoother surface. Ultimately, N1 with higher surface roughness possesses higher hydrophobicity than N2 and N3. The nature of surface roughness can directly influence the MD performance of the developed membranes. For example, N_13 with higher roughness can minimize the membrane wettability and prevent fouling due to the re-entrant structure following the Cassie-Baxter theory. On the other hand, N_13 with lower roughness might be prone to wetting and allow the passage of ions due to the smoothness of the surface. This analysis indicates that it is paramount to select the best polymer concentration to obtain membranes with higher porosities, optimized thickness, and surface roughness to achieve higher vapor permeability and better MD performance.

Table 8. Bulk properties of the NIPS membranes.

Membrane	WCA (°)	Roughness R_q (nm)	LEP (bar)	Mean pore size (μm)	Thickness (μm)	Porosity (ε%)
N_13	84 ± 4	12.3 ± 2.12	2.1 ± 0.4	0.21 ± 0.01	52.76	81.63
N_15	78 ± 3	4.25 ± 1.72	2.2 ± 0.1	0.19 ± 0.01	62.30	76.43
N_17	60 ± 4	3.31 ± 0.57	2.5 ± 0.1	0.16 ± 0.02	87.04	65.02

3.5.3.1 Membrane roughness and wettability-NIPS

WCA values are essential in determining the wettability of membrane surfaces and provide insight into the roughness of the surface. While 6FDA-*m*PDA was anticipated to exhibit inherent hydrophobicity due to the fluorine atoms in its polymer backbone, membranes prepared via the NIPS method showed relatively lower WCA values as presented in insets in **Figure 16a-c** and **Table 8**. This can be attributed to the smoother surface morphologies of the NIPS membranes, as evident from the SEM and AFM images in **Figure 16** and **Figure 22**. The non-solvent type directly influences the surface morphology of membranes developed through NIPS. As can be seen from **Table 8**, the pristine membrane (P) prepared using a water bath showed the lowest WCA value of $56 \pm 1^\circ$. This may be attributable to the affinity between water and DMF solvent, facilitating a faster demixing rate and resulting in a hydrophilic membrane with a smoother surface due to smaller membrane pores. Since MD requires a hydrophobic membrane to achieve vapor-liquid equilibrium and achieve optimum solute rejections and overall process efficiency, the pristine membrane developed with a water bath does not represent an ideal membrane for MD applications. As a result, another non-solvent was employed.

The change of non-solvent type from water to ethanol increased the surface roughness, translating into higher WCA values. For instance, N2, with the same dope concentration of 15 wt.% % as P, had an approximately 40 % increase in WCA. Additionally, because of the direct influence of surface roughness and morphology, and the fact that these parameters all rely on the nature of the phase separation, which is also affected by the

polymer concentration, it is expected that membranes with higher surface roughness should possess higher WCA. As a result, N1 possessed the highest WCA of $84 \pm 4^\circ$. This is due to the roughness of the membrane, morphology, and interconnected pores as evidenced by the SEM and AFM characterizations. The lower value of N3 is attributed to its smoother surface. The explanation for the smoothness of this membrane has been provided in the morphological analysis.

3.5.3.2 Roughness and wettability of W-VIPS and W/E membranes

The AFM images of the W-VIPS membranes presented in **Figure 23** show that increasing exposure time also increases the roughness of the membranes. For instance, as the exposure time increases from 3 to 5 minutes, the roughness of the membranes also changes from 352.53 to 354.08 nm. This is also reflected in the membranes' WCA values, with V_W5 having a higher value of 90° relative to V_W3, which had a value of 76° , as shown in **Table 9**. The highest surface roughness of 432.17 nm observed for V_W8 is also reflected in the membranes' WCA (97°), further linking the nature of surface morphology to surface roughness, following the Cassie-Baxter theory.

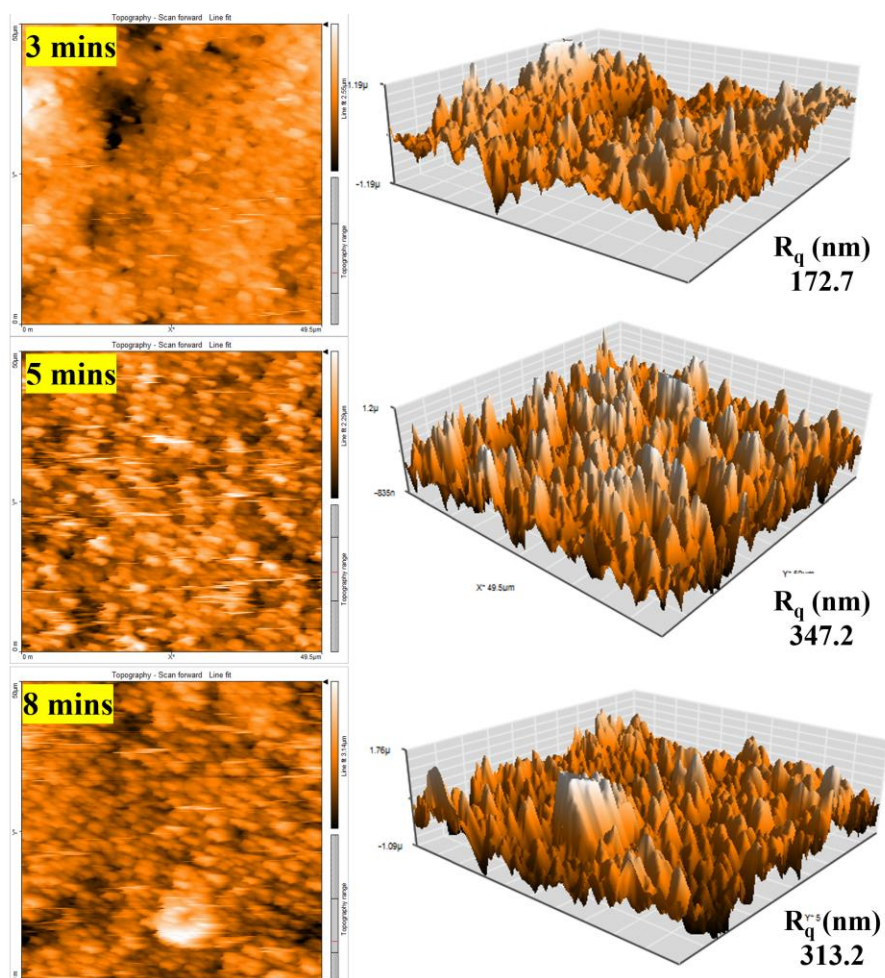


Figure 23. AFM analysis showing surface characteristics of the water VIPs membranes with exposure times of 3, 5, and 8 minutes for V_W3, V_W5, and V-W8, respectively.

Table 9. Bulk properties of the W-VIPS and W/E membranes.

Membrane	WCA (°)	Roughness S _q (nm)	LEP (bar)	Mean pore size (μm)	Thickness (μm)	Porosity (ε%)
V_W3	76	352.53	0.9 ± 0.1	0.31 ± 0.05	98.0	55.60
V_W5	90	354.08	1.4 ± 0.3	0.77 ± 0.03	61.5	68.06
V_W8	110	432.17	1.2 ± 0.1	0.54 ± 0.01	106.0	82.13
V_W/E_3	114	947.01	1.1 ± 0.2	0.46 ± 0.01	101.5	86.41
V_W/E_5	134	559.85	1.6 ± 0.3	0.35 ± 0.01	162.0	75.23

Another reason for the increase in the membrane's hydrophobicity with increasing exposure time might be due to changes in the surface chemistry in the sense that, as the membranes become more open with interconnected morphology, the -CF₃ hydrophobic groups become more exposed to the surface and therefore increase the water repellency of the membranes. In contrast to the trend of increasing surface roughness with longer exposure times observed for the W-VIPS membranes, the membranes prepared with the binary non-solvent of water-ethanol showed a decrease in roughness with longer exposure time, as shown in **Figure 24**. The decrease in the surface roughness of the water-ethanol membranes is related to their surface morphology. For instance, V_W/E_3 with a shorter exposure time of 3 minutes possessed a more porous surface morphology than V_W/E_5 with an exposure time of 5 minutes. This variation arises from the more compacted morphology observed with longer exposure time, as discussed in the morphological

analysis of these membranes. Ultimately, the kinetics and thermodynamics of the phase separation mechanism have a direct influence on membrane roughness by determining the membrane morphology and surface chemistry.

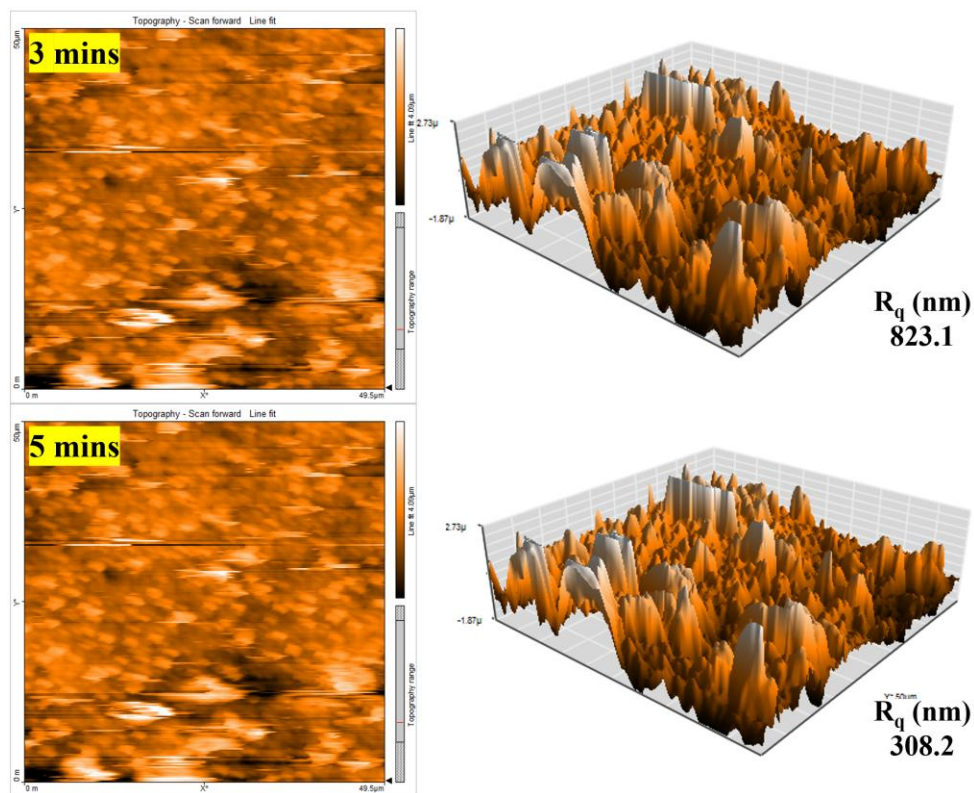


Figure 24. AFM analysis showing surface characteristics of the water/ethanol VIPS membranes with exposure times of 3 and 5 minutes for V_W/E_3 and V_W/E_5, respectively.

3.5.3.3 Surface roughness and wettability of E-VIPS membranes

The ethanol-VIPS membrane's roughness, evaluated with AFM, is depicted in

Figure 25. The membrane V15_E with a lower polymer concentration had a higher surface

roughness (R_q value of 23 nm) than the subsequent membranes with a higher polymer concentration. Membranes with lower polymer concentrations usually possess higher surface roughness due to spherulite structures on the membrane's surface. Faisal et al. [155] observed nano-scale nodules on a PVDF membrane surface with a lower concentration of 8 %. As a result, this membrane had a higher roughness and WCA.

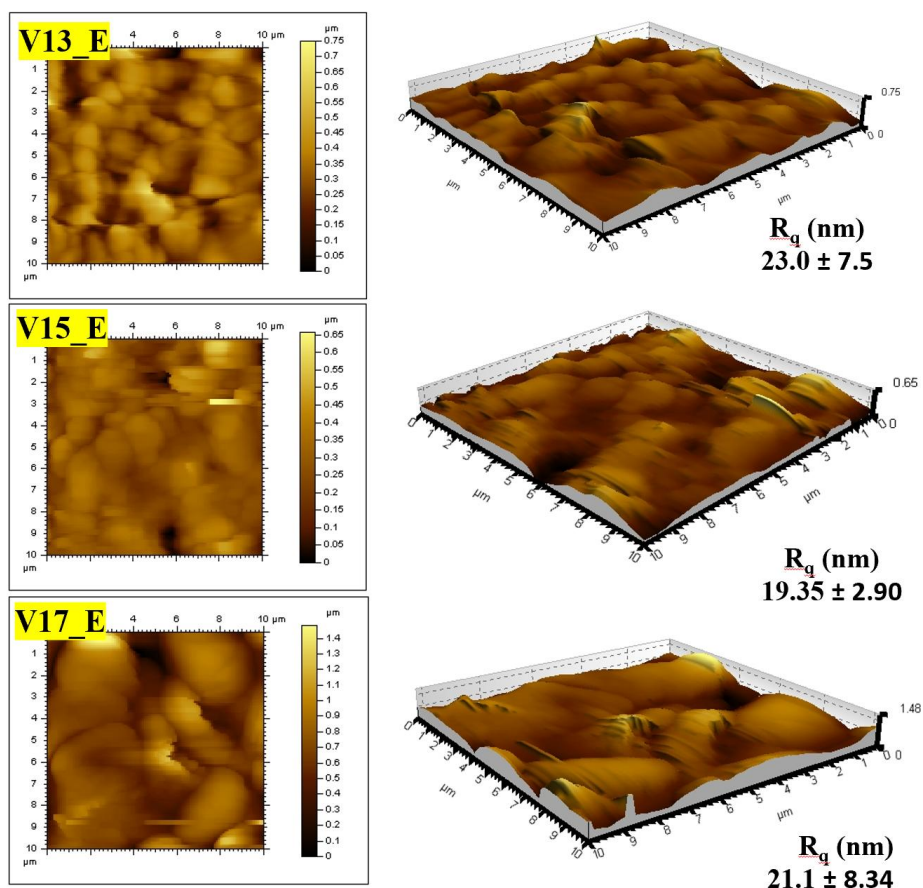


Figure 25. AFM analysis showing surface characteristics of the ethanol VIPS membranes with polymer concentrations of 13, 15, and 17 wt.% for V13_E, V15_E, and V17_E, respectively.

The increase in dope solution concentration increases the solution viscosity, subsequently increasing polymer chain entanglement and preventing efficient and ordered arrangements of polymer molecules during crystallization. This ultimately led to surfaces with lower roughness but raised the WCA values as seen in **Table 10**. Nonetheless, surface roughness is not the only parameter controlling membrane wettability. The highest WCA can be attributed to the interplay between surface chemistry, molecular orientation, and surface morphology. For instance, V15_E displayed the highest WCA of 150° despite its lower roughness, relative to V13_E and V17_E, suggesting that the membrane surface possesses a more uniform distribution and orientation of hydrophobic fluorine groups, inherent to the 6FDA-*m*PDA polymer backbone. This uniform arrangement minimizes water spreading and maximizes water droplet stability on the surface, leading to the observed high WCA.

Table 10. Bulk properties of the E-VIPS membranes.

Membrane	WCA (°)	Roughness R _q (nm)	LEP (bar)	Mean pore size (μm)	Thickness (μm)	Porosity (ε%)
V13_E	136 ± 2	23.0 ± 7.50	0.9 ± 0.3	0.37 ± 0.03	62.50	82.06
V15_E	150 ± 6	19.35 ± 2.9	1.9 ± 0.1	0.45 ± 0.01	63.32	88.13
V17_E	142 ± 3	21.1 ± 8.34	1.9 ± 0.2	0.43 ± 0.01	79.20	75.23

3.5.3.4 Surface roughness and wettability of P-VIPS membranes

The AFM analysis of the propanol VIPS membranes in **Figure 26** revealed a decrease in surface roughness with increasing polymer concentration. For instance, the R_q

value decreased from 58.3 to 34.5 and 29.5 nm upon increasing the dope solution concentration from 13 to 15 and 17 wt. %, respectively. These changes in surface roughness were also reflected by the reduction in the WCA, which was reduced from 138° for **V13_P** to 131° and 108° for **V15_P** and **V17_P**, respectively. The decrease in surface roughness upon increasing dope solution concentration could be attributed to the smoother membrane surface observed with fewer pores, as explained in the morphological analysis.

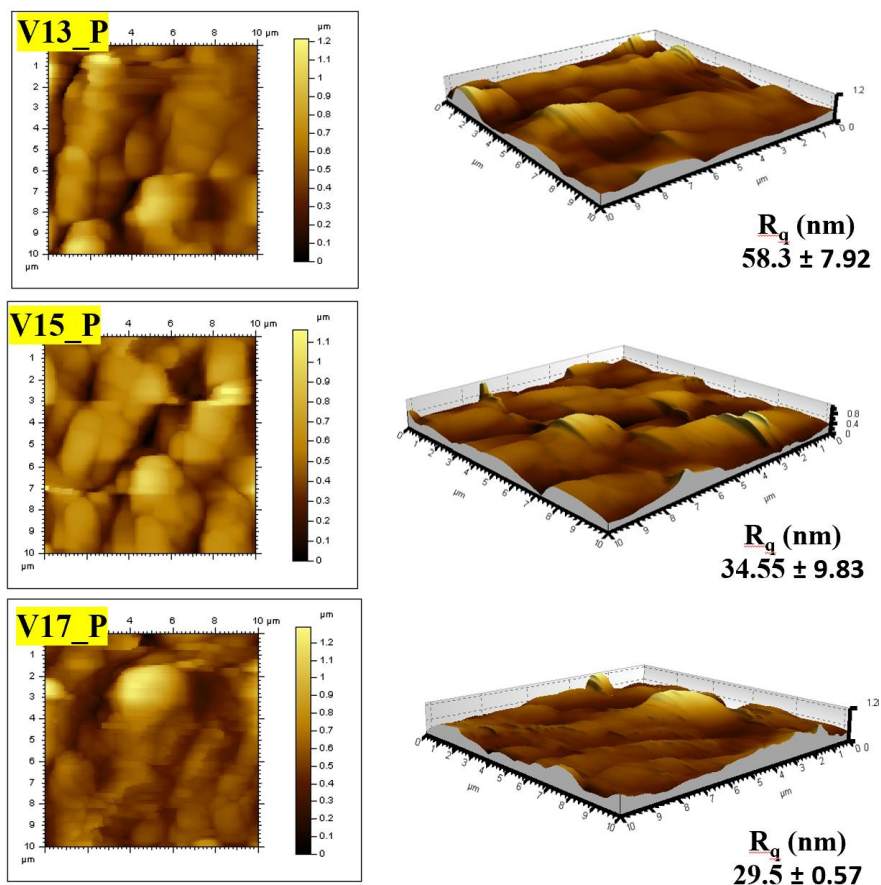


Figure 26. AFM analysis showing surface characteristics of the propanol VIPS membranes with polymer concentrations of 13, 15, and 17 wt.% for V13_P, V15_P, and V17_P, respectively.

The membranes prepared from a similar approach with propanol vapor also showed improved properties compared to those from the NIPS. However, a similar trend of change in WCA with concentration was observed, just as the membranes prepared from the NIPS, contrasting the behavior of those prepared with the same approach using ethanol vapor. As presented in **Table 11**, **V13_P** with a lower dope solution concentration of 13 wt.% has the highest WCA of 138°. As confirmed by the SEM image, this membrane possesses an increased surface roughness and topography compared to **V15_P** and **V17_P**. The difference and change in surface morphologies from ethanol to propanol might be attributed to the affinity of the non-solvent vapor toward the cast polymer solution, which subsequently alters the thermodynamics and kinetics of the phase separation mechanism that resulted in the polyimide membranes. It is worth mentioning that a slight alteration in the mass transfer mechanism, as well as other thermodynamic parameters such as the heat of vaporization of the solvent, chemical potential, and temperature of the environment, can alter the phase separation mechanism and therefore result in a different surface morphological property.

Table 11. Bulk properties of the P-VIPS membranes.

Membrane	WCA (°)	Roughness R _q (nm)	LEP (bar)	Mean pore size (μm)	Thickness (μm)	Porosity (ε%)
V13_P	138 ± 3	58.3 ± 7.92	2.1 ± 0.4	0.37 ± 0.03	50.20	81.76
V15_P	131 ± 5	34.5 ± 9.83	2.2 ± 0.3	0.24 ± 0.01	52.30	77.13
V17_P	108 ± 2	29.5 ± 0.57	2.6 ± 0.1	0.23 ± 0.02	69.60	68.40

3.5.4 Bulk properties of the 6FDA-mPDA membranes

3.5.4.1 Membrane surface porosity

The membrane surface porosity is directly related to its permeability and overall performance due to enhancement in mass transfer across the membrane, selectivity, and thermal efficiency of the process. The type of non-solvent bath, polymer concentration, and additives directly influence membrane porosity. Since no pore-forming agent was employed in this study, the non-solvent type and polymer concentration are the main discussion points.

3.5.4.2 Influence of non-solvent type

The type of non-solvent in NIPS has a direct relation to the membrane properties. **Table 8** clearly shows that membrane P has lower porosity (60.13 %) than N2 (76.43 %), even though both were prepared with the same concentration. It is important to note that in the NIPS method, the rate of solvent extraction from the polymer solution to the non-solvent significantly influences the membrane pore structure. When water was used as the non-solvent, polymer precipitation occurred rapidly due to the high exchange rate of water, resulting in lower interconnected pores and porosity. On the other hand, the lower exchange rate of ethanol relative to water favors a slower polymer precipitation and subsequently, larger interconnected pores with higher porosities.

In addition to the solvent-non-solvent exchange rate, the difference in solubility parameter is another factor that influences solvent-non-solvent-polymer interaction. The lower solubility parameter of water, compared to ethanol, also facilitates moderate polymer

precipitation and enhances surface porosity. Additionally, the higher viscosity of water leads to rapid polymer gelation and reduces the likelihood of polymer chain enlargement before solidification. In contrast, the lower viscosity of ethanol allows for chain movement before solidification, which may increase surface porosity. To conclude this part, the water system leads to instantaneous demixing, which produces a dense skin layer with low porosity, while the ethanol system favors the formation of more interconnected pores with higher porosity due to the delayed demixing rate. Thus, it implies that changing water with ethanol as a non-solvent enhances the porosity and permeability due to a slower exchange rate, lower viscosity, and a gradual phase inversion. Therefore, selecting the right non-solvent is one of the important factors for tailoring the membrane properties for any desired application.

3.5.4.3 Influence of polymer concentration on porosity of NIPS membranes

Polymer concentration has been shown to influence membrane final morphology (i.e., surface roughness and porosity). From the SEM images in **Figure 16**, N_13 depicted a higher network of interconnected pores and surface porosity. This is attributed to the lower polymer concentration leading to a larger area of polymer-lean phases. Increasing the dope solution concentration increases the polymer-rich phases and lowers the membrane surface porosity. This is because gelation occurs rapidly at higher concentrations, leading to membranes with denser structures and decreased porosity and pore connectivity. Moreover, increasing the polymer concentration increases the viscosity of the casting solution, which hinders solvent-non-solvent interaction, while lower concentrations favor instantaneous demixing during phase separation. For instance, N_13

with a lower polymer concentration (13 wt%) showed larger pores and higher porosity (81.63%) relative to N_15 and N_17, which demonstrated porosities of 76.4 and 65%, respectively, as shown in **Table 8**. The higher porosity of N_13 could facilitate a higher vapor transport in MD. On the other hand, while the lower porosity of N_17 might enhance the membrane-wetting resistance, it will lead to a reduction in vapor flux.

3.5.4.4 Effect of VIPS on the surface porosity

Because the surface porosity is directly related to the surface morphology, membranes with a more porous and interconnected morphology are expected to have higher porosity. The porosity of the membranes prepared with water vapor increases with increasing exposure time. For instance, V_W3, with relatively less pore connectivity relative to V_W5, has a lower porosity of 64 % compared to V_W5 with 77.23 %. When the exposure time increased to 8 minutes for V_W8, the surface morphology became interconnected with numerous pores, raising the surface porosity to 81.2 %. These variations in surface morphology have been discussed in the morphological analysis of these membranes.

In the case of the membranes prepared with the binary non-solvent vapor, V_W/E_3 exhibits a higher porosity of 84 % compared to V_W/E_5, which has a porosity of 76.62 %. This reflects the characteristic nature of the surface of these membranes, as observed in the SEM images.

As shown in the SEM images of ethanol VIPS membranes in **Figure 19a-c**, the membrane surface structure becomes more open as the solution increases from 13 wt. % to 15 wt. % for **V13_E** and **V15_E** respectively. This is also reflected in membrane porosity

measurements. For instance, the porosity increases from 82 to 88 % as the solution increases to 15 % for the same membranes. The variation in morphologies of these membranes has been explained to have occurred due to the nucleation and growth mechanisms. The larger sizes of the surface granules and their agglomeration due to the delayed demixing can be said to result in the lower surface porosity (75 %) of the **V17_E** membrane. The deviation in porosity trends observed in ethanol VIPS membranes compared to NIPS membranes arises from the distinct mechanisms of phase separation and the influence of key process parameters in the VIPS method.

3.5.5 Liquid entry pressure (LEP) of the polyimide membranes

The membrane's LEP is an essential parameter for long-term MD performance, since a higher LEP prevents the feed solution from passing through the membrane pores. The results of the LEP of the membranes, determined as previously described, are summarized in **Figure 27**. The LEP is related to the WCA, maximum pore size, and geometrical factor of the membrane pore as established by Young's equation. All the membranes prepared from the NIPS method showed higher LEP values of 2.1, 2.2, and 2.5 bar for **N_13**, **N_15**, and **N_17**, respectively. As expected, **N_17** with a higher polymer concentration showed a higher value than **N_13** and **N_15**. This is due to the lower maximum pore size value of the membrane. Also, the increased polymer concentration makes it difficult for the water molecules to penetrate the membrane due to increased final membrane thickness, as shown in SEM images. From the morphological nature of the cross-section shown in SEM images of the NIPS-based membranes, it can be observed that the pore geometry is not cylindrical, varying the geometrical coefficient from close to unity. Following Young's equation, membranes with higher WCA values and smaller pore

sizes tend to have higher LEP values. However, in some instances, if membrane wetting occurs due to loss of hydrophobic characteristics, the value is decreased. For example, the lower WCA value of 76° for V_W3 resulted in its lower LEP of 0.9 bar. In the case of V_W5 and V_W8, which have larger pore sizes, their re-entrant morphologies and increase in WCA values increase their LEPs to 1.4 and 1.2 bar, respectively.

While V_W5 had a higher WCA of 90° relative to V_W5 with 97°, the larger pore size of V_W5 resulted in a relatively lower LEP. This is also observed in the case of water-ethanol membranes. As shown in **Table 9**, V_W/E_3 had a larger pore size, but lower WCA compared to V_W/E_5; subsequently, it depicted a lower LEP. As the WCA increased to 134° for V_W/E_5, the hydrophobic properties of the membrane decrease water penetration through the membrane pores, leading to a higher LEP of 1.9 bar.

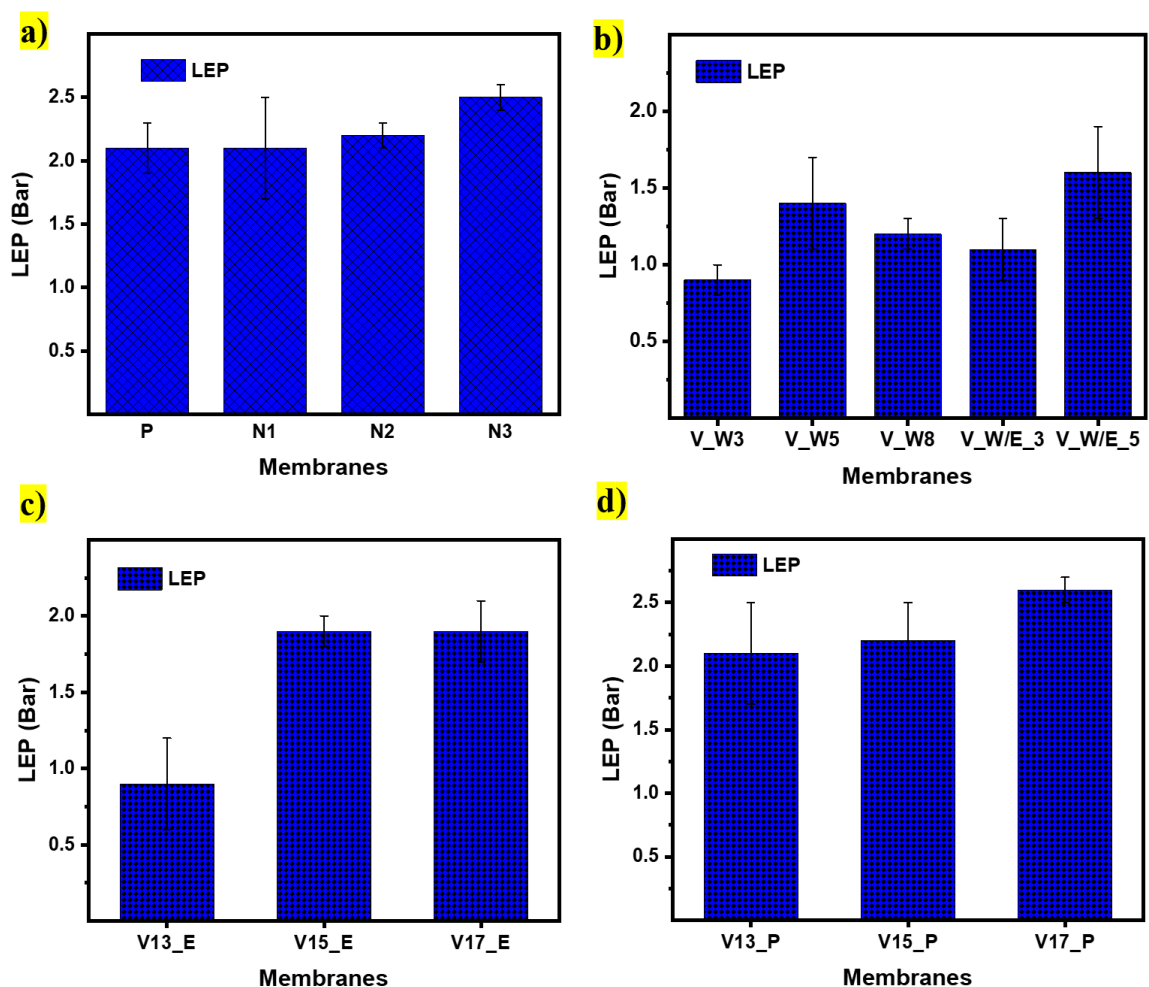


Figure 27. liquid entry pressure of the 6FDA-*m*PDA membranes: (a) NIPS-based membranes; (a) W and W/E-VIPS-based membranes; (a) E-VIPS-based membranes; (a) P-VIPS-based membranes.

Due to the change in morphology from NIPS to VIPS, membranes prepared from NIPS displayed considerably higher LEP values than those prepared by VIPS due to their smaller pore sizes and denser surfaces. For instance, at the same dope solution concentration (i.e., 13 wt.%), N1 displayed an LEP of 2.1 ± 0.4 bar, while **V13_E** exhibited an LEP of 0.9 ± 0.3 bar. Moreover, it was noticed that in the case of N1 – N3, as the dope solution concentration increases, the LEP remains almost the same (from 2.1 ± 0.4 to 2.5 ± 0.1 bar),

while for **V13_E** – **V17_E**, the LEP displayed significant enhancement when increasing the concentration from 13 wt% to 17 wt% which resulted in LEP of 0.9 ± 0.3 and 1.9 ± 0.2 bar, respectively. The changes in LEP upon increasing dope solution concentration could be attributed to the tighter pore formation, which requires higher pressure to allow the liquid to go through. Moreover, in the case of membranes prepared from VIPS, they showed lower LEP values compared to the NIPS membranes despite having higher WCA values. This disparity might be explained by the membranes' modified cross-section and surface characteristics, the pore size increase, and the change in pore geometry. These data were in line with the contact angle and pore size measurements, which are involved in the LEP calculation.

Considering the bulk properties and morphologies of the P-VIPS membranes, i.e., the pore sizes and the surface morphologies relative to those of ethanol. A change in the membrane's LEP is expected. Interestingly, by changing the vapor from ethanol to propanol, membranes exhibit higher LEP values like the NIPS membranes. However, in contrast to the previous trend, **V13_P** with a lower dope concentration possesses a higher LEP value than **V15_P** and **V17_P** with higher concentrations. This is due to the increase in surface roughness and WCA value of the membrane. These interesting variations arise from the morphological changes observed in these membranes, further indicating the role of surface engineering in tuning the properties as well as the performance of the polyimide membranes.

3.5.6 Pore size and distribution of the 6FDA-mPDA membranes

Due to the dense and flat-surface morphologies of the NIPS membranes, they showed relatively smaller pores. It is important to note that the NIPS mechanism leads to faster demixing and phase separation, leading to higher nucleation and a relatively shorter growth time, and subsequently results in more ordered crystallization and small-size particle distribution. As a result, N₁₃–N₁₇ showed considerably smaller pores. Interestingly, all the membranes exhibit pore sizes within the required range for MD applications. The influence of polymer concentration on morphology and surface porosity is similar to the scenario on pore sizes, and to some extent, their distribution. Thus, the variation of pore sizes follows the same trend. Because the N₁₃ membrane has a higher surface porosity and more open and interconnected pores, it has a larger pore size due to a larger area of polymer-lean phase compared to other membranes with higher polymer concentrations. For example, N₁₃ has a 25 % increase relative to N₁₇, and about 10 % relative to N₁₅. On the other hand, the change of non-solvent from water to ethanol resulted in an almost 50 % increase between N₁₃ and the pristine membrane. In terms of distribution, N₁₃ depicted a larger pore size distribution due to its higher porosity and lower solution viscosity, while both N₁₅ and N₁₇ have a narrow distribution due to the slower demixing process, due to an increase in polymer concentration and solution viscosity.

Because the NIPS membranes showed considerably smaller pores due to the faster demixing rate of the process. Conversely, the slower evaporation rate of solvent demixing in VIPS results in a larger interconnected pore structure, as confirmed by the SEM micrographs.

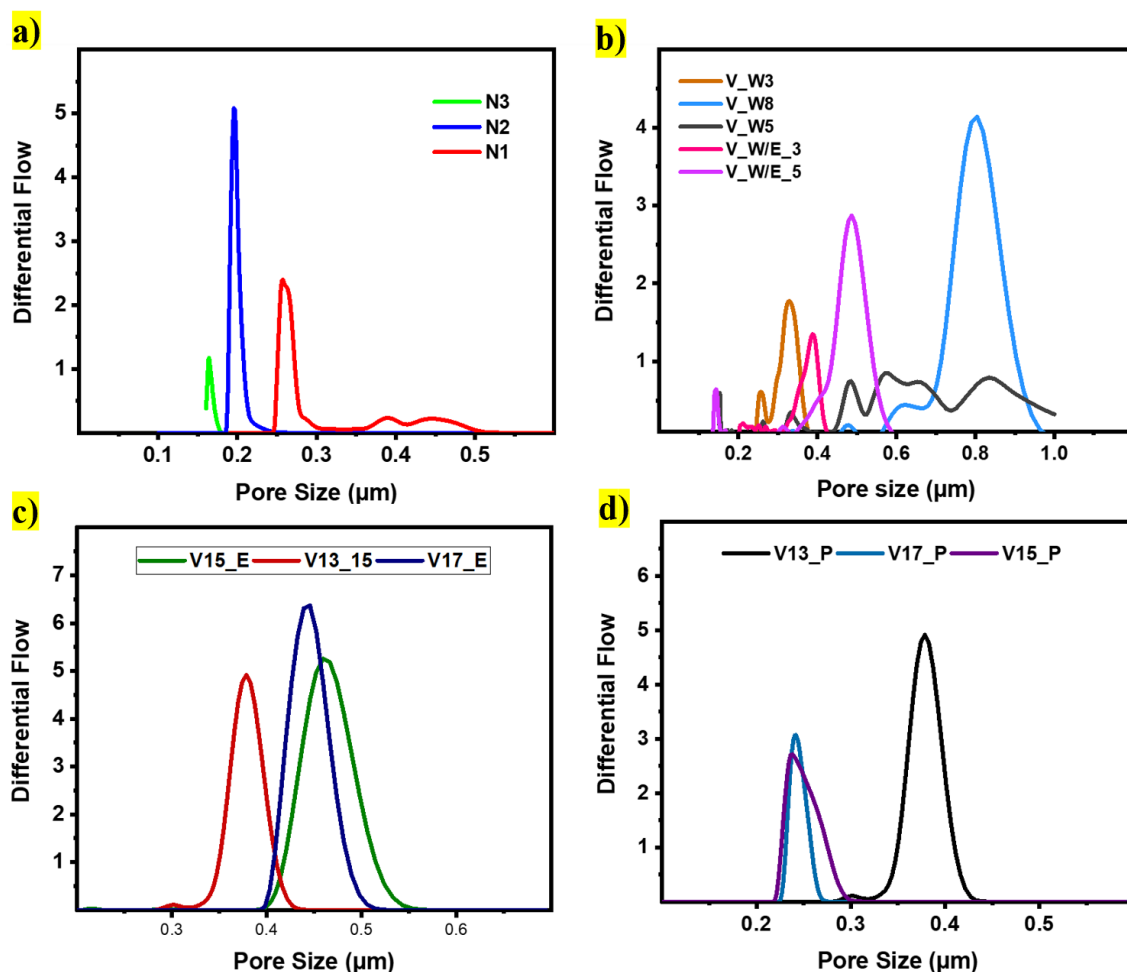


Figure 28. Pore size distribution of the 6FDA-*mpDA* membranes: a) NIPS-based membranes; b) W and W/E-VIPS-based membranes; c) E-VIPS-based membranes; d) P-VIPS-based membranes.

As explained in the morphological analysis, the phase separation with ethanol was driven by nucleation and growth. Due to the smaller sizes of the surface granules of V13_E, the membrane possesses smaller pore sizes (0.37 μm) relative to the rest of the VIPS membranes. As the dope solution increased to 15 wt.% % for V15_E, the sizes of the surface granules increased while maintaining good porosity and increased the pore size to 0.45 μm . While there was a similar increase in the size of the granules for the V17_E

membrane, the formation of a dense skin layer due to the higher viscosity of the solution and delayed demixing resulted in a decrease in pore size to 0.43 μm relative to V15_E. Interestingly, the uniform and slow phase inversion process of the VIPS resulted in membranes with a uniform pore size distribution, as shown in **Figure 28**. The uniform pore size distribution is important to membranes' stability and wetting resistance for MD applications. For instance, membranes with moderate pore sizes that are uniformly distributed tend to have better LEP than those with a broader distribution. In addition to enhancing mechanical properties, the permeability and selectivity of the membranes can be affected by their pore size distribution, especially in size-selective applications.

From the morphological characteristics of the P-VIPS membranes, V13_P possesses a more open structure than the other membranes. This structure is reflected in the pore size of 0.37 μm as shown in their bulk properties. Among the P-VIPS, this membrane had larger crystalline granules, thus having larger pore sizes and distribution. The crystalline granules become smaller as the concentration increases, resulting in a closer arrangement, and hence, smaller pore sizes and distribution. Despite increasing the concentration from 15 to 17 wt. %, the difference in pore size between V15_P and V17_P was not significant (0.24 and 0.23 μm for V15_P and V17_P respectively). The variations in pore sizes are attributed to the influence of propanol vapor on the number of voids and separation mechanisms when the polymer concentration varies.

Like the membranes prepared with ethanol vapor, P-VIPS membranes also depicted narrow pore size distributions relative to the NIPS membranes. A narrow pore size distribution prevents membrane wetting and ensures long-term performance and stability. Ultimately,

polymer concentration must be carefully optimized in VIPS to produce membranes with suitable characteristics for MD applications.

3.5.7 Mechanical properties of the 6FDA-mPDA membranes

Although MD does not require much pressure to operate like pressure-driven membrane processes, the mechanical properties of the membranes are paramount for long-term stability. Before the MD performance testing, the mechanical properties of the fabricated membranes were evaluated and presented in **Figure 29**. N₁₃-N₁₇ displayed an elongation at break ranging between 4% and 9%. Moreover, all membranes demonstrated tensile strength higher than 3 MPa.

Generally speaking, increasing polymer concentration increases the number of polymer chains per unit volume, subsequently increasing rigidity and networking. Therefore, a direct relation was expected. However, in the case of NIPS-based membranes, the trend was only observed for N₁ and N₂, in which the tensile strength increased from 4.8 to 10.5 MPa after increasing the dope solution concentration from 13 to 15 wt%. Nevertheless, the membranes with higher concentrations have higher strength and rigidity. For instance, N₃ has higher tensile strength and rigidity but lower ductility than N₂. In the case of membranes prepared with water vapor, their tensile strength decreases with increasing exposure time due to an increase in porosity.

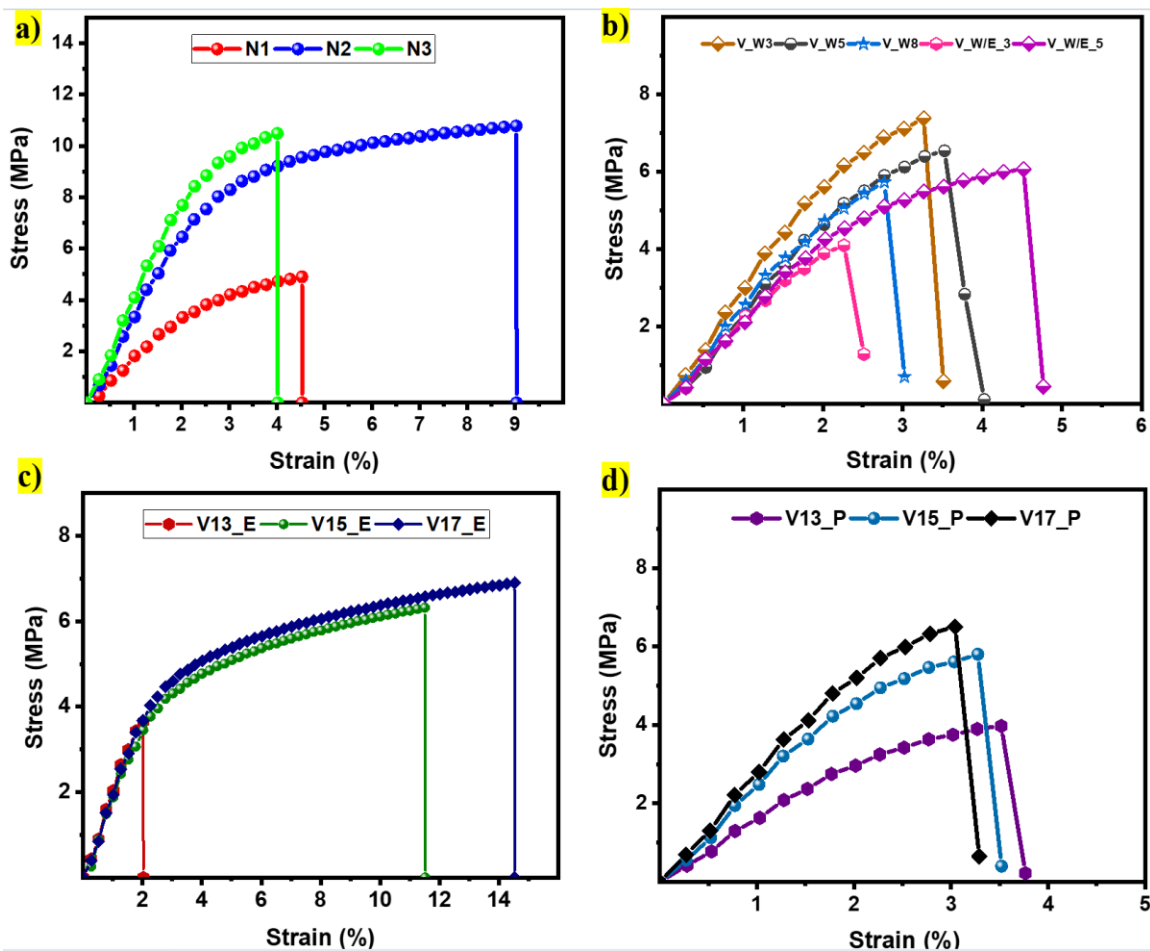


Figure 29. Mechanical properties of the 6FDA-mpDA membranes: a) NIPS-based membranes; b) W and W/E-VIPS-based membranes; c) E-VIPS-based membranes; d) P-VIPS-based membranes.

For instance, the value drops from ~7.5 to 6.2 MPa for V_W3 and V_W5, and finally to ~5.8 MPa for V_W5, respectively. However, their elongation at break does not follow this trend. This might be due to the wider pore size distribution associated with these membranes. For the water-ethanol membranes, the longer exposure time decreases the membrane porosity as discussed in the previous section. Subsequently, V_W/E_5 had

higher tensile strength (6.8MPa) and higher elongation at break (4.7 %) compared to V_W/E_3 with 4MPa and 2.5 % respectively.

Generally, the increase in polymer concentration increases the number of polymer chains per unit volume, subsequently increasing rigidity and networking. Subsequently, membranes with higher concentration should have higher mechanical characteristics. Following this, V13_E with the lowest concentration has the least tensile strength of about 3.5 MPa as presented in the mechanical analysis in the Figure. Increasing the dope solution concentration to 15 and 17 wt. % for V15_E and V17_E increased the tensile strength to 6 and 6.7 MPa, respectively. Moreover, these membranes with higher concentrations depicted higher elongation at break. For instance, V17_E has an elongation at a break value of 14.5 % while the V15_E value decreases to about 12.5 %. A drastic decrease was observed for V13_E as the value dropped to about 2 %. This might be attributed to the dense nature of the membrane compared to the rest of the ethanol VIPS membranes.

From **Figure 29 (c-d)**, It can be seen that the membranes prepared with propanol showed similar tensile strengths but shorter elongation at break compared to ethanol-based membranes. For instance, with the same polymer concentration, V15_E had ~6MPa tensile strength against V15_P with ~5.8MPa. However, this membrane depicted an elongation at break of 11.5 % compared to 3.5 % for V15_P. These variations are attributed to the morphological characteristics brought by differences in non-solvent properties. Nevertheless, the 6FDA-mPDA membranes depicted good mechanical properties and were good enough for MD testing.

3.5.8 Air-gap membrane distillation performance

To evaluate the membrane distillation performance of the 6FDA-*m*PDA-based membranes, highly saline water with a concentration of 70000 ppm NaCl was utilized under the process conditions and parameters presented in **Table 7**. N_13, depicted a flux of $13.03 \text{ kg m}^{-2} \text{ h}^{-1}$ with a stable salt rejection of 99.98%, as shown in **Figure 30 (a and b)**. A reduction in flux was observed as the dope solution concentration increased. For instance, as the concentration increased from 13 to 17 wt%, the flux was reduced from 13.03 to $8.32 \text{ kg m}^{-2} \text{ h}^{-1}$ for N_13 and N_17, respectively. In the case of N_15, an average flux of $11.08 \text{ kg m}^{-2} \text{ h}^{-1}$ was observed, attributable to the membrane porosity and pore sizes falling between N_13 and N_17. Nonetheless, salt rejection was maintained above 99.98% in all membranes. This reduction in flux and enhancement in rejection with increasing concentrations could be attributed to the reduction in pore size and overall porosity, in which the porosity was reduced from 81.63% to 65% after increasing the dope solution from a concentration of 13 to 17 wt.%, respectively (**Table 8**).

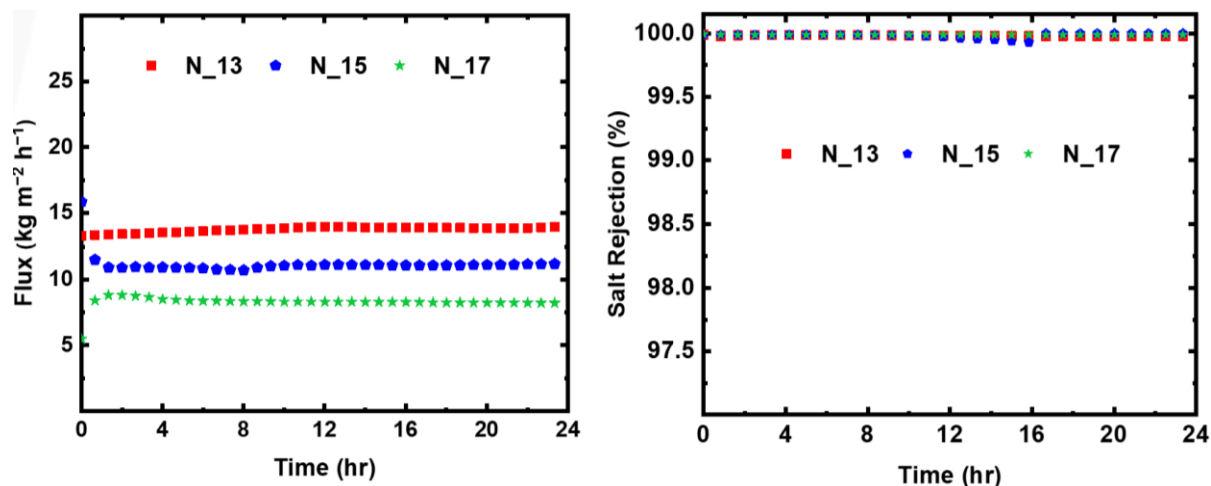


Figure 30. Membrane distillation performance of the NIPS membranes: a) showing the flux, and b) representing the salt rejections of N_13, N_15, and N_17, with polymer concentrations of 13, 15, and 17 wt.%, respectively.

One of the most crucial membrane properties is the polymer concentration, which substantially impacts the membrane's structure and functionality [156]. It can be noted that, as the dope solution concentration increases, the porosity of NIPS-based membranes (N_13-N_17) decreases, leading to a lower flux.

3.5.8.1 Effects of VIPS on MD performance

The morphological characteristics and bulk properties of the VIPS-based membranes displayed significant enhancement over the NIPS-based membranes. For instance, the NIPS-based membranes are characterized by minimal surface porosity, low WCA, and a finger-like cross-section. By applying VIPS, these properties that directly influence the performance were significantly enhanced. Subsequently, the membranes developed by VIPS demonstrated significantly higher performance than those developed by NIPS. For instance, at the same dope solution concentration of 15 wt.%, V13_E

exhibited a flux of $19.98 \text{ kg m}^{-2} \text{ h}^{-1}$, 53% higher than N_13. However, the salt rejection dropped to 99.6% in V13_E due to the larger pore size and lower LEP (0.9 bar) relative to N_13 (**Figure 32b**). The increase in flux observed for the V13_E membrane can be directly associated with its interconnected surface morphology and a sponge-like cross-section that enhances vapor transport compared to the finger-like cross-section observed in N_13. Similarly, at the same dope solution concentration of 15 and 17 wt. %, V15_E and V17_E displayed significantly higher flux of 26.26 and $22.08 \text{ kg m}^{-2} \text{ h}^{-1}$, 137% and 165% higher than N_15 and N_17, respectively. This increase in performance of the VIPs membranes resulted from the change in surface and cross-sectional morphologies observed for the VIPs membranes. These changes also resulted in an increase in pore sizes and surface porosities of the VIPs membranes, which enhances vapor transport across the membrane. For instance, N_15 possesses a low porosity of 76.43 % compared to 88.13 % for V15_E. Moreover, there is a noticeable increase in pore sizes from $0.21 \text{ }\mu\text{m}$ to $0.45 \text{ }\mu\text{m}$, respectively. Ultimately, these improvements in properties are reflected in the performance of the membranes. For the MD performance of W and W/E VIPs-based membranes in **Figure 31(a-d)**, a significant enhancement in flux was observed compared to the NIPS membranes. From the morphological perspective, while these membranes also showed finger-like morphologies like the NIPS membranes, the porous nature of the membrane surface penetrated the membrane thickness as seen in the SEM images. Moreover, there is a significant increase in pore sizes compared to the NIPS membranes. For example, both V_W5 and V_W/E_5, prepared with the same concentration as N_15, possessed larger pore sizes of 0.77 and $0.46 \text{ }\mu\text{m}$, respectively.

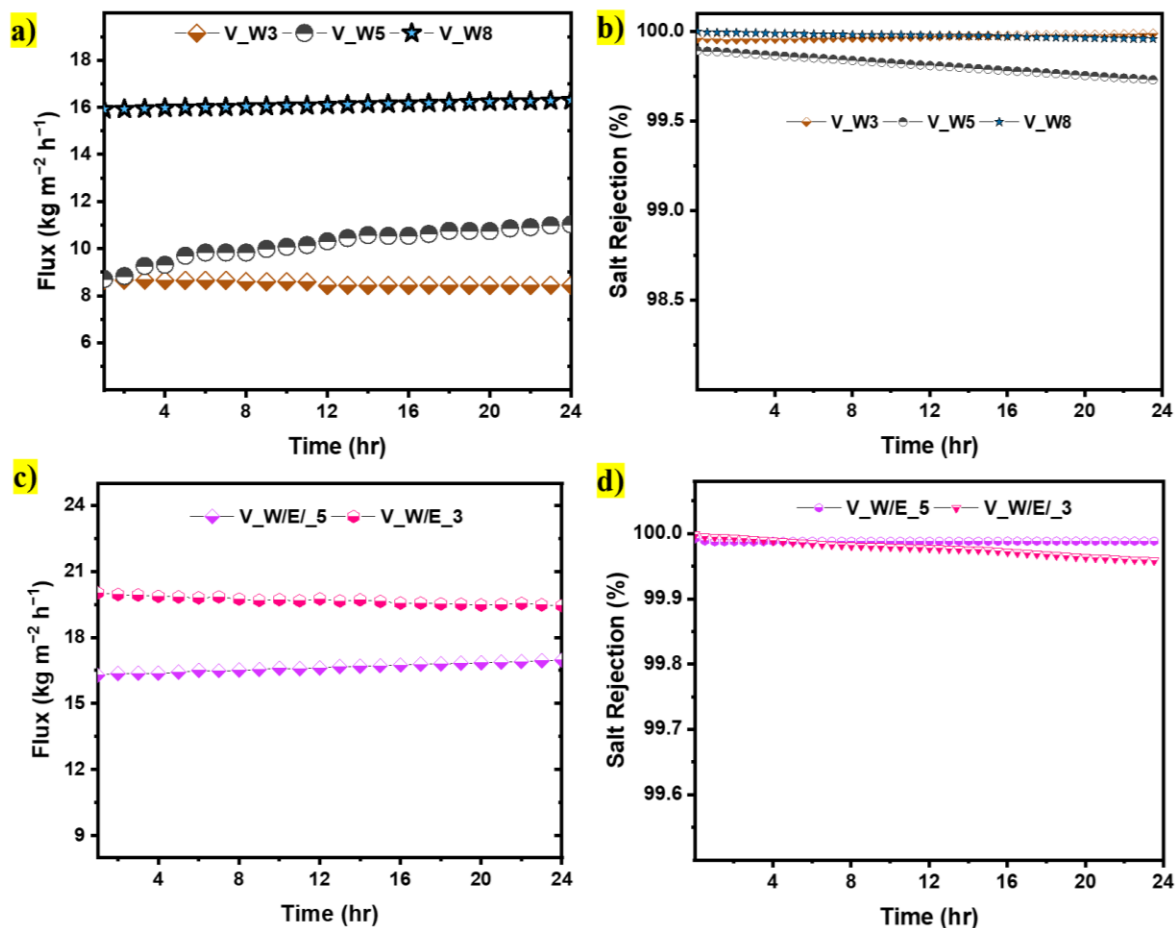


Figure 31. Membrane distillation performance of the water and water/ethanol VIPS membranes: (a–b) show the flux and the salt rejections of membranes prepared with water vapor with exposure times of 3, 5, and 8 minutes for V_W3, V_W5, and V_W8, respectively. (c–d) representing the flux and salt rejections of water/ethanol membranes with exposure times of 3 and 5 minutes for V_W/E_3 and V_W/E_5, respectively.

For example, despite having the same concentration as N_15, all the membranes showed higher fluxes (between 16–20 $\text{kg m}^{-2} \text{h}^{-1}$) except V_W5, which demonstrated a similar flux ($\sim 10 \text{ kg m}^{-2} \text{h}^{-1}$). The lower performance of the V_W5 membrane is associated with its lower porosity (68 %) despite having larger pores; on the other hand, V_W8 and V_W/E_5

porosities range between 82% and 86%, respectively. Moreover, the higher WCA values of V_W8 and V_W/E_5 (110 and 134° respectively) enhance their wetting resistance. Subsequently, these membranes maintain a stable salt rejection of ~99.99 % over the testing period. In the case of V_W5 and V_W/E_3, their WCA values of 90 and 114°, larger pores, and a wide pore size distribution contributed to the observed minimal drop in salt rejection.

3.5.8.2 Effects of concentration on performance of E-VIPS membranes

One of the most crucial properties of membranes is the polymer concentration, which significantly impacts the membrane's structure and functionality [14]. For the membranes prepared with NIPS, the permeability decreases with an increase in polymer concentration. Conversely, a different trend was noted for the ethanol VIPS-based membranes. This has been explained in the morphological analysis and was attributed to the mechanism of phase separation. Due to the small crystalline granules that led to the smaller pore sizes of V13_E, a lower permeate flux of 19.98 kg m⁻² h⁻¹ was observed for this membrane. As the dope solution concentration increased from 13 to 15 wt.% %, the flux rose from 19.98 to 26.26 kg m⁻² h⁻¹ for V15_E (Figure 7c). This increase in membrane vapor permeability is due to the increase in pore size and porosity of this membrane. As can be seen from **Table 10**, the pore sizes and porosities changed from 0.37 µm and 82 % to 0.45 µm and 88 % for V13_E and V15_E, respectively. Moreover, the higher WCA and LEP of the membrane contributed to its higher salt rejection due to an improved wetting resistance.

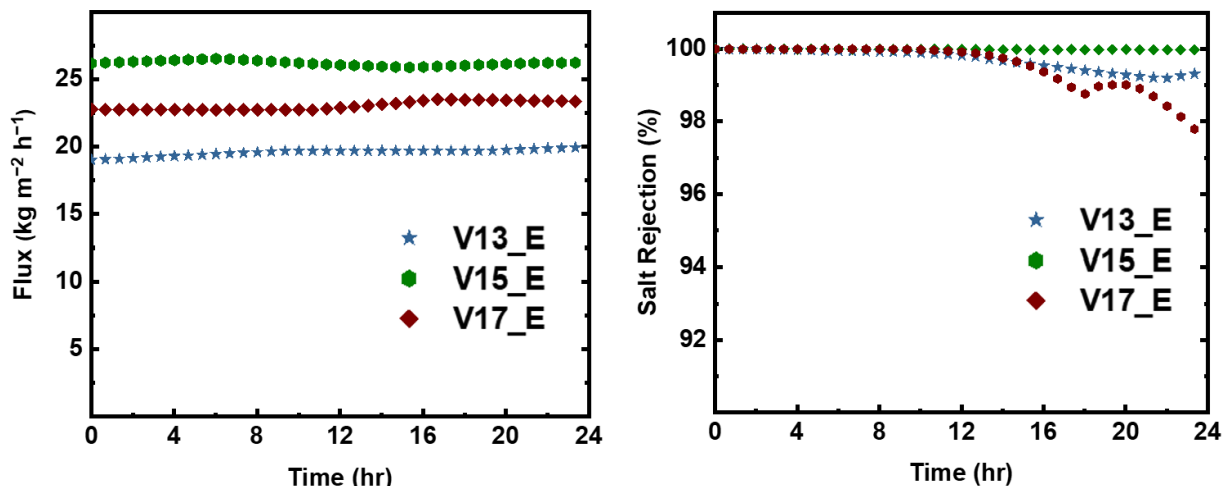


Figure 32. Membrane distillation performance: (a–b) representing the flux and salt rejections of the ethanol VIPS membranes with polymer concentrations of 13, 15, and 17 wt.% for V13_E, V15_E, and V17_E, respectively.

The decrease in vapor flux was observed from 26.26 to 22.08 kg m⁻² h⁻¹ for V15_E and V17_E as the concentration increased to 17 wt. % is due to the change in surface and cross-sectional characteristics of this membrane as seen in the SEM images. In addition to a decrease in pore size to 0.43 μm, a noticeable change in the cross-section can be observed for this membrane. The presence of a dense bottom layer increases mass transfer resistance and subsequently results in a reduction of membrane flux. The lower rejection observed for this membrane might be due to partial membrane wetting due to the decrease in WCA. In addition, the fluctuations in salt rejection associated with V17_E might be attributed to partial membrane wetting and self-sealing brought by scaling or cleaning capabilities. As discussed by Tijging et al. [157] and Warsinger et al. [158], wetting-induced rejection drops can be temporarily reversed by scaling (rejection enhancement). However, long-term fouling leads to irreversible decline, aligning with the observed performance of V17_E. Consequently, wetting-induced leakage may have happened in the case of V17_E and was

momentarily reduced by scaling, but in the end, it resulted in an irreversible performance reduction. This emphasizes the necessity of membranes with improved fouling resistance and LEP.

3.5.8.3 Influence of concentration on the performance of P-VIPS membranes

The MD performance of P-VIPS membranes with different polymer concentrations is presented in **Figure 33**. The highest performance is observed from V13_P. As shown in **Table 11**, this membrane has higher pore sizes and surface porosity relative to the rest of the P-VIPS membranes, associated with its lower polymer concentration.

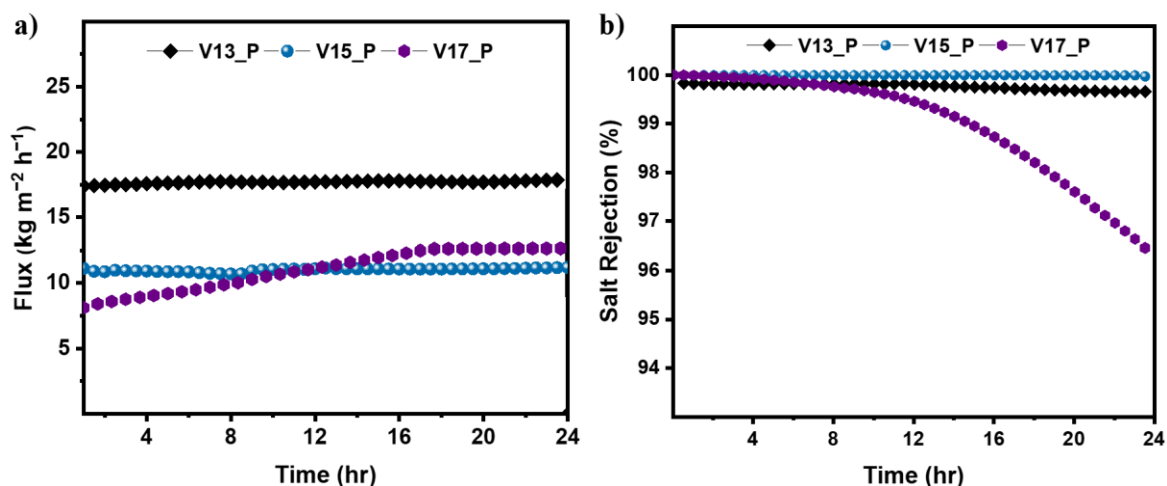


Figure 33. Membrane distillation performance: (a–b) representing the flux and salt rejections of the propanol VIPS membranes with polymer concentrations of 13, 15, and 17 wt.% for V13_P, V15_P, and V17_P, respectively.

These properties are reflected in the membrane performance, resulting in a flux of $\sim 17.5 \text{ kg m}^{-2} \text{h}^{-1}$, comparable to the performance of V13_E with $19.98 \text{ kg m}^{-2} \text{h}^{-1}$. Additionally, the membrane maintains a stable salt rejection higher than V13_E despite having similar

WCA values. This might be due to the more uniform pore size distribution associated with this membrane. As the polymer concentration increases to 15 wt.% for V15_P, the membrane pore size and porosity are reduced to 0.24 μm and 77 %, respectively. Subsequently, the flux dropped to about 12 $\text{kg m}^{-2} \text{h}^{-1}$. Additionally, due to the roughness of 34.5 nm and good WCA and high LEP, this membrane maintained a stable rejection of ~99.99 %. Ultimately, this membrane showed a balance between membrane permeability and selectivity. Following the trend in the change in membrane pore size with a change in concentration, the V17_P membrane started with the lowest flux of about 8 $\text{kg m}^{-2} \text{h}^{-1}$. This is attributable to the smaller pore sizes (0.13 μm), relative to the rest of the P-VIPS membranes. Nevertheless, due to a large number of small crystalline granules of this membrane, it possessed higher porosity, thereby depicting similar MD performance with V15_P. The observed increase in flux for the V17_P membrane may be attributable to the increase in vapor transport due to an increase in the thermal conductivity of the membrane over time. This partial or surface wetting may bring water closer to the membrane surface or within the membrane layers due to the accumulation of adsorbed vapor. Ultimately, this improves the efficiency of vapor transport by reducing membrane thermal resistance and increasing the evaporation-condensation cycles. However, this wetting, caused by the lower WCA of the membrane, resulted in a drop of salt rejection to 96 % after about 24 hours. Ultimately, the membrane pore structure and polymer concentration are paramount in striking a balance between membrane properties and performance.

Ultimately, VIPS was able to tune the membrane's porosity and roughness, which led to a significant increase in the hydrophobicity and membrane performance. This behavior can be attributed to the sponge-like nature, especially for ethanol and propanol VIPS-based

membranes, which feature interconnected pores that enhance the flux through the membranes. However, V17_E did not follow this trend of increased flux with rising dope solution concentration, possibly due to its unique morphology, which combines finger-like and sponge-like cross-sections, resulting in reduced pore connectivity and consequently, lower flux. Moreover, due to the trade-off between permeability and selectivity, the increase in flux could subsequently lead to a decrease in salt rejection, as observed by some VIPs-based membranes. Therefore, these findings suggest that the performance of MD membranes could be controlled by several parameters, including the membrane's hydrophobicity, pore size, LEP, and surface porosity.

3.5.9 Comparison of 6FDA-mPDA membranes with commercial membranes and previous studies

To further evaluate the potential of the newly developed membranes for MD applications, the performance of V2 was compared to the performance of commercial hydrophobic PTFE and PVDF membranes (obtained from TISCH Scientific), and the obtained results are presented in **Figure 34 (a and b)**. The commercial PVDF membrane demonstrated a flux of $8.2 \text{ kg m}^{-2} \text{ h}^{-1}$ with a salt rejection of 99.61%, while the PTFE membrane showed an average flux of $9.62 \text{ kg m}^{-2} \text{ h}^{-1}$ with a salt rejection of 99.8% over the 24-hour testing period. However, V2 displayed significantly higher flux and rejection relative to PVDF and PTFE. For instance, under the same experimental conditions, V2 displayed a flux of $26.26 \text{ kg m}^{-2} \text{ h}^{-1}$, which is 220% and 173% higher than the flux obtained from PVDF and PTFE, respectively. Furthermore, V2 maintained an excellent salt rejection of 99.98%, which demonstrates its great potential for MD applications.

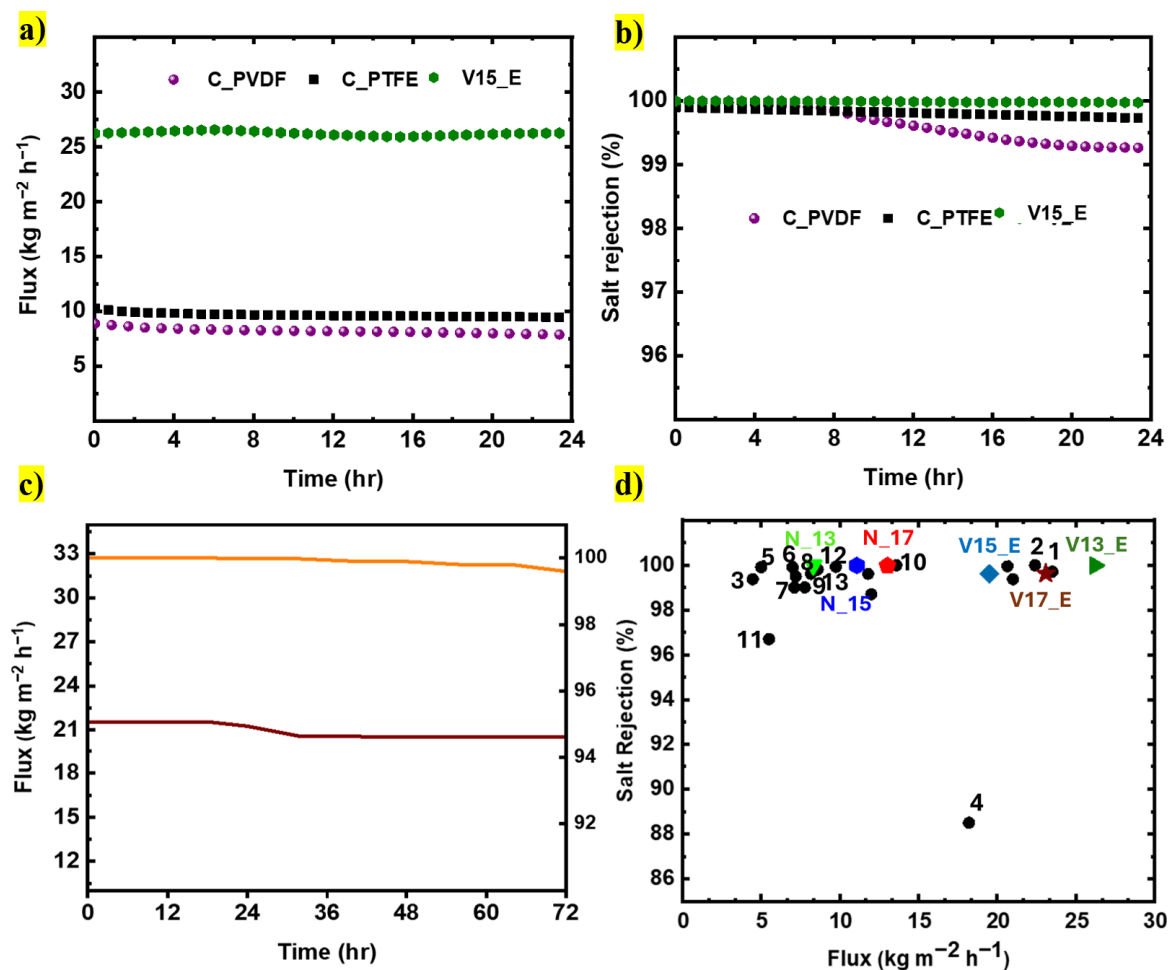


Figure 34. Comparison of MD performance and long-term stability test: (a-b) representing the flux and salt rejection of commercial PTFE and PVDF membranes with V_15_E, (c) depicting the long-term AGMD test of V17_E with seawater as feed; (d) performance of selected 6FDA-*m*PDA membranes against previously reported membranes (black dots represent membranes from the literature (**Table 12**)).

Furthermore, the 6FDA-*m*PDA-based polyimide membranes were compared to previously reported membranes, as shown in **Figure 34c** and **Table 12**. Interestingly, the membranes developed from NIPS surpassed previously reported membranes' rejection while maintaining similar flux. While the VIPS-based membranes surpassed the previously

reported ones by flux and rejection. This indicates that the surface engineering of the 6FDA-*m*PDA polyimide could fine-tune the performance and significantly improve it. Interestingly, some of these reported membranes required additional modifications, including the addition of porogen, to achieve the resulting performance, in contrast to the 6FDA-*m*PDA membranes prepared without additional modifying agents.

While this study does not fully optimize the 6FDA-*m*PDA membranes but rather introduces a new membrane material for desalination application in MD, our results are comparable to, and in some instances, superior to some reported hydrophobic and superhydrophobic membranes for MD, as presented in **Table 12**. Theoretically, both DCMD and VMD have higher flux than our AGMD module used in this work, yet our membranes outperform some of these reported membranes. In addition, while most of the reported membranes were tested under moderate feed salinity, the 6FDA-*m*PDA membranes performed in a harsher environment, further depicting their potential for desalination applications. The results obtained in this work have proven that polyimide membranes can compete with or outperform the commercially available and already developed membranes for MD.

3.5.10 Long-term MD and fouling tests

Membrane fouling and wetting are critical issues that reduce the performance of membranes in MD. The loss of membrane hydrophobicity typically leads to wetting, enabling foulants to pass through the membrane with the permeate. The feed solution penetrates the membrane pores when the hydrostatic pressure across the membrane exceeds the liquid entry pressure or when solutions containing organic or inorganic pollutants absorb or deposit on the membrane's surface. Depending on the nature of pore wetting, it

can lead to a decrease in permeate flux in cases of partial wetting or a decline in permeate quality when the membrane is fully wetted. To ensure stability against challenging contaminants in water desalination and to explore the potential of the 6FDA-*m*PDA membranes for industrial applications, the V3 membrane, which showed a decrease in salt rejection over a 24-hour testing period, was evaluated with real seawater for 72 hours to understand its performance mechanism.

The long-term MD performance in Figure 8d indicates that the membrane exhibited exceptional performance, maintaining a stable water flux of $20.54 \text{ kg m}^{-2} \text{ h}^{-1}$ and salt rejection of 99.99% until after 60 hours, when the rejection decreased to approximately 99.57%. The observed reduction in rejection during the short-term MD test could be attributed to partial wetting, which was mitigated by the membrane's self-cleaning capability during the long-term testing. The stability of the membrane surface, even after extended MD testing with seawater, was evaluated using SEM, as shown in **Figure 35 (a-c)**, where the membrane retained its porosity after three days of testing in highly saline water.

Furthermore, the self-cleaning capabilities of the fabricated polyimide membranes were assessed by immersing the membranes in a 1% methylene blue solution as a model. Remarkably, the membranes demonstrated excellent self-cleaning performance, remaining clean and free of discoloration after immersion (**Figure 35d**). This behavior underscores their ability to resist the adsorption of methylene blue, a positively charged and hydrophilic dye, indicating their robust anti-fouling properties. The membranes' stability and self-cleaning ability can be attributed to their advanced material properties, which include high

thermal and chemical resistance, hydrophobic surface characteristics, and resistance to salt scaling.

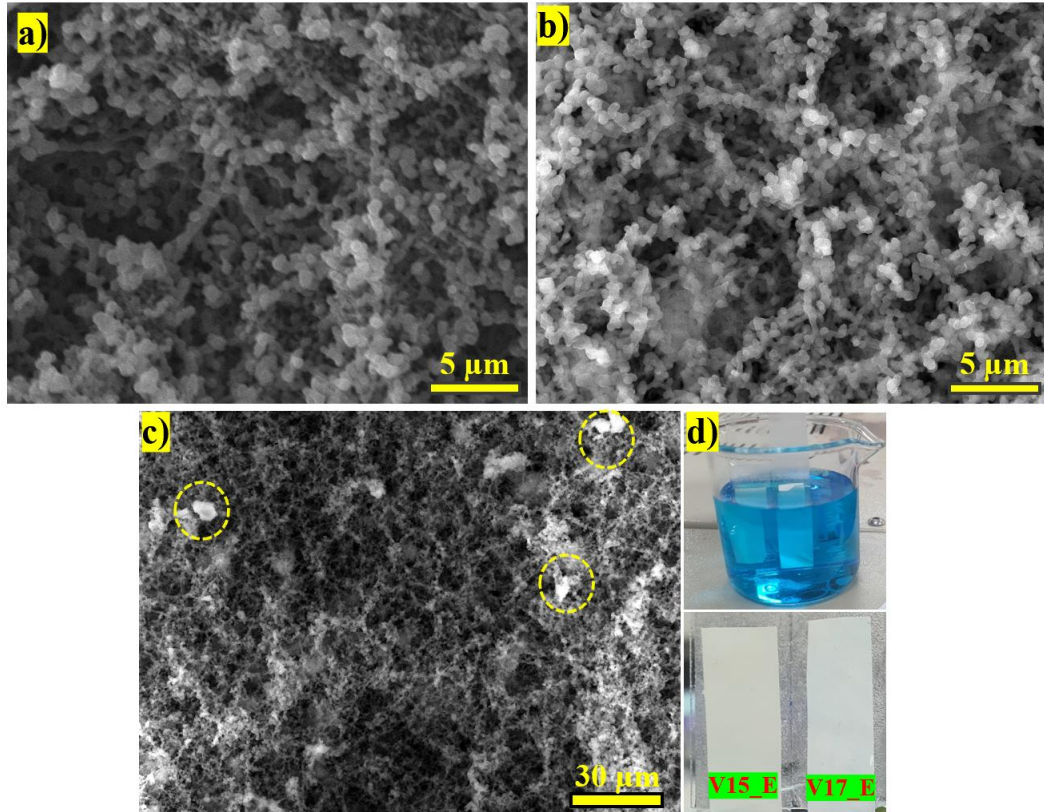


Figure 35. Field Emission Scanning Electron Microscopy (FESEM) images illustrating the fouling and long-term stability of the V_17 membrane. (a) Top surface before membrane distillation (MD) testing; (b) and (c) after prolonged MD operation; (d) membrane surface following a self-cleaning treatment using a 1% methylene blue solution.

These attributes are vital for sustaining membrane distillation (MD) processes, especially when treating high-salinity feedwater like seawater. Such self-cleaning capabilities are crucial for long-term performance in membrane distillation (MD) applications, where

fouling from organic and inorganic contaminants poses a significant challenge. The membranes' ability to maintain functionality without extensive chemical cleaning reduces maintenance needs, extends operational lifetimes, and enhances economic feasibility for large-scale MD processes. Consequently, these polyimide membranes show considerable potential for use in sustainable water purification systems, particularly in challenging environments with a high propensity for fouling.

3.6 Membrane Recycling

To demonstrate the industrial applicability and sustainability of the 6FDA-*m*PDA-based membranes, we explored their performance after recycling. After conducting the MD experiment in highly saline medium, the membranes were recycled following the procedure mentioned in Chapter 3. The FTIR analysis demonstrated that both the pristine and recycled membranes are the same, indicating the high stability of the polymer chemical structure (**Figure 36**).

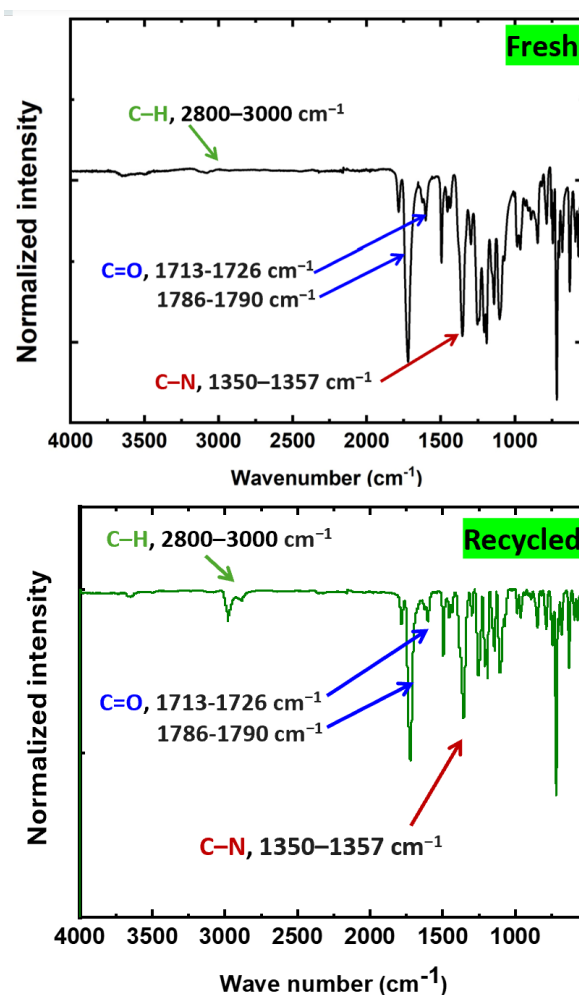


Figure 36. FTIR spectrum of fresh and recycled polymer.

Interestingly, the recycled membranes demonstrated comparable performances with the pristine ones, as shown in **Figure 37 (c-d)**. For instance, N_13 only lost 7% of its initial flux of $13.03 \text{ kg m}^{-2} \text{ h}^{-1}$ before recycling, compared to the flux of $12.12 \text{ kg m}^{-2} \text{ h}^{-1}$ after recycling. Moreover, this membrane maintained its salt rejection rate of 99.98%, even after recycling. On the other hand, V15_E lost 13.5% of its flux (from 26.26 to $22.71 \text{ kg m}^{-2} \text{ h}^{-1}$) but retained its high salt rejection without any observed loss (**Figure 37c-d**). Similarly, only marginal changes in membranes' hydrophobicity and pore size were observed, as

depicted in **Figure 37a-b**. For instance, the WCA of the fresh membrane ($84 \pm 4^\circ$) is almost the same as that of the recycled membranes (85 ± 5). Moreover, a slight increase in pore size from 0.21 to 0.23 μm was observed after recycling for the N_13 membrane. Similarly, despite a slight decrease in pore size from 0.45 to 0.42 μm , the error bar indicates that these values are almost the same.

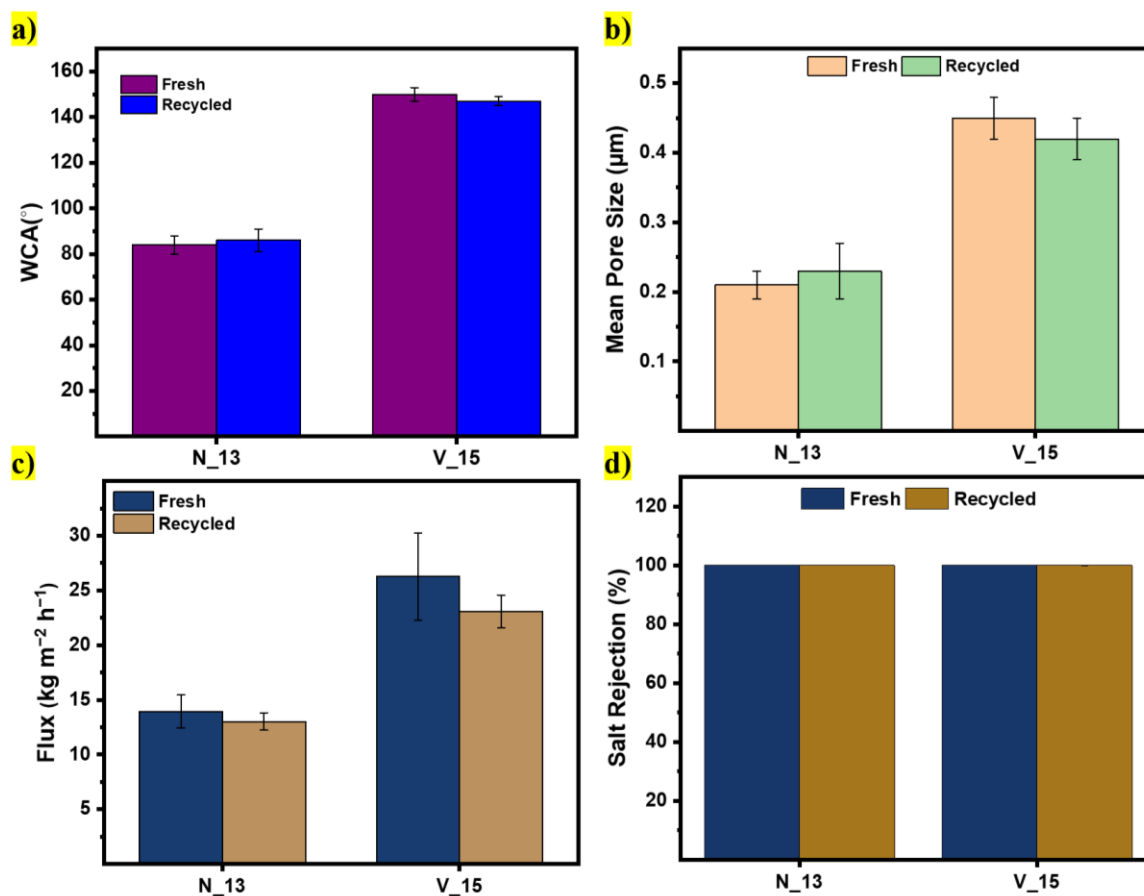


Figure 37. Properties and performance of the recycled membranes compared to the pristine ones: a) representing WCA; (b) representing mean pore sizes; and (c-d) representing the flux and rejections of N_13 and V_15 from fresh and recycled polymer, respectively.

The possibility of recycling and reusing the 6FDA-*m*PDA-based membranes without affecting the chemical structure or compromising performance highlights their potential as

cost-effective and environmentally friendly solutions for water purification and sustainable resource management.

Table 12. Comparison of 6FDA-*m*PDA-based membranes to previously reported hydrophobic membranes for MD. (^aMembranes prepared by NIPS; ^bMembranes prepared by VIPS).

Membrane Type	WCA (°)	Feed Solution (ppm)	MD Type	Flux (kg m ⁻² h ⁻¹)	Rejections (%)	References
PVDF ^{a,b}	123	(35000)	DCMD	23.5	99.7	[159] ¹
PVDF ^b	84.3 ± 0.7	35000	VMD	22.4	99.9	[128] ²
ZIF-8/TFC ^a	84.16 ± 0.7	35000	AGMD	4.47	99.37	[160] ³
GO/PVDF ^a	141 ± 1.8	35000	AGMD	18.20	88.50	[161] ⁴
Modified PES ^a	119	42400	AGMD	4.47	99.37	[162] ⁵
PVDF/GO ^a	77 ± 1	35000	AGMD	6.2	99.90	[163] ⁶
PVDF/h-BN (M2) ^a	114 ± 0.8	35000	AGMD	7.10	99.00	[164] ⁷
PVDF/0.5 wt% 15.5-rGO ^a	59 ± 2	35000	AGMD	7.0	99.90	[165] ⁸
6FDA-TMPD (M1) ^a	75 ± 2	70000	AGMD	9.75	99.92	[118] ⁹
6FDA-TMPD (M6) ^a	96.8 ± 2	70000	AGMD	13.11	99.99	[118] ¹¹
PES/TNT ^a	-	35000	VMD	5.5	96.70	[166] ¹²
PVDF ^a	74 ± 3	70000	AGMD	8.2	99.61	This work
PTFE ^a	82 ± 4	70000	AGMD	9.62	99.80	This work
N_13 ^a	84 ± 4	70000	AGMD	13.03	99.98	This work
V_W8 ^b	110 ± 3	70000	AGMD	16.08	99.99	This work
V_W/E_5 ^b	134 ± 4	70000	AGMD	16.5	99.98	This work
V15_E ^b	150 ± 6	70000	AGMD	26.26	99.98	This work
V15_P ^b	138 ± 3	70000	AGMD	17.34	99.8	This work

CHAPTER 4

CONCLUSION AND RECOMMENDATIONS

4.1 Conclusion

In summary, we have successfully developed porous and hydrophobic 6FDA-*m*PDA membranes using VIPS and NIPS methods and used them in membrane distillation to desalinate highly saline water. Being a relatively fast-demixing process, NIPS produced membranes with smooth surfaces and minimal surface porosity. Ultimately, the highest performance was obtained with N_13, displaying a maximum flux of $13.03 \text{ kg m}^{-2} \text{ h}^{-1}$ with a stable salt rejection of 99.98%. To induce a slower and more uniform phase inversion and enhance the performance of the polyimide-based membranes, VIPS was employed. The influence of vapor type on membrane formation, morphology, and subsequently, performance was investigated.

The optimum membrane porosity with water vapor was achieved with a longer exposure time. On the other hand, introducing ethanol to create a binary non-solvent vapor produces membranes with higher porosity, with a shorter exposure time. This motivated the use of ethanol as the non-solvent. Interestingly, membrane porosity was further enhanced, in addition to modifying the surface and cross-sectional morphology from finger to sponge-like and ultimately enhancing the membrane hydrophobicity and permeability. The formation of porous structure throughout the membrane cross-section was attributed to the low density of ethanol and its affinity towards the cast polymer film compared to water, facilitating a higher mass transfer of vapor through the film.

When denser and higher molecular weight vapor, i.e., propanol, was employed, the pore sizes of the membranes decreased due to smaller crystalline granules and fibrous surface morphology relative to ethanol vapor membranes. As a result, the hydrophobicity and permeability of the membranes decreased.

VIPS achieved fine-tuning of membrane porosity and showed notable enhancement in membrane morphology and performance.

Interestingly, VIPS-based membranes displayed higher porosity and water contact angle, leading to the best membrane with a maximum flux of $26.26 \text{ kg m}^{-2} \text{ h}^{-1}$ with a salt rejection of 99.98 % for V15_E. These findings suggest that the choice of vapor type is vital in determining the membrane morphology and performance.

The resulting membranes displayed stable performance during the long-term experiment without observing any fouling behavior. The recyclability of the developed membranes was investigated, and the recycled membranes demonstrated similar flux and salt rejection to the pristine ones. The developed membranes' ability to continue performing without requiring intensive chemical cleaning and sustainability through recycling lowers maintenance requirements, increases operating lifespans, and improves the viability of large-scale MD operations from an economic standpoint. These polyimide membranes, therefore, show great promise for application in environmentally friendly separation systems, especially in harsh settings with a high anti-fouling tendency.

4.2 Recommendations and outlook

This research has established the difference between membrane fabrication methods and their effects on the properties and performance of the developed polyimide-based membranes, specifically, using NIPS and VIPS, exploring different vapors. Additionally, the effect of polymer concentrations and the nature of vapor and how they influence membrane structure, wettability, and performance has been investigated. While this study is the first of its kind, the need for further investigations and elaboration of the mechanisms of the VIPS method is paramount. Given this, the following recommendations have been put forward:

4.2.1 Enhancement of the NIPS method through electrolyte non-solvent-induced phase separation

The results obtained from the NIPS method showed that the 6FDA-*m*PDA NIPS-based membranes are relatively dense, hydrophilic, and lack the ideal pore structure for long-term MD applications. This stems from the quick precipitation that occurs during the process, especially with water as the non-solvent.

Moreover, since pore-forming agents are not expected to be added to enable better recyclability, employing an electrolyte solution (i.e., water that contains ionic salts) might be a viable alternative for producing membranes with better properties. The improvement of properties is expected to occur due to the change in mechanisms as follows:

Osmotic effects: The application of an electrolyte solution will induce osmotic effects, lowering the precipitation rate and facilitating better and controlled pore formation.

Polymer-ion interactions: Rather than direct interaction between the polymer and the non-solvent, ions dissolved in the non-solvent solution can diffuse into the polymer matrix, hindering the efficient packing of polymer chains. This might result in membranes with increased porosity and interconnected pore structures.

Crystallization effects: With higher concentrations of salt in the non-solvent solution, supersaturation might contribute to producing a membrane with better microvoid structures.

4.2.2 Enhancing the sustainability of the VIPS by employing green non-solvents

The VIPS method is a promising method with advanced polyimides for generating membranes with good properties for MD applications. It is recommended to use non-toxic or less toxic and biodegradable vapors to enhance the sustainability and environmental friendliness of the VIPS. Therefore, solvents such as methyl lactate, ethyl acetate, and limonene, amongst others. In addition to sustainability, exploring these solvents might bring out new morphologies due to differences in diffusion coefficients and polymer-vapor affinities, and may open new doors for eco-friendly membrane fabrication methods for various applications.

4.2.3 Developing models for more VIPS systems by incorporating more vapors

The current VIPS models describing the membrane formation mechanisms are limited to using water as a non-solvent. The findings from this study demonstrate the need for models accounting for the phase separation mechanism with ethanol, propanol, or a binary non-solvent to describe the diffusion rate or mass transfer of vapor, polymer-vapor interaction, and precipitation rate. Moreover, developing a vapor-diffusion-induced precipitation phase diagram with more solvents, considering the vapor polarity, vapor-polymer affinity (i.e., the Flory-Huggins parameters), and the partial pressure and swelling effects will help in predicting morphological and physical properties of VIPS membranes using non-documented vapors or binary mixtures. Ultimately, this can make the process more practical for large-scale applications.

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Vitae

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Research Interests

Polymer and Porous Materials Synthesis

Materials for Clean Water and Energy Applications

Education

M.S. **King Fahd University of Petroleum and Minerals** **Jan. 2023 – May 2025**

Materials Science and Engineering

Thesis: Engineering of Recyclable 4,4'-(Hexafluoroisopropylidene) Diphthalic Anhydride
(6FDA)-based Polyimide Membranes for Efficient Water Desalination in Membrane Distillation.

Advisors: Dr. Turki Nabieh Baroud and Dr. Mahmoud Abdulhamid

B.S. **Ahmadu Bello University, Zaria, Nigeria** **February 2020**

Chemistry

Research Experience

Graduate Student

Supervisors: Dr. Turki Nabieh Baroud and Dr. Mahmoud Abdulhamid

- Fabrication and engineering of 6FDA-based polyimide membranes as new membrane materials in membrane distillation (phase inversion, electrospinning).
- Surface modification of polymeric membranes.
- Surface characterizations such as SEM, AFM, EDX, etc.
- Data analysis

Undergraduate Student

Dec. 2018 – Nov. 2019

Supervisors: Professor C. E. Gimba and Dr David Arthur

- Worked on preparing a composite material from an epoxy matrix reinforced with bagasse fiber.
- Performed a phytochemical screening and antimicrobial activity of the leaf extract of *Annona Senegalensis*.
- Assessed the level of bioaccumulation of some selected heavy metals in Rice consumed within Funtua Metropolis was analyzed using Atomic Absorption Spectroscopy.

Teaching Experience

King Fahd University of Petroleum and Minerals, Saudi Arabia

Materials Science and Engineering Department

- MSE 202: Materials Lab Instructor **Aug 2024 – May 2025**
- MSE 435: Corrosion Prevention and Control **Jan-May 2024**
- MSE 509: Circular Materials Economy **Aug – Dec 2023**

College of Health Sciences and Technology, Tsafe, Zamfara-Nigeria **Nov. 2020-2021**

Graduate Assistant

- Taught a class of 50 students a general chemistry course with an excellent success rate.
- Created a suitable approach to engage 20 students during bi-weekly chemistry experiments and enhanced their understanding of chemistry phenomena.
- Performed necessary administrative tasks such as invigilation and marking of students' exams.

Honours and Awards

King Fahd University Scholarship Award **2023-2025**

Fully funded scholarship for a master's program

Katsina State Scholarship Award**2015-2019**

Tuition fees scholarship for undergraduate studies

Materials Science and Engineering, KFUPM**2023**

Second-best seminar presentation award

Working Experience

Dangote Fertilizer, Ibeju Lekki, Lagos, Nigeria**May-Dec 2022***Process Engineer***ABJ NIG. LTD., Funtua, Katsina-Nigeria****June-Nov 2018***Internship: Quality Control Chemist***Publications and Manuscripts** (<https://orcid.org/0000-0002-5418-8067>)

- **Yakubu A.** Muhammed Azeem, Dahiru Lawal, Turki N. Baroud, Mahmoud A. Abdulhamid. Fine-tuning surface porosity of polyimide-based membranes for membrane distillation. Accepted in the Journal of Separation and Purification Technology.
- Jamilu Usman, **Yakubu A.**, Muhammad Usman, Abdulazeez Ismail, Mohammed Abdul Azeem, Sani I. Abba, Dahiru Lawal, Turki N. Baroud. Water-Stable Eco-Friendly ZIF-90 Embedded PVDF Membranes for High-Efficiency Desalination of Saline Water Using Air-Gap Membrane Distillation (Prepared Manuscript).
- **Yakubu, A.**, Arthur D.E., Peter F.M., Aroh A., Arthur C.C. An assessment to determine the level of some selected heavy metals in rice (*Oryza sativa*) consumed within Funtua Metropolis. Journal of Chemical Review and Letters. **2021**. **4**(3):164-170. DOI: [10.22034/crl.2021.272598.1102](https://doi.org/10.22034/crl.2021.272598.1102)
- **Yakubu, A.**, Haruna, I., Maidaula, A.T. Phytochemical Screening and Antimicrobial Activity of Leaves Extract of Crude *Annona Senegalensis*. International Journal of Research and Innovation in Applied Sciences. **2021**. **6**(10): 49-54. <http://dx.doi.org/10.51584/IJRIAS.2021.61104>

Leadership/Volunteering Activities

Lab Manager, Membrane Engineering Lab, KFUPM

Jan – Aug 2024

Member, Arewa Mentorship and Support Initiative

Dec 2023 – Present

- Providing mentorship and guidance to undergraduate students in Northern Nigeria

Chemistry Tutor, Govt Senior School, Funtua

2022

- Taught general chemistry to high school students in preparation for the West African Examination Council exam

Academic Officer, Students' Chemical Society, ABU Chapter

Jan. 2019 – Nov. 2019

- Organized and monitored tutorials across departmental levels, which enhanced students' performance

Group Discussion Leader

2016 – 2019

- Led and tutored a group of my colleagues to help simplify complex courses for easy assimilation.

Language and Other Skills

Language: English (proficient), Hausa (mother tongue), Arabic (intermediate)

Tools: Microsoft Excel, PowerPoint, and Origin Software.

Soft Skills: Time Management / Ease at grasping concepts / quickly adapting to new environments.

Other skills: Materials Characterization (SEM, XRD, AFM, etc.), Data Analysis, Business, and Innovative Skills. |