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Perspective

Toward the Next Generation of Sustainable Membranes from Green Chemistry Principles

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ABSTRACT: Large-scale membrane technology has been widely implemented and rapidly growing for roughly 40 years. However, considering its entire life cycle, there are aspects being characterized by low sustainability, and this industry certainly cannot be defined as green. In the membrane manufacturing process, raw materials mainly rely on nonbiodegradable petroleum-based polymers and hazardous solvents. These materials are thus associated with the energy crisis and with disposal burdens at the end of their lifetime, and they pose risks to workers and the environment. Therefore, biobased polymers and green solvents should be employed within the membrane preparation process and replace traditional ones. Moreover, the wastewater generated from membrane fabrication processes contains an important amount of organic solvents and should be efficiently treated or recycled before discharge. The application of artificial intelligence in membrane manufacturing and use processes can also improve efficiency significantly. Finally, a large number of spent membrane elements should also be reused and recovered, rather than landfilled. This review critically evaluates the recent advances in methods to improve the sustainability of membrane technology, specifically emphasizing the progresses made, with regard to the above aspects. This review thus analyzes the needs for membrane industry transformations in the light of circular economy.

KEYWORDS: *Membrane technology, Biobased polymers, Green solvents, End-of-life management, Sustainability*

INTRODUCTION

Membrane technology has been increasingly applied in diverse industrial processes, for example, water treatment and gas separation, the chemical and pharmaceutical industry, the food and beverage industry, hemodialysis, or textile processing.[1−3] In the water treatment field, membrane technology plays a key role in promoting safe potable water supply, wastewater reuse, desalination, and environmental protection.[4−6] Hydrogen recovery, nitrogen enrichment, oxygen separation, carbon dioxide capture, and natural gas purification can be realized efficiently by gas separation membranes.[7,8] In addition, membrane technology has also been applied in metallurgy, energy, electronics, and progressively more novel fields.[1]

Membrane technology has several key advantages over traditional technologies.[9] Membrane-based separation is characterized by sharp selectivity, while being associated with simple equipment and conveniently compact structures.[10] It is also highly adaptable and flexible, in terms of installation and operation. Furthermore, low energy consumption, low pollution, and little use of chemicals in membrane separation processes reduce the total CO_2 emission and environmental effects, compared to traditional technologies.[8,9,11,12]

Although the advantages of membrane technology are apparent, drawbacks are gradually exposed in large-scale production and deployment. For instance, petroleum-based nonbiodegradable polymers are the typical materials used for membrane fabrication. Moreover, large amounts of toxic organic solvents are involved in the membrane manufacturing process, posing a series of health and environmental risks. In another typical example, hollow fiber modules are difficult to repair if broken, and this feature shortens their average lifetime. In the light of the increasingly severe energy crisis and environmental pollution problems, improving the sustainability of membrane

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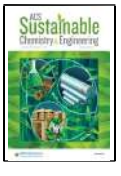

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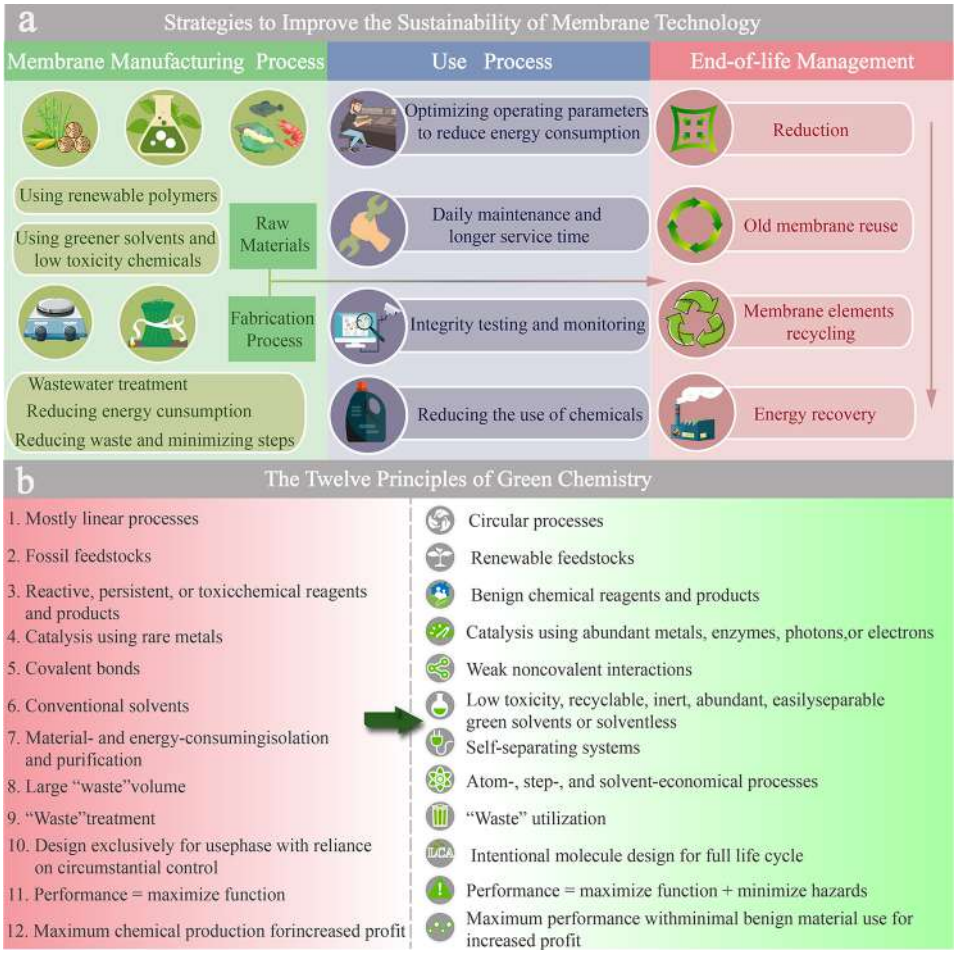

Figure 1. Sustainable membrane industry transformation strategies from manufacturing to end-of-life management: (a) strategies to improve the sustainability of membrane technology, and (b) characteristics of today's and tomorrow's chemical sectors. [Revised with permission from ref 14. Copyright 2020, American Association for the Advancement of Science.]

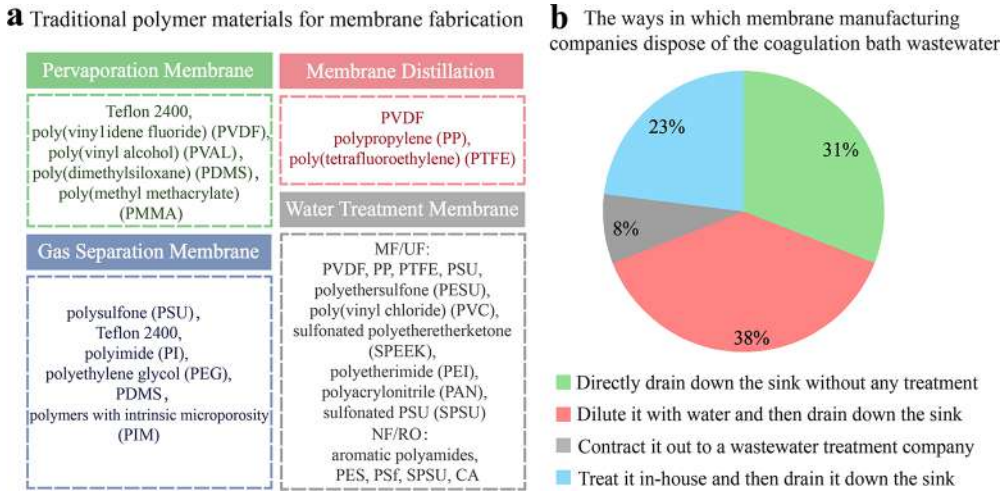

Figure 2. (a) Traditional polymer materials for membrane fabrication. (b) The main outcome of a survey from Razali et al. regarding the way in which membrane manufacturing companies dispose of the wastewater from the phase inversion coagulation bath. [Revised with permission from ref 19. Copyright 2015, Royal Society of Chemistry, London.]

technology and promoting the green transformation of this engineering field is imperative.

In Figure 1a, promising strategies focusing on cradle-to-grave considerations are summarized, considering membrane manufacturing, use, and end-of-life management. These approaches are guided by the Twelve Principles of Green Chemistry, which are shown in Figure 1b.[13,14] We believe that gradual improvements of already existing manufacturing platforms are likely to be implemented in the foreseeable future.

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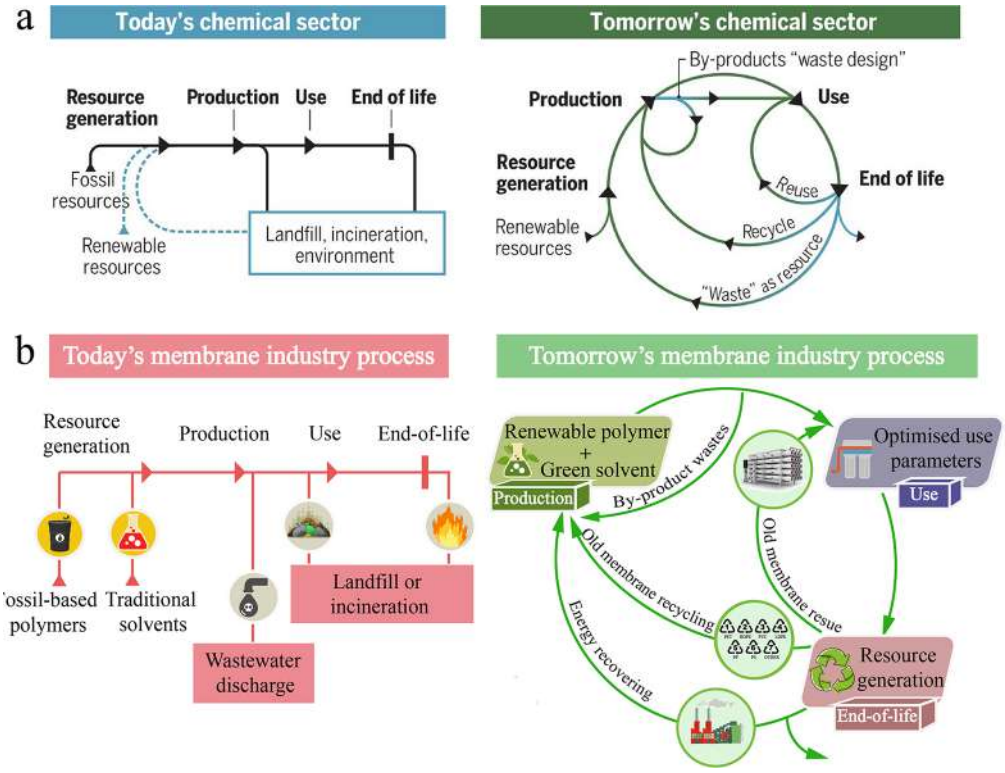

Figure 3. (a) From linear processes to circular processes in the chemical sector. [Revised with permission from ref 14. Copyright 2020, American Association for the Advancement of Science.] (b) Membrane industry transformation: from a linear process to a circular process.

We propose five different ways to improve the sustainability of the membrane manufacturing process. The first is using the polymers from renewable sources (also called biobased polymers) to partially or entirely substitute nonbiodegradable petroleum-based ones. Biobased polymers may be used as membrane materials, nonwoven membrane supports, or additives. Nowadays, the typical polymers for membrane manufacturing are poly(vinylidene fluoride) (PVDF), poly(ether sulfone) (PESU), polysulfone (PSU), poly(ethylene terephthalate) (PET), and poly(ethylene glycol) (PEG), etc. (see Figure 2a). They are nonrenewable and difficult to degrade: both their production and disposal are not sustainable. Partial substitution may be a relatively easy first step in the efforts to substitute these materials.[15−17] However, it is worth noting that not all biobased polymers are biodegradable. Some nonbiodegradable biobased polymers, such as bio-derived PET, can be applied to fabricate membranes for wastewater treatment, whereby biodegradable membranes are not suitable. Moreover, they can be recycled or reused in circular economy.[18]

Furthermore, the greener solvents should be used to substitute traditional ones. Traditional solvents typically used for membrane fabrication, such as *N*,*N*-dimethylacetamide (DMAc), 1-methyl-2-pyrrolidinone (NMP), and dimethylformamide (DMF), are harmful to the environment and pose risks to the health and safety of membrane manufacturing workers;[13,20,21] the European REACH Regulation has identified them as substances of very high concern (SVHC).[22] Therefore, greener alternatives are urgently needed. In the past decade, there have been some advances around the use of green solvents for membrane fabrication, and a series of nontoxic, biodegradable, and recyclable green solvents (e.g., PolarClean and Cyrene) have been applied and shown to provide comparable or even superior performance, compared to traditional solvents.[9,23−26]

Third, the wastewater (mainly containing organic solvents and polymers) generated from membrane fabrication should be treated and recycled. It is estimated that membrane production generates over 50 billion liters of wastewater annually worldwide, contributing to more than 95% of the total waste generated during the membrane fabrication process.[19,27] However, only 31% of this waste is being somehow treated nowadays,[19] as presented in Figure 2b. The fourth strategy in the manufacturing process is reducing the number of steps for membrane fabrication, which would translate to a reduction of toxic waste, energy consumption, and costs. From this point of view, tuning of the membranes via blending is a best option rather than surface grafting, while surface physical coating is to be preferred over elaborate chemical functionalizations involvoing several pre- and post-modification steps. Finally, the membrane casting solutions should be dissolved at room temperature to reduce energy consumption.

In the membrane use phase, we propose four strategies to improve sustainability. First, measures to reduce the energy consumption should be taken into consideration, including optimizing the transmembrane pressure, membrane modules structure, physical backwashing time, and other operating parameters. Artificial intelligence and related in silico fields may provide help, which can also improve the efficiency of the membrane fabrication process. Second, daily maintenance is of vital importance to extend the service time of membrane modules. Third, integrity testing and continuous monitoring are useful to ensure the stable and efficient operation of membrane modules and guarantee the quality of the permeate. The direct integrity testing is a physical process that is sufficiently sensitive to detect a 3-μm breach in membrane modules, and it should be

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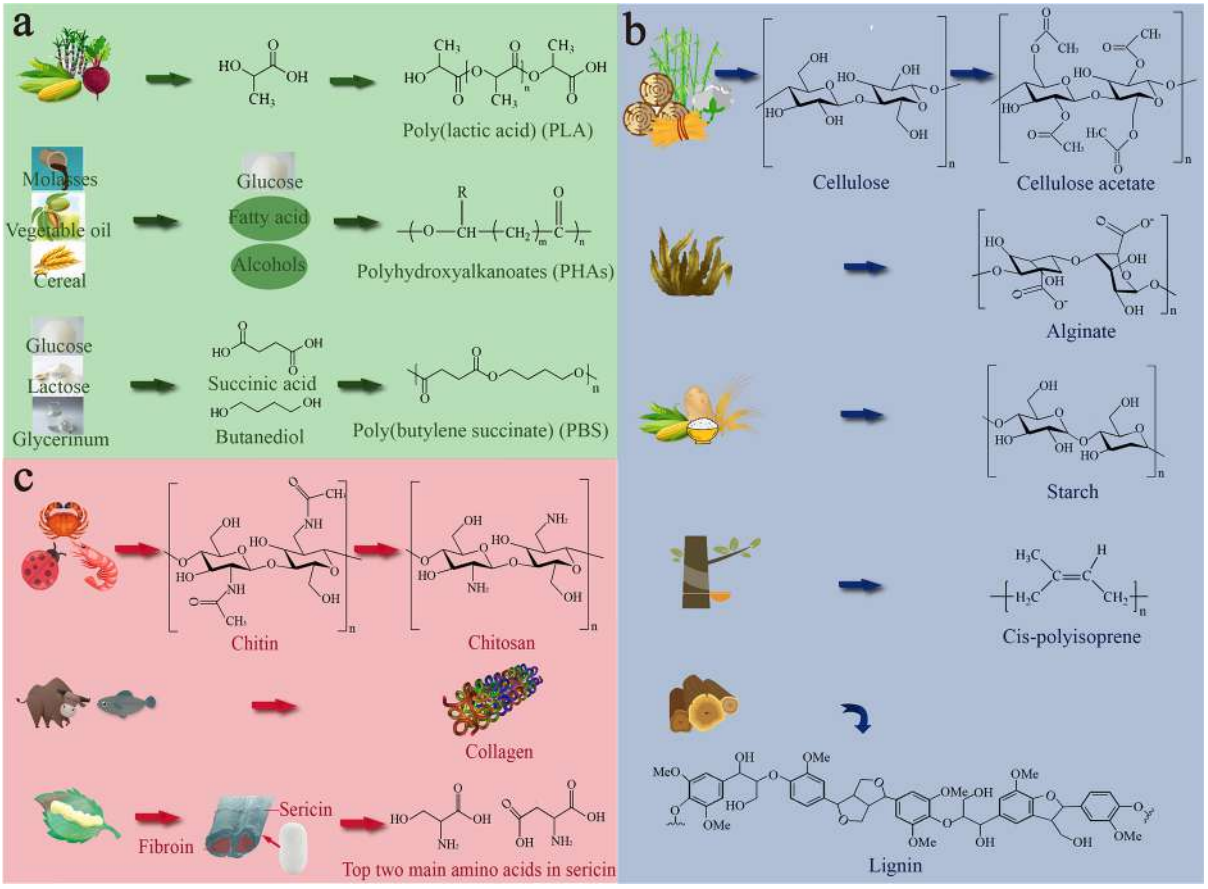

Figure 4. Structural formula of typical biobased polymers derived from (a) bacterial fermentation products, (b) vegetable sources, and (c) animal sources.

conducted at least once per day. The continuous indirect integrity monitoring is the measurement of the product stream quality parameter, which should be taken at least every 15 min. The membrane fibers, fabricated by high-molecular-weight polymers, are difficult to repair once they are fractured. In order to prolong their lifetime and improve sustainability, readily repairable polymer materials or self-healing materials for membrane fabrication are of interest for many researchers and engineers.[28,29] Fourth, in the chemical cleaning process, the number of chemicals should be as few as possible.

The end-of-life management of spent membrane modules is also an important aspect, given that large numbers of membrane elements are discarded annually. Considering reverse osmosis (RO) alone, over 14 000 tons of RO modules are discharged annually worldwide, while this number is even higher for ultrafiltration (UF) and microfiltration (MF) membranes.[1,30] All of these numbers are continuously increasing. Typical methods to dispose of these spent membrane elements are landfilling or incineration, neither of which is satisfactory from a sustainability viewpoint. When landfill disposal is chosen, one must consider that the current petroleum-based elements do not degrade biologogically and will persist in the environment, threatening the soil and underground water. As for incineration, this process produces air pollution and greenhouse gases. The correct end-of-life management methods should encompass reuse, recycling, and recovery, constructing a circular economy (see Figure 3b).

This review covers the following cutting-edge aspects required to improve the sustainability of membrane technology: (i) biobased polymers for membrane manufacturing, (ii) green solvents for membrane manufacturing, (iii) treatment and recycling of the wastewater from membrane manufacturing, (iv) the application of artificial intelligence in membrane technology, and (v) end-of-life management of spent membrane modules. We believe that lower toxicity, lower environmental persistence, a smart platform, and circular economy are key factors of next-generation membrane technology.[31] This review introduces recent advances regarding these aspects to provide some inspiration for membrane scientists and enterprise manufacturers, guiding and promoting the sustainable transformation of the entire industry.

BIOBASED POLYMERS FOR MEMBRANE MANUFACTURING

In the last decades, petroleum-based polymers have dominated the membrane market. There is no doubt that these polymers are economical and versatile, as well as thermally and chemically stable,[32] but their negative impacts on the environment are not negligible. The exploitation, transportation, and refining processes of crude oil may cause marine pollution and air pollution, as well as an increase in the carbon footprint. Also, petroleum is nonrenewable and is being depleted worldwide.[33]

To cope with these problems, we should incorporate biobased polymers into the membrane preparation process. Some biobased polymers are found naturally, such as cellulose and chitin, while biosynthetic routes may be pursued to obtain many others. These materials usually exhibit high hydrophilicity, biocompatibility, and biodegradability, as well as low toxicity,

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Table 1. Solvents Used for Cellulose Membrane Manufacturing

solvent	classification	features	ref
NMMO[a]	organic solvent	commercially used	72
hydrazine/LiSCN, NaSCN, or KSCN	hydrazine/thiocyanate salt	toxic	73
DMAc/LiCl	organic solvents with dissolved salts	toxic	70
NMP/LiCl	organic solvents with dissolved salts	toxic	74
NaOH/urea/DI water (7:12:81 by wt %)	alkali	low cost and low toxicity	75
$LiOH{\cdot}H_2O$/urea/DI water (8:15:77 by wt %)	alkali	low cost and low toxicity	71
AMIMCl[b]	ionic liquid	low toxicity, expensive, and difficult to commercialize	76
[EMIM][OAc][c]	ionic liquid	low toxicity, expensive, and difficult to commercialize	77, 78
[DMIM][DMP][d]	ionic liquid	low toxicity, expensive, and difficult to commercialize	79
[EMIM] [DEP][e]	ionic liquid	low toxicity, expensive, and difficult to commercialize	79
[C_4mim] [Cl][f]	ionic liquid	low toxicity, expensive, and difficult to commercialize	80

[a]NMMO = *N*-methylmorpholine-*N*-oxide. [b]AMIMCl = 1-allyl-3-methylimidazolium chloride. [c][EMIM] [OAc] = 1-ethyl-3-methyl imidazolium acetate. [d][DMIM][DMP] = 1,3-dimethylimidazolium dimethyl phosphate. [e][EMIM] [DEP] = 1-ethyl-3-methyimidazolium diethyl phosphate. [f][C_4mim][Cl] = 1butyl-3-methylimidazolium chloride.

carbon footprint, and environmental impact. Bacterial fermentation, vegetables, and animals are the dominant resources of biobased polymers, as depicted in Figure 4.

Biobased Polymers from Bacterial Fermentation. *Poly(lactic acid) (PLA).* PLA is an environmentally benign aliphatic polyester. It is derived from the activity of lactic acid bacteria, using agricultural products and byproducts, such as corn, sugar cane, and sugar beets, as the initial substrate; it is biodegraded naturally by hydrolysis, generating H_2O, CO_2, and humus.[34] PLA has suitable mechanical and physical properties, which can be compared to those of many petroleum-based polymers. The price of PLA was very high before the late 1980s;[35] however, a patented, low-cost continuous production process was developed by Cargill Dow LLC, decreasing the price and promoting commercial production and the promotion of PLA.[34] Today, the applications of PLA have expanded to packaging, the medical and automotive industries, textiles, films, personal hygiene products, and three-dimensional (3D) printing,[34,36−38] showing a bright future.

Because of its good biocompatibility, PLA in membrane fabrication was first applied in health and medical sciences, as a scaffold for human cell growth and as a support for the controlled release of medicines.[39−41] In addition, PLA can be effectively used alone or blended with other polymers to fabricate MF and UF membranes via various methods: nonsolvent induced phase separation (NIPS),[42] thermally induced phase separation (TIPS),[35,43] vapor-induced phase separation (VIPS),[38,44−46] and electrospinning.[41,47] In the future, 3D or four-dimensional (4D) printed membranes may be produced with PLA, which is a promising green method for membrane manufacturing.

In composite membranes, support layers can be fabricated via the same routes. For example, Le Phuong et al.[27] fabricated sustainable, biodegradable, nonwoven composite membrane supports from PLA and bamboo fiber (consisting of cellulose, lignin, and hemicellulose), which provided a sustainable alternative for conventional membrane backing materials.

Polyhydroxyalkanoates (PHAs). PHAs can be produced from renewable resources such as lipids, carbohydrates, alcohols, and organic acids.[48] They are environmentally friendly biobased polymers with suitable biocompatibility and biodegradability.[48−50] Therefore, their main application is in biomedical fields.[51−53] More than 150 types of different monomer structures of PHAs have been reported.[54] However, only a few have been commercialized: poly(3-hydroxybutyrate) (PHB), poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV), and poly(3-hydroxybutyrateco-3-hydroxyhexanoate) (PHBHHx).[55]

There has been little research on PHAs for membrane fabrication. Note that PHAs are totally insoluble in water and most organic solvents, except some halogenated solvents, such as chloroform.[32] Therefore, PHB, PHBV, and PHBHHx membranes can be produced by VIPS with chloroform as the solvent.[49,51] However, given that chloroform is toxic, this specific system is not sustainable. Whether there is a possibility of PHAs application in membrane engineering and in other fields is a question worth exploring.

Poly(butylene succinate) (PBS). PBS is one of the most promising biodegradable aliphatic polyesters with suitable biocompatibility, biodegradability and excellent processability, as well as thermal and chemical resistance.[56,57] It can be obtained by polymerization of butanediol and succinic acid, both of which are from biobased renewable resources. The cost of PBS is relatively low, compared to many other biopolymers.[58]

There has been some research using PBS to fabricate membranes. Jeong et al.[56] prepared the first PBS membranes by electrospinning, obtaining uniform nanoporous threads by dissolving PBS in chloroform.[59] However, it was found that the membranes were soft and had low separation performance.[60] Therefore, gelatin, a natural protein, was used to blend with PBS or as a coating layer to improve its mechanical properties.[57,61] Overall, PBS membranes have been limited, because of the poor mechanical properties. To overcome this issue, PBS may be blended with PLA,[62−64] PESU,[65] or cellulose acetate (CA):[66,67] the resulted membranes have shown improved mechanical characteristics.

Biobased Polymers from Vegetable Sources. *Cellulose and Its Derivatives.* Cellulose, which is the most abundant polymer on Earth, is a linear polysaccharide primarily derived from plant fiber, for example, wood, cotton, bamboo, straw, reeds, hemp, mulberry bark, and bagasse. In addition, it can also be generated by bacteria (e.g., *Acetobacter xylinum* or *Acanthamoeba castellani*) and algae (e.g., *Valonia ventricosa*).[68,69]

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Cellulose exhibits suitable hydrophilicity and biocompatibility, excellent mechanical strength (the ultimate tensile strength of cellulose is estimated to be 17.8 GPa, seven times higher than that of steel),[70] and easy chemical modification with low production cost.

However, its high crystallinity and strong intermolecular hydrogen bonds reduce the solubility in common solvents, limiting the membrane fabrication.[71] The solvents that have been used to obtain cellulose-based membranes are listed in Table 1.

Creatively, Eggensperger et al.[28] utilized the symbiotic culture of yeast and bacteria with kombucha tea, and the cellulose fibers they produced can form a living water filtration membrane. The surface of the membrane can heal after a puncture or incision. This interesting self-healing living membrane avoided petroleum-based polymers and harmful solvents, and the low-tech process potentially brought accessible water treatment to anyone and anywhere.

Cellulose derivatives have been developed to overcome some cellulose limitations. Such derivatives are the products of esterification or etherification of hydroxyl in cellulose macromolecules,[69] and some have been used as membrane materials, such as cellulose acetate (CA), cellulose acetate butyrate (CAB),[81] hydroxyethyl cellulose (HEC),[82] cellulose triacetate (CTA),[83] and ethyl cellulose (EC).[84] CA, the most common and promising cellulose derivative, can be produced by treating cellulose with acetic acid, acetic anhydride, and sulfuric acid as a catalyst.[85] It can be dissolved in many common organic solvents, such as acetic acid, acetone, DMAc, and DMF. Also, it has a tunable polymeric network with pore sizes customizable over a wide range for MF, UF, NF, RO, and FO membrane fabrication.[86−88] Abundant research has encompassed the fabrication of CA membranes for oil/water separation,[89,90] desalination,[91] and wastewater treatment.[92,93] Important drawbacks of CA membranes are that they function well in a narrow pH range of 3−8 and have limited lifespan.

Cellulose derives biobased nanomaterials—namely, nanocellulose, including nanofibrillated cellulose (NFC), cellulose nanocrystal (CNC), and bacterial nanocellulose (BNC)—are also emerging green materials for membrane fabrication.[94,95] Their inherently high crystallinity and hydrogen-bonding propensity promote the formation of films with excellent gas-barrier properties.[95]

Lignin. Lignin is the second-most abundant polymer on Earth after cellulose, serving as structural support to cell walls.[96] It can be biodegraded by some micro-organisms, such as white-rot fungi. Lignin has high potential, being the only renewable aromatics feedstock.[97,98] However, it is also among the most challenging biobased polymers, because of its complexity. Currently, commercial lignin-based polymeric products are almost negligible in volume.

In the membrane manufacturing process, lignin has been blended with other polymers, such as poly(vinyl alcohol) (PVAL)[99] and polyacrylonitrile (PAN),[100] to compensate for the poor mechanical properties of lignin fibers. Moreover, it has also been used as a component of nonwoven membrane supports.[27] Lignin is a promising membrane or nonwoven support material, but the research is limited, because of its complexity in extraction, purification, effective blending, and defragmentation.[18] The current utilization of lignin is in two major approaches, both of which suffer from challenges: lignin as a whole, or defragmentation of lignin into monomers and then polymers. Using lignin as a whole may lead to poor performance, while defragmentation is too costly.[18,101] More efforts from chemistry, materials, and processing should be made to transform lignin to available materials.

Alginate. Alginate is a natural polysaccharide extracted from brown algae. It can combine with Na^+ or Ca^{2+} and produce sodium alginate (NaAlg) or calcium alginate (CaAlg). Alginate is nontoxic and has suitable biocompatibility,[102] with potential applications in the biomedical field for cell growth, drug delivery, and tissue engineering.[103]

Alginate has been increasingly employed in membrane fabrication processes in the last two decades. Its unique structure helps absorption of water, dyes, and heavy metals,[104] and alginate-based materials can be applied in pervaporation dehydration, water treatment, oil−water separation, and organic solvent nanofiltration. Alginate membranes in pervaporation dehydration have outstanding separation characteristics, exceeding PVAL, ion-exchange resins, and other polysaccharides, such as chitosan and cellulose.[105] In water treatment applications, alginate membranes can adsorb trace heavy metals and dyes.[102] Alginate membranes are also ideal candidates for oil−water separation, because of their superhydrophilic and underwater superoleophobic properties.[106] However, note that alginate intrinsic water-soluble properties are associated with the presence of carboxyl and hydroxyl groups, which also lead to chemical instability under aqueous conditions.[107] Therefore, it may be a good idea to blend polyanionic alginate with polycationic chitosan or to cross-link it with polyvalent metal cations (e.g., Ca^{2+}), forming a stable and insoluble polyelectrolyte complex or strong gel in water.[107−109] The alginate layer treated by Ca^{2+} ions also demonstrated good stability for organic solvent nanofiltration.[110]

Starch. Starch, containing ∼30% amylase, 70% amylopectin, and <1% lipids and proteins from plants, is an abundant natural polymer with high biodegradability and low cost. It has been widely used in the food industry to provide functional properties.[111] However, when used for membrane fabrication, starch has some intrinsic shortcomings. First, it is very hydrophilic, leading to low stability under different environmental conditions. Second, its mechanical strength and elongation behavior are poor. In order to overcome these problems, starch may be blended with other polymers, such as chitosan, CA, and PVAL. Plasticizers may also be incorporated, including glycerol and sorbitol.[32,111−113]

Polyisoprene. Polyisoprene is produced from the *Hevea brasiliensis* tree (cis-polyisoprene) or *Pallaquium gutta* tree (trans-polyisoprene).[32] In addition, it can also be obtained from petroleum refining, but synthetic polyisoprene has inferior performance than natural polyisoprene in strength and processability. Polyisoprene has wide applications in producing tires, shoes and boots, machinery, medicines, sports equipment, and latex.

The reports on fabricating polyisoprene membranes have been very few and focused on self-assembly. Mulvenna et al.[114] synthesized polyisoprene-b-polystyrene-b-poly(*N*,*N*-dimethylacrylamide) (polyisoprene−PS−PDMA) triblock polymers. This polymer then was used to prepare membranes by NIPS and self-assembly. This membrane may be used in water treatment, pharmaceutical separations, sensors, and drug delivery. Zhang et al.[115] fabricated polyisoprene−PS−PDMA hollow fiber membranes, exhibiting high flux and high selectivity in nanofiltration. In addition, polyisoprene-b-polystyrene-b-poly-4-vinyl pyridine membranes[116] and polystyrene-b-polyisoprene-b-polystyrene

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(SIS) membranes[117] were fabricated, showing tunable structures.

Biobased Polymers from Animal Sources. *Chitosan (CS).* CS is obtained from chitin via deacetylation. The amino group in CS molecular is more active than the acetyl amino group in the chitin molecule, imparting CS with excellent biological function and chemical modification potential.[118] When the deacetylation of chitin reaches 60%, it becomes CS,[119] but, this material only can be used as a valuable industrial product at more than ∼70% deacetylation. Chitin exists in the outer shells of crustaceans, the cell membranes of fungi and algae, the shells and bones of mollusks, and the cell walls of higher plants; hence, it is widely distributed in nature. CS is nontoxic and biodegradable, and it has suitable biocompatibility and low cost. It can also be used as membrane materials for biomedical applications, pervaporation, water treatment, gas separation and proton exchange of fuel cells, supercapacitors, and solid-state batteries.[120]

CS-based membranes in water treatment have been mainly applied with two objectives: (i) adsorptive membranes for phase transfer of contaminants from the aqueous solution, and (ii) composite NF/RO/FO membranes for surface separation with high solute rejection. CS-based membranes have an interesting ability to adsorb contaminants, especially heavy metals, because the amino and hydroxyl groups of CS can serve as coordination sites.[121,122] The main application of CS membranes in pervaporation has been to dehydrate aqueous−organic mixtures, and CS is arguably the most studied biodegradable material for pervaporation membranes.

However, pure CS membranes will suffer from excessive swelling and poor mechanical resistance in aqueous solutions, impairing their performance. Therefore, avoiding CS as the bulk membrane material and using it only as the skin layer of composite membranes may be the best option, because the CS skin layer can be reinforced by cross-linkers such as glutaraldehyde, glyoxal, formaldehyde, epichlorohydrin, and isocyanates, etc. to suppress excessive swelling, and the proper support layer can improve the mechanical property of composite membranes.[123,124]

The amino groups of CS also make this polymer a promising membrane material for CO_2 gas separation, because these moieties act as fixed carriers to facilitate the transport of acidic gases through membranes. However, it was found that the gas permeability of dry CS membranes is very low, because of their dense structure. Some studies induced the swelling of CS membranes with water vapor to cope with this problem, and the swollen membranes exhibited higher CO_2 gas permeabilities and selectivities.[15−17]

Collagen. Collagen exists in animal connective tissues in the skin, tendons, cartilage, and bones. In fact, animal production processes produce large amounts of collagen solid waste. The recycling of this waste will also prevent the spread of harmful pathogens in the environment.[125] Collagen-based membranes are widely studied in tissue engineering, because of low immune response, which can be used as a substrate or scaffold for cell attachment, proliferation, and differentiation.[126−128]

Other collagen-based membrane applications include pervaporation[129,130] and oil/water separation,[125,131] but studies have been limited because collagen-based membranes biodegrade rapidly and are sensitive to extreme pH and high-temperature conditions. Moreover, collagen generally fails to achieve desired mechanical characteristics, since it is unable to retain its structural integrity and because of swelling in aqueous environments.[132]

Sericin. Silk fiber is a natural polymer produced by Lepidopteron insects of the family *Bombycidae* and *Saturniidae*, and it is composed of a fibrous core protein fibroin with sericin protein surrounding it.[133] In the textile industry, sericin is the waste from degumming processes. However, it has some other applications in skin care, food, tumor suppression, and wound healing, or as an antioxidant, antiapoptotic, and anticoagulant.[134−136]

As for membrane fabrication, sericin is hydrophilic and water-soluble. Pure membranes are easily swollen, thus associated with weak mechanical properties.[32] However, the structure of sericin consists of polar side chains rich in hydroxyl, carboxyl, and amino groups that enable easy cross-linking, copolymerization, or blending with other polymers to prepare membranes with high performance.[133] Sericin membranes may be applied in the biomedical field or for CO_2 separation, because the serine and glycine amino acids in its polypeptide chain can facilitate CO_2 transport. Prasad et al.[137] fabricated a CS/sericin/Na_2CO_3 active layer on a PESU support for CO_2/N_2 separation.

Dopamine (DA) and Other Biophenols. Recently, dopamine-bioinspired coatings have been widely used for membrane surface modification.[138−142] They are utilized to simulate superior bioadhesion of marine mussel byssus from nature for their similar functional moieties.[143] Via self-polymerizing in an aerobic, alkaline environment, a polydopamine (PDA) layer can be formed and adhere to almost all types of substrates with high binding strength, including hydrophobic membrane surfaces. PDA layer is characterized by long-time stability, easy formation, high hydrophilicity, and antifouling and antibacterial properties.

Wang et al.[138] reported a simultaneous polymerization of dopamine and hydrolysis of commercial tetraethoxysilane in a facile single-step process on the PVDF membrane substrate, dramatically enhancing the hydrophilicity and oil-in-water emulsion separation ability. They also proved that other molecules dissolved with DA can be immobilized onto the substrate during the PDA polymerization process. Recently, Zhang et al.[142] reported the use of glucose, PDA, and Zr-based metal organic frameworks (MOFs) UIO-66-NH_2 to fabricate ultrathin nanocomposite membranes and realized ultrafast, low-pressure, precise separations in the NF process. Other biophenols, including tannic acid, vanillyl alcohol, eugenol, morin, and quercetin, were also investigated as surface coatings on membrane surfaces, showing good performance in organic solvent nanofiltration processes.[140]

Recycled Materials for Membrane Manufacturing. Although most recycled materials do not belong to biopolymers, and will persist in the environment, the utilization of them for membrane fabrication is also one of the pathways forward, especially in the situations that are not suitable for biodegraded membranes (e.g., wastewater treatment).

Recycled PET can be obtained via simply dealing with commercial water bottles; it was then used as feedstocks of membrane fabrication.[144−146] Park et al.[146] used recycled PET as the porous support and fabricated a green TFC membrane via the reaction of tannic acid and priamine. Polystyrene (PS) from plastic cups was also blended with CA to fabricate MF or UF membranes.[147] The waste brick powders (WBP) and sodium-alginate-coated membrane can separate crude oil-in-water emulsions.[148]

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Table 2. Properties of Some Biobased Polymers and Petroleum-Based Polymers[a]

polymer	density (g/cm^3)	melting point (°C)	tensile strength (MPa)	Young's modulus (GPa)	price (USD/kg)
PLA	1.21−1.25	150−162	40−60	3−4	3−5
PHB	1.18−1.26	168−182	24−40	3.5−4	4
PHBV	1.23−1.25	144−172	20−25	0.5−1.5	3.5
PBS	1.26	114	34	0.441	NA[b]
CA	1.3	230−300	NA	NA	10−100
lignin	NA	NA	NA	NA	<0.5
sodium alginate	NA	NA	NA	NA	12−35
starch	1−1.39	110−115	5−6	0.125−0.85	2−5.5
CS	1	102.5	NA	NA	20−40
PP	0.9−1.16	161−170	30−40	1.1−1.6	1.1−1.5
PVDF	1.75−1.79	160−175	30−70	1.8−2.5	19−32
PESU	1.37−1.51	365−388	85−125	2.7	9−26
PSU	1.24−1.34	315−371	70−107	2.5−8.5	19−30
PVC	1.38	185−205	41−52	2.9−3.4	0.6−1.5
PAN	1.184	317	NA	NA	4−4.25

[a]The presented values have been collected from other studies.[151,152] [b]NA = not available.

Challenges and Outlook. In summary, biobased polymers may be used as membrane materials or nonwoven membrane supports, showing a bright future. Biobased membranes have been widely investigated for application in the medical field. Their biocompatibility, biodegradability, and nontoxicity are ideal characteristics for drug delivery, hemodialysis, blood oxygenation, and tissue engineering. Moreover, biobased membranes can also be applied in water treatment, oil−water separation, pervaporation, organic solvent nanofiltration and gas separation, but there are some typical drawbacks:

(i) biobased membranes usually have inferior mechanical properties (see Table 2) and poor performance in harsh chemical environments;
(ii) the membranes can be biodegraded, so their long-time durability is often impaired, especially in water treatment applications and organic solvent nanofiltration;
(iii) some biopolymers used as membrane material partially or completely dissolve in water, so the related membranes will swell in aqueous environments;
(iv) the hydrophobic membranes for membrane distillation, membrane crystallizers, membrane contactors, etc. can hardly be prepared by biobased polymers;
(v) the production of biobased polymers is still small and the price of these materials is high, reducing economic interest over petroleum-based materials (see Table 2).

To overcome these problems, adding additives (e.g., natural plasticizers, nanoparticles), cross-linking with cross-linking agents, blending with other polymers, or fabricating composite membranes, whereby the biopolymer is used only in one of the different layers, are all feasible options to increase the membrane performance. Le Phuong et al.[149] reported that 23% of the papers on fabricating organic solvent nanofiltration membranes used renewable and biodegradable materials, demonstrating solvent-resistant property after adopting these modification methods. However, the degradability of these materials has yet to be demonstrated. There is no doubt that further research is needed to obtain biobased membranes having comparable or even superior performance, with respect to petroleum-based membranes. Hybrid membranes consisting of petrobased and biobased polymers together, or biobased nonbiodegradable polymers, or polymers from recycled materials may represent the first step with commercial success. Another critical factor is cost, which requires performing technological innovation in production, constantly reducing the cost and expanding output.[150]

GREEN SOLVENTS FOR MEMBRANE MANUFACTURING

The current membrane fabrication process relies heavily on traditional solvents chloroform, DMF, NMP, and DMAc, posing risks to the environment and human health. Using green solvents to substitute traditional ones is the inevitable trend in the future in both NIPS and TIPS processes. In NIPS, one of the prerequisites is that the polymer must dissolve in the solvent. The affinity between solvent and polymer also influences the phase separation pathway and the performance of the resulting membranes; therefore, selecting a proper green solvent with suitable affinity with the polymer is critical. Such affinity can be described by the R_a value, which is calculated by the Hansen solubility parameters (HSP), using the following equation:[153]

$$R_a = \sqrt{4(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2} \quad (1)$$

where δ_d is the dispersion parameter, δ_p the polar parameter, and δ_h the hydrogen bonding parameter.[153] A small R_a value indicates high polymer−solvent compatibility, and the polymer will most probably be soluble in that solvent, as shown in Figure 5.

TIPS is another method commonly used to fabricate membranes. The polymer is dispersed in a diluent at high temperature. The homogeneous dope solution is then cooled to low temperature, and phase inversion is thus induced. Because of the high temperature, the polymer concentration can be higher than in NIPS (up to 50%), leading to a denser membrane surface, better mechanical strength, narrower pore size distribution, and a lower probability of defect formation, compared to membranes fabricated via NIPS. In contrast, TIPS is associated with more energy consumption. The diluents mostly used in TIPS are harmful, including dioctyl phthalate (DOP), dibutyl phthalate (DBP), dimethyl phthalate (DMP), diethyl phthalate (DEP), diphenyl ketone (DPK), diphenyl carbonate (DPC), glycerin triacetate (GTA), NMP, and DMAc.

In this chapter, we discuss green organic solvents, deep eutectic solvents (DES), polyelectrolyte complexation, and

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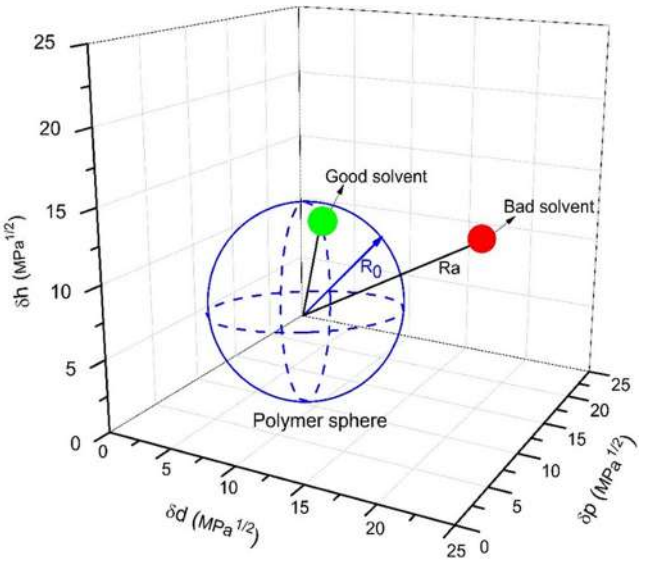

Figure 5. Radius of interaction of the Hansen solubility sphere (R_0) and the position of a good and a bad solvent for a specific polymer. [Reproduced with permission from ref 154. Copyright 2019, American Chemical Society, Washington, DC.]

solvent-free systems. The HSP values of several green solvents and of typical polymers are summarized in Table 3 and Figure 6.

Green Organic Solvents. *Methyl/ethyl Lactate.* Methyl lactate and ethyl lactate are lactate acid esters, which are biobased nontoxic solvents with low vapor pressure. They can be biodegraded via the activity of hydroxyl radical by photochemical oxidation in the vapor phase.[158,168]

Concerning membrane manufacturing, both methyl lactate and ethyl lactate are good solvents for cellulose-based polymers, such as CA.[9] The HSPs are given in Table 3. Gonzalez et al.[169] prepared CA UF membranes with LiCl as an additive and methyl lactate as a solvent. They evaluated the pollution potential and the ecotoxicity of this membrane, and both were determined as negligible. Furthermore, a cellulose diacetate (CDA) UF membrane prepared with LiCl and methyl lactate was assessed via holistic metrics-based approach, considering technical as well as environmental and health and safety (EHS) issues. Results showed that this membrane had great renewable intensity and required a low number of solvents for its preparation.[157] Moreover, CA NF membranes prepared by methyl lactate were also reported.[158] There are also some studies on the use of ethyl lactate, such as for the synthesis of tris-(2,4,6-trimethoxyphenyl) phosphonium functionalized poly(2,6-dimethyl-1,4phenylene oxide) (PPO−TPQP) anion exchange membranes,[170] polycaprolactone (PCL) membranes loaded with hydroxyapatite (HA) nanoparticles scaffolds,[171] and PLA membranes for pervaporation.[172]

PolarClean. Methyl-5-(dimethylamino)-2-methyl-5-oxopentanoate (Rhodiasolv PolarClean, abbreviated as PolarClean) is a new highly promising member of the green solvent family. This solvent is miscible with water and is derived from 2-methylglutaronitrile (MGN), which is a byproduct in the hydrocyanation of butadiene used to manufacture adipodinitrile (ADN).[173,174] It is completely biodegradable (97% after 18 days) with no environment and health hazards.[175] It is nonflammable and has very low vapor pressure.[175] The boiling point of PolarClean is 280 °C. According to the Rhodia raw material database, PolarClean can reduce the carbon footprint, compared to other traditional solvents.

Table 3. HSP Values and Radius of Interaction of the Hansen Solubility Sphere (R_0) of the Polymers and HSP Values of Green Solvents

polymer or solvent	δ_d ($MPa^{1/2}$)	δ_p ($MPa^{1/2}$)	δ_h ($MPa^{1/2}$)	R_0 ($MPa^{1/2}$)	ref
CTA	18.4	11.9	10.1	NA[a]	154
CA	18.6	12.7	11	8.8	153
PVDF	17.2	12.5	9.2	5	155
PESU	19.6	10.8	9.2	6.2	153
PSU	19.7	8.3	8.3	8	153
Matrimid 5218	18.7	9.5	6.7	NA[a]	156
PVC	17.6	7.8	3.4	8.2	153
PAN	21.7	14.1	9.1	10.9	153
lignin	20.61	13.88	15.25	11.83	153
chitosan	21.9	32.5	24.6	NA[a]	154
ethyl lactate	16	7.6	12.5	–	153, 157
methyl lactate	15.8	6.5	10.2	–	158
PolarClean[b]	15.8	10.7	9.2	–	155, 159
DMSO[c]	18.4	16.4	10.2	–	160
TEP[d]	16.8	11.5	9.2	–	161
γ-BL[e]	19	16.6	7.4	–	162
PC[f]	20	18	4.1	–	154
ATBC[g]	16.02	2.56	8.55	–	162
ATEC[h]	16.6	3.5	8.6	–	163
TEC[i]	16.5	4.9	12	–	163
TEGDA[j]	16.45	2.14	9.78	–	164
Cyrene[k]	18.8	10.6	6.9	–	165
DMI[l]	17.6	7.1	7.5	–	166
TamiSolve NxG	17.8	8.2	5.9	–	167

[a]NA = not available. [b]PolarClean = methyl-5-(dimethylamino)-2-methyl-5-oxopentanoate. [c]DMSO = dimethyl sulfoxide. [d]TEP = triethyl phosphate. [e]γ-BL = gamma-butyrolactone. [f]PC = propylene carbonate. [g]ATBC = acetyl tributyl citrate. [h]ATEC = acetyl triethyl citrate. [i]TEC = triethyl citrate. [j]TEGDA = triethylene glycol diacetate [k]Cyrene = 1,6-anhydro-3,4-dideoxy-D-glycero-hex-3-enopyranos-2-ulose (or dihydrolevoglucosenone). [l]DMI = dimethyl isosorbide.

Hassankiadeh and co-workers fabricated PVDF hollow fiber membranes via a combined NIPS-TIPS (N-TIPS) method, using PolarClean as the green diluent.[175] This is the first report using PolarClean for membrane fabrication. It was found that the PVDF/PolarClean system resulted in a dense membrane structure, while additive poly(*N*-vinylpyrrolidone) (PVP) increased the membrane porosity. Jung et al.[155] reported PVDF flat sheet membranes fabricated with PolarClean via the N-TIPS method. This membrane was modified by using one of the following additives: Pluronics F-127, PVP, LiCl, or glycerol. The Pluronics F-127-modified membrane exhibited the highest water permeability, with the value up to 2800 L m^{-2} $h^{-1}bar^{-1}$, with narrow pore size distribution. Jung and co-workers also fabricated PVDF hollow fiber membranes from PolarClean.[176] Recently, Tocci et al.[177] found the PolarClean can promote the β-phase formation of PVDF membrane.

PolarClean has good affinity with many polymers other than PVDF, and it has been used for membrane fabrication with PESU,[178] CA,[179] PSU,[179−181] PVC,[159] and novel Matrimid 5218[156] via the NIPS method. The affinity of PolarClean with these polymers is shown in Table 3. Considering its versatility, PolarClean is regarded as a promising alternative for traditional solvents. However, the multicomponent nature and multistep

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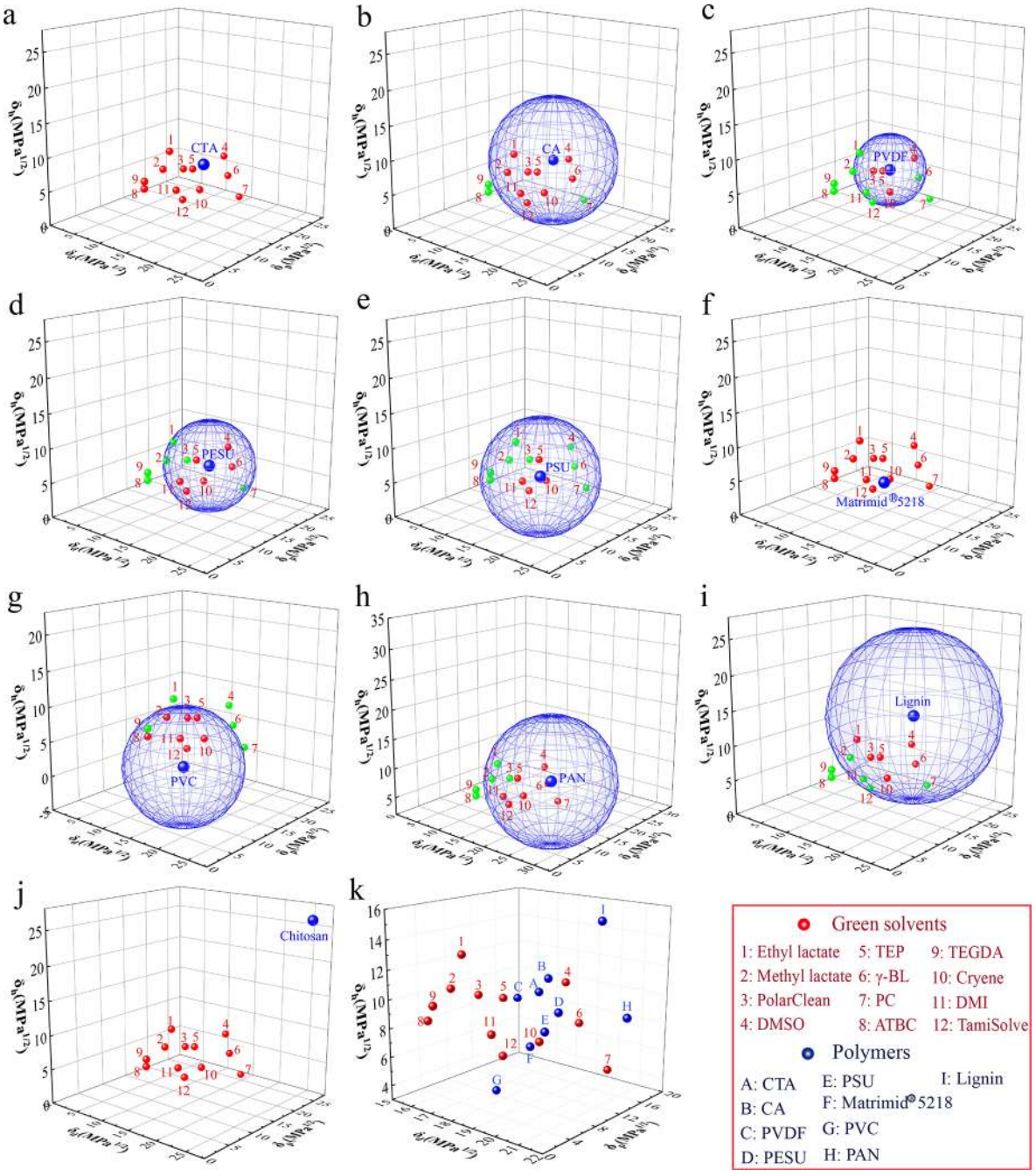

Figure 6. (b–e, g–i) Three-dimensional Hansen solubility parameter spheres of typical polymers (red dots are inside the sphere, green dots are outside the sphere). (a, f, j) Three-dimensional Hansen solubility parameters of green solvents and CTA, Matrimid 5218, and chitosan (the radiuses of the Hansen solubility spheres of these polymers are not available). (k) Three-dimensional Hansen solubility parameters of all green solvents and all polymers.

synthesis of this solvent are an obstacle for its widespread use, and the price is still high (9.5 USD/kg, while traditional solvents, such as NMP or DMF, are usually in the range of 2–4 USD/kg).[178] Cseri and co-workers[182] proposed a more advanced and shorter synthetic route, which was more sustainable than the patented route, showing great potential in reducing costs.

Dimethyl Sulfoxide (DMSO). DMSO is a nonhazardous, biodegradable, and recyclable solvent, which is extracted from lignin or synthesized via the oxidation of dimethyl sulfide. It has a high boiling point (189 °C at 760 mmHg) and a very low vapor pressure (0.6 mmHg at 25 °C). Moreover, it has good solvent power for many polymers. To date, there have been reported works regarding CA,[183] CTA,[184] PVDF,[183,185,186] PAN,[183,187] PESU,[23,183,188,189] polyimide (PI),[190] PVC,[160] and Nafion[191] membranes fabricated using DMSO as the solvent, proving its versatility.[192] Mu and co-workers[183] fabricated PVDF, CA, PESU, and PAN microporous membranes using a simple freeze-gelation method. Moreover, Meringolo et al.[185] prepared PVDF membranes with DMSO as the solvent via a combined vapor-induced phase inversion (VIPS) and NIPS method (V-NIPS). No chemical additive was used, and the resulting membrane exhibited a permeate flux up to 12.1 kg m^{-2} h^{-1} with salt rejection of 99.8% in membrane distillation (MD). These tests

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showed performance comparable to that observed with commercial PVDF membranes.

Using DMSO as the solvent, Evenepoel et al.[23] fabricated PESU UF membranes, which showed a higher permeability and rejection of bovine serum albumin (BSA) and rose Bengal (RB), compared to an analogous membrane fabricated from NMP. Prihatiningtyas et al.[184] fabricated CTA/cellulose nanocrystal (CNN) pervaporation membranes via the VIPS method, and the effect of solvents, including DMSO, dioxane, NMP, and DMF, was investigated. Among all solvents, the DMSO-based membranes resulted in homogeneously distributed CNCs on the membrane surface and a matrix with self-assembled structure.

As for economical evaluation, the cost of DMSO is much lower than that of many other green solvents, and is almost at the same level as traditional solvents. It has been reported that the approximate prices of the following green solvents are 1.6 USD/kg for DMSO, 2.6 USD/kg for triethyl phosphate, 1.9 USD/kg for acetyl tributyl citrate, and 19.4 USD/kg for triethylene glycol diacetate.[160]

Triethyl Phosphate (TEP). While TEP is a safer solvent for human health and worker safety, compared to traditional solvents, it cannot be defined as "green". On the one hand, it is harmful when being swallowed or when in contact with the eyes.[193] On the other hand, the use of TEP will expand the amount of phosphorus in the Earth's crust.[9] However, by only taking into account the direct harm to people and the environment, TEP is still a better alternative to other toxic solvents. Moreover, it has a high boiling point (215 °C).[193]

TEP has good affinity with PVDF (see Table 3), so the research on TEP has mostly focused on PVDF membrane fabrication. Karkhanechi and co-workers found that the TEP-based dope solution was more viscous than the NMP solution. Therefore, a macrovoid-free structure was observed.[194] However, Chang et al.[161] reported a more porous PVDF membrane structure resulting from a TEP-based system, with respect to an NMP-based system. They prepared PVDF hollow fiber membranes with no additive for application in MD, which not only possessed robust mechanical properties but also exhibited an average flux of 20 kg m^{-2} h^{-1} at a feed temperature of 60 °C, with almost-complete NaCl rejection. Other studies[195−198] compared PVDF membranes fabricated using TEP with others obtained with toxic solvents, namely, hexamethyl phosphoramide (HMPA), trimethyl phosphate (TMP), DMF, DMAc, and NMP, showing that TEP was a good solvent for PVDF, leading to a symmetric structure with interconnected pores. The comparison between TEP and DMSO as the solvent for PVDF membrane fabrication was also investigated, and it was found that DMSO resulted in higher porosity.[199] A combined V-NIPS method was also used to fabricate PVDF membranes with TEP as the solvent, promoting the formation of a highly porous surface.[199−202] In addition, there are some reports of fabrication of PVDF membrane via the N-TIPS method. The membrane fabricated by NIPS often had numerous fingerlike voids, leading to poor mechanical strength. The combined method effectively prevented this phenomenon and promoted the formation of an interpenetrating network structure.[203]

Gamma-Butyrolactone (γ-BL). γ-BL is a nontoxic solvent with high boiling point (204 °C) and high flashing point (98.3 °C), and it can be mixed with water. Interestingly, it can easily dissociate lithium salts.[204] In industry, γ-BL is a common solvent as a superglue remover, a paint stripper, and an aroma in foods. For membrane fabrication, there have been some reports on the use of γ-BL as a nontoxic solvent. Bey et al.[205] first used γ-BL to fabricate polyetheretherketone (PEEK) hollow fiber membranes via NIPS. This membrane was successfully used for chromium(VI) removal from aqueous solutions, with an extraction value of up to 99%. Polyetherimide (PEI) gas separation membranes were also prepared using γ-BL.[206] Experiments showed that PEI could not be dissolved in other green solvents, such as methyl lactate, ethyl lactate, propylene carbonate (PC), tributyl *o*-acetylcitrate (ATBC), tributyl citrate (TBC), and TEP, even at temperatures up to 140 °C. However, PEI was dissolved in γ-BL at 100 °C. The membrane obtained from this dope solution had a denser layer than that present in the membrane fabricated with NMP, resulting in slightly better hydrogen−methane selectivity but much lower permeability.[207]

Organic Carbonates. Stable organic carbonates are obtained from the diesterification of carbonic acid with hydroxy compounds, and their general structure is $R_1-O(C=O)O-R_2$.[154,208] Their synthesis in supercritical CO_2 may be considered as being environmentally friendly. The most common carbonate solvents are propylene carbonate (PC), glycerol 1,2-carbonate, and butylene carbonate. These cyclic carbonates are nontoxic, eco-friendly, and biodegradable, with high boiling points. Organic carbonates for membrane fabrication have been rarely reported. PC has been used as a diluent for PVDF membrane fabrication via TIPS.[209] Moreover, Rasool et al.[154] studied seven types of organic carbonates, namely, dimethyl carbonate (DMC), diethyl carbonate (DEC), PC, 1,2-butylene carbonate (BC), glycerol 1,2-carbonate, 1,2-hexylene carbonate, and styrene carbonate (SC), to dissolve PESU, PSU, PAN, PVDF, CS, PI, CTA, and CA at room temperature. Experiments showed that CA was the only polymer that could be dissolved in carbonates BC and DMC, while other polymers were not dissolved in any of the solvents. Since the affinity of these organic carbonates and polymers were poor, traditional solvent NMP was mixed with organic carbonates for membrane preparation via NIPS. Membranes with either spongy or macrovoid structures were successfully prepared, and the filtration experiment results were satisfactory, as depicted in Figure 7.

Acetyl Tributyl Citrate (ATBC), Tributyl Citrate (TBC), Acetyl Triethyl Citrate (ATEC), and Triethyl Citrate (TEC). ATBC, TBC, ATEC, and TEC, are all family members of citric acid esters, commercially known as "Citroflex". They are nontoxic and eco-friendly. ATBC is a widely used plasticizer in food contact polymers, medical plastics, aqueous pharmaceutical coatings, extracorporeal tubing, wraps and films, beverage tubing, and children's toys.[210] It can be used as a diluent for PVDF UF membrane fabrication via the TIPS method. Cui et al.[211] first used ATBC for the preparation of PVDF flat sheet and hollow fiber membranes, proving that it was a competitive and promising compound. Hassankiadeh et al.[210] then reported the poor mechanical strength of PVDF membranes fabricated using ATBC. Therefore, Kim et al.[212] increased the PVDF concentration up to 50 wt %, obtaining membranes with suitable mechanical strength. ATBC was also used for poly(ethene-*co*-chlorotrifluoroethene) (E-CTFE) membrane preparation.[213] The resulting membrane possessed a spherulite structure, high surface hydrophobicity, suitable mechanical strength, promising permeate flux (22.3 L $m^{-2}h^{-1}$), and almost-complete salt rejection in MD.

TBC is another ester diluent used to manufacture PVDF membranes. Liu et al.[214] first reported PVDF membrane

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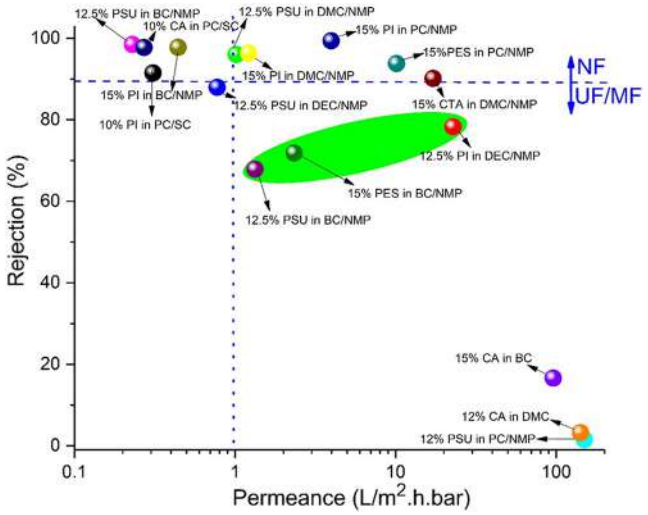

Figure 7. Permeance versus rejection of membranes prepared from carbonate-based solvents or carbonate/traditional solvent mixtures, categorizing them as either NF or MF/UF membranes. [Reproduced with permission from ref 154. Copyright 2019, American Chemical Society, Washington, DC.]

preparation using TBC, with di-(2-ethylhexyl) phthalate (DEHP) as the nonsolvent. Zhang et al.[215] then studied the kinetics of a PVDF/TBC system with five different PVDF concentrations (30, 40, 50, 60, 70, and 80 wt %) for four different cooling rates (5, 10, 15, and 20 °C/min). It was found that PVDF took a shorter time to crystallize as the cooling rate and polymer concentration increased.

As for ATEC and TEC, it is known that the solubility power to PVDF is improved in the order of ATBC< ATEC < TEC, by calculation of the Hanson solubility parameter (see Table 3). Sawada et al.[163] explored the effect of different diluents on the morphology and performance of the membrane. It was found that PVDF/ATEC and PVDF/TEC membranes formed spherulites, while PVDF/ATBC membranes formed only fibrillar structures. These three membranes had similar porosity (56.1%−58.9%) with average pore sizes in the following order: ATBC (0.82 μm) < ATEC (2.88 μm) < TEC (4.29 μm).

Triacetate Ester of Glycerol (Triacetin). Triacetate is slightly miscible with water but highly miscible with alcohol and ether. It can be used as an additive in food, perfumes, and cosmetics.[9] As for membrane fabrication, triacetin has been used for PVDF membrane preparation via TIPS method.[24,216] Ghasem et al. investigated the effects of quenching temperature,[217] PVDF concentration,[218] and polymer extrusion temperature[219] on the performance of PVDF membranes for CO_2 absorption and removal. The results showed that the membrane obtained at lower quenching temperatures was dense, leading to low gas permeability. Complete removal of CO_2 was possible using a membrane contactor deploying PVDF hollow fiber membranes fabricated at high quenching temperatures. As the PVDF concentration in the dope solution increased, CO_2 flux decreased, because of a thicker and denser outer skin layer. Moreover, it was found that the PVDF membranes exhibited improved removal efficiency of CO_2 with increased extrusion temperature.

Triethylene Glycol Diacetate (TEGDA). TEGDA is not classified as dangerous to the environment, with no acute or chronic effects. It is also not called as a "PBT" substance (Persistent, Bioaccumulative and Toxic) nor a "vPvB" substance (Very Persistent and Very Bioaccumulative).[164] TEGDA is generally employed as a plasticizer, and only one report can be found regarding its use as a low-toxicity diluent for PVDF membrane fabrication via the TIPS method.[164] The crystals of this PVDF membrane were α-phase and a specific fibrillar structure was formed, which yielded PVDF membranes with high elongation and permeability properties.

Dihydrolevoglucosenone (Cyrene). Cyrene, dihydrolevoglucosenone or 1,6-anhydro-3,4-dideoxy-D-glycero-hex-3-enopyranos-2-ulose, is a sugar-based solvent derived from cellulose.[165] The synthesis route only contains two steps, as depicted in Figure 8a, ensuring atom economy and low environmental impact. Also, there are no nitrogen or sulfur heteroatoms in Cyrene, which prevents NO_x and SO_x emissions upon incineration. Moreover, it is nontoxic, and it has high boiling point (227 °C) and high flashing point (108 °C) at 760 mmHg, with very low vapor pressure (0.28 Pa at 25 °C). Cyrene is considered as a prospective green alternative to traditional solvents NMP, DMAc, and DMF in membrane fabrication process, because of similarities with these compounds, in terms of solubility parameter, polarity, density, and miscibility with water.

Marino et al.[220] employed Cyrene for the first time to manufacture PVDF and PESU membranes via the V-NIPS method. Without any pore-forming agent, a short exposure time

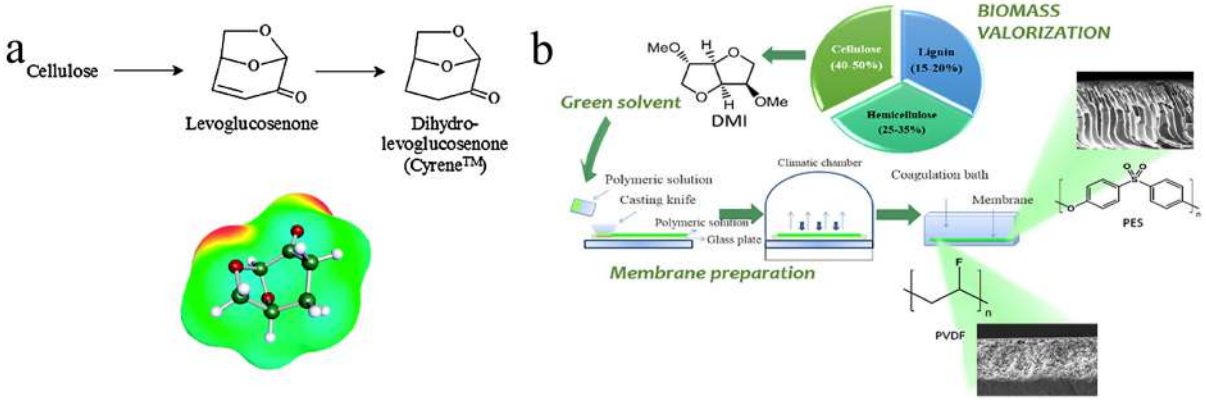

Figure 8. (a) Scheme for the production of Cyrene and its σ-surface (COSMO surface). [Revised with permission from ref 165 . Copyright 2014, Royal Society of Chemistry, London.] (b) Dimethyl isosorbide as a green solvent for PVDF and PESU ultrafiltration and microfiltration membrane preparation via N-VIPS method. [Reproduced with permission from ref 166 . Copyright 2020, American Chemical Society, Washington, DC.]

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Table 4. Average Molar Mass (M_{ave}) and Hanson Solubility Parameters (δ_t) of Choline Chloride-Based DESs[a]

HBA	HBD	HBA:HBD (molar ratio)	M_{ave} (g/mol)	δ_t (MPa$^{1/2}$)
choline chloride	urea	1:2	86.57	31.8
choline chloride	ethylene glycol	1:2	87.91	29.1
choline chloride	glycerol	1:2	107.93	31.5
choline chloride	malonic acide	1:1	121.84	35.6
choline chloride	oxalic acide	1:1	114.83	33.4

[a]Data taken from ref 235.

(0−5 min) to a relative humidity (RH) of 55% achieved tunable pore sizes from 0.55 μm to 0.03 μm (PVDF membrane) and from 0.12 μm to 0.02 μm (PESU membrane). Therefore, the pure water permeability could also be controlled. This work identified the feasibility of Cyrene in the fabrication of water treatment membranes. A recent study found that Cyrene is capable of dissolving PVC and CTA at 60 °C, but the resulting polymer inclusion membranes (PIMs) were inhomogeneous and opaque, exhibiting different appearances from those fabricated from traditional solvents. However, they worked adequately for Zn(II) extraction.[221] Cyrene is a promising green solvent for membrane manufacturing, but only two research works have been reported, and more efforts to improve its applicability are encouraged.

Dimethyl Isosorbide (DMI). DMI is another sugar-based green solvent, synthesized via methylation of the anhydro sugar isosorbide or directly derived from D-sorbitol, which is ranked in the top-10 biobased platform chemicals.[222] DMI is nontoxic and water-soluble, with a high boiling point of 235−237 °C at 760 mmHg.[166] Russo et al. published the only research so far on DMI for membrane fabrication.[166] They confirmed that DMI possessed the required physical/chemical properties to cast PVDF and PESU membranes, in terms of Hansen solubility parameters, relative energy difference, and viscosity. Membranes were manufactured via the V-NIPS method without any pore-forming additive: porous structures with a tunable pore size in the range of UF and MF could be obtained by controlling the exposure time to humidity. The process is depicted in Figure 8b. DMI is a new green solvent with a bright future in membrane preparation strategies.

TamiSolve NxG. TamiSolve NxG is a nonreprotoxic and biodegradable solvent. Itexhibits similar properties with traditional organic, polar aprotic solvents for membrane fabrication, such as NMP. TamiSolve NxG has been used for poly(vinylidene fluoride-hexafluoropropylene) P(VDF-HFP) MF or UF membranes fabrication for direct contact membrane distillation (DCMD), showing comparable performance to commercial PP membranes.[167]

Deep Eutectic Solvents (DESs). In 2003, Abbott et al.[223] first published a paper on DESs as alternative of ionic liquids (ILs). DESs are composed of a mixture of organic compounds and consist of strong hydrogen bond interactions between suitable hydrogen bond donors (HBDs) and hydrogen bond acceptors (HBAs).[223,224] They share many properties with ILs (e.g., low melting point, low vapor pressure, and high thermal stability), but they have lower toxicity and are biodegradable, eco-friendly, and associated with low costs.[225] In addition, they possess the additional features of ease of preparation, 100% atom economy, extensive tunability, and universal dissolution abilities.[226] A large number of HBAs and HBDs are available to prepare DESs. Among them, the top candidates are choline chloride (ChCl) and urea, for HBA and HBD, respectively.

The environmental impacts of DESs are investigated in terms of biodegradability and toxicity. It was found that cholinium-based DESs suffered a degradation of up to 80% after 21 days.[224] Meanwhile, the toxicity of DES is found to be dependent on its composition and concentration. It was reported that cholinium-based DESs has a greater cytotoxic effect than their singular components. However, they demonstrated no toxic effect on the studied bacteria.[227] Overall, DESs are much greener solvents than ILs, in terms of EHS impacts.

Recently, the utility of DESs has been explored in membrane technology, mainly focusing on using DESs as additives, as surface modifiers, or using DESs for liquid membranes fabrication.

Bin et al.[228229] first used DESs as additives of membrane casting solutions for PESU UF membrane fabrication. They found that DESs played the role of pore-forming agents rather than surface modifiers. Moreover, a small added amount (2 wt %) in the casting solutions can greatly enhance the water permeabilities, but their antifouling properties were not promoted. Then, very recently, Seyyed Shahabi et al.[230] added a choline-chloride−urea-based DES to the MPD aqueous solution to modify the PA layer of RO membranes during synthesis via interfacial polymerization. They observed a smoother surface, enhanced water flux, and salt rejection.

Maalige et al.[231] reported three different choline-chloride-based DESs as surface modifiers for surface treatment and cleaning of thin-film composite polyamide membranes (TFC-PAs). The enhanced surface wettability and surface smoothness of the DES-treated membranes resulted in remarkable increases in the flux rate and flux recovery without substantial changes in the solute rejection efficiencies. This phenomenon was attributed to the presence of hydrogen bonding between DES and PA moieties.

DESs for liquid membranes fabrication were also investigated.[232−234] DESs were imbedded into the pores of a solid porous framework of membranes via immersing or pressure impregnation. These liquid membranes then can be used for efficient CO_2 separation, ethylene/ethane separation, or fuel cell application, because of the enhanced proton conductivity.

However, to the best of our knowledge, DESs have never been investigated as green solvents to prepare membranes. The Hansen solubility parameters of ChCl-based DESs are depicted in Table 4, translating to relatively far distances from polymers materials (seen in Table 3). Therefore, maybe such specific DESs do not have good solvent power to typical polymers. However, given that the properties of DESs can be easily tuned by changing the HBD and HBA components, there may be combinations resulting in mixtures that would dissolve polymers for membrane manufacturing. Whether this proposal is feasible, however, remains to be explored.

Polyelectrolyte Complexation Induced Aqueous Phase Separation. Water is the greenest and most abundant natural solvent in the world. The possibility to utilize water as

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both a solvent and nonsolvent for membrane fabrication has attracted considerable interest. Traditional polymers (for example, PVDF, PVC, PESU, PSU) cannot dissolve in water. Polyelectrolytes (PEs) are charged polymers with either positive or negative charges on their repeating units, surrounded by small counterions, which stand out because of their water solubility. When two oppositely charged polyelectrolytes are mixed, they can form a water-insoluble solid known as polyelectrolyte complex (PEC), which can be cast as a thin film. Sadman et al.[236] used the coacervate of anionic poly(styrenesulfonate) (PSS) and cationic poly(*N*-ethyl-4-vinylpyridinium) (QVP-C2) dissolved in KBr solution to form a complex coacervate. The behavior of the complex in highly concentrated KBr was exploited to form membranes with porosities ranging in size from nanometers to micrometers, using water−water phase inversion via immersion precipitation in a low ionic strength solution. Recently, Baig et al.[237] reported a similar approach by using water solutions with different pH values. They prepared a homogeneous solution of the strong polyanion PSS and the weak polycation poly(allylamine hydrochloride) (PAH) at high pH, whereby PAH is not charged (pK_a ~8.8). The solution was cast and immersed in a low pH bath to charge the PAH and resulted in controlled precipitation, forming a porous water-insoluble PEC membrane. By tuning parameters, such as PE concentration and molecular weight, the membrane pores can be tuned from MF, UF, to NF. This novel membrane fabrication process eliminates the use of organic solvents and the membranes can be cast with tunable pore size ranging from MF to NF. However, this process still has some drawbacks. Extensive time and cumbersome protocols are needed for solution preparation and for the following coagulation process, thus impairing mass production.

Solvent-Free Systems for Hydrophobic or Hollow Fiber Membrane Manufacturing. Melt spinning and cold stretching (MSCS) is regarded as the simplest membrane fabrication method, given that it does not involve any phase inversion process. During this process, the polymer melt is spun at a temperature close to its melting point, and then the micropores of the membrane are formed by the mechanical force acting on the material in a subsequent cold-stretching step.[238] Because no solvents or additives are required, this method is both economical and clean. However, the membrane fabricated via MSCS usually suffer from poor filtration performance and membrane fouling problems. To address these issues, Ji et al.[239] used poly(ethylene oxide) (PEO) as a pore-forming agent and melted it together with PVDF, obtaining a membrane with tunable pore size and tensile strength. The mean pore size of the prepared membranes with 100% stretching was ~0.317 μm, which showed a high dye rejection (<93.9%) for Direct Black 19. On the basis of the MSCS method, some new ideas have emerged: melt/solution integrated homogeneous-reinforcement method, homogeneous braid reinforced hollow fiber membranes, melt spinning-stretching interfacial phase separation method, and nanofibers-covered hollow fiber membranes via continuous electrospinning, which should improve the membrane performance while also relying on the sustainability of the process.[238]

These methodologies above can also be used for hydrophobic membrane fabrication. In the very near future, we will have to produce more hydrophobic porous membranes for new membrane operations, such as membrane distillation, membrane crystallizers, membrane contactors, etc. It might be more complicated to consider the appropriate green solvents and polymers than the hydrophilic materials. However, these solvent-free methodologies might be useful for their large-scale productions. But the massive amount of energy consumed to melt the polymers is not negligible.

Challenges and Outlook. In the European Union (EU), the use of NMP has been restricted. The regulations state that, as of May 2020, NMP can no longer be used in concentrations above 0.3%, unless the manufacturers and consumers take appropriate risk management protocols. It is obvious that a similar fate awaits other traditional solvents with environmental and health risks. Therefore, it is very important to substitute traditional solvents with greener ones in the chemical industry, including the membrane manufacturing processes. However, this substitution must be based on two conditions: (i) the membrane performance is not impaired and, if possible, it is improved; and (ii) the price of green solvents is competitive. Currently, some researches showed that it is feasible to achieve both goals simultaneously, showing competitive and even better performance when green solvents are applied. Meanwhile, Cseri et al.[240] reported that there is no direct correlation between the greenness and the price of the solvents. Replacing a traditional solvent with a greener alternative may be less expensive. Another important factor is that life cycle assessment (LCA) is needed to compare "green" and traditional membranes. The production, use, and disposal phases all must be assessed, with detailed statistics of environmental impacts. This LCA method may provide a robust comparison between traditional and green solvents, and it may illustrate when the use of green solvent would indeed reduce the environmental impacts of the membrane.

SOLVENT WASTEWATER TREATMENT AND RECYCLING

Wastewater is an inevitable problem during the membrane preparation processes, especially those based on the NIPS method. It has been reported that 100−500 L of wastewater is generated per square meter of membranes, and the contamination in wastewater generally exceeds the minimum allowable level of 100 ppm. Therefore, treatment is required before disposal. However, the reality is that >69% of the wastewater produced by membrane fabrication factories is discharged without effective treatment.[19] This wastewater generally contains organic solvents and a small amount of additives and polymers. Its direct discharge endangers aquatic life and damages the ecosystems, seriously reducing the sustainability of membrane technology. If the wastewater were to be treated effectively, the in-house reuse could be accomplished, and the concentrated organic solvents could be recycled. However, purification should be accomplished with low cost and high efficiency.

To date, there have been few reports of organic wastewater treatment from the membrane fabrication process. Razali et al.[19] used adsorption and seven different classes of adsorbents, namely, graphene, polymers with intrinsic microporosity, molecularly imprinted polymers (MIPs), zeolites, metal organic frameworks, activated carbon, and resins, to remove NMP or DMF from membrane industrial wastewater. Results showed that most adsorbents exhibited feasible performance to treat the membrane wastewater, and >99% of the organic impurities in the wastewater were successfully removed; the recycled water may be reused without adverse effects on the performance of the membranes. Meanwhile, the adsorbent regenerability was confirmed for up to 10 wastewater treatment cycles. This is an effective technology with low price, applicable in the membrane

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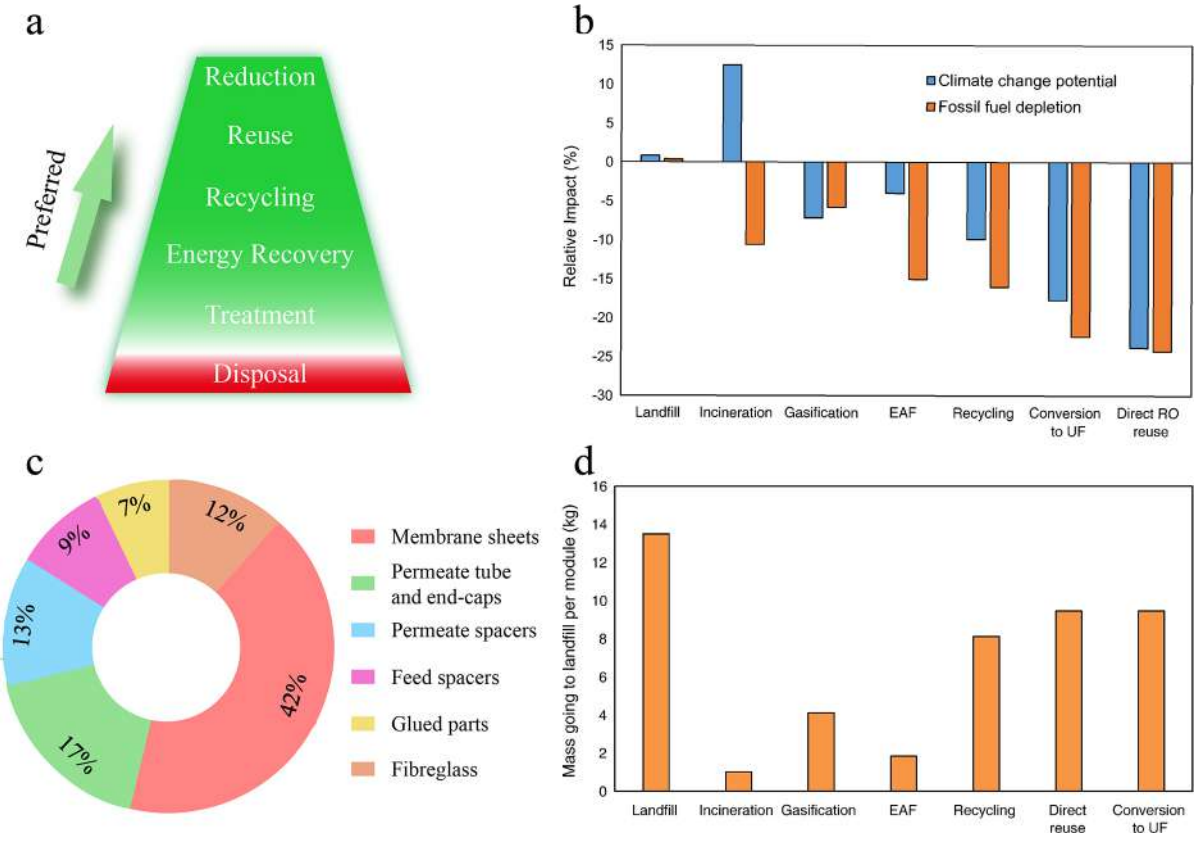

Figure 9. (a) Waste management hierarchy from most to least preferred options. [Revised with permission from ref 245. Copyright 2012, Elsevier.] (b) Greenhouse gas emissions and resource depletion for the disposal of one RO membrane element. [Reproduced with permission from ref 246. Copyright 2014, Elsevier.] (c) Composition of a typical RO membrane element. [Revised with permission from ref 245. Copyright 2012, Elsevier.] (d) Mass of waste material requiring landfill disposal for each of end-of-life scenarios for one RO membrane. [Reproduced with permission from ref 246. Copyright 2014, Elsevier.]

fabrication process. In another study, the wastewater was treated by membrane filtration, and both the extracted resource and water were recycled into the membrane fabrication process.[239]

THE APPLICATION OF ARTIFICIAL INTELLIGENCE IN MEMBRANE TECHNOLOGY

In recent decades, artificial intelligence (AI) technology and related in silico fields have developed rapidly and made great breakthroughs. Under these circumstances, membrane scientists began to think about applying AI to membrane preparation, as well as membrane processes, for the purpose of optimizing the process and improving efficiency.

The major challenge is the lack of a reliable model that predicts the influence of the preparation parameters on the resulted membrane performances.[241] On one hand, the mechanism of different parameters affecting membrane performance is very complex, which requires designers to have a systematic knowledge of all parameters for membrane fabrication (e.g., polymers, solvents, additives, temperature, humidity), and how they affecting membrane performances. On the other hand, AI is based on big data analysis. Therefore, compiling as much data as possible and finding their relationships are of vital importance to modeling and model domestication. But, in the actual membrane preparation process, their relationships are multidimensional and complex.

However, there have been some breakthroughs recently. Zhou et al.[242] used models to evaluate the performance of 12 723 MOF adsorbents or membrane materials from the CoRE 2019 database for D_2/H_2 separation. The subsequent machine-learning methods enabled predictions of novel nanoporous material features. Rall et al.[241] used artificial neural networks and machine-learning techniques to realize simultaneous membrane and separation process optimization for layer-by-layer NF membrane modules. Other works utilized AI for performance prediction of organic solvent nanofiltration membranes[243] and PVDF, PESU, and PSU micro/ultra/nanofiltration membranes.[244]

AI technology and related in silico fields have great potential to improve the efficiency of membrane technology, coupling the membrane fabrication and the design of the membrane processes. Much work needs to be explored, pushing membrane technology into the era of AI.

END-OF-LIFE MANAGEMENT OF SPENT MEMBRANE MODULES

Membrane elements have limited lifetime. For RO membranes, it is typically 3−7 years, while for MF and UF membranes, it is usually 7−10 years.[1] For gas separation membranes, the lifetime is much shorter, because of their exposure to harsh conditions. Therefore, large quantities of discarded membrane elements are generated annually. Over 14 000 tons of RO membrane modules are discharged every year, whereas, for UF and MF membranes, this number is even higher. For hemodialysis, over 600 000 tons of potentially hazardous dialyzer waste is produced every year, while the waste from gas separation activities is ∼10 times less

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than that for RO.[1,30] All of these numbers are unceasingly increasing.

Although faced with a tremendous amount of waste, people paid little attention to the end-of-life management and the environmental impact assessment of membrane modules.[1] Usually, the solid wastes are disposed in landfills or by incineration, but both treatment methods pose risks to the environment. The waste management hierarchy of the European Directive 2008/98/EC (Figure 9a) proposes the priorities and the most sustainable strategies for the management of spent membrane modules. The CO_2 emissions and resource depletion for each strategy are summarized in Figure 9b.

Reduction. Reducing the amount of wasted membrane elements is the first priority, and several approaches can be taken to this purpose. First, the membrane should be made with high performance, including suitable mechanical property, superior antifouling properties, and minimal aging or swelling. These characteristics would ensure a relatively long lifetime. Second, the choice of daily operational parameters is important and membrane lifetime can be extended under lower transmembrane pressure and mild conditions. Daily maintenance is also critical to rapidly identify damaged fibers and repair them in time. Third, as detailed in the section entitled "Biobased Polymers for Membrane Manufacturing", biobased materials can be included into the membrane manufacturing process to replace petroleum-based ones, with the goal of biodegradation after disposal, thus reducing the ultimate amount of solid waste.

Spent Membrane Reuse. The reuse of membrane elements means their direct application in lower throughput systems. Although a spent RO membrane usually no longer satisfies the initial selectivity criteria, it can still maintain a rejection rate of >96%, and it may be applied in seawater pretreatment or selective demineralization of brackish water. Direct RO reuse has both the greatest reduction in CO_2 emissions and fossil fuel depletion among all strategies (Figure 9b).

Membrane Element Recycling. Recycling of RO membranes includes direct recycling and indirect recycling. Direct recycling means the chemical conversion of RO membrane into NF or porous UF membranes.[247−249] Most RO membranes are composed of a thin and dense PA layer, a thicker porous PSU layer, and a nonwoven polyester backing layer. By controlled degradation of the PA layer, RO membranes may be converted to NF or UF membranes. It was reported that the best chemical agent to degrade PA layer is sodium hypochlorite (NaOCl): the exposure level (expressed in units of ppm h) determines the permeability and rejection of the resulting membrane.[247] Potential applications for the converted RO membranes are in pretreatment filtration for desalination, advanced treatment of wastewater, and freshwater production in rural zones.[250] According to Figure 9b, this conversion is only slightly worse than the RO reuse method, in terms of sustainability, because of the extra chemical treatment steps involved.

Indirect recycling means mechanical and chemical recycling of all plastics of membrane elements, containing not only PA, PSU, and polyester, but also PP for the feed spacer, polyester for the permeate spacer, acrylonitrile butadiene styrene (ABS) for the permeate tube and end-caps, fibreglass for the outer casing, and glued parts containing proprietary epoxy-like components. The composition of a typical RO membrane is shown in Figure 9c. All of these materials may be extracted and recycled via diverse recycling routes, such as mechanical recycling and chemical recycling (recycling to monomer).[251]

Energy Recovery. If or when reusing and recycling markets cannot absorb all membrane waste, energy recovery could be a valid solution to provide heat energy for electricity generation or other heat-related processes.[252] Incineration, syngas production, and electric arc furnace (EAF) are categories of energy recovery. Incineration is the most convenient for electricity generation. However, because of lack of selectivity, pollutant emissions in gas stream may be very high, especially in terms of dioxins and fly ash, as well as considerable CO_2 emissions. The gasification process provides greater environmental benefits, compared to incineration, because of electricity production through the combustion of the generated syngas.[245,252] The third energy recovery approach involves the use of the membrane material as a polymeric carbon source in EAF for steelmaking, to reduce the use of metallurgical coke.[246]

Waste Materials Requiring Landfill. The waste materials include components that cannot be treated (e.g., the fiberglass in EAF), and the residue waste generated from the recovery, recycling, or treatment processes themselves (e.g., slag from the gasification and incineration processes). These waste materials ultimately need to be landfilled, and the mass of waste for each end-of-life strategy is demonstrated in Figure 9d. Although membrane reuse and recycling provide prominent environmental benefits, they will still produce large amounts of waste, requiring eventual disposal. Therefore, if the absolute priority is the aversion of waste from landfills over all other impacts, incineration, or better, incineration following reuse/recycling remains the best option.

Challenges and Outlook. End-of-life membrane management is crucial to transform a traditional linear process to a circular process. Different strategies may be adopted, while landfill is the worst one, in terms of environmental effects. However, when it comes to the mass of waste requiring landfill, incineration generates the least amount of mass, while membrane reuse alone is associated with the second largest after direct landfill. Therefore, the best scheme for end-of-life management mustr combine the actual situation and the final demand. Obviously, obtaining both economic gains and environmental benefits is the ideal goal. In this process, LCA is useful to compare the different options quantitatively and to identify the optimal scheme.

However, current reports on membrane elements end-of-life management are limited, and the few that are available all focus on RO membranes, neglecting other membrane types. Faced with the continuous growth of discarded membrane elements, we should exert more effort to conduct research of their end-of-life management and promote practical applications of the spent modules, thus greatly increasing the sustainability of the membrane industry.

CONCLUSIONS AND FUTURE PERSPECTIVES

When confronted with an increasingly serious energy crisis and environmental pollution, green chemistry and green engineering may provide important help in our endeavor to overcome these challenges. The Principles of Green Chemistry advocate the use of renewable materials and production processes with lower impact on the environment. Membrane technology has been implicitly considered as a green and sustainable technology. However, starting from membrane manufacturing all the way to membrane disposal, there are problems that negatively affect the sustainability.

The use of petroleum-based polymers as membrane materials is related to a series of environmental issues, and biobased

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polymers are feasible options to improve membrane sustainability. However, some drawbacks hinder the deployment of biopolymers, such as poor mechanical properties, long running instability, and high costs. There is no doubt that further research is needed to master membrane preparation using biobased materials while simultaneously achieving comparable or even superior performance, with respect to current petroleum-based membranes. Biobased membranes may be more readily applied in the medical fields and other fields that are not impaired by microbial degradation.

The utilization of green solvents to substitute current toxic ones is another important strategy to improve the sustainability of the membrane manufacturing process. However, environmental advantages alone most likely cannot enable the widespread adoption of green solvents, and other factors related to performance, health, and cost should also be taken into account. Therefore, identifying suitable green solvents for membrane fabrication is a challenge. More-sustained studies are needed to identify alternative solvents and exploit their advantageous properties in membrane manufacturing.

Given the fact that there are still challenges to the effective application of green solvent alternatives, the treatment and recycling of organic solvent wastewater may be a viable approach to reduce pollution. If the wastewater is treated effectively, the reuse of wastewater may be accomplished, and the concentrated organic solvents may be recycled. However, reports in this field are very limited, and more research is urgently needed to find ways to purify the wastewater at low price and with high efficiency.

To improve the efficiency of membrane fabrication and use processes, AI technology and related in silico fields have great potential. The literature is emerging, and we believe that more works can push membrane technology into the era of AI.

The end-life-management of spent membrane elements is another important issue of great concern. The reduction, reuse, recycling, and/or energy recovery of used membrane elements, rather than their direct landfill or incineration, should be pursued to drive membrane technology into a circular economy approach.

That being said, quantification of the real impacts of new materials or processes and evaluation of their sustainability are complex analyses, and a complete LCA, including the production, use, recycling, and disposal phases, should be established to consider the real burdens related to membrane technology. One cannot judge whether a solvent is greener or not merely by considering one or a few metrics. LCA can more robustly inform with regard to which raw materials or processes contribute the greatest impacts; therefore, engineers should target those to rapidly reduce the associated problems, by applying the strategies that are found to contribute the most to reducing such impacts. An important limitation is that the necessary data and information to perform robust LCA studies are difficult to obtain, both in databases or from experiments, and progressively better and more appropriate databases should be established.

In the future, the definition of membrane performance should be expanded, including sustainability considerations. This transformation requires the innovation of science and technology coupled with new emerging systems thinking and systems design, resulting in a positive impact on a global scale.

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