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Alternative materials for interfacial polymerization: recent approaches for greener membranes

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Thin-film selective layers fabricated *via* interfacial polymerization (IP) form the core of membrane-based water purification and desalination, as well as other molecular separations. The monomers and organic solvents used in the reaction are for the most part toxic chemicals, likely to be banned in the near future, for environmental protection. There is, therefore, a growing need to find alternative, sustainable, materials that can produce adequate membranes for industrial applications, fabricated *via* IP. The present work summarizes recent studies on fabricating RO/NF/OSN membranes *via* IP using sustainable solvents and/or monomers, in comparison to the toxic chemicals used to fabricate polyamide, the chosen polymeric material for the commercial selective membrane layer. The properties of these 'green' materials are described, as well as the properties of the resultant membranes, discussing possible limitations in the fabrication techniques and the benefits of the process. Furthermore, an eco-scale score is calculated for representative membranes, demonstrating the utility of this tool for assessing the 'greenness' of the fabricated membranes. Overall, the presented literature shows that there is a great potential for fabricating more sustainable and scalable membranes. However, studies exhibit various limitations, for example, no standardization for performance tests and performance criteria for every membrane type, which prevents accurate and true comparisons among different membranes. Suggestions are made, where applicable, for future work to add aspects that assess the potential of fabricated membranes to future industrial applications. Finally, and most importantly, there is still a need for improved fundamental understanding of IP, with which to facilitate the search of alternative sustainable materials for membrane fabrication with desired properties.

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1. Introduction

Thin films fabricated *via* interfacial polymerization (IP) are widely used in industrial applications, such as micro-encapsulation and the separation layer for water purification

membranes.^{1–3} IP comprises various condensation chemistries, most commonly polyamides, polyesters, polyureas, *etc.* The selected IP chemistry for the state-of-the-art water separation membranes is polyamide (PA),¹ which was first synthesized in the late 1970s by Cadotte and co-workers, and turned out to be the most significant breakthrough in desalination technology, achieving >99% salt rejection in seawater.^{4,5} With their exceptional performance, along with facile and readily up-scalable manufacturing, PA membranes have become the industry standard for Nanofiltration (NF) and Reverse Osmosis (RO) applications.^{6–8} Furthermore, they are integrated in various other industrial processes, such as wastewater treatment, water purification, microencapsulation, and industrial substances separation.^{9–11} Nonetheless, since their first fabrication, TFC membranes have not undergone significant improvements.^{12–14}

TFC PA membranes comprise a thin, dense, and cross-linked PA selective layer synthesized *via* a rapid, exothermic Scotten–Baumann (acylation) polycondensation reaction of two polyfunctional monomers. The commonly-used mono-

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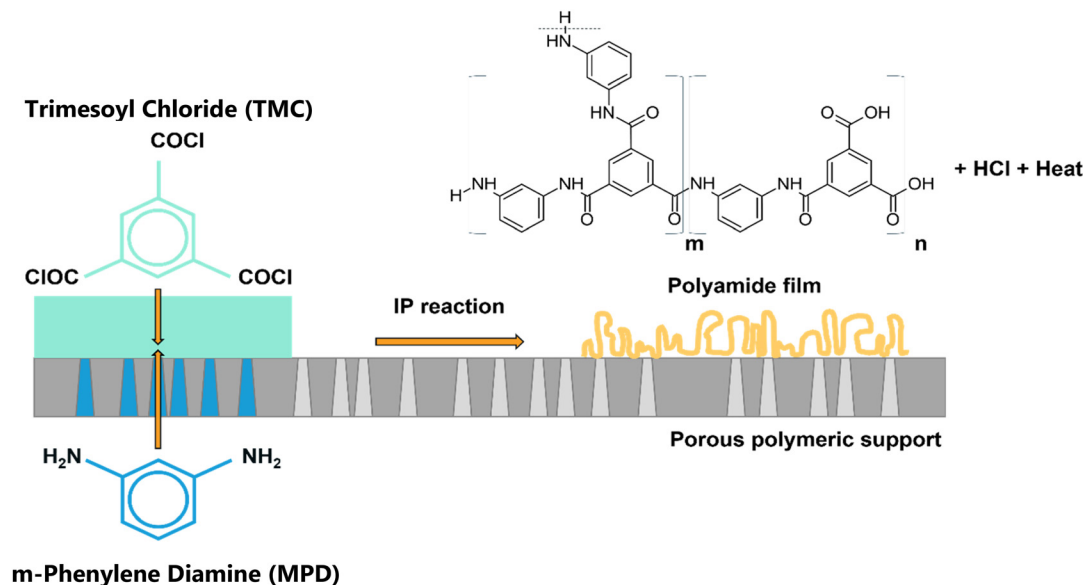


Fig. 1 IP reaction between MPD in the aqueous phase and TMC in the organic phase producing cross-linked polyamide, HCl and heat are by-products.¹⁵

mers for RO membranes are Trimesoyl-Chloride (TMC), dissolved in hexane, and *m*-Phenylene Diamine (MPD) or Piperazine (PIP, for NF) in water (Fig. 1).¹⁵

The acyl group in TMC is added to the amine monomer forming an amide bond, releasing HCl and heat as by-products of the reaction.^{15–18} The amine monomers are better soluble in hexane than TMC in water; therefore, the reaction occurs at the organic side of the interface and is diffusion limited.¹⁵ Besides the mentioned monomers, IP can be performed using other monomers with a variety of chemical structures. However, the success of the IP process for continuous scale-up production not only mandates a complete reaction leading to a defect-free selective layer, but potentially benefits from being very rapid, which may limit the industrial implementation of many reported approaches.

IP has been optimized by the industry for decades, making it a highly competitive process, but only recently has its sustainability begun to be questioned. The reaction involves the use of hazardous organic solvents, such as hexane, heptane, benzene, and cyclohexane, as well as petroleum-based and toxic monomers.^{19–22} Among the common chemicals for the fabrication of RO membrane by IP (MPD, TMC, and hexane), MPD is the most hazardous and toxic, while hexane is used in much larger quantities but is less hazardous.²³ These chemicals have serious health and environmental adverse effects, to the point that recent European legislation has classified some of them as carcinogenic, designated to be banned from industrial use in the near future.^{20,21} The search for green alternatives for organic solvents would assist the global solvent market, which is estimated to produce 37.4 million metric tons by 2030,²⁴ to align with the United Nations' sustainable development goals (SDGs) for 2030.^{25,26} The global membrane manufacturing has a great share in the production of toxic

wastewater, as well as to pollute the environment through the evaporation of organic solvents.²⁰ It was estimated in the last decade that 10 billion liters of wastewater (containing mostly organic solvents and polymers) were produced annually by desalination membrane production processes solely.²⁷ Therefore, there is a growing need to fabricate membranes using sustainable materials, eliminating the adverse effects the membrane industry has on the environment. Thus, our focus in this work will be on the alternative greener approaches within the framework of IP related membrane production.

To design greener industrial processes and achieve the international target of sustainability that arose since the concept of green chemistry was first formulated in 1990s,²⁸ chemists use the Twelve Principles of Green Chemistry that were introduced in 1998 by Paul Anastas and John Warner.²⁹ In the light of these principles, Szekely *et al.* (2014) outlined the main principles needed for producing more sustainable organic solvent nanofiltration (OSN) membranes, which are relevant for NF and RO membranes as well because they encompass similar processes.³⁰ The principles are as the following (a) utilization of green solvents, (b) the use of low-toxicity chemicals, (c) the use of renewable and sustainable raw materials, (d) fabrication of membranes at room temperature, and (e) design of degradable membranes.³⁰

The present work focuses on recent published attempts made to substitute the hazardous organic solvents and the toxic amine monomers by bio-based or otherwise more sustainable materials in an IP process solely, to derive TFC membrane for NF/OSN/RO processes, and to replace the existing polyamide chemistry. Finding 'green materials' that perform IP, following the five principles of Szekely *et al.*³⁰ and using them to fabricate a greener membrane without compromising

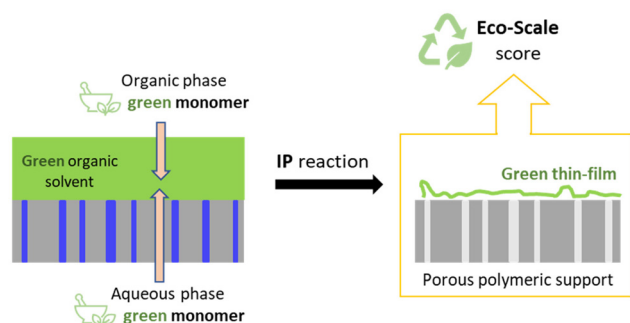


Fig. 2 A schematic representation of the review's concept: summarizing the 'green' options for monomers and organic solvents to perform IP, the corresponding properties of the resultant TFC membrane fabricated, and presenting the 'eco-scale score' calculation for the fabricated membranes.

its performance, is challenging. We summarize the resultant 'greener' membrane performance, while considering these principles. We also demonstrate the calculation of an Eco-Scale score, that provides a quantitative value of the membrane greenness (Fig. 2). Lastly, the underlying motivation of this work is to understand where the process of moving towards sustainable RO/NF membranes stands and to address the gaps and limitations it experiences.

2. Sustainable materials for IP-based membrane fabrication

In recent years, several studies have successfully incorporated bio-based polymers and either less toxic solvents or without the use of solvents for membrane fabrication *via* IP. Herein, we review studies that use 'green solvents' and/or 'green monomers', mentioning their origin, properties, the resultant membrane performance, their advantages, and disadvantages. The fabricated membrane properties are summarized in Tables 2 and 3, and a demonstration of how to calculate the 'greenness' of the membrane is presented later in section 3.

2.1 'Green' solvents

The properties of organic solvents have a major influence on the IP reaction as it involves many aspects that affect the resultant membrane morphology and performance. The main properties affecting the reaction and resultant morphology are its vapor pressure (high vapor pressure solvent may cause vaporization of the organic phase during IP and crumpling of the formed film),³¹ interfacial tension with the aqueous phase (low interfacial tension increases the partitioning of the aqueous monomer to the organic phase and hence the reaction rate; furthermore, the interface will be more easily deformed resulting in film crumpling), the aqueous monomer solubility in the organic solvent, and viscosity (the latter two will increase the aqueous monomer's diffusion rate and hence the polymerization rate), for a more detailed mechanistic

description of the organic solvent effects on IP reaction, see ref. 15. The main characteristic required for an organic solvent in IP is its water-immiscibility to create a biphasic system that contains an interface, and the ability of the organic monomer to dissolve in it. The physical properties of representative 'greener' solvents from different categories, used for NF/OSN/RO membrane fabrication *via* IP, are summarized in Table 1.

2.1.1 Ionic liquids (ILs). Mariën *et al.*³⁸ were the first to use ILs as the organic solvent in IP. ILs are formed by a variety of organic ions possessing either hydrophilic or hydrophobic characteristics. Their interaction with monomers and polymers can be electrostatic and by hydrogen bonding, promoting the solubility of materials such as cellulose, which are barely soluble in other solvents. ILs are non-volatile; therefore, non-toxic in terms of emission during membrane fabrication, and generate less waste of solvent due to evaporation. However, not all ILs are considered 'green', some can be toxic when disposed and not easily biodegrade, but they can be designed to be more sustainable than other organic solvents.^{39,40} Mariën *et al.*⁴¹ used the common imidazolium cation, 1-butyl-3-methylimidazolium [C₄mim], and the anion bis(trifluoromethylsulfonyl)imide [Tf₂N] as the IL, its physical properties are mentioned in Table 1. The water-IL interfacial tension is lower comparing to water-hexane; therefore, a more diffuse interface is formed increasing the partitioning of the aqueous monomer, and hence the polymer formation rate, which may reduce the use of surfactants as well as the aqueous monomer concentration. Lower concentrations of the amine monomer were used (0.1 wt% here vs. 2 wt% in the conventional system with hexane) to receive good performing membrane. However, ILs have a higher viscosity than hexane, leading to lower diffusion of the monomers to the reaction zone reducing the reaction rate, hence higher concentration of TMC is needed (0.5 wt% here vs. 0.1 wt% in the conventional system). The high viscosity minimizes mass transfer at the interface and the resultant membrane is thinner and smoother, with high water permeance and comparable selectivity to a conventional system (with hexane as a solvent) fabricated under similar conditions. The membranes are reported to have a lower tendency for organic and mineral fouling. IL and TMC can in principle be recycled by evaporating residual water from the IL/TMC phase and reused in IP, because IL prevents TMC from hydrolyzation (when hydrolyzed it loses its reactivity) and it is not

Table 1 Physical properties of selected organic solvents used for IP reaction at 20 °C, unless mentioned otherwise^{32–37}

Solvent	Water-solvent interfacial tension [mN m ⁻¹]	Viscosity [mPa s]	Vapor pressure [Pa]
<i>n</i> -Hexane	50.8	0.31	20 398.3
[C ₄ mim][Tf ₂ N]	13.69	63.05	—
Hexyl acetate	18.8	0.86–1.17	176
Decanoic acid	—	4.3@50 °C	0.048@25 °C
α -Pinene	—	1.3@25 °C	630@25 °C
<i>p</i> -Cymene	36.41	0.8333	200

volatile, reducing the solvent volume required for the process.⁴¹ However, ILs are more expensive than regular solvents and do not always completely meet the principles for sustainable membranes.³⁰ A more affordable class of hydrophobic ionic liquid with tricaprylmethylammonium as cation (the trade name Aliquat), has been investigated as a solvent for IP by Van den Mooter *et al.*⁴² Unfortunately, Aliquat was not successful in promoting the polyamide thin-film formation, since the presence of tertiary amines functioned as a catalyst for the hydrolysis and esterification of TMC. However, Aliquat was successful as an organic phase for IP using epoxy as monomer, as an alternative to polyamide chemistry. Other, less expensive options of green ILs are emerging and should be explored for IP.

Hartanto *et al.*²⁰ used a mixture of 50 : 50 [C₄mim][Tf₂N] (IL) and hexyl acetate, to reduce the costs and make IL-based processes more feasible for the industry. Hexyl acetate is an environmentally friendly solvent and cheaper than IL. The mixture has higher interfacial tension and lower viscosity than the pure IL⁴¹ (Table 1), resulting in a higher MPD concentration required (0.5 wt%) and lower TMC concentration (0.3 wt%).²⁰ Considering large-scale usage, the membrane performance achieved using IL and IL + hexyl acetate has lower NaCl rejection (94–97%) than membranes used for RO applications (>99%), but it is still considered a good performance, that can be used for various industrial applications. In this case, ILs are still expensive compared to hexane, but the use of a mixture with hexyl acetate reduces the costs and makes it feasible for industrial use.

Zheng *et al.*⁴³ fabricated polyamide/poly(*m*-phenylene isophthalamide) (PMIA) TFC membranes for OSN, using a novel IL-assisted method. Dope solutions formulated by an environmentally benign IL [EMIm][OAc] were used to cast the porous PMIA membrane substrates. The IP reaction between amine monomers (*i.e.*, piperazine and polyethyleneimine) in the aqueous phase and aromatic acyl chlorides (*i.e.*, phthaloyl chloride and 1,3,5-benzenetricarboxylic chloride) in the IL [BMIm][Tf₂N] phase led to the synthesis of the selective layer on the PMIA surface. When a fabricated TFC membrane with a favourable selection of monomers with the IL as the organic solvent was compared to a membrane with the same monomer composition but with *n*-hexane as the organic phase solvent, the newly synthesized membrane had up to three times enhanced permeance and maintained high rejections for Congo Red and vitamin B12; however, this is not an adequate comparison, because the monomer selection was optimized for this IL system. The enhancement in the membrane permeance was attributed to the high viscosity of the ILs, which reduced the rate of monomer diffusion in the organic phase; further reducing the mass transfer at the interface, causing the selective layer formed to be much thinner and less cross-linked. Furthermore, the residual IL phase containing the organic monomers can be reused to fabricate more membranes. In subsequent work, Yao *et al.*⁴⁴ retained ILs as a replacement for organic phase and ventured into developing TFC OSN membranes with sandwich-like structures *via* IP on

metalorganic framework (MOF) nanosheet-modified microporous polyvinylidene fluoride (PVDF) substrate surface. The IP monomers are mixed amine (polyethyleneimine and PIP) in the aqueous phase and TMC in the hydrophobic IL phase. The IL was 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([BMIm][Tf₂N]), which was similar to the earlier reported study.⁴³ MOF nanosheets of micrometer lateral dimensions and nanometer thickness (1.5 ± 0.6 nm) could be deposited on the PVDF substrate as an interlayer to facilitate the IP reaction.

The low volatility of ILs comparing to hexane has advantages relating to the IP reaction in addition to lower toxicity. One example is the preparation of covalent organic frameworks (COFs) by IP, which is affected by a disturbance in the liquid–liquid interface as the volatile solvents evaporate. To overcome this limitation, Gao *et al.*,⁴⁵ proposed the synthesis of several imine-linked freestanding COF membranes having varying thickness and morphology at tuneable IL–H₂O interfaces. In both, the water and ILs, the monomer diffusion was controlled due to the hydrogen bonding between the amine monomers and the catalyst (*p*-toluenesulfonic acid), and the high viscosity of ILs. The crystallinity of the COF membranes could further be improved by varying the alkyl chain length of cations in the ILs (enabling regulation of the interfacial tension and interfacial region size). However, a main disadvantage of COF approaches is the long time required for an adequate selective layer formation, which is usually much larger than a fabrication process in a continuous mode allowed by the instrumental set-up.

While the examples focus on IL in the organic phase, there are reasons to use hydrophilic IL as the polar phase when working with monomers of limited solubility in water.^{46,47} Although the performance seems to increase, these studies cannot be classified as a greener approach when ILs replace water as aqueous phase. Lastly, in most cases, the IL is used as an additive.^{48,49}

2.1.2 Bio-based solvents. Ong *et al.*²¹ used decanoic acid in the IP organic phase, which is a medium chain fatty acid found in coconut oil, palm kernel oil, and animal fats. The resultant NF polyamide membrane had very high water permeance and excellent separation performance for different dyes; moreover, its stability in organic solvents was high.²¹ However, decanoic acid's melting point is 31.5 °C, and therefore the IP reaction was performed at 60 °C. Conducting the reaction at a significantly higher temperature than the ambient results in more energy consumption and doesn't follow green principles for OSN membranes.³⁰

In subsequent work, Falca *et al.*,⁵⁰ used oleic acid as a replacement for hexane in the organic phase. The resulting high-performing composite membrane was selective for small molecules with a molecular weight cut-off (MWCO) of 650 g mol^{−1} and a high permeance of ~57 L per m² per h per bar. Oleic acid, a green solvent derived from coconut, has a low vapor pressure and high boiling point. These properties may be favorable in synthesizing TFC membranes, but like decanoic acid, the high viscosity would require higher temperatures for an effective membrane formation.

Abdellah *et al.*⁵¹ used alpha-pinene, an organic compound extracted from plants (*e.g.* rosemary, basil, pine), as the organic solvent for IP reaction between terephthaloyl chloride (TPC) and catechin or quercetin in two different studies. Catechin or quercetin are both considered 'green' monomers and will be described in the next section. Alpha-pinene has a lower vapor pressure than hexane and this reduces the amounts of solvent used and eliminates the possibility of explosion. However, its vapor pressure is not negligible (Table 1) and higher than other solvents mentioned here. The resultant membrane showed high stability in harsh aprotic solvents, and its performance is competitive with other membranes in literature (see Table 2 and previous reports^{51,52}) with relatively high DMF permeance of 2.6 L per m² per h per bar and MWCO of 300 g mol⁻¹. The effect of solely changing the solvent to alpha-pinene cannot be deduced because these membranes had other variations from the commonly used membrane. Alpha-pinene has a slightly higher viscosity than hexane, which would slightly decrease the MPD and TMC diffusion rate to the reaction zone. This membrane followed almost all of the 'green' principles³⁰ except that the organic monomer used was not considered 'green'.

2.1.3 Vapor phase interfacial polymerization. A creative study reported by Paseta *et al.*⁵³ eliminated the use of the organic solvent by carrying out the IP reaction in the vapor phase. They used the common monomers (MPD and TMC), while the TMC was vaporized in an oven at 40 °C reacting with MPD on a PI (polyimide) support in an upside-down Petri dish. The low melting point of TMC (32–38 °C) allowed for the process to occur in the vapor phase, because of increased TMC vapor pressure, at a reasonable temperature (40 °C). The authors demonstrated that by using this technique, the consumption of TMC monomer is reduced by 96.2% because there is no excess of TMC in a residual solution. The membrane permeance was higher than conventionally-fabricated membranes, but the rejection was similar. Nevertheless, higher permeance with similar rejections translates to higher salt permeability as well. Moreover, the MWCO was lower than most other membranes in this review. The technique is more environmentally friendly as it reduced the amount of TMC used and eliminates the need for hexane, and more economical due to the same reasons. However, its preparation requires heating for 60 minutes at 40 °C which is a drawback from an industrial perspective. Future work should examine the industrial suitability of this process and its overall environmental impact. In a similar study, Karki *et al.*⁵⁴ developed thin film nanocomposite (TFN) membranes, by the vapor-phase IP method, in which TMC was vaporized. Carboxylic acid-functionalized TiO₂ (COOH–TiO₂) nanoparticles were incorporated in the TFN membranes. The surface of the membrane was modified by IP using diethylenetriamine and TMC. However, the low functionalization required the incorporation of large amounts of nanomaterials (and subsequent large amounts of monomers) to make the IP process feasible.

Welch *et al.*⁵⁵ used molecular layer deposition to produce polyamide by gas phase deposition. Within 48 cycles, a 15 nm

film was fabricated by the reaction between vaporized MPD and TMC, without solvents, and thus, RO membrane performance was achieved. The process requires high temperatures (115 °C) and low pressure, and the reaction time is higher than conventional IP. Fabrication in a large scale of robust films is a challenge.

Promoting the IP reaction from the vapor phase might be an alternative to the classical organic solvent liquid system, but optimization and further investigation are still needed.

2.1.4 Alternative IP methods based on non-organic solvents. An aqueous two-phase interfacial assembly method was proposed by Wang *et al.*⁵⁶ for the fabrication of covalent organic framework (COF) membranes. The aqueous two-phase system contained polyethylene glycol and dextran which spontaneously segregated into two water-rich phases. At the water–water interface, COF membranes were fabricated by the distribution of aldehyde and amine monomers into the two aqueous phases. The membrane fabrication was dependent on the reactants' weight ratio, pH value, and reaction time. The membranes had high NaCl rejection of 93.0–93.6% and water permeance reaching 1.7–3.7 L per m² per h per bar. It was also observed that the structure of the membranes was highly dependent on the interfacial tension. Tight and compact COF membranes were formed for high interfacial tension (0.1–1.0 mN m⁻¹), while loose and fragmented COF membranes were formed for low interfacial tension (0.001–0.1 mN m⁻¹). This method has also been adapted to fabricate other COF and metal–organic polymer membranes. The fabrication of membranes in an all-aqueous system for the very first time confers a green and generic method for advanced membrane manufacturing systems. Here again, the proper COF formation might require time, compromising the feasibility of the membrane formation in continuous machines.

Table 2 compiles a list of studies using IP to prepare membranes by using green solvents. The key components and results of the studies, along with the advantages and disadvantages, are mentioned. The comparison must be carefully analyzed since the membranes were not tested under the same conditions. An agreement on testing protocols in the nanofiltration and reverse osmosis field would be highly advantageous to guide the development of new membranes. Recently OSN and RO database of membrane performance were released.^{57,58} These databases serve as an essential tool of comparison among different membranes; however, the comparison should be carefully assessed because the testing procedure was not uniform.

2.2 Green aqueous monomers

Replacing the toxic amine monomer in an IP reaction is challenging. The monomer should be sufficiently reactive to create a highly crosslinked thin film and must be soluble in appropriate, immiscible liquids (ideally green solvents).⁶¹ Green monomers are a sort of natural reagents, the building blocks of polymers, which are abundant, nontoxic, cheap, environmentally friendly, renewable, and sustainable as they are usually sourced from biorefineries, bioplastics, plants, bio wastes or

Table 2 Summary of the NF/OSN/RO membrane properties fabricated via IP using sustainable organic solvents

Ref.	Organic solvent	Origin	Membrane type	Aqueous monomer	Organic monomer	Support	Product	MWCO [g mol ⁻¹]	Rejection [%]	Permeance [L per m ² h per bar]	Advantages	Disadvantages
41	[C ₄ mim][Tf ₂ N]	IL	RO	MPD	TMC	PI	PA	N/A	96.8% NaCl	Water: 1.09	<ul style="list-style-type: none"> • Reduced surfactants • Reduced amine conc. • Reduced fouling • Increased permeance • Recycled organic phase • Non-volatile • Relatively inexpensive IL 	<ul style="list-style-type: none"> • Increased TMC conc. • High costs • Moderately toxic
42	Aliquat	IL	SRNF/STNF	MPD/HDA	TMC/BADGE	PSF/PI	PA/Epoxy	N/A	~45% of ethyl acetate	Water/ethanol mixture: < 0.05	<ul style="list-style-type: none"> • Additional need of co-solvents • No satisfactory performance • Long reaction time of 72h • Increased TMC conc. 	
20	50 : 50 [C ₄ mim][Tf ₂ N] : hexyl acetate	IL, hexyl acetate from plants	FO, RO	MPD	TMC	PI	PA	N/A	94.5% NaCl	Water: 0.41	<ul style="list-style-type: none"> • Better performance than pure IL • Lower costs than pure IL • Hexyl acetate is derived from plants 	
43	[BMIm][Tf ₂ N]	IL	OSN	PIP + PEI	TMC/PDC	PMIA	PA/PIPA	320–479	>99% for both congo red and vitamin B12	Water: 2.15, (with Congo red), Water: 3.6, (with, vitamin B12)	<ul style="list-style-type: none"> • Strong tolerance to various organic solvents with good stability • Enhanced separation performance • Recycle of IL for greenness 	<ul style="list-style-type: none"> • Requires heating to 60 °C for crosslinking • Expensive IL
44	[BMIm][Tf ₂ N]	IL	OSN	PIP + PEI	TMC	Modified Cu-TCPP nano-sheets on PVDF	PVDF/t-Cu-TCPP/PA	N/A	98.9% brilliant blue; 95% congo red	Water: 2.7	<ul style="list-style-type: none"> • Steady performance throughout the 36 h NF of the Rose Bengal/ethanol mixture • Good performance in the concentration of lecithin in methanol 	<ul style="list-style-type: none"> • Cu-TCPP nanosheets and ILs are expensive

Table 2 (Contd.)

Ref.	Organic solvent	Origin	Membrane type	Aqueous monomer	Organic monomer	Support	Product	MWCO [g mol ⁻¹]	Rejection [%]	Permeance [L per m ² h per bar]	Advantages	Disadvantages
45	[CnMim][Trf ₂ N]	IL	OSN	BD	TFB	Nylon	COF	N/A	98% Alcacian blue	Acetonitrile using C ₁₂ M IL: ~523	• High permeance for acetonitrile, acetone, water, methanol, and ethanol • Excellent selective rejection of dyes • Amino acid IL acts as humectant to preserve wettability and prevents permeability reduction after heating for storing membrane at dry-state • Higher selectivity for sodium than the commercial membranes mentioned	• Extremely long reaction time • Difficulty in scale-up • Longer reaction time • TFC membrane is submerged in the amino acid IL for up to 12 h. • Selectivity towards MgSO ₄ is lower than pristine TFC standard membrane
59	Hexane in first step and then [αN1111][Gly] amino acid IL	Crude oil and IL	NF	PIP	TMC	PES	Amino acid based IL-TFC	267	MgSO ₄ : 91.4%	Water: 12.6		
60	Toluene and then [MimAP][Trf ₂ N]/dichloromethane	Crude oil and IL	NF	PIP	TMC	PAN	PA	500–600	Mg ²⁺ : 81.9; Li ⁺ : 45.2	Water: 37.8	• Stable performance for Mg ²⁺ /Li ⁺ separation • Possibility of using Li from brine with high Mg ²⁺ /Li ⁺ ratio. • High stability • Excellent separation performance • Non-volatile • Solvent derived from plants • Non-volatile	• Requires annealing temperature of 80 °C
21	Decanoic acid	plants	OSN	PEI	TMC	PAN	PA	650	99% congo red	Methanol with congo red: 60		• High energy costs
50	Oleic acid	Bio based	OSN	MPD	TMC	PAN	PA	650	99.9% direct red 80	Water: 57		• Requirement of post-heat treatment

Table 2 (Contd.)

Ref.	Organic solvent	Origin	Membrane type	Aqueous monomer	Organic monomer	Support	Product	MWCO [g mol ⁻¹]	Rejection [%]	Permeance [L per m ² h per bar]	Advantages	Disadvantages
52	Alpha-pinene	Plants	OSN	Catechin	TPC	CA	Polyester	500	92% amido black; 87% Sudan Blue	DMF: 1.4	• Good performance	
51	Alpha-pinene	Plants	OSN	Quercetin in NaOH	TPC	Cellulose	Polyester	300	90% methyl orange; 96% amido black	DMF: 2.6	• Solvent derived from plants	• Flammable
61	<i>p</i> -Cymene	plants	OSN	Tannic acid	Priamine	PET	TA/ Priamine free-standing film	395	90%styrene dimer	Acetone: 13.7	• Excellent performance • Solvent derived from plants	• Relatively high vapor pressure
53	Vapour	—	OSN	MPD	TMC (vapour)	PI	PA	260	98.5% Rose Bengal	Water with Rose Bengal: 2.4	• Decreased liquid waste. • Increased permeance • Enhanced performance obtained against heavy metal ions	• Increased energy costs • Designing a new process • Requires additional step of introducing nanoparticles to form
54	Vapour	—	NF	DETA + COOH-TiO2	TMC (vapour)	PSf	PA	N/A	Na ⁺ :87% Cu ²⁺ : 87% Hg ²⁺ : 77% Pb ²⁺ : 83%	Water: 37.8	• Incorporated TiO ₂ -NPs enhanced the antifouling tendency. • Reduces liquid waste	• nanocomposite (TFN) membrane. • Large amount of TMC required
62	No solvent	—	NF	APPD	β CD	P84 PI	Polyester	N/A	Congo red/ NaCl: 99.1/7.87	Water: 209 at 2 bar	• Single step crosslinking and IP simultaneously • Excellent antifouling characteristics • High dye rejection and salt permeation for dye/salt mixtures	• Initial tendency of fouling of membranes
56	No solvent	—	RO	DHTA in phase 1 TMGC or BTTH in phase 2	—	PAN	COF	N/A	NaCl: 93–93.6%	Water: 1.7–3.7	• Eliminates organic phase completely. • No use of heat during IP and thus, is a green manufacturing method	• Requires NaOH • More efforts to realistically scale-up

Table 2 (Contd.)

Ref.	Organic solvent	Origin	Membrane type	Aqueous monomer	Organic monomer	Support	Product	MWCO [g mol ⁻¹]	Rejection [%]	Permeance [L per m ² h per bar]	Advantages	Disadvantages
55	No solvent	—	RO	MPD	TMC	NF270	PA	N/A	NaCl: 97–99%	Water: 1.4–1.6	<ul style="list-style-type: none"> • A controlled process to fabricate consistent films • Scalable 	<ul style="list-style-type: none"> • High temp. (115 °C) • Vacuum • Long and challenging fabrication process

PIPA: poly(*m*-phenylene isophthalamide), DHTA: 2,5-dihydroxyterephthalaldehyde, TMGC: triaminoguanidinium chloride, BTTH: 1,3,5-benzenetriamine trihydrochloride, DETA:

renewable oil.^{63,64} Table 3 summarizes the ‘green’ aqueous monomers used for IP in recent studies and the fabricated membrane properties, and a calculation tool to assess the ‘greenness’ of the membrane is demonstrated in section 3.

2.2.1 Bio-polyphenols. Various studies used different kinds of plant-derived polyphenols as the aqueous monomer replacing the toxic amines, to derive a polyester film. Polyester is produced by a reaction between an organic acyl chloride and a diol, here we focus on a bio-polyphenol, that can cross-link resulting in a thin, well-performing membrane.^{51,65} Phenols behave like weak acids that have a low reactivity towards acylation (the characteristic reaction that occurs during IP); therefore, initial activation of the phenol with a strong base is sometimes used which results in a more reactive specie towards the acyl group, phenoxide ions. The added base also neutralizes the by-product acid.⁵² Pérez-Manríquez *et al.*⁶⁵ used morin hydrate, a natural polyphenolic compound derived from the Guava plant, as the aqueous monomer, and terephthaloyl chloride (TPC) as the organic monomer. The morin/TPC TFC membrane was stable in harsh organic solvents. The monomer is low-cost; however, morin has low solubility in water and hence methanol was used as the aqueous solvent reducing the potential for upscaling.⁶⁵ Abdellah *et al.*^{51,52} used two different bio-polyphenols, catechin and quercetin, in two separate studies. The polyphenols were first reacted with sodium hydroxide that was added to the aqueous solution for their activation and then performed an IP with TPC, Fig. 3 is an example for the fabrication of polyester from catechin and TPC. Catechin and quercetin have many cross-linkable hydroxyl groups, increasing their potential to produce an adequate membrane. However, the reaction time was 3 hours compared to the 1–2 minutes of the reaction to fabricate commercial membranes. The organic solvent they used to dissolve TPC is also derived from plants, alpha-pinene, its properties appear in section 2.1. The fabricated membranes showed high DMF permeance of 1.4 and 2.6 L per m² per h per bar and MWCO of 500 and 300 g mol⁻¹, while quercetin being superior. The reason for the better performance is not clear. In both studies they used the same procedure for membrane fabrication, same support, and the same monomer concentrations. Moreover, understanding the effect of changing the aqueous monomer should be studied when solely the aqueous monomer is changed comparing to commercial membrane, here multiple parameters were changed.

Zhang *et al.*,⁶⁶ Pérez-Manríquez *et al.*,²² and Park *et al.*⁶¹ used tannic acid, a type of polyphenol found in plants, as the aqueous monomer. They used different organic monomers, organic solvents, and supports (Tables 3 and Table 4). The resultant membranes varied in their performance, while the best performing membrane was that of Park *et al.*⁶¹ Zhang *et al.*⁶⁶ fabricated membranes with excellent antifouling properties probably due to the enrichment of hydroxyl groups in the polyester thin film. Pérez-Manríquez *et al.*²² produced a stable membrane that could in principle be scaled up.

Zhang *et al.*⁶⁷ used polyphenol from green tea, epigallocatechin gallate (EGCG), to fabricate NF membrane. They first per-

Table 3 Summary of the NF/OSN membrane properties, fabricated via IP using sustainable monomers

Ref.	Aqueous phase	Origin	Membrane type	Organic monomer	Organic solvent	Support	Product	MWCO [g mol ⁻¹]	Rejection [%]	Permeance [L per m ² per h per bar]	Advantages	Disadvantages
65	Polyphenol: morin hydrate in methanol	Guava	OSN	TPC	Cyclohexane	PAN	Polyester	800	96% Brilliant blue	Brilliant blue in NMP: 0.3	<ul style="list-style-type: none"> Simple fabrication method. Easy to upscale. Stable in harsh organic solvents. Excellent performance. Low-cost 	<ul style="list-style-type: none"> Morin isn't soluble in water. Usage of methanol
52	Polyphenol: catechin	Apples and other fruits	OSN	TPC	Alpha-pinene	Cellulose	Polyester	500	92% amido black; 87% sudan blue	1.4: DMF	<ul style="list-style-type: none"> Easy fabrication. High stability 	A prior reaction of the polyphenol in base conditions to better react in IP.
51	Polyphenol: quercetin	Caper black-tea etc.	OSN	TPC	Alpha-pinene	Cellulose	Polyester	300	90% methylenorange; 96% amido black	2.6: DMF	<ul style="list-style-type: none"> Easy fabrication. High stability 	<ul style="list-style-type: none"> Good antifouling properties Stable. Cost-effective. Optional scale-up process
66	Polyphenol: tannic acid	Tea, berries, wood, etc.	NF	TMC	Hexane	PES	Polyester	N/A	42% Na ₂ SO ₄ ; 99% congo red	20	<ul style="list-style-type: none"> Good antifouling properties Stable. Cost-effective. Optional scale-up process 	Salt rejection is not high
22	Polyphenol: tannic acid	Date fruit	OSN	TPC	Cyclohexane	PAN	Polyester	800	95% Brilliant blue, 88% congo red	Brilliant blue in NMP: 0.08	<ul style="list-style-type: none"> Stable. Cost-effective. Optional scale-up process 	Fair performance
67	Polyphenol: EGCG – PEI	Green tea	NF/OSN	TMC	Hexane	PTFE	EGCG-PEI-TMC/ PTFE membrane	380	99.9% methyl orange, 95.5% Na ₂ SO ₄	Water: 9.15	<ul style="list-style-type: none"> Robust and stable membrane 	PEI was used which is a toxic amine monomer.
68	Polyphenol: Allylated Gallic acid in phosphate buffer solution	Gall nut, oak bark & other plants	NF	TMC	Isopar G	PAN	Polyester	327 with the use of co-monomer MPD	>99% congo red, 81% methyl orange, 59% Na ₂ SO ₄	Water: 47.6	<ul style="list-style-type: none"> High water flux Synergistic use of polyphenol based monomer 	For increasing the rejection of dyes, MPD was used as a co-monomer
69	Cyclodextrin (CD): cyclic oligosaccharide, in 1 M NaOH	Starch	NF/OSN	TC	Hexane	PAN	Polyester	—	91–95% Methyl orange	Water: 20	<ul style="list-style-type: none"> Low-cost materials. 	<ul style="list-style-type: none"> Relatively high concentration of cyclodextrin (6.5%w/v). Reaction in high pH
											<ul style="list-style-type: none"> Commercially available reagents. Repeatable fabrication process. 	

Table 3 (Contd.)

Ref.	Aqueous phase	Origin	Membrane type	Organic monomer	Organic solvent	Support	Product	MWCO [g mol ⁻¹]	Rejection [%]	Permeance [L per m ² per h per bar]	Advantages	Disadvantages
70	Cyclodextrin (CD): α-CD, β-CD and γ-CD in NaOH solution	wheat/maize/potato starch	OSN	TMC	Hexane	Matrimid	Polyester	α-CD (320 Da) <β-CD (400 Da) <γ-CD (550 Da)	99.4% rose Bengal, 98.6 brilliant blue, 86.3% methyl orange	Water: 5.5, Methanol: 4.9, Ethanol: 3.8, DMF: 0.9, NMP: 0.8, Cyclohexane: 4.5, Hexane: 6.0	• Only work on Janus membrane using cyclodextrin as a monomer • Molecularly engineered IP reaction allows permeance for organic & non-organic solvents • High water flux	• NaOH was used as a catalyst in the aqueous phase. • Fair performance of permeance of solvents
71	Cyclodextrin (CD): β-CD	Starch	NF	TMC	Heptane	PES	Polyester	N/A	95.6% congo red, 94.4% methyl blue	Water: 104.6 (0.1% β-CD), Water: 197.6 (1.8% β-CD)	• Requires post heat treatment of 60 °C. • Requires 1.8 wt% β-CD • Requires post heat treatment of 60 °C. • Use of expensive and low toxic graphene quantum dots as additives	• Requires post heat treatment of 60 °C.
72	Cyclodextrin (CD): β-CD with graphene quantum dots as additives	Starch	NF	TMC	Heptane	PES	Polyester	860 (1.8% β-CD and 0.3% graphene quantum dots)	>93.0% Eriochrome black T and congo red	Water: 122 (1.8% β-CD), Water: 474.7 (1.8% β-CD and 0.3% graphene quantum dots as additives)	• Highly chlorine resistant • Extremely high water flux	• Requires 1.8 wt% β-CD • Requires post heat treatment of 60 °C.
73	Cyclodextrin (CD): β-CD with triethylamine	Starch	NF	TMC	Hexane	Multi-walled carbon nanotubes (MWCNTs) on PVDF membrane	Polyester	590 (2% β-CD on MWCNTs substrates)	96.4% congo red, 97.4% brilliant green	Water: 179.93 (2% β-CD on MWCNTs substrates)	• Extremely high water flux • Highly chlorine resistant • Good separation performance for dye/salts mixture	• Use of MWCNTs • Use of NaOH and triethylamine
74	Polysaccharide chitosan	Crustaceans	NF	TMC	Hexane	PSF	Polyamide	800	91.9% Na ₂ SO ₄	5.22	Chitosan reduces the amount of the amine monomer needed.	Chitosan has to be dissolved in acidic solution (pH~2) and heated. • NaOH was used as a catalyst in the aqueous phase. • High concentration (5 wt%) of aqueous monomer
75	Glucose - mono, maltose - di, and raffinose - trisaccharides with 1 M NaOH	Tissues of most plants, honey and fruits	NF	TMC	Hexane	PES	Polyester	464 (glucose), 495 (maltose) 485 (raffinose)	~95% Na ₂ SO ₄	Water: 33.7 with glucose	Completes circular economy as sugar-based membranes were used to separate sugar from aqueous solution	• NaOH was used as a catalyst in the aqueous phase. • High concentration (5 wt%) of aqueous monomer

Table 3 (Contd.)

Ref.	Aqueous phase	Origin	Membrane type	Organic monomer	Organic solvent	Support	Product	MWCO [g mol ⁻¹]	Rejection [%]	Permeance [L per m ² per h per bar]	Advantages	Disadvantages
76	Glucose - mono, sucrose - di, and raffinose - trisaccharides with 1 M NaOH	Tissues of most plants, honey and fruits	Loose NF	TMC	Hexane	PES	Polyester	783 with optimized 0.6 wt% sucrose	Congo red/Na ₂ SO ₄ : 99.4/11.2, direct blue 23/NaCl: 98.8/3.3	Water: 52.4 with sucrose	• Reasonable dye/salt rejection	NaOH was used as a catalyst in the aqueous phase
77	Sugar alcohol: meso-erythritol	Corn	Loose NF	TMC	Hexane	PES	Polyester	N/A	Congo red/Na ₂ SO ₄ : 99.6/11, direct red 23/NaCl: 95.2/5.6	Water: 53.2	• Good antifouling ability	
78	Glucose - mono, sucrose - di, and raffinose - trisaccharides, Cyclodextrin (CD); β-CD	Tissues of most plants, honey and fruits, and starch	NF	TMC	Heptane	PAN	Polyester	440 with glucose as optimized monomer	99.5% Na ₂ SO ₄ 5.6	Water: 16.1	• Highly chlorine resistant	• NaOH was used as a catalyst in the aqueous phase.
79	Dopamine (DA)	Mussels	NF	TMC	Heptane	PES	DA/TMC		64% Na ₂ SO ₄ , 97% congo red	Water: 7.5	• Very high rejection of Na ₂ SO ₄ salt	• Use of heat at the cost of money
80	Sulfonated dopamine (SDA)	Mussels	NF + OSN	TMC	Cyclohexane	HPAN	SDA-TMC	2000	90% Na ₂ SO ₄ , 99.9% congo red, methyl blue.	Water: 10.4	• Stable	• Its performance is not good enough for NF.
81	Dopamine hydrochloride (PDA), norepinephrine (PNE) and tannic acid (TA)	PDA: Mussels PNE: neurotransmitter TA: Trees, fruits	NF	TMC	Isol-C	PSF	Polyester	650 (PDA) 715 (PNE), 832 Tannic acid	~93% Na ₂ SO ₄ for 2 wt% PDA	Water: 8.4	• High permeance	• NaOH was used as a catalyst with PDA/PNE in the aqueous phase.
82	Dopamine hydrochloride (PDA) and glucose with MOFs additive	Mussels and tissues of most of plants	NF + OSN	TMC	Hexane	PI	PA	N/A	99.9% Na ₂ SO ₄ , 98.9% MgSO ₄ , 97% MgCl ₂ , 92.3% NaCl	Water: 39.3, IPA: 18.5 Acetone: 30.1 EA: 18.3 DMF: 5.5	• Excellent chemical and mechanical stability	Use of low-toxic MOFs as additives
83	Amino acid: L-lysine	Diet of poultry, fish, beans etc.	NF	TMC	Hexane	PSF	PA	1150	Naphthol green B/NaCl: 99.2/2.75	Water: 36.15	• Multifunctional TFN membranes	High MWCO

Table 3 (Contd.)

Ref.	Aqueous phase	Origin	Membrane type	Organic monomer	Organic solvent	Support	Product	MWCO [g mol ⁻¹]	Rejection [%]	Permeance [L per m ² per h per bar]	Advantages	Disadvantages
84	Lignin alkali (LA)	Plants' cell walls	NF + OSN	TMC	Hexane	PSF	Polyester	630	97.3% Brilliant blue; 97.8% Congo red.	Water: 1.7	• Stable • Low cost • Easy reaction	Moderately low salt rejection for NF application.
85	Tris (hydroxymethyl) aminomethane (THAM) in 0.1 M NaOH solution	Condensation of nitromethane with formaldehyde	NF + OSN	TMC	Hexane	PES	Poly(ester amide)	N/A	51.4% MgSO ₄ 99.9% Na ₂ SO ₄ (7.5% THAM), CR/NaCl: 98.8/7.5 (0.5% THAM)	Water: 11.1 (7.5% THAM), water: >45 (0.5% THAM)	• Multifunctional TFC membranes • Easy membrane fabrication with alternating ester and amide linkages	• Use of NaOH solution as a catalyst • Requires post heat treatment

formed a Michael addition/Schiff base reaction between the pyrogallol groups in EGCG and amine groups in polyethyleneimine (PEI), later amidation reaction with TMC onto poly(tetrafluoro ethylene) (PTFE) resulted in a cross-linked EGCG-PEI-TMC/PTFE product (see Fig. 4). The use of PEI, which is considered a toxic amine monomer, reduces the sustainability of the membrane; however, its optimized concentration is 1 w/v%, half the MPD concentration commonly used. The use of EGCG for the production of NF membranes compared to those produced solely by the reaction between PEI and TMC increased the stability of the membrane due to the stronger adhesion to the support.⁶⁷ The resultant membrane had very good performance and stability.

Alhazmi *et al.*⁶⁸ used allylated gallic acid as IP monomer to react with TMC. The MWCO was tuned between 700 and 327 g mol⁻¹ by changing the chemical composition and reaction time. The allyl functionality integrated into the membrane network offers the chance for post-functionalization.

To conclude, membranes fabricated using bio-polyphenols showed overall competitive performance, as seen in Table 3, were easily fabricated, and have good potential to replace or to come in addition to the aqueous monomer commonly used for OSN/NF membranes.

2.2.2 Polysaccharides. Recent literature suggests alternative monomers to those of petrochemical sources by simply exploring sugar-based monomers for replacing the amine monomer. Zheng *et al.*⁷⁵ employed the classical examples of mono-, di- and tri-saccharides such as glucose, maltose and raffinose for facile IP. However, as in the case of polyphenols, the pH had to be adjusted and therefore NaOH had to be used in the aqueous solution for accelerating the reaction. The reactivity of the primary –OH groups was lesser than secondary and tertiary –OH groups of saccharides and was much lower than the –OH groups of amine monomers (MPD/PIP) with aqueous monomer TMC. Hence, the sugar monomer concentrations were increased to promote IP reaction rate. Additionally, a high porosity commercial PES (with a MWCO as high as 100 kDa) was applied as the support to improve the sugar transfer rate to the polymerization zone. The optimized sugar-based TFC-NF membrane exhibited a water permeance of 33.7 L per m² per h per bar and Na₂SO₄ rejection of ~95%. The glucose-based TFC-NF membrane had a MWCO of 464 g mol⁻¹, slightly larger than the MWCO of PIP/TMC NF membranes. However, the rejection of Na₂SO₄ was similar due to a high density of negative charges on the surface. Polysaccharides are large molecules, that hinder the rapid IP reaction by their slow diffusion to the interface. The resulting TFC membrane is inferior in its performance to membrane fabricated by polyphenols. Nevertheless, in terms of sustainability, sugar-based monomers open a new window of opportunity to replace toxic monomers as sugar is abundantly available in the nature offering non-toxic and harmless trait to human beings and environment, and the matured industrial methods to extract sugar makes it a cheap and a greener alternative. Additionally, the authors closed the loop by fabricating sugar-based TFC-NF membrane, and subsequently, by

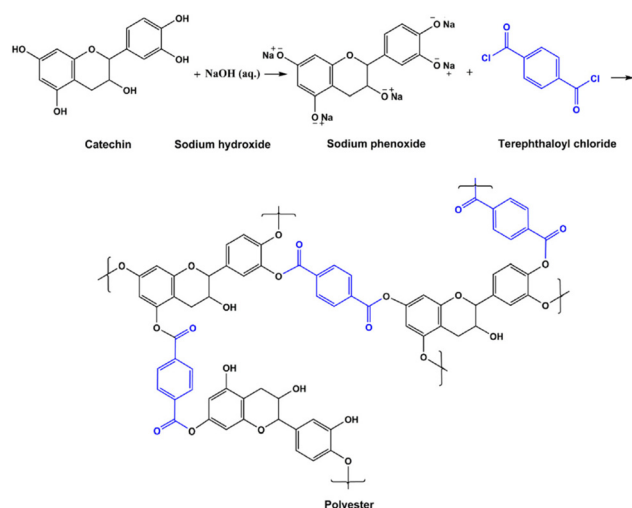


Fig. 3 The IP reaction between catechin and TPC, yielding polyester.⁵²

using these membranes, sugar was recovered from water for its further production.⁷⁵

In continuation, Jin *et al.*⁷⁷ reported the use of a sugar alcohol, meso-erythritol, followed by sugar bio-monomers such as sucrose⁷⁶ replacing the amine monomer. These membranes were evaluated for the wastewater treatment of textile industries, as they offered adequate dye/salt separation, wherein 99.6% of Congo Red dye was rejected and 89% of Na₂SO₄ salt was permeated (at a water flux of 53.2 L per m² per h per bar)⁷⁷ and 99.4% of Congo Red dye was rejected and 88.8% of Na₂SO₄ salt was permeated (at a water flux of 52.4 L per m² per h per bar).⁷⁶

Cyclodextrins (CDs) constitute a family of cyclic oligosaccharides, which are plant-based produced derived from starch. They have abundant active –OH groups for crosslinking as well as a cavity in the middle of their structure, named alpha, beta, or gamma macrocycles. The cavity enables selective transport of molecules with a sizes range of 0.47–0.95 nm. When they are used as IP monomers in a fully crosslinked network, the cavities can act as “preformed” pores. However, to have full advantage of CD cavities as selective pathways, the space between the CD unities must be minimized. CDs also have disadvantages compared to MPD: their hydroxyl groups are less reactive towards acyl-chloride than amines, and they tend to agglomerate in aqueous solutions. A pioneering approach to effectively produce CD membranes was proposed by Villalobos *et al.*,⁶⁹ they used CD as the aqueous monomer and succeeded in optimizing the preparation conditions (high concentration of the aqueous monomer, hydrophilic and highly porous support, high pH). CD reacted with terephthaloyl chloride (TC) to produce polyester. The fabricated membrane had high performance: its permeance was an order of magnitude higher than commercially available OSN membranes, and its rejection of methyl orange is slightly lower than polyamide TFC membranes.

Table 4 Summary of the NF/OSN greener membranes properties, fabricated via IP using greener monomers and greener organic solvents

Ref.	Aqueous phase	Origin	Membrane type	Organic monomer	Organic solvent	Support	Product	MWCO [g mol ⁻¹]	Rejection [%]	Permeance [L per m ² per h per bar]	Advantages	Disadvantages
61	Polyphenol: tannic acid	Trees, plants nuts and fruits	OSN	Priamine	<i>p</i> -Cymene	Recycled PET	Priamine-TA	395	90% styrene dimer	13.7 (acetone)	• Excellent performance ⁸⁸ • All membrane's components are 'green'	• Extensive OSN studies need to be performed • Need of organic catalysts: TMG/DMAP/TEA
23	2% acetic acid in chitosan	Shrimp shells	OSN	plant-based 2,5-furandicarboxaldehyde (FDA)	3% TamiSolve in eucalyptol solution	Recycled PET	Chitosan	317	100% Rose Bengal in acetone, 96% methyl orange in acetone	12 (acetone)		
86	Genipin in 0.1% citric acid solution	hydrolysis of geniposide extracted from the fruits	OSN	Priamine	Eucalyptol solution	PLA fibers support with TBAB	Polyamide	281	90% styrene dimer 99.6% oil separation from water mixture	10 (acetone), 5.6 (water) in oil/water separation	• Multifunctional to permeate organic solvents and to separation oil from water • All membrane's components are 'green'	• Expensive technique to obtain electrospun fibers

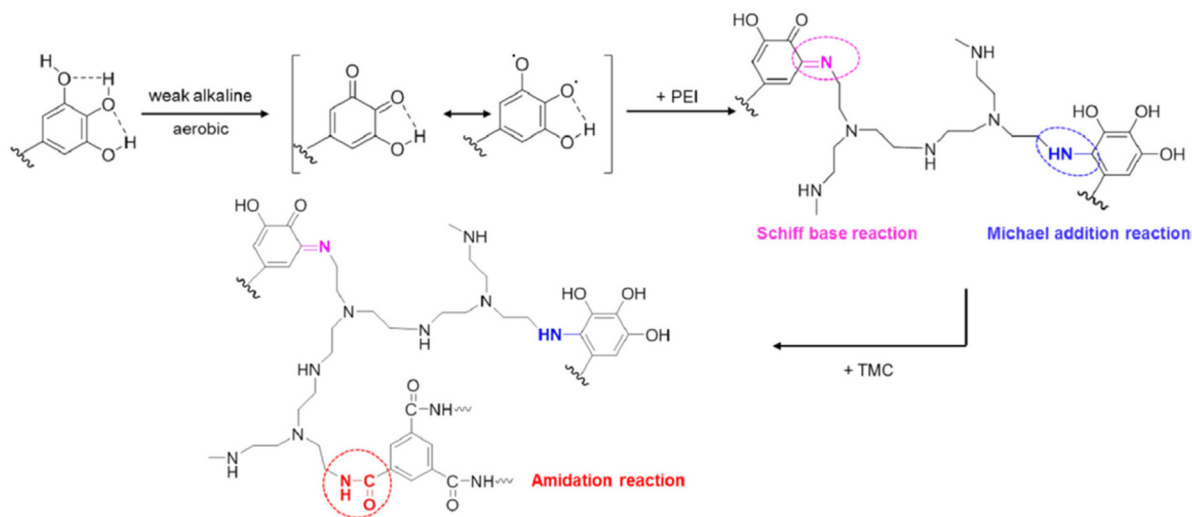


Fig. 4 Reaction mechanism between pyrogallol groups of EGCG, amine groups of PEI, and acyl-chloride.⁶⁷

In a practically identical approach, Liu *et al.*⁷⁰ further explored the fabrication of membranes by molecularly engineering the IP of CD and TMC to construct precise molecular sieving architectures (Fig. 5). Preferential transport for polar solvents is claimed to occur outside the cavities, while the methylene (–CH₂–) groups located at the interior of CD's cavities generate inner hydrophobic cavities for the transportation of non-polar solvents, giving a double character to the membrane recognized as a “Janus” system, as depicted in Fig. 5. The study employed positron annihilation spectroscopy (PAS) to confirm that larger free volume and higher microporosity are generated with a larger inner cavity of the type of CD. Based on the rejection ratio of various dyes, the estimated MWCOs of various CDs and TMC based nanofilms are 320 g mol^{−1}, 400 g mol^{−1} and 550 g mol^{−1} for α, β and γ-CDs respectively. These are in accordance with the free volumes and inner cavity sizes of α-CD < β-CD < γ-CD. Lastly, the chosen β-CD and TMC based freestanding nanofilms exhibited shape-selective functions for 3D molecules and reasonable permeances for both polar (methanol, 4.9 L per m² per h per bar) and nonpolar solvents (*n*-hexane, 6.3 L per m² per h per bar).

Polyester, the selective layer network when using unmodified CD or polyphenol as monomers can have advantages over polyamide chemistry, which has been highly successful for TFC membranes, in term of chlorine resistance.^{71,87} Polyamide is not resistant towards chlorine which is a drawback for large-scale desalination plants that cannot clean the RO system with sodium hypochlorite.^{71,88,89} Xue *et al.*⁷¹ therefore explored the potential advantages of CD polyester membranes, prepared by a procedure similar to that described above, in terms of their chlorine resistance. High fluxes ranging from 104.6 L per m² per h per bar to 197.6 L per m² per h per bar were reported by altering the concentration of β-CDs in between 0.1 to 1.8 wt% and the rejection of Congo red and methyl blue dyes was 95.6% and 94.4%, respectively. The desirably high flux was attributed to the synergistic effect of the intrinsic cavity and

inactive –OH groups of β-CD which resulted in the formation of water channels and a loose selective layer. The most striking result of this work was indeed the confirmation of a remarkable chlorine resistance even when exposing to 10 000 ppm of sodium hydrochloride solution for 96 h. Besides the low reactivity and need for high pH during synthesis, a drawback of this work was that heat treatment is needed to promote cross-linking of the selective layer and to remove the *n*-heptane organic solution.

With the objective of achieving even higher permeability, while maintaining solute selectivity, more sophisticated approaches were investigated, such as introducing graphene quantum dots or carbon nanotubes as an additive to the β-CD monomer in the aqueous solution.^{72,73} However, the cost of graphene quantum dots and the complex pre-steps of obtaining not-so-economical MWCNTs poses a disadvantage. Nevertheless, the increase of the complexity for the membrane preparation is not an advantage for the industrial fabrication and application.

Regarding the high-performance properties of CD membranes, the availability and low cost of the reactants make the process feasible for large-scale usage; however, the requirement of high pH reduces their attractiveness. A much more effective approach was later proposed and demonstrated by Huang *et al.*,⁹⁰ they functionalized CDs with amino groups and then used them as monomers for IP. Amines are more reactive; hence a thin, defect-free selective layer was formed, which was able to separate molecules efficiently with MWCO around 350 g mol^{−1}. By using this procedure, the selective layer is highly crosslinked and constituted by 61.5% of β-CD, each unit covalently connected with four others. The membranes rejected more than 99% brilliant blue. The rigid CD cavities rejected molecules with kinetic size larger than 0.61 nm. They distinguish molecules by shape as well, the rejections of Safranin O and methylene blue were 72% and 38%, respectively, even though their size is similar (351 and

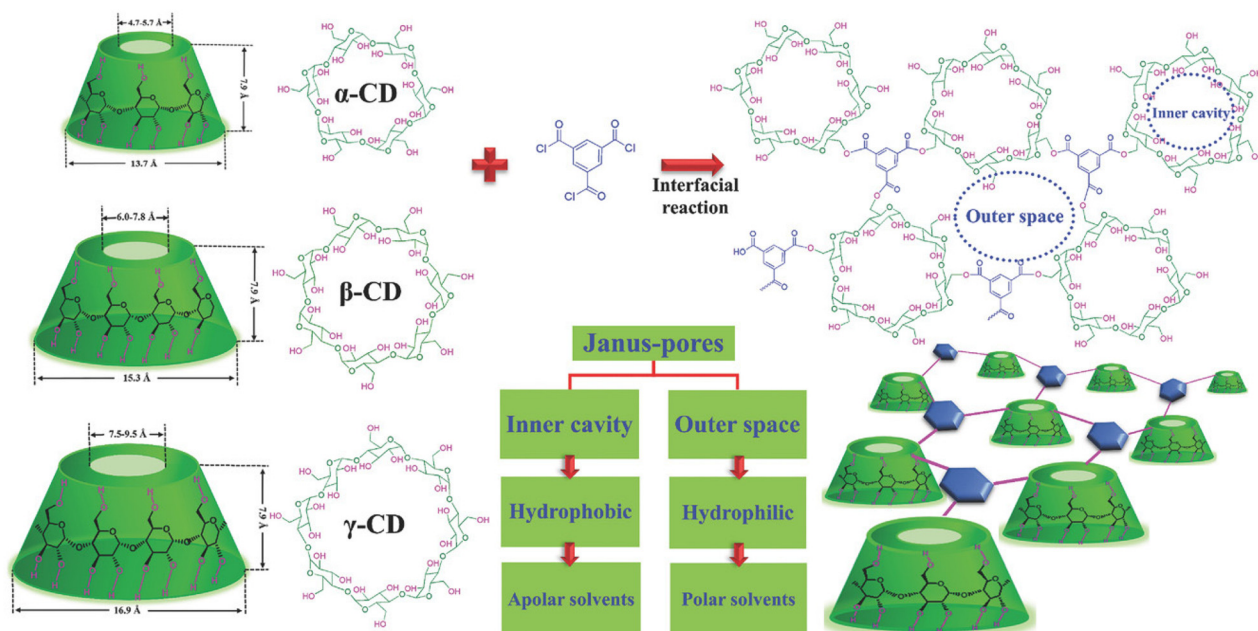


Fig. 5 Chemical structures and architectures of the crosslinked cyclodextrins and TMC, to produce molecular sieving nanofilms by IP.⁷⁰

320 g mol⁻¹). With the fast reactivity of the amino functionalization, the IP reaction can be easily translated to machines analogous to those used in the industry. The scalability should be therefore straight forward. The amino functionalization preferentially occurs in the narrow rim of the β -CD molecule and the reaction with the acid chloride is regiospecific.⁹⁰ The resulting layer is therefore asymmetric, having different degrees of hydrophilicity on each side, reflected by water contact angles of 29° (high density of unreacted hydroxyl groups) and 72°. This fact has been further explored by Jiang *et al.*⁹¹ with the perspective of obtaining aligned macrocycle pores for nanofiltration practically with the approach again applied to CD and extended to 4-sulfocalix[4]arene.

Tang *et al.*⁷⁴ used chitosan, a polysaccharide abundant in crustaceans, to fabricate a NF membrane. First, chitosan was used as the only aqueous phase monomer (0.8% w/v) reacting with TMC in hexane (0.8% w/v); next, together with PIP (0.55% w/v chitosan, 0.25% w/v PIP) in the aqueous phase, the IP reaction with TMC was performed to produce polyamide (Fig. 6). Chitosan is a polymer with long chain molecules that reduce its penetration ability to the organic phase, as opposed to PIP which diffuses more easily to the organic phase and reacts with TMC. Therefore, the addition of PIP increases the polymerization rate and a significant increase in pure water flux (~5 L per m² per h per bar) was reported, and a slight decrease in salt rejection (~3%) in comparison to the performance of the pure chitosan NF membrane which has salt rejection of 91.9% for Na₂SO₄ and water permeance of 5.22 L per m² per h per bar, moreover the addition of chitosan could reduce the usage of the amine monomer concentration (0.8% vs. 2%).⁷⁴ However, to dissolve chitosan in the aqueous phase

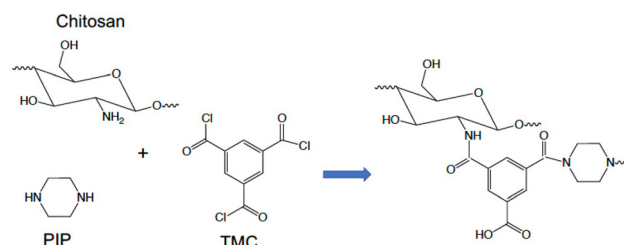


Fig. 6 The IP reaction between chitosan and PIP with TMC to produce polyamide.⁷⁴

it must be heated and under acidic conditions, which reduces process sustainability and upscaling potential.

In a recent study, Abdi *et al.*⁶² explored the separation of mixtures of dye/salt wherein P84 co-polyimide was modified with β -CD by a green method. In this research work IP between *N,N*-bis(3-aminopropyl)-1,3-propanediamine (APPD) and β -CD in a green solvent formulated novel β -CD incorporated P84 co-polyimide nanofiltration (NF) membranes. The difference in this method was that the chemical crosslinking between the P84 co-polyimide membranes and APPD, and the IP with β -CD would take place in one step. Initially, APPD would be dissolved in water at different β -CD concentrations and since all the mixed solutions would have a pH higher than 12.33, this would favor the reactivity of the β -CD leading to a strengthening of the electrostatic attraction of β -CD with APPD. When the P84 membrane is immersed in this solution, chemical crosslinking and IP would simultaneously occur. The unreacted hydroxide groups on the outer surface of β -CD would help

increase water permeability and form a negatively charged surface, while the interior cavity of the 3D bowl-like structure would enhance the size-sieving capability of the membrane. As a result, the dye/salt separation efficiency of the β -CD incorporated NF membranes increases and turns it to a favorable system for the treatment of salt-containing dye wastewater treatment.

2.2.3 Amino acid-based monomers. Dopamine (DA) is a bio-molecule known as a mussel-inspired 'bio-glue'; it consists of a catechol structure with one amine group. The amine and phenol groups can all react with acyl chloride groups forming amide and ester bonds in the dense thin film composite membrane.^{79,80} Zhao *et al.*⁷⁹ (2014) were the first to use DA as the aqueous monomer in the preparation of TFC membrane *via* IP. They reported a strong bio-adhesion of DA from the active layer to the support, producing a stable membrane. The membrane salt rejection is not good enough for NF applications, MWCO wasn't measured, but the membrane excellent chemical stability turns it to be an adequate candidate for wastewater applications.⁷⁹

Ding *et al.*⁸⁰ added sulfonic acid groups to dopamine, resulting in sulfonated dopamine (SDA) as the aqueous monomer reacting with TMC *via* IP (Fig. 7). They reported that the sulfonic acid groups contribute to the restraining of IP and to the hydrophilicity of the fabricated membranes. The salt rejection of the SDA-NF membrane was lower than of the DA-NF membrane they fabricated, whereas the SDA-NF membrane water flux was higher. The SDA-NF membrane performed an excellent dye rejection ($\sim 99.9\%$) even for dyes with MW of 320 g mol^{-1} ; however, the MWCO is very high (2000 g mol^{-1}), which does not go along with the dye rejection performance reported. The preparation of SDA included the addition of propanesulfonate and ammonia to DA, following heating of the solution to 50°C for 18 h. This may reduce the sustainability and the feasibility of industrial usage.

Along a similar line of research, Shah *et al.*⁸¹ employed bio-monomers, namely dopamine hydrochloride (PDA) and DL-nor-

epinephrine hydrochloride (PNE), which are derivatives of amino acids, for replacing toxic monomers in the aqueous phase. The amine, phenol and catechol functional groups of PDA and PNE aid in forming a dense thin-film selective layer with enhanced chemical and structural stability even in harsh environments compared to the previously mentioned amino acid derivatives based monomers. TMC was used in the organic phase, constituted by a light alkylate Isol-C solution. The permeation was tested with poly(propylene glycol) oligomers with varied molecular weights, revealing that PDA, PNE and tannic led to membranes exhibiting approximate MWCOS of 650 g mol^{-1} , 715 g mol^{-1} , and 832 g mol^{-1} , respectively. Comparing all three NF membranes, the PDA based-membrane exhibited a relatively higher flux and rejection rate for bivalent ions. The water permeability was $8.14 \text{ L per m}^2 \text{ per h per bar}$ and with a Na_2SO_4 rejection of $\sim 93\%$. Thus, in comparison to the two earlier works of DA and SDA-based monomers, the dopamine hydrochloride-based TFC membranes had better permeability and salt rejection. Lastly, as concluded by the authors in this work, these TFC-NF membranes require further fine-tuning of the properties for their implementation in various industrial applications.

Another work by Zhang *et al.*⁸² extended the protocol of using DA hydrochloride as an aqueous monomer by combining it with glucose and MOFs to prepare nanocomposite membranes for precise and ultrafast molecular separations. The IP reaction of polydopamine and glucose in the presence of compatible MOF additives enabled the formation of ultrathin selective layers on the surface of porous substrates. These ultrathin nanocomposite membranes derived from natural compounds offered enhanced chemical stability and water flux permeability of $39.3 \text{ L per m}^2 \text{ per h per bar}$. Due to the synergistic effects of each of the components, the reported solvent permeances of these ultrathin nanocomposite membranes were two orders of magnitude higher than that of commercially available OSN membrane.⁹² However, the incorporation of MOFs compromises the green

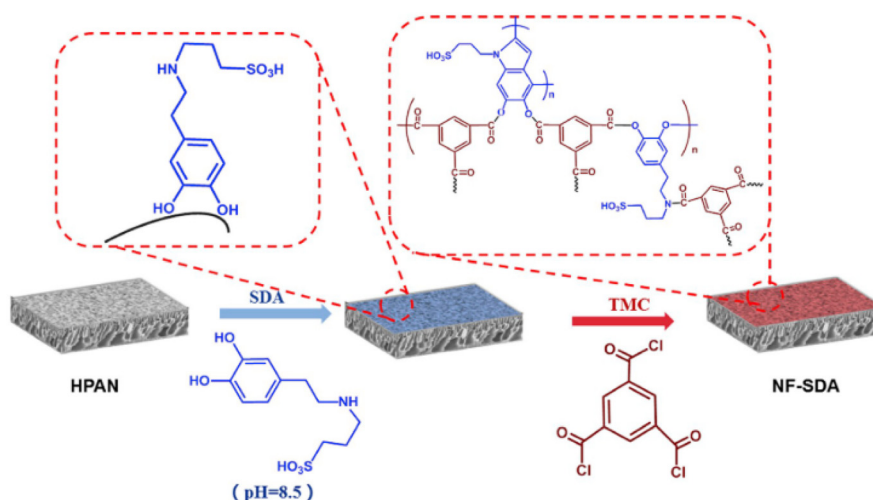


Fig. 7 Preparation of NF membranes by IP, using sulfonated dopamine (SDA) and TMC as monomers.⁸⁰

advantage of DA and glucose and makes the scaling-up processes more difficult.

Another amino acid-based monomer, L-lysine, was explored as an aqueous monomer in IP with TMC. Xu *et al.*⁸³ used readily available, non-toxic, and cheaper amino acids like L-lysine with two amino groups that can rapidly react with TMC. The membrane is presented as charge-mosaic. By using L-lysine, a loose inner structure was obtained for fast transport of salts and water and efficient rejection of dyes. Extensive discussions related to the plausible mechanisms of the salt concentration sensitivity (the water flux of the L-lysine based membrane had a linear increase with the salt concentration in the feed solution) of the charge-mosaic NF membranes were presented in this work. The optimized membrane exhibited desirably high separation efficiency to salts/dyes mixtures (retention of over 99.2% for Naphthol green B dye and NaCl rejection of 2.75%) coupled with an unusual salt concentration sensitivity. The measured water flux of 36.15 L per m² per h per bar was 13 times higher than the pure water flux reported in the literature and these findings were confirmed after rigorous cycles of repetition. This study could open doors for potential industrial applications such as in textile industry where separation of salts and dyes are inevitable or during pre-treatment in salination.

2.2.4 Lignin. Zhan *et al.*⁸⁴ used lignin alkali (LA) as the aqueous monomer. Lignin is a polymer derived from plant cell walls; it is the second largest natural macromolecule in nature. Lignin has many benefits, being renewable, bio-degradable, abundant, cheap, and non-toxic. Zhan *et al.*⁸⁴ were the first to perform IP with lignin as the aqueous monomer to produce a NF membrane. The phenol groups in LA reacted under alkaline conditions with acyl groups in TMC forming a dense thin polyester layer. The fabricated membrane has high rejection towards dyes (>97%); however, not satisfying salt rejection (51.4% for MgSO₄), excellent structural stability, and an easy, low-cost preparation process. However, lignin is a complex material, and the reproducibility of the membrane will depend on the source of lignin.

2.2.5 Trisaminomethane. Tris(hydroxymethyl)amino-methane or THAM, a low-cost and green monomer was reported used to prepare poly(ester amide) (PEA) thin-film composite membranes *via* IP.⁸⁵ THAM contains one amino group and three hydroxyl groups and exhibits tetrahedral-like geometry which is uncommon among most of the monomers as they are either linear or planar. Moreover, THAM is extensively used in the medical field, specifically in molecular biology or biochemistry, and is featured as an integral component in buffer solutions.⁹³ Furthermore, THAM demonstrated high water solubility and thus, Zhang *et al.*⁸⁵ were particularly interested to investigate the relationship between membrane structures and aqueous monomer concentration for IP with TMC in the organic phase. Additionally, detailed experimental work revealed that the coexistence of functional groups with different reactivities enabled THAM to showcase moderate reactivity which in turn was beneficial for tuning the crosslinking density of the resultant polymeric network.

Therefore, low and high THAM concentrations and the subsequent tunable crosslinking densities led to loosen and dense structures, respectively.

This interesting study shows THAM as a potentially suitable monomer for controlled IP, which was difficult to achieve with the traditional polyamide or polyester membranes. The controlled tunability provides a wide range of structures, as higher THAM concentration was tested for desalination application wherein a water permeance of 11 L per m² per h per bar and Na₂SO₄ salt rejection of 97.1% was recorded. Contrarily, lower THAM concentration, a loosely crosslinked structure showed dye removable rate of 95% and a lowered NaCl rejection of <7.5% with high water permeance of >45 L per m² per h per bar. Therefore, tunable crosslinked membranes can be further exploited for task-specific separation processes. Lastly, as THAM contains three hydroxyl groups, lower reactivity with TMC was addressed, by adding NaOH to the aqueous phase the OH groups are deprotonated⁶⁹ and aid in forming alkoxide ions with improved reactivity. However, during IP, extended time was required to promote the reaction as well as thermal post-treatment, which needs to be considered for further scale-up.

2.3 Pursuit for greener membranes combining green solvents and green monomers

Recent studies reported pioneering work in preparing green membranes wherein both the toxic organic solvents and toxic monomers have been replaced by green alternatives.^{23,61,86} Furthermore, these membranes were fabricated at room temperature, thereby fulfilling all sustainable principles by Szekeley *et al.* (2014).³⁰ Park *et al.*⁶¹ fabricated a totally green membrane for the first time. *p*-Cymene was used as the organic sustainable solvent in the IP reaction, it is derived from plants, such as organum, eucalyptus, *etc.* It has low viscosity and moderate to high vapor pressure, is considered flammable and its interfacial tension with water is lower than hexane (Table 1). The product was not polyester because they did not use acyl chloride as the organic monomer, but priamine. The polymerization reaction was Schiff-base and Michael-addition between the pyrogallol groups of tannic acid (they were first converted to quinone) and the amine groups of priamine resulting in the formation of imine and amine groups (see Fig. 8). Its performance show high permeance of different solvents (*e.g.* 13.7 L per m² per h per bar for acetone) and a low MWCO (395 g mol⁻¹). The fabrication process is easy and can be scaled up; however, the costs of the green solvent and the green monomers may be much higher than the commonly used ones.

Following the above work, Park *et al.*²³ designed thin-film composite (TFC) membranes *via* IP of chitosan, a shrimp farming waste material, in the aqueous phase and plant-based 2,5-furandicarboxaldehyde in the organic phase, on an upcycled polyethylene terephthalate porous support. TamiSolve was employed as a green solvent for the first time, to activate the selective layer of the chitosan-based TFC membrane. This resulted in significant enhancement in the permeance of various pure solvents including ethanol, methyl

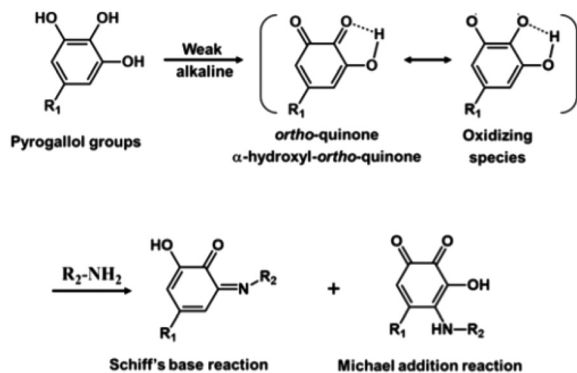


Fig. 8 Reaction mechanism between pyrogallol groups of TA and amine groups of priamine.⁶¹

ethyl ketone, acetone, and acetonitrile, with no remarkable defects and high solute rejections. This work successfully targeted the replacement of toxic and fossil-based solvents and reagents in developing high-performance and solvent-resistant nanofiltration membranes.

Yang *et al.* fabricated a biodegradable electrospun nanofibrous support, made of polylactic acid (PLA) and gelatin as an interlayer.⁸⁶ PLA and gelatin were dissolved using dimethyl carbonate (a green solvent) and water. The hydrophilicity of the support was enhanced due to the presence of the interlayer, gelatin. IP of natural monomers was employed to fabricate green polyamide TFC membranes on the porous support. The natural monomers (plant-based) used were genipin in the aqueous phase and priamine in organic solvent eucalyptol. The fabricated final membranes showed excellent acetone permeance up to 10 L per m² per h per bar and a 99.6% of oil removal rate in water treatment at a water permeance of 5.6 L per m² per h per bar. These membranes have excellent solvent stability and OSN performance which potentiates its use in sustainable membrane manufacturing. Considering the underlying motivation of this review, more efforts from the scientific community can be directed towards producing greener membranes by IP which include both green solvents and green monomers, exhibiting enhanced process performance.

3. Eco-Scale greenness assessment tool towards IP

Green chemistry encourages reducing the use of toxic chemicals/reagents, employing energy-efficient equipment, and generating minimal waste.²⁸ Recent trends in chemical processes focus on the miniaturization of the sample preparation devices, the development of solventless or solvent-minimized extraction techniques, and the utilization of less toxic solvents.⁹⁴ The twelve principles of green chemistry serve as a basic guideline for inducing greenness in the design of chemical procedures.²⁹ Several metrics have been developed for the evaluation of the greenness of chemical processes, of which Analytical Eco-Scale,

Green Analytical Procedure Index, and Analytical Greenness Metric are among the important tools for assessing the greenness of chemical processes.^{95,96} All these metrics take different aspects of the analytical/chemical procedure into account to provide the green index of the procedure. However, Eco-Scale is the most widely employed greenness assessment tool due to its simplicity in calculation and as it provides a quantitative assessment of the method's greenness in the form of a number that can be compared with an ideal score of 100.^{94–96}

Although the membrane community has been continually seeking to harness the sustainability metrics offered by membrane technologies, there is a sporadic distribution of works reported on utilizing 'greenness assessment tools' in this field of research. Here, we attempt to uphold the principles of green chemistry by exploring the analytical Eco-Scale tool to compare the greenness of the IP reaction for the fabrication of representative membranes, each one from the three categories described in the previous sections, namely, green solvents, green monomers, and total green membranes. For comparison, the Eco-Scale of the standard membrane fabricated *via* IP using MPD/TMC as monomers and hexane as organic solvent, is calculated as well. Briefly, the underlying motivation of this section is to evaluate the effective greenness of the materials/procedure for performing IP to obtain TFC membranes. It also distinguishes between the overlapping perception of green and sustainable chemistry, wherein the former concerns the *environment*, and the latter deals more broadly towards *economics, ecology and society*.⁹⁷

The Eco-Scale assessment tool was proposed by Gałuszka *et al.*⁹⁸ based on the calculation of a numerical total score classifying the greenness level of the investigated analytical method. An ideal green procedure has a total score of 100 with no penalty points. Penalty points representing the harmful impacts of the method on the environment are subtracted from the total score. Negative effects on the environment include hazardous solvents consumed, high energy consumption, and the amount of waste generated. According to this assessment tool, there are three classifications: a green method, which has a final total score of more than 75 points; a non-green method, which has a final total score between 50 and 75 points; and inadequate green analysis and extremely harmful to the health/environment if the final score is below 50 points. The penalty points of hazards are calculated based on the following criteria: non-hazard, which has no pictogram and 0 penalty points; less severe hazard chemical, which has only one penalty point and a more severe hazard, which has two penalty points. The penalty points are also extended towards energy consumption and purification steps of the materials involved, if any, during the process.

The Eco-Scale assessment in this review was carried out using the freely available Eco-Scale calculator (<https://ecoscale.cheminfo.org/calculator>) and the software is based on the paper by Aken *et al.*⁹⁹ There were following assumptions while carrying out the analysis: (i) The materials and process employed only for the IP section were considered, (ii) The type of membrane support and its procedure to obtain them was not considered, (iii) The technical set-up for IP was assumed

Table 5 Eco-Scale scores of the work on classical interfacial polymerization (IP), selected work on use of green monomer (section 2.1) or green solvent (section 2.2), and of green membranes employing both green monomers and solvents (section 2.3)

Aqueous monomer	Organic monomer	Organic solvent	Category of IP work	Eco-Scale score	Ref.
MPD	TMC	<i>n</i> -Hexane	Classical IP	73	100
MPD	TMC	Oleic acid	Green solvent	88	50
Allyl gallic acid	TMC	Isopar G	Green monomer	90	68
Tannic acid	Priamine	<i>p</i> -Cymene	Green membrane	90	61
Chitosan	FDA	Eucalyptol	Green membrane	95	23
Genepin	Priamine	Eucalyptol	Green membrane	95	86

to be a common set-up without the need for any special glassware/glove box/unconventional set-up, (iv) the pre- and post-treatment steps like heating were considered.

As seen in Table 5, it is clearly evident that the classical example of IP has an undesirable Eco-Scale score of 73 as it uses toxic monomers like TMC and MPD along with hexane as an organic solvent and requires post-heat treatment for cross-linking.¹⁰⁰ Merely by replacing hexane with greener organic solvent alternative like oleic acid increased the Eco-Scale score of the IP process to 88.⁵⁰ Furthermore, the same group chose an alternative greener monomer allylated gallic acid and instead of *n*-hexane, isopar-G was used as a solvent and the crosslinking was performed at room temperature conditions.⁶⁸ This resulted in the Eco-Scale score of 90. Avoiding toxic substances like MPD monomer and *n*-hexane organic solvent saved 10 penalty points each. However, 5 penalty points each were attributed to the usage of TMC and a non-green solvent like Isopar-G. Lastly, sub-section 2.4 dealt with green membranes produced by combining both greener monomers and green organic solvents, and no post-heat treatment at elevated temperatures was involved. The Eco-Scale score of the first work by Park *et al.*,⁶¹ was 90 as *p*-cymene was used as the organic solvent and priamines were used as the organic monomers.⁶¹ The penalty points were applied for these two as *p*-cymenes, a bio-derived green solvent imparts irritation to the eyes and skin, and priamines are a bit expensive and not so readily available. The other two works on green membranes by Park *et al.*, and Yang *et al.*, from the same research group^{23,86} obtained the highest Eco-Scale scores of 95 each. In the former work, chitosan from shrimp shells was used and the latter work used priamines as the green monomer. Although both are bio-derived greener options, their cost and availability are a concern. Anyhow, a clear distinction can be witnessed from Table 5 as alternatives uphold the spirit of green chemistry by increasing the Eco-Scale score and substantially contributing to more sustainable processes, which was the essence of the contribution of the present review.

4. Conclusions

This work summarizes the recent advances reported on sustainable variations of organic solvents and monomers used for NF/OSN/RO membrane fabrication *via* the IP reaction. Clearly, there is a wide variety of sustainable solvents and

monomers that can be used, and there is a need for more specific criteria of what makes a better solvent or monomer. To this end, better understanding of IP fundamentals provides insight on the desired properties of materials involved in the reaction. Another noteworthy outcome of this review is the apparent lack of agreed-upon criteria for performance tests of a specific membrane type. For example, in the case of OSN membranes, different dyes were used in different studies to measure rejection, the permeance was measured using different liquids, and the MWCO was not consistently reported. These variations make it very difficult to compare between membranes and scrutinize the impact of variations in materials and fabrication conditions. Ideally, every membrane type should have specific criteria and an experimental protocol for evaluating its performance. Moreover, when studying an effect of a specific parameter on the fabricated membrane performance, this parameter should be the only one changed, if possible, otherwise it is not possible to clearly gauge its impact on the reaction and on the resultant membrane.

Furthermore, the objective of these studies is to find alternate, sustainable materials to replace the commonly used toxic materials; therefore, it would be very useful to include an industrial perspective, *e.g.*, estimated costs, reaction times, upscaling potential, and possibly other aspects of industrial relevance. In lieu of this, many 'green' membranes will remain in the academic literature without their application in industry.

The last aspect of this review is the evaluation of the greenness of the membrane materials used in the IP process by employing an Eco-Scale greenness assessment tool. The results clearly distinguished the importance of using greener solvents and greener monomers as they had less environmental penalty points when compared with the classical monomers (TMP and MPD) and organic solvent (*n*-hexane) used in IP for producing membranes.

Author contributions

Adi Ben-Zvi: conceptualization, investigation, visualization, writing – original draft, writing – review & editing. Usman Taqui Syed: conceptualization, investigation, visualization, writing – original draft, writing – review & editing. Guy Z. Ramon: conceptualization, supervision, writing – review &

editing, funding acquisition. Suzana Nunes: supervision, writing – review & editing, funding acquisition.

Conflicts of interest

The authors confirm that they are not affiliated with or involved in any organization or entity that has a financial or non-financial interest in the subject matter or materials covered in this article.

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