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A review on microporous polyvinylidene fluoride membranes fabricated via thermally induced phase separation for MF/UF application

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ABSTRACT

To date, remarkable success has been achieved in the fabrication and industrialization of poly(vinylidene fluoride) (PVDF) membranes both in lab-scale and full-scale via thermally induced phase separation (TIPS) method for microfiltration/ultrafiltration (MF/UF) applications in water treatment. This article provides a comprehensive and heuristic overview of the fabrication, development, and industrialization of PVDF microporous membranes via TIPS during the recent several decades. Firstly, detailed information about the PVDF material was given to illustrate why PVDF was widely considered as a prominent material and how to choose a suitable polymer raw material for membrane production. Then from a historical developing perspective, this paper reviewed two commonly applied preparation methods for PVDF microporous membranes and highlighted the advantages of the TIPS method. Thirdly this work presented a deep review on the fast development of PVDF membrane fabrication and modification to show how to prepare and improve the polymeric microporous membranes via TIPS, following a line of thermodynamic formula design, experimental kinetics study, dynamic analysis of the preparation process based on modeling and simulation methods, and hydrophilic modification analysis based on an industrial and application perspective. Next based on the production and application status of present worldwide commercial PVDF membrane manufacturers, we summarized vital challenges to realize industrial-scale fabrication and extensive MF/UF applications for PVDF membranes via TIPS, and then aiming at the urgent issues to be addressed during the membrane application, some emerging advanced techniques based on TIPS were introduced to point out the next possible method for realizing commercialization. Finally, conclusions and future challenges are presented. This paper provides new insights about polymeric membrane fabrication and industrialization via TIPS from technology development and membrane application perspectives.

1. Introduction

Global water demand is expected to amount to an increase of 20–30% above the current level of water use, mainly due to rising demand in the industrial and domestic sectors [1,2]. According to a market report, the global water treatment technology market accounted for $5242.73 Million in 2017 and is expected to reach $12.4 billion by 2026, while the purification technologies for cleaning water include biological treatment, oxidation, precipitation, flocculation, and membrane technology, etc. [3]. Among the different technologies, membrane technology can be regarded as one of the most effective and promising ways. It has been pointed by Orion Market Research Private Limited that the global membrane filtration market is estimated to be valued at USD 13.5 billion in 2019 and is projected to reach USD 19.6 billion by 2025, at a CAGR (compound annual growth rate) of 6.4%, while microfiltration/ultrafiltration (MF/UF) is expected to have a significant share in the market due to their pretty wide application in different industries [3–5].

Polymeric membrane materials dominate the existing MF/UF membrane market because of their low cost and flexibility [6]. Examples of organic polymers include polysulfone (PSU), poly (ether sulfone) (PES), polyamide (PA, such as PA6, 66, and PA12), polypropylene (PP), high-density polyethylene (HDPE), polytetrafluoroethylene (PTFE), polyvinyl chloride (PVC) and poly(vinylidene fluoride) (PVDF). Herein,

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PVDF is one of the most used polymer materials and has received significant attention concerning its outstanding properties [7]. According to a market report, amid the COVID-19 crisis, the global market for PVDF membranes estimated at US$624.8 Million in 2020 is projected to reach a revised size of US$958.2 Million by 2027, growing at a CAGR of 6.3% over the period 2020–2027, while Asia-Pacific region dominates the market across the globe with the largest consumption from countries such as China, India, and Japan [8]. Some of the leading players in the global PVDF membrane market are Merck, Koch Membrane Systems, Bio-Rad Laboratories, Thermo Fisher Scientific, Pentair, Pall Corporation (Asahi Kasei), Citic Envirotech, GE Healthcare, Toray Industries etc.

To date, remarkable progress has been made in the fabrications of PVDF membranes with high performance for the MF/UF applications in wastewater treatment, and most of the commercial membranes are produced via phase inversion (PI) methods mainly due to their simplicity and flexible production scales [9]. The PI processes, in which the thermodynamic state of a homogeneous polymer solution is changed by contacting with another phase (liquid or vapor), and possibly changing temperature as well, to promote the formation of a solid phase, are the most commonly used techniques for manufacturing microporous polymeric membranes [10–14]. Depending on the state and property of the contact phase, PI processes can be divided into nonsolvent induced phase separation (NIPS) [5,13] (more commonly wet casting or immersion precipitation (IP)), evaporation/vapor induced phase separation (VIPS) (dry casting) [14] and thermally induced phase separation (TIPS) [15]. Among the preparation of PVDF membranes for wastewater treatment, NIPS and TIPS are the two most commonly employed methods [16,17].

In the recent decade, several influential review papers have been published and given an overview of the preparation, development, and application of PVDF membranes [6,9,12,15–24]. Some of them covered a very wide scope of topics that involved the production and modification of PVDF membranes in flat sheet and hollow fiber configurations via different methods such as phase inversion, use of inorganic particles as a filler or as an additive, sintering, electro-spinning, and track etching [16,17,22]; Some paid more attention to the different methods such as NIPS [24], TIPS or electrospinning [12,20], rather than the specific PVDF membrane; Some papers focused more about the progress of the modification and application of the PVDF membranes both in the lab-scale and commercial scale, instead of aiming at a particular preparation method [6,18,21]; While the others cared more about the effect of the physical properties of the PVDF membranes including crystallization behavior and electrical property on the application [19,23]. It can be known from these review works that since the 1980s, most of the available PVDF membranes have been produced via the NIPS method because PVDF is easily dissolved in common organic solvents [16]. While TIPS, as a process invented and introduced in the 1980s, has been developed and gradually become a hot research theme of membrane science in the past two decades [25]. The first research work on the PVDF membrane preparation via TIPS should be traced back to a PVDF membrane that presented isotropic spherulitic microstructure with large macrovoids and irregular porous prepared by Lloyd in the 1990s [26]. Since then, significant effort has been paid to realize controllable production of PVDF microporous membranes with high performance via TIPS, meantime several manufactures have realized industrial production and commercial application, which leads to this article that aims to comprehensively and heuristically review the significant literature and accomplishment associated with the lab-scale researches and industrial development of PVDF membranes via TIPS for water treatment. Also, critical issues, emerging advanced techniques, and challenges are brought out to provide new insights for future technology development.

Section 2 firstly provides detailed information about PVDF to illustrate why it was regarded as a prominent polymer for MF/UF membrane fabrication and how to choose proper PVDF raw material for commercialization; Then from a historical perspective, the development status of PVDF microporous membranes preparation till 2005 was reviewed when TIPS process was not widely applied in PVDF membrane preparation and research, and two preparation methods including NIPS and TIPS are introduced and compared for the PVDF membrane fabrication. Meanwhile, we highlighted the advantages of the TIPS method. In section 4 the paper focuses more on how to fabricate and improve the membranes via TIPS by taking PVDF membrane preparation as an example, following a line of thermodynamic formula design, experimental kinetics study, dynamic analysis of the preparation process based on modeling and simulation methods, and membrane hydrophilic modification. In Section 5, taking the production and module development of a commercial PVDF membrane manufacture as an example, we intend to summarize key issues to realize industrial-scale fabrication and wide MF/UF applications for PVDF membranes via TIPS. Then aiming at the urgent issues to be addressed during the membrane application, some emerging advanced techniques based on TIPS were introduced to point out the next possible method for realizing commercialization. Finally, conclusions and outstanding challenges are presented.

2. PVDF material for UF/MF membrane

Commercial PVDF is generally produced by polymerization of vinylidene fluoride (VDF) in emulsion or suspension using free-radical initiators, leading to the formation of repeat units of $–CH_2–CF_2–$, whose structure is shown in Fig. 1 [21,27,28]. Due to the characteristics of PVDF materials which include high mechanical strength, good chemical resistance, and thermal stability as well as excellent chemical resistance against corrosive chemicals, PVDF received considerable attention as an essential membrane material to produce microporous membrane for the water treatment process [16]. Based on the information provided by one of the major PVDF suppliers, Solvay Inc. (Solvay®PVDF Chemical Resistance, https://www.solvay.cn/chemical-resistance-matrix-pvdf), in contrast with other polymers that commonly applied in membrane fabrication such as polyvinyl chloride (PVC), HDPE, PP, PES, PA, PS and PSU, the chemical resistance of PVDF against most of the chemicals, including saline solution, acids, halogens, oxidizers, aliphatic, aromatic, polar protic and polar aprotic solvents, can be considered as relatively excellent, as shown in Fig. 2, which aroused most attention of people who were working on the preparation of MF/UF membranes. Because the MF/UF membrane application for the water treatment market mainly includes recycling of industrial wastewater, discharge of municipal sewage, purification of drinking water, and pretreatment for seawater desalination. These applications require the MF/UF membranes should have a high mechanical performance to withstand repeated physical and chemical cleaning. Thus with its high mechanical strength, good chemical resistance, and thermal stability, PVDF gradually occupied the most share of the MF/UF market. Table 1 lists a summary of selected manufacturers of polymeric MF/UF membranes popular in the US municipal water treatment market of 2012

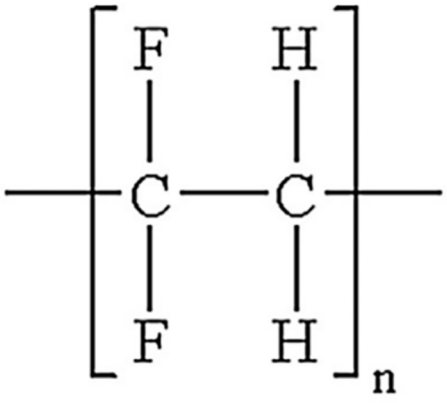


Fig. 1. Chemical structure of the repeat unit of PVDF.

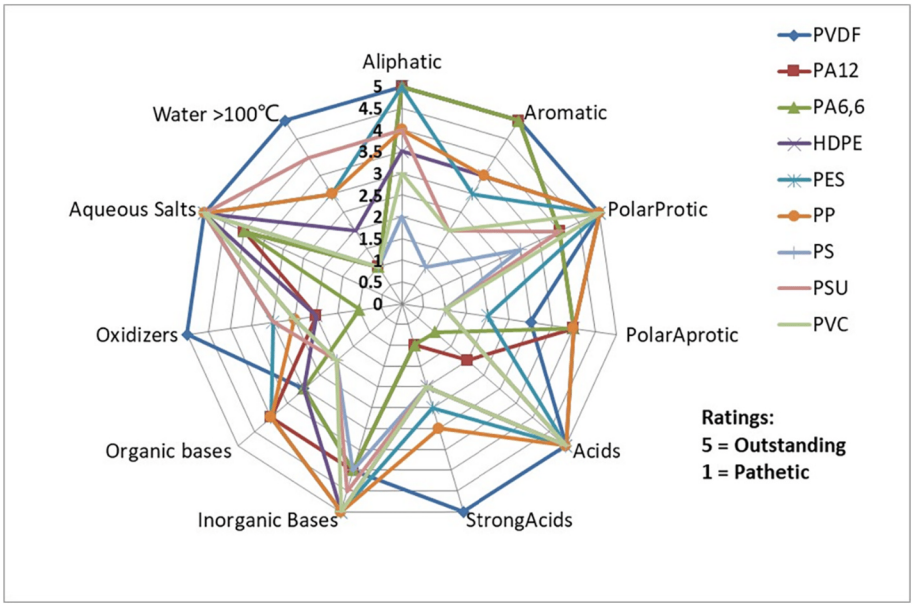


Fig. 2. Chemical resistance of PVDF and some organic polymers that are commonly applied in membrane fabrication.

Table 1
A summary of selected low-pressure manufacturers of polymeric MF/UF membranes in the municipal water treatment market of 2012 [29].

System Manufacturer	Membrane Material	Flow Configuration	Manufacturer Reported Pore Size, μm	Configuration
GE Zenon Zeeweed	PVDF	Outside–in	0.02–0.04	Submerged
GE Zenon 1500	PVDF	Outside–in	0.02–0.04	Pressurized
Pall (Asahi)	PVDF	Outside–in	0.1	Pressurized
Siemens Memcor	PP	Outside–in	0.2	Submerged/ Pressurized
Siemens Memcor	PVDF	Outside–in	0.1	Submerged/ Pressurized
Dow	PVDF	Outside–in	0.03	Pressurized
Toray	PVDF	Outside–in	0.01–0.02	Submerged/ Pressurized
Hydranautics	PVDF	Outside–in	0.1	Pressurized
Pentair X-flow	PES	Inside–out	0.05	Pressurized

[29]. According to Table 1, many manufacturers have developed commercially successful products based on PVDF, which should be attributed to the ease of manufacture owing to its relative cost, its operational advantages, physicochemical resistances (including free chlorine and both acidic and basic pHs), and mechanical strength.

As a semicrystalline polymer, PVDF normally presents a degree of crystallinity between 35% and 70%, while the melting and glass transition temperatures are around 155–192 °C and −40 to −30 °C, respectively [27]. Depending on its different chain conformations of trans (T) and gauche (G), semi-crystalline PVDF possesses many complicated structures with at least four crystalline polymorphs, including α (TGTG′), β (TTTT), γ (T_3GT_3G'), and δ (polarized α) phases [30]. Generally, crystallization behavior involving different polymorphs, crystallinity, and crystallization rate is a significant factor in determining the mechanical properties and the resistance of the membranes. There are several parameters such as solvent or diluent, thermal history, cooling rates, polymer molecular weight, molecular weight distribution, and polymerization method affecting the crystallization behavior. Therefore, understanding the effect of the PVDF crystalline behavior on the phase separation and membrane formation has also aroused much attention during the recent three decades [15,20].

The global PVDF market is consolidated, and the top four players accounted for a market share of over 90% of the global market. Leading players of commercial PVDF manufacturers include Arkema (France), Solvay S.A. (Belgium), SABIC, Dyneon GmbH (Germany, 3 M Company), Kureha Corporation (Japan), Shanghai 3F New Materials Company Limited (China), Daikin Industries Ltd (Japan), and others [31]. Concerning literature about the PVDF membrane preparation, Solvay, Arkema, and 3F New Materials have been considered as the most significant and popular suppliers of the raw PVDF materials. Table 2 lists the main properties of the most employed grades for commercial PVDF materials. Some grades such as Kynar® 760 from Arkema were used to be applied in some literature but are not available commercially

Table 2
Main properties of the most employed grades of the commercial PVDF raw materials.

PVDF Manufacturer	Grades	Molecular Weight $\overline{M_w}$ /kDa	Forms	Melt flow rate (ASTM D1238)/g/ 10min	Melting Point/°C
Solvay [38]	6010	320 [39]	Pellets/ powder	4.0–8.0 (230 °C/5.0 kg)	[redacted]
	[redacted]	670-700 [40]	Powder	<2.0 (230 °C/ 21.6 kg)	[redacted]
	[redacted]	255-268 [35,41]	Pellets	16.0–30.0 (230 °C/5.0 kg)	[redacted]
	[redacted]	352 [37]	Pellets	4.0–8.0 (230 °C/5.0 kg)	[redacted]
	[redacted]	573 [42]	Powder	2.8–4.6 (230 °C/ 21.6 kg)	171–175
3F [43]	FR904	600 [44]	Powder	1.0–6.0 (230 °C/ 12.5 kg)	160–168
	FR905	900 [45]	Powder	–	160–168
Arkema [46]	Kynar® 761	441 [47]	Powder	2.0 - 6.0 (230 °C)	165–172
	Kynar® MG-15	1458 [48, 49]	Powder	–	162–170

anymore, as a result, it is not included in table. As listed in Table 2, the molecular weight of the PVDF materials changes around from 300 kDa to 700 kDa, while the value of melt flow rate (MFR) differs considerably, which implies that molecular weight as well as MFR, have considerable impacts on the resultant membranes.

It has been indicated that during the free-radical polymerization process, molecular defects are easily introduced when $CF_2{=}CH_2$ monomers are added onto the growing chain in an inverted manner rather than all in the same direction (isoregically) [32]. Such inverted addition normally takes place to an extent of ca. 3.5–6.0 mol% (depending upon temperature), and leads to the well-known head-head (HH) defects (i.e. $–CF_2\text{-}CF_2\text{-}$) and tail-tail (TT) defects (i.e. $–CH_2\text{-}CH_2\text{-}$) [33]. And these regio-defects were proven to influence crystal structure and polymorphism. People also studied the effect of copolymerized hexafluoropropylene segments on the phase characteristics and crystallization behavior of PVDF. The results indicated that compared with pure PVDF, the crystallization (melting) temperature, equilibrium melting point and crystallinity of the copolymer were all lower [34,35]. What's more, polymer molecular weight and molecular weight distribution are other important factors impacting membrane preparation. It was proven that as the PVDF molecular weight increased, the phase separation and the viscosity slowly increased, which resulted in higher mechanical properties and denser structure [36,37]. Also, the shape of raw PVDF material including particles and powders affects processability and then has considerable effects on membrane production. In summary, the selection of PVDF raw materials is very significant for membrane preparation. For membrane fabrication and development, it is more practical to try more product samples for a particular solvent or diluent system.

3. PVDF membrane preparation: a historical perspective

3.1. The early stage (till 2005)

Fig. 3 presents the record count evolution of publications retrieved from the "Web of Science" database by taking "PVDF membranes Paper & Patent" as the key "title words". As shown in this figure, the earliest attempt to prepare PVDF membranes for water treatment was mainly from the early 1980s when a large amount of research on membrane formation had been carried out on cellulose acetate (CA) membranes and cellulose derivatives via NIPS [50–53], but less attention was focused on PVDF [54]. There are more than 100 pieces of literature from 1980 to 2005, and most of the literature belongs to the topic of the research of PVDF membranes prepared via NIPS. The NIPS for PVDF is a process that PVDF is firstly dissolved with a solvent (sometimes also with some nonsolvents or additives) to form a homogeneous casting solution mostly around the room temperature, then the casting solution is shaped into a film with desired configurations like a flat sheet or hollow fiber, and exposed in the air for a few seconds, and subsequently, the film is immersed in the coagulation medium which is a nonsolvent of PVDF and compatible with the solvent to allow mutual mass transfer between the casting solution and the coagulation to induce phase separation and PVDF solidification to form a nascent membrane. The final membrane would be obtained after some post-treatments including washing the residual solvents and additives in the nascent membranes.

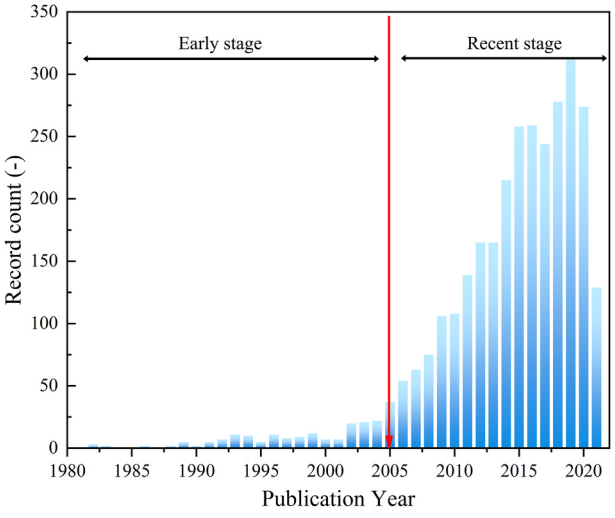


Fig. 3. Record count evolution of publications retrieved from the "Web of Science" database by taking "PVDF membranes Paper & Patent" as the key "title words".

Particularly after 2000, the amount of research was markedly increased, which implied that during this period researches of PVDF membrane via NIPS were gradually actively pursued. After reviewing them, it can be found that these works aimed at selecting more systems to regulate and control the membrane structure, studying the effects of various preparation conditions on membrane morphology and performance, as well as understanding the relationship between membrane structure with its formation process. Table 3 summarizes various preparative parameters adopted during the decades from the 1980s to 2005 including solvents, coagulation mediums, coagulation additives, polymer additives, organic additives, and inorganic additives. Necessary additional explanations were also added in the 'Comments' column of Table 3.

From Table 3, it can be easily found that because PVDF can be easily

Table 3
Preparation parameters of PVDF membranes fabricated via NIPS method during the period from the 1980s to 2005.

Preparative parameters	Species	Comments
Solvents	DMAc [51,66–75], DMF [7,51,52,76–88], NMP [52,69,78,82,83,86,87,89,90], triethyl phosphate (TEP) [57,77,78,83,89,91,92], dimethyl sulfoxide ($DMSO_2$) [77,78,80,86,92,93], dimethyl acetamide (DMA) [77–79,82,83,86,94,95], hexamethyl phosphoramide (HMPA) [78,83], tetramethylurea (TMU) [78], trimethyl phosphate (TMP) [78,86], acetone [52,96]	Can dissolve PVDF and is compatible with coagulation mediums.
Coagulation medium	Water (the most commonly applied), tetrachloromethane [76], trichloro methane [76], ethanol [69,95], 1-octanol [88]	Nonsolvents of PVDF and commonly be water due to economic considerations.
Coagulation additives	Methanol [76], ethanol [67,69,72,76], glycerol [76], DMF [76], butanol [76]	Help to regulate the compatibility between the solvents and the coagulation mediums.
Polymer additives	Poly-(ethylene glycol) (PEG) [51,73,80,81,85], poly (styrene sulfonic acid) [80], polymethyl methacrylate (PMMA) [94,97], polyvinyl-pyrrolidine (PVP) [66,69,74,77,86,95,97], polyvinyl acetate (PVAc) [70]	Help to improve the membrane porosity and performance such as hydrophilicity and water permeability.
Organic additives	Methyl ethyl ketone (MEK) [7], glycerol [91,92], ethanol [66,67,92], 1-propanol [67], tetrahydrofuran (THF) [51,81,93], acetic acid (HAc) [69], propionic acid [69], ethylene glycol [72], 1-butanol [96], pentane [96]	Casting solution additives and some are pore-forming agents while others are used to regulate the demixing rate.
Inorganic salt additives	Lithium chloride [52,67,77,79,82,90], water [68], zirconium dioxide [89], lithium perchlorate [75,84], titanium dioxide [85], alumina [74], silicon dioxide [87]	Some are pore-foaming agents, such as lithium chloride and lithium perchlorate, while others are nanoparticle additives.

dissolved in common organic solvents such as N, *N*-dimethylacetamide (DMAc), N, *N*-dimethylformamide (DMF), *N*-methyl pyrrolidone (NMP), and dimethyl sulfoxide ($DMSO_2$), which facilitate the formation of porous PVDF membranes via the NIPS process. During this period, researchers initially focused on regulating and improving flat sheet PVDF membrane structures by selecting a proper solvent, or adding some additives (organics, inorganics, or polymers) into the casting solution or the coagulation medium, or blending other polymers like polymethyl methacrylate (PMMA) with PVDF. Depending upon how the phase separation occurred, the resultant membrane may have quite different structures, namely asymmetric skinned with cavities of varying size and shape beneath the upper layer, and symmetric skinned with cellular pores or spongy pores, as shown in Fig. 4(A). The research results have indicated that for PVDF, the kinetic process of the diffusion between the solvent and the nonsolvent (coagulation medium) is the controlling factor in the design and engineering of a membrane suitable for a specific given UF process. However, most of the free membranes were brittle and thus have no potential in industrial applications, which lead to an introduction of non-woven supports. Since the 1990s, investigators gradually paid more attention to the preparation of hollow fiber PVDF membranes (as shown in Fig. 4(B)). After 2000, nanoparticles like zirconium dioxide or alumina et al. were increasingly dispersed in the casting solution to suppress the macropores and increase the permeability.

Based on the research works of this period, people gradually mastered appropriate techniques to fabricate PVDF membranes both in flat sheet and hollow fiber configurations with good UF performance via NIPS, and the mechanism of membrane formation and the influences of various controlling parameters have also been investigated using thermodynamic and dynamic modeling methods [55–57]. Fig. 5 shows a phase diagram that includes three components-polymer (PVDF), solvent, and nonsolvent (usually water), which is necessary to address guidance for understanding the outcome of the NIPS process [58]. In this period, people have also established some relatively accurate dynamic models to investigate the relationship between membrane structure and its formation process by tracking a composition path on the phase diagram to describe the mass transfer associated with the membrane formation [55,59–64]. The theoretical calculation of these composition paths has been considered as a useful tool to reason how mass transfer affects membrane morphology [55,64,65].

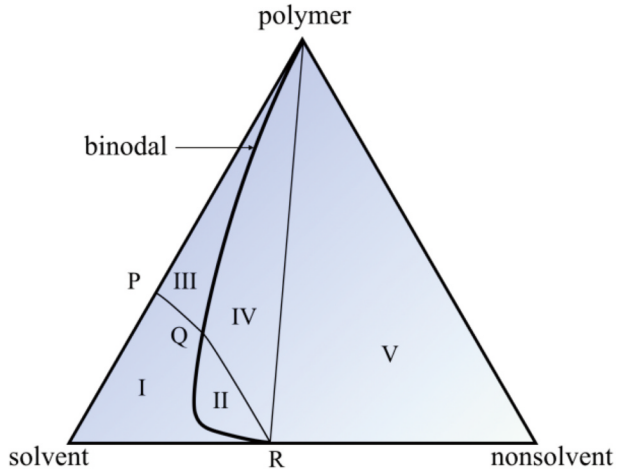


Fig. 5. A schematic phase diagram for a ternary polymer-solvent-nonsolvent system at a fixed temperature, relevant to the NIPS process. This is a general example of a semicrystalline polymer that includes the possibility of five different regions: homogeneous liquid (I), liquid-liquid coexistence (II), solid-liquid (S–L) coexistence (III), solid-liquid-liquid coexistence (IV), and another S-L coexistence (V).

3.2. The recent stage

As reviewed above, PVDF membranes prepared via the NIPS process are too brittle for practical application without non-woven supports. Whereas, it is well known that MF/UF membranes should have a high mechanical performance to attain a long service life. Therefore, since 2005, more people have tended to adopt other techniques to fabricate PVDF microporous membranes. The TIPS process, which was invented by Castro in the 1980s, can be applied to a wide range of amorphous or semi-crystalline polymers [25]. It is a technique that a polymer is firstly mixed at a specified temperature with a diluent (also called "latent solvent") of a high boiling point to form a homogeneous solution, then the induced phase separation and polymer solidification can occur by quenching (or heating) the polymer solution with an upper critical solution temperature (or lower critical solution temperature) on the desired shape surface. In the last step, the diluent trapped in the polymer matrix is removed to obtain a microporous membrane structure [98,99]. Compared to NIPS, TIPS has several advantages: firstly, it is a process with strong controllability which can be easily extended to industrial scales; secondly, membranes of the same polymer prepared by TIPS normally possess higher mechanical strength, fewer defects, and narrow pore size distribution than those prepared via the NIPS process; Finally, TIPS process has less controlling parameters thereby allowing the

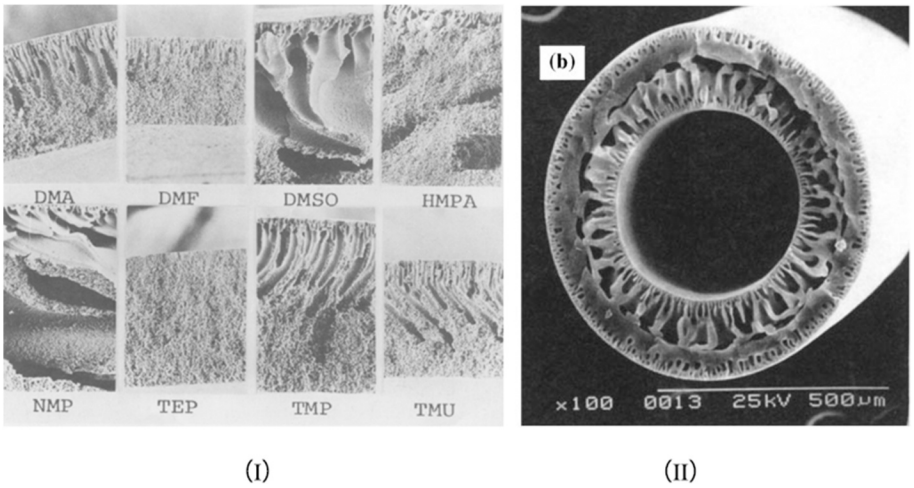


Fig. 4. Various cross-section structures of PVDF membranes in two geometries: (I) flat sheet shape, adopted from Ref. [78] with permission; (2) hollow fiber shape, adopted from Ref. [95] with permission.

shortening of the time spent on the development period [100–103]. There are more than 1500 pieces of literature retrieved by taking "TIPS, Paper & Patent" as the keywords from the 1980s to 2020. The annual amount shows a remarkable increase after 2000 and keeps rising in the recent five years, which demonstrates that during the past decades, several polymers such as PVDF, PP, PVC, PSU, PTFE, HDPE, and CA, have all been successfully employed to fabricate commercial polymeric membranes [20,104–109]. Besides, more than 300 of this literature is related to the PVDF membrane preparation, and this amount ranks the first among the different polymers, which implies that people have accumulated much information about TIPS by preparing PVDF membranes. Therefore, in the subsequent section, a comprehensive review and discussion on the researches of thermodynamics, membrane formation kinetics, process dynamics, and membrane modification via the TIPS process will be presented, taking PVDF membrane preparation and modification as an example.

4. Fundamentals on the PVDF membrane formation via TIPS

This section mainly discusses the fundamentals to prepare and improve PVDF microporous membranes via TIPS on the lab scale. Firstly, a full summary of diluent selection as well as the resultant membrane structures during the recent decades was presented, which provides an overall perspective for the PVDF membrane preparation via TIPS. Secondly, all criteria that have been proposed to estimate the interaction between the polymer and diluents were underlined to realize thermodynamic formula design. Thirdly, considering the actual membrane formation is always very fast and quite far from an equilibrium process, the kinetics of the membrane formation was studied both by off-line speculation and in-situ observation. Fourthly, modeling and simulation works that were developed to study the dynamics of the membrane formation via TIPS were reviewed. Finally, due to the low surface energy and hydrophobic characteristics of PVDF materials, hydrophilic modification has been extensively conducted and reviewed.

4.1. Thermodynamic phase diagrams and diluent selection

A binary phase diagram, which is based on Flory–Huggins polymer-solvent solution theory, is normally regarded as the basic thermodynamic guide to understand the mechanism of the membrane formation via TIPS, and two representative examples can be found in Fig. 6. Generally, the TIPS processes can be classified into two kinds: liquid-liquid (L-L) phase separation and solid-liquid (S–L) phase separation [11]. As shown in Fig. 6, the area between the binodal curve and the crystallization temperature curve is the L-L phase separation region while the area below the crystallization temperature curve is considered as the S-L phase separation region. The location of the binodal curve is strongly determined by the interaction between polymer and diluent, which is considered to be characterized by a parameter called χ. As the polymer–diluent interaction is strong, which means χ is relatively small, the binodal curve would be lower than the crystallization curve, which results in a phase diagram like Fig. 6 (II). Meanwhile, as the polymer-diluent interaction is getting weak, which means the parameter χ is relatively higher, part of the binodal curve rises above the crystallization curve thus the phase diagram looks like Fig. 6 (I) [58,99,110]. The idea here is that thermal quenches along different vertical paths will follow different TIPS processes and produce different membrane morphologies due to the influence of thermodynamics. Four different possibilities can be predicted, corresponding to the four arrows in Fig. 6. Passing through the L-L equilibrium spinodal curve before entering the S-L equilibrium region, as shown in Path (A), leads to bi-continuous, open-pore morphologies due to the process of spinodal decomposition in which rapid local phase separation results in the formation of liquid-phase microstructures that coarsen over time and govern the ultimate pore structure, as shown in Fig. 6 (a). Passing through the metastable region, as shown in Path (B), will lead to cellular morphologies due to the process of nucleation and growth of a polymer-lean liquid phase, as shown in Fig. 6 (b); the rate at which these solvent-rich nuclei grow and coalesce, as determined by their inherent kinetics and the rate at which the polymer solidifies, will determine the size and openness of the cellular structure. Thirdly, passing through the S-L equilibrium curve, as shown in Path (C), leads to compact spherulitic structures due to the process of nucleation and growth of a solid phase getting out of the liquid phase, as shown in Fig. 6 (c); Finally, passing through the S-L equilibrium curve, as shown in Path (D), leads to a particle-like structure connected by leaves, tied fibrils, fuzzy spheres, and leafy spherulites; And the pore structure is governed by the size and connectedness of the solid polymer particles.

Therefore, it can be known that the compatibility between the polymer and the diluent, plays a key role in determining the phase separation process and the resulting membrane morphology; hence affecting the membrane properties, such as pore size and distribution, mechanical strength, and flux. The determination principles of diluent selection in the TIPS process should comply with the following schemes:

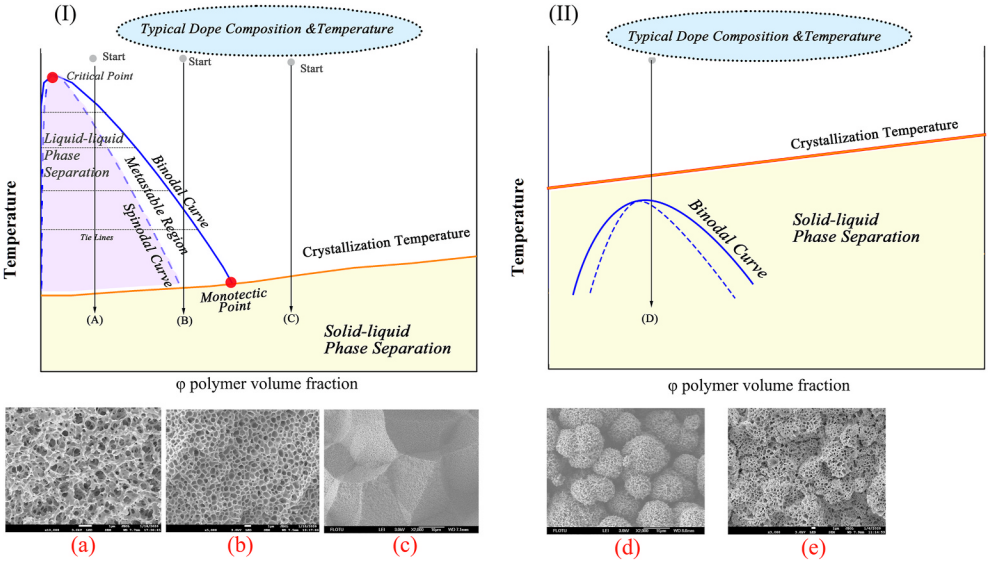


Fig. 6. Different temperature-composition phase diagrams for polymer-diluent systems, relevant to the different TIPS processes. Thermal quenching through different regions of the phase diagram (paths A, B, C, and D) yields different porous structures like (a), (b), (c), (d), and (e).

(1) the principles for diluent determination should vary with polymer categories. As a polar semi-crystalline polymer, PVDF can be soluble in a polar solvent or a solvent with similar polarity. (2) Since a homogeneous solution can be formed at an elevated temperature by blending the polymer with a high-boiling, low molecular weight diluent, the initial temperature must be less than the boiling point of diluent and is typically 25–100 °C greater than the melting temperature (T_m) or glass transition temperature (T_g) of pure polymer. The polymer must be stable and the diluent should have low volatility at the high temperature. For PVDF, the melting point of which is around 160–175 °C, thus the diluent with a boiling point higher than 200 °C is desirable for preventing severe volatilization. (3) The solution is supposed to be fabricated into the desired shape (a sheet, tube, or hollow fiber) only at appropriate viscosity [17]. Thereby diluents with low fluidity and mobility would be not desirable for membrane fabrication. (4) Chemicals with low toxicity and low corrosivity are preferred. (5) Commercial products with low prices are favorable to control the membrane production cost.

Much effort has been paid to the diluent selection for the microporous PVDF membrane prepared via TIPS since the 1990s because it determines the essential phase behavior of the system. Table 4 summarizes the study history of the diluent selection during the recent decades. It shows that for PVDF, almost all alcohol solvents cannot dissolve PVDF even at a high temperature due to its strong polarity. Only some ester, ketone, or sulphone compounds can be used as diluents, such as dibutyl phthalate (DBP), glyceryl triacetate (GTA), γ-butyrolactone (GBA), and propylene carbonate (PC), etc. Whereas, most of the single diluent systems only undergo the TIPS (S-L) phase separation process and lead to membranes with the spherulitic structure that looks like Fig. 6 (d, e). The UF performance including permeability and mechanical strength of these membranes was kind of unsatisfactory. As a result, many researchers tended to add a second diluent such as diethylene glycol (DEG), or bis(2-ethylhexyl) phthalate (BEHP) to decrease the compatibility of the systems and induce L-L phase separation. The results showed that only a few diluent groups were effective to change the structure. Therefore, whether for PVDF or other polymers, a criterion to evaluate the interaction between the polymer and diluents and to help to choose appropriate single diluents to prepare membranes with bicontinuous interconnected porous structure and high performance via

Table 4
a brief study history of diluent selection for membrane preparation of PVDF via TIPS.

Period	Main author & Institution	Diluent + additive	Result
1985–1987 [111,112]	C. Josefiak Akzona Inc., USA	cyclohexanone (CO); GBA; propylene carbonate (PC); carbitol acetate (CBA); glycerin triacetate (GTA) + dioctyl adipate (DOA); butyl carbitol acetate (BCA);	Membranes prepared presented spherulitic structures and sphere-shaped pores. A membrane with a 3-dimensional network of pores, separated by narrow intermediate bridges was obtained using BCA as the diluent.
1990 [98]	Douglas R. Lloyd University of Texas Austin, USA	DBP;	Membrane prepared presented a spherulitic structure.
1991, 2000 [113,114]	Yoshinao Doi, Haruo Matsumura Asahi Kasei, Osaka (JP)	dioctyl phthalate (DOP) + SiO_2 nanoparticles; DBP + bis(2-ethylhexyl) phthalate (BEHP) + SiO_2 nanoparticle;	A membrane with a three-dimensional network structure was obtained by adding SiO_2 nanoparticles that were dissolved by NaOH solution into the PVDF-DBP system.
1996 [115]	Thomas W. Beck Memtec. Limited, Australia	GTA + DEG	A membrane with microporous structure was obtained after quenching and stretching the PVDF-diluent mixture system.
2006–2019 [13, 36,116–125]	Xianfeng Li, Xiaolong Lu, Zhenyu Cui, Tianjin Polytechnic University, China	DBP + $CaCO_3$; DBP + DOP; PC; PC + dioctyl terephthalate (DOTP); GTA + triethylene glycol (TEG); sulfolane (SFL);	For the systems of pure DBP, pure PC, pure SFL, DBP with $CaCO_3$ nanoparticles and PC with DOTP, S–L phase separation occurred and membranes with the spherulitic structure were obtained; L–L phase separation could take place and membrane with uniform porous structure as a specific amount of DOP was added;
2006–2009 [126–129]	Jun Zhang, Zhaoliang Cui, Nanjing University of Technology, China	dimethyl phthalate (DMP); DBP; DMP + DOA; DMP + dioctyl sebacate (DOS); DPK; diethyl malonate (DEM); methyl benzoate (MB); methyl salicylate (MS); DMP + dibutyl sebacate (DBS); DBP + DBS; dibutyl maleate (DBM)	Membranes with different spherulitic structures including interconnected, jagged, sharp-edged and porous, were obtained as different diluents were applied.
2007–2008 [130,131]	Cuixian Chen Tsinghua University, China	DBP; GBA; DBS; PC; GBA + CO; DBP + CO;	Membranes with the spherulitic structure were prepared for all the diluent systems.
2007–2008 [42, 132–136]	Liping Zhu, Baoku Zhu, Youyi Xu Zhejiang University, China	DBP + DEHP; SFL; triacetin;	S-L phase separation and membranes with spherulitic structures were found.
2008–2015 [137–141],	Hideto Matsuyama Kobe University, Japan	GTA + glycerol; diethyl phthalate (DEP);	The hollow fiber membranes presented spherulitic structures.
2010–2018 [142,143],	Zhengliang Xu, East China University of Science and Technology, China	tributyl citrate (TBC) + DEHP;	For the system of TBC and DEHP, S-L phase separation could be found and membranes with the particle-packing porous structure were formed.
2013–2016 [37, 144–147],	Young-moo Lee, Enrico Drioli, Hanyang University, Korea	acetyl tributyl citrate (ATBC); acetyl triethyl citrate (ATEC); triethyl citrate (TEC);	At low PVDF concentration, the membranes showed a more bicontinuous structure, while the structures produced with higher polymer concentrations were fuzzy spherical porous.
2013–2015 [148–150]	Zhikang Xu, Zhejiang University, China	$DMSO_2$; PC; CO;	Irregular tubular pores were observed as $DMSO_2$ was the diluent due to the crystallization of $DMSO_2$; Porous spherulites were formed from PVDF/CO system, whereas smooth particles resulted from PVDF/PC system;
2015–2018 [41, 151,152],	Pingli Li, Baoan Li, Tianjin University, China	GTA + DBS; GBA + DOP; GBA + DOA; GBA + DOS;	Membranes with cellular structure could be obtained for these systems.
2016–2020 [44, 153–156],	Wanzhong Lang, Shanghai Normal University, China	DBP; DBP + SiO_2@graphene oxide (GO) nanohybrid; DBP + oxidized multi-wall carbon nanotube (O-MWCNT);	Membranes with bicontinuous porous and fuzzy spherulitic structure could be observed;

TIPS is crucial and necessary. Through these researches, people have summarized some methods about how to estimate the interaction between the polymer and diluent, which will be discussed in the next section.

4.2. Estimating the interaction of PVDF and the diluents

Section 4.1 has demonstrated that diluent selection plays an important role in improving the membrane structure and such a diluent searching step that is time and cost-consuming limits the application broadening of TIPS. Since 2006, a lot of people have tried to pursue a simple criterion or guidance to estimate the interaction between the polymer (especially PVDF) and different organic solvents or solvent mixtures, so as to help find a proper environmental-friendly diluent to prepare membranes with a bicontinuous structure and excellent UF performance including high water permeability, good selectivity, and satisfying tensile strength. At present, three ways have been proposed to calculate or evaluate the PVDF-diluent interaction parameter χ, including solubility parameter, dielectric constant, and molecular structure. In the following part, basic principles and applications of the three ways will be presented.

4.2.1. Solubility parameter

Solubility parameters are also sometimes called cohesion energy parameters as they are derived from the energy required to convert a liquid to a gas. There are two kinds of solubility parameter systems involving the Hildebrand solubility parameter [157] and the Hansen solubility parameter [158]. The Hildebrand solubility parameter ($\delta_{\text{hildebrand}}$) was firstly proposed and defined as the square root of the cohesive energy density:

$$\delta_{\text{hildebrand}} = \left(\frac{E}{V}\right)^{1/2} = \left(\frac{\Delta H_V - RT}{V}\right)^{1/2} \quad (1)$$

where V is the molar volume of the pure solvent, and E is its (measurable) energy of vaporization, which can also be calculated by '$\Delta H_V - RT$', where ΔH_V is molar heat of vaporization, R and T are the gas constant (8.314 J/(mol·K)) and temperature (K). Solution thermodynamics indicates that the noncombinatorial molar free energy of solution, $\Delta G^M_{noncomb}$ which includes all free energy effects of a mixing process, must be zero or negative for the solution process to occur spontaneously. According to Ref. [158], $\Delta G^M_{noncomb}$ can be calculated by Eq. (2) as follows,

$$\Delta G^M_{noncomb} = \phi_1 \phi_2 V_M (\delta_1 - \delta_2)^2 \quad (2)$$

Where the δ is volume fraction and V_M is the volume of the mixture, while 1 and 2 represent the solvent and polymer. As a result, the Hildebrand solubility parameter provides a numerical estimate of the degree of interaction between materials, especially for polymers and solvents. It can be a good indication of solubility of the target polymer in different solvents, particularly for nonpolar polymers, and the idea here is that the polymers and solvents with similar values of $\delta_{\text{hildebrand}}$ are likely to be miscible. Nevertheless, since the polarity of PVDF is a little high, the Hildebrand solubility parameter has been rarely used to evaluate the PVDF-diluent interaction. Instead, Hansen solubility parameter (HSP), which is based on the idea that is that the total cohesion energy consists of several individual parts, which arise from (atomic) dispersion forces, (molecular) permanent dipole–permanent dipole forces, and (molecular) hydrogen bonding (electron exchange) [158]. So, the square of HSP δ can be regarded as the sum of the squares of the Hansen dispersion (D), polar (P), and hydrogen (H) components, as shown in the equation below,

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \quad (3)$$

Similar to $\delta_{\text{hildebrand}}$, herein the materials with similar HSP δ have a high affinity for each other. Since 2008, several researchers have adopted HSP to analyze the mutual affinity between components of the systems [41,42,110,147,151,159–165]. Based on HSP, the interaction parameter between the PVDF and each diluent can be calculated by

$$\chi_{ij} = \frac{V}{RT}\left[(\delta_{D,i} - \delta_{D,j})^2 + 0.25(\delta_{P,i} - \delta_{P,j})^2 + 0.25(\delta_{H,i} - \delta_{H,j})^2\right] \quad (4)$$

where V is the molar volume of the diluent, R is the gas constant, T represents the temperature, and subscripts i and j represent PVDF and the single diluent, respectively. If the diluent is an organic solvent mixture, a mixing rule to calculate the HSP of the mixture is needed and a widely applied example is shown as,

$$\delta_{x,m} = \varphi_i \delta_{x,i} + \varphi_j \delta_{x,j} \ (x = D, P, H) \quad (5)$$

where φ is the volume fraction, while subscripts i and j represent different solvents [159]. As mentioned above, many researchers added a second diluent to decrease the compatibility of the systems and induce L-L phase separation, when only S-L phase separation occurs in the original system. HSP can also help to choose the nonsolvent additive. Among these research works, some people employed HSP to estimate the interaction, calculate the parameter χ, and draw the phase diagram of the corresponding polymer-diluent systems [110,159]. Recently, some people consider that the miscibility between the polymer and diluents should be related to another parameter [41,145,147,151,161,162], the so-called 'solubility parameter distance, Ra', which is calculated by the following equation,

$$R_a = \left[4(\delta_{D,i} - \delta_{D,j})^2 + (\delta_{P,i} - \delta_{P,j})^2 + (\delta_{H,i} - \delta_{H,j})^2\right]^{0.5} \quad (6)$$

According to Hansen, the smaller the Ra value is, the stronger compatibility between polymer and diluents is. Generally, HSP of common polymers and organics can be looked up in the HSP handbook [158], and they were provided based on abundant experimental data. With the help of HSP and Ra, diluent searching can be more effective and convenient. Whereas, people found that one's HSP can be very different based on different experimental methods, especially for polymers [158]. A change in the molecular weight or provider can result in completely various values. Besides, some component's HSPs are not covered by the HSP handbook, and it is would cost a lot of experimental effort to get a precise value. Besides, sometimes the parameter χ obtained by Eq. (2) cannot agree with data acquired by other experiment methods, such as binodal light measurement or light scattering. Therefore, some people tried to develop new methods for better representing the interaction between PVDF and the diluents. Since 2008, the author team of this manuscript has paid a lot of effort into this issue and has found several diluent systems that with PVDF can undergo the TIPS (L–L) process. Based on the research work, two criteria were proposed to estimate the interaction between PVDF and the diluents, which will be described below.

4.2.2. Dielectric constant

The dielectric constant, or also called relative permittivity, of a material, is its (absolute) permittivity expressed as a ratio relative to the vacuum permittivity [166]. In the chemistry field, the dielectric constant of a solvent is a relative measure of its chemical polarity. Considering adopting HSP is not always reliable to select a proper diluent for a specific polymer, such as PVDF, in 2008, Dr. Yang from our author team firstly found that dielectric constants could be regarded as an important parameter to measure the interaction among polar molecules, after studying the effect of the dielectric constant difference between PVDF and many diluents, including 1,4-butyrolactone, DMP, MS, GTA, PC, and DBP on the morphology of PVDF membranes [167–170]. According to these researches, the attractive interaction among PVDF molecules leads to the aggregation of PVDF and crystallization when the dielectric constant of PVDF is apparently larger than that of the diluent, accompanying membranes with incompact particle structure, as shown in (c)

and (d) of Fig. 6. When PVDF and diluents have similar dielectric constants, attraction and repulsion exist in a state of equilibrium, thus accompanying a channel-like structure. If the dielectric constant of PVDF is smaller than that of diluent, PVDF molecules crystallize difficultly in the diluent due to the repulsive interaction. Based on these, a novel diluent diphenyl ketone (DPK) which could result in an L-L phase separation with PVDF was selected for the preparation of PVDF membranes, and PVDF membranes with the bicontinuous structure were obtained without adding other components or a stretching process posttreatment. Recently, the dielectric constant criterion has been accepted by some researchers to estimate the polarity of the diluents [41]. People tend to combine the HSP and dielectric constant to analyze the interaction between the polar polymer and diluent when choosing a proper diluent for a specific polymer.

4.2.3. Molecular structure

Based on the HSP and dielectric constant, DPK was found to be a proper diluent for PVDF that could satisfy the five requirements mentioned in Section 4.1, and the binary phase diagram of the PVDF/DPK system is shown in Fig. 7 (a). Nevertheless, the L-L phase separation region of the system is a little narrow, so that the PVDF concentration is not able to be increased to more than 30 wt% if the resultant membrane with bicontinuous structure is needed. As described in Section 4.1, the compatibility of polymer and diluent directly affects the binodal temperatures and crystallization temperatures. When the compatibility becomes lower, the binodal curve is shifted to a higher temperature but the crystallization temperature is less influenced, which would result in an extension to the L-L phase separation region. The L-L phase separation region of the PVDF/DPK system is relatively narrow, which means the compatibility between PVDF and DPK is relatively good. As a subsequent work, Dr. Lin of our team found a new diluent called “diphenyl carbonate (DPC)” which’s structure is shown in Fig. 8. Dr. Lin compared the molecular structures of different diluents including DPK, DPC, and diphenylmethane (DPM). It is easy to find that the three diluents all have a homologous symmetrical diphenyl structure, but differ in functional groups between diphenyl structures. The polarity of DPK almost results from the stronger electron-withdrawing ability of the oxygen atom in the carbonyl group. In DPC, because of the existence of two oxygen atoms on the two sides of the carbonyl group, the electron clouds move away from the oxygen atom of the carbonyl group in contrast to DPK. Therefore, the polarity of DPC is a little weaker than DPK. In contrast, the polarity of DPM is much weaker than DPK and DPC due to its whole symmetrical structure and the methylene group. Besides, DPM cannot be compatible with PVDF even at a very high temperature, while DPK has relatively good compatibility with PVDF. Since the polarity of DPC is in the middle of DPK and DPM, the interaction between PVDF and DPC should be weaker than DPK but better than DPM. Based on the speculation, our team found that the PVDF/DPC has a broader L-L phase separation region and the corresponding monotectic point is increased to more than 50 wt%, as shown in Fig. 7 (b) [171]. Therefore, the diluent searching job can not only depend on combining HSP and the dielectric constant but also can be completed by modifying the diluent molecular structure [147,161].

Until now, the three criteria have been generally acknowledged to estimate the interaction between the diluents and polymer for selecting a proper diluent to prepare membranes via TIPS. Commonly, HSP, especially Hansen HSP as well as the derived Ra parameter, is more convenient and straightforward to apply, since it can be available for most cases. Nevertheless, if the polarity of the system is much higher, the dielectric constant may be more effective. Besides, if one would like to select a diluent from a homologous series, combining the molecular structure with the other two criteria can save much effort.

4.3. Experimental kinetics

Although thermodynamic phase diagrams have been regarded as a critical ingredient for understanding the membrane formation process, one must be aware that such diagrams represent only the equilibrium properties of a system, while the actual membrane formation is always very fast and quite far from an equilibrium process. The resultant membrane structure is highly dependent on the process kinetics, like polymer concentration, cooling rates, aggregation kinetics, and crystallization kinetics. As a result, studying the kinetics of the membrane formation seemed more necessary to control the membrane structure formation process and prepare a membrane with good properties.

4.3.1. Off-line speculation

So far, two kinds of methods have been applied to study the membrane formation process via TIPS. The most widely used approach is to speculate the membrane formation mechanism from the membrane structure and performance to understand the effects of different process factors, including the polymer concentration, cooling rate, evaporation time, and so on, on the membrane formation. Among these process factors, the polymer concentration is the most essential factor, and almost each membrane preparation research work evolves its effect on the morphology, pore size, and porosity of the resultant PVDF membranes for a specific PVDF-diluent system [172]. For a system involving the L-L phase separation, when the polymer concentration was lower than the monotectic point [as shown in Fig. 6 (I)], the PVDF membranes showed a more bicontinuous structure due to the L-L phase separation mechanism. In contrast, the structures of the PVDF membranes produced with polymer concentrations higher than the monotectic point were more spherical due to the S-L phase separation mechanism. The membrane pore size and porosity show a decreasing tendency with increasing PVDF concentration because the fraction of the polymer-lean phase was reduced during the phase separation [144,167]. For example, our group found that the monotectic point of the PVDF/DPC system was about 56 wt %. As PVDF concentration increased higher than the

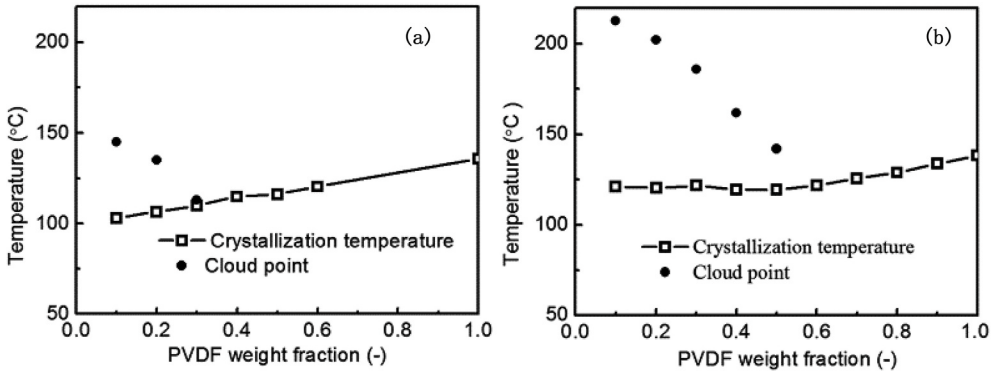


Fig. 7. Phase diagrams of different systems: (a) PVDF-DPK [167] (b) PVDF-DPC system [171].

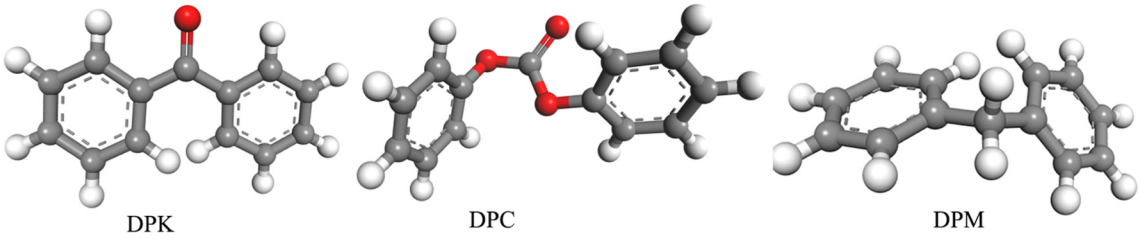


Fig. 8. Molecular structures of different diluents including DPK, DPC, and DPM.

monotectic point, the membrane structure gradually changed from bicontinuous to cellular until spherulitic. Also, the tensile strength gradually increased over the high concentrations while the porosity declined [171]. For the system only involving the S-L phase separation, the spherulitic structure is normally obtained for different initial polymer concentrations, and spherulites would become larger as the polymer concentration increased. Moreover, the increase of polymer concentration brings about a decrease in a space volume between spherulite but a promotion in the tensile strength [131,132,140]. For the system involving a crystallizable diluent such as $DMSO_2$, the pore size decreased from 3.5 μm to 1.5 μm with the PVDF concentration was changed from 10 wt % to 30 wt %, which is because higher polymer concentration resulted in higher solution viscosity. As a result, the crystallization of $DMSO_2$ was impeded, and smaller pores were formed [148].

The cooling rate (or quenching depth) is another critical factor influencing the phase separation process and crystallization of the PVDF-diluent system during the TIPS process, and two main effects should be noticed. Note that different cooling rates can be generated by different conditions, such as varying the quenching temperature or bore fluid temperature, or even changing the coagulation solution. Firstly, due to the phase separation and crystallization are both induced by the temperature change, different cooling conditions lead to different times for them to develop, which inevitably change the membrane structure; For the system involving an L-L phase separation process, an increase of cooling rate resulted in smaller pore size due to the shorter growth time of the polymer-lean phase [171]. For the system that only involving an S-L phase separation process, it was found that the higher quenching temperature provides a lower cooling rate and more time for nuclei to grow and results in a spherulitic structure with a bigger crystal size, providing more porosity and lower tensile strength [37,133,139]. And this always resulted in the low mechanical strength of porous membranes. As reported by Gu et al., when the membranes were quenched in ice water, the high crystal potential and cooling rate made the crystallization very fast without coarsening [127]. While at room temperature with relatively low cooling and crystallization rate, the size of the spherulitic structure with a more regular shape increased. Secondly, the heat transfer during the cooling process would certainly result in a temperature gradient in the casting solution, which always generates an asymmetric cross-section structure. For example, Li's group and Wu's group both experimentally found that the temperature gradient induced by the heat transfer can result in the pore size near the outer surface is usually smaller than that near the inner surface of the hollow fiber membranes [110,123]. Lang's group studied the addition of NaCl to the coagulation on the membrane structure [44]. The results revealed that with the addition of NaCl in quenching bath, rougher top surfaces could be obtained due to the decline of cooling rate with the addition of NaCl in quenching bath. This phenomenon can also been explained by modeling work, which will be mentioned in Section 4.4.

As described in Section 2.1, PVDF macromolecules can crystallize into at least four distinct phases, including α, β, γ, and δ [173,174]. The permeability and mechanical performance of the membranes are closely related to the crystalline phase-type and crystallization behavior of PVDF [126,174]. During the TIPS membrane preparation, PVDF crystallization is induced by quenching or cooling the melting solution blended with diluents, while diluent, polymer concentration, and quenching temperature (or cooling rate) are the crucial controlling factors determining the resulting crystalline form. In the TIPS process, PVDF usually crystallizes at the temperature at which the solution is unstable to allow the occurrence of a phase separation, which may induce the α phase even when the crystallization temperature is very low [19]. Therefore, it has been generally found that the most common polymorph of PVDF formed via TIPS is α-phase, and the degree of the crystallinity of PVDF can range between 30% and 70% [30,36,41,44,117,175–178]. Normally An increase in the PVDF concentration always promotes the crystallization temperature and crystallinity [36,116,177,179], and there are two reasons behind this. Firstly, the phenomena are due to the classical [180] thermodynamics phase equilibrium theories that diluents with smaller molecules (plasticizers, monomers, and insoluble additives) can cause melting and crystallization point depression in crystallizable polymers. Secondly, the number of nuclei of PVDF increases as the polymer concentration increased, resulting in high crystallinity [177].

The cooling rate and diluent also affect the PVDF crystal forms. Gu et al. obtained α-phase crystal by quenching a PVDF-DMP system to different temperatures above 40 °C. While the β-phase crystal was formed when the system was quenched into liquid nitrogen and crystallized for 24 h in a water bath of 25 °C since β-phase often appears when it crystallizes under 30 °C. In comparison, α-phase was formed for quenching between 80 °C and 140 °C and γ-phase is formed for a higher temperature of 165 °C [126]. While for some diluents such as benzophenone, which is solid at room temperature, α-phase PVDF membranes were formed even when the quenching temperature fell to − 8 °C [181]. In another study [130], it was found that a CO/DBP binary diluent promoted the formation of the α-phase, whereas the addition of GBA led to the formation of the γ phase. Meanwhile, two kinds of membrane cross-section morphologies, including the spherulite-like crystallite and sheaf-like, crystallite were obtained, and plenty of sheaf-like crystallites may exhibit good tensile strength and permeability for pure water. Shi et al. studied the effect of quenching temperature on the morphological and crystalline properties of PVDF membranes [182]. They found that when the quenching temperature was below crystallization temperature, the S-L phase separation dominated the process. The size of spherulites and inter-spherulite microvoids increased with an increase in the quenching temperature. The spherulites became more regular, and the crystallinity was decreased at a higher quenching temperature. Yang et al. from our research group discovered that the diluent also significantly affected the phase separation mechanism of the polymer–diluent system, thereby leading to differences in the morphologies and crystalline forms of membranes [170].

Because the PVDF microporous membranes derived from the S-L phase separation usually have loosely packed α-phase crystals, which would weaken the microporous membranes' strength. Adding some additives or altering the temperature and the property of the coagulation bath is effective to adjust the interaction between the polymer and the diluents to raise the crystallization and form β-phase polymorphism more efficiently, which are helpful to improve the mechanical strength and other properties of the resultant PVDF membranes [44,178,183,184]. Ma et al. from our research group examined the effect of four types

of nanoparticles [MMT, montmorillonite (MMT), SiO_2, $CaCO_3$, and polytetrafluoroethylene (PTFE)] with 1.0 wt% addition on the crystallization of PVDF, as well as the non-isothermal crystallization behaviors and non-isothermal crystallization kinetics of PVDF/nanoparticles composites [185,186]. The results were shown that the nucleation enhancement and the growth rate of the spherulites were decreased in the order of SiO_2>$CaCO_3$>PTFE > MMT. As a result, it was found that when the S-L TIPS process occurred, the supramolecular organization was formed because of the rejection of the diluent (DPK) by the growth of PVDF crystals. Thus, a higher-strength PVDF microporous membrane with network interpenetrating lamellar crystals was prepared. Due to the efficient nucleation of nanoparticles, uniform spherulites were formed [187]. He demonstrated that the symmetrical backbone chains favored the β-crystals with fiber-like structures via the TIPS method [188]. He also focused on the supramolecular organization of PVDF lamellae formed from the PVDF/MMT/DPK diluted system with PMMA additions via S-L TIPS [189]. As shown in Fig. 9, the supramolecular organization occurred in the PVDF/MMT/PMMA/DPK mixture, in which MMT nanoparticles dispersed in the dilutions and had an excellent nucleation agent for PVDF crystals (especially for the β-PVDF). The SEM pictures revealed that lamellar stacks exhibited branching and interpenetration further emphasized the pronounced advantage of the β-PVDF and nucleation effect. As for M3 and B of Fig. 9, a reinforcing network of PVDF lamellae offered the membrane the highest tensile strength and elongation at break.

Similarly, other nanoparticles like ZnO or TiO_2 have also been added to the PVDF/diluent systems but these research works focused more on membrane performance improvement. Some organic nucleating agents such as dicyclohexyl benzene amide (TMB-5), 2,2-methylene bis(4,6-tertiary butyl phenol) sodium phosphate (TMP-1), and 1,3: 2,4-di-p-methyl benzylidene sorbitol (DMLO) were also added into the PVDF/TBC (30 wt %)+DEHP (70 wt %) systems to test their effects on the structure and performance of the resultant membranes [143]. It turned out that the nucleating agents only influenced the S-L separation, and they can improve the crystallization rate, nucleation ability, and structures.

To summarize the PVDF membrane preparation with different process kinetics, polymer concentration, cooling rates, and diluent are all important to influence the crystallization process as well as the membrane morphology and performance. For commercial production of PVDF membrane, considering the coagulation medium is normally water and the membrane product cost, it is not very easy to make a wide range of adjustments to the polymer concentration and cooling temperature, and then the optimum polymer concentration and cooling temperature are normally easy to be found by a few experiments based on the rules mentioned above. Nevertheless, the effects of the various polymorphs and crystallization kinetics on membrane performance are more complicated, and this manuscript only focused on PVDF membranes prepared via TIPS. For readers who are interested in the topic can refer to Ref. [19] which systematically summarized PVDF crystals with different polymorphs and reviewed the crystallization and applications of different PVDF polymorphs in membrane separation.

4.3.2. *In-situ observation*

Except for the off-line speculation, people have established several in-situ techniques to directly observe and study the membrane formation process, including time-resolved light scattering, optical microscope with a hot stage, temperature-dependent Fourier Transform Infrared (FTIR) spectroscopy, and a membrane stiffness measuring device [139,149,190–195]. Among these techniques, the optical microscope with a hot stage is the most widely applied apparatus to obtain the cloud points of the phase diagram and observe the phase separation evolution mechanism including the formation and growth of the droplet and crystallization nuclei [149,171,190,194]. The time-resolved light scattering method was mostly adopted by Matsuyama's group to characterize the phase separation kinetics for different polymer-diluent systems [139,191–193]. The induced phase separation led to a change in the scattering intensity and based on the change, interphase periodic distance, and solidification rates can be measured, so that the phase separation mechanism (spinodal decomposition or nucleation and growth) as well as the membrane structure can be clarified and predicted [139,190–193]. Besides, the temperature-dependent FTIR

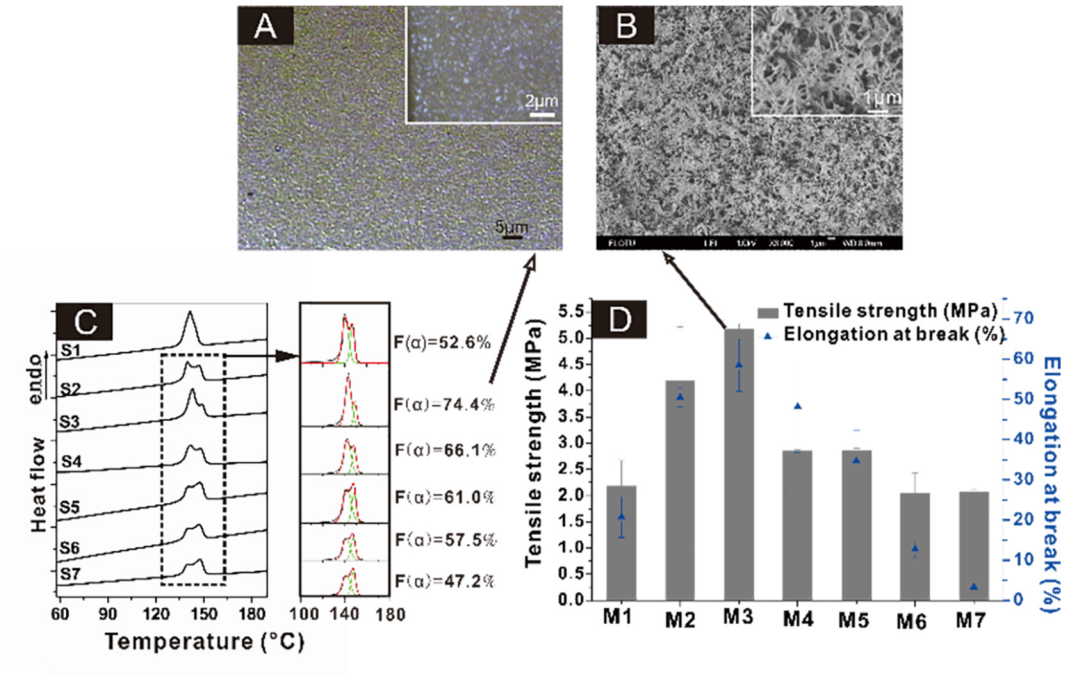


Fig. 9. Polarized optical micrographs (A), cross-sections of membranes (B), DSC melting traces (C), tensile strength, and elongation at break for membranes derived from PVDF/DPK diluted systems with or without MMT nanoparticles and PMMA. Note: the mark S1 to S7 represents the different compositions of the mixtures; readers interested may refer to Ref. [189].

spectroscopy can reflect the transformation of chain conformation and crystalline polymorphs during the membrane formation [149]. Although the researches primarily aforementioned focused on other polymers like PE or PP, other than PVDF, it still can be known that these in-situ techniques have their particular advantages in studying the membrane formation mechanism. However, two issues limit these techniques to get more popular. The first would be it is a little hard and time-consuming to conduct this in-situ observation research; the second thing is the link between the information provided by these observations and the resultant membrane structure and performance is still unknown, thus at present most of these techniques play an assistant verification role in studying the membrane formation via TIPS.

4.4. Dynamic modeling and simulation

The membrane formation via TIPS is a complex multiscale process governed by thermodynamic potential differences, transfer rates, and the kinetics of phase formation [196]. For simplicity, one might consider three key scales. At the molecular scale, solvent molecules and polymer segments interact and move on the nanometer (*nm*) and nanosecond (*ns*) length and time scales, respectively. At the mesoscale, phase domains and other ordered structures with characteristic length scales of 10–100 nm form over time scales of 10–1000 ns [197–199]. At the production scale, the membrane is normally several micrometers (μm) thick with pore sizes on the order of 100–1000 nm, and the formation operation may take several seconds (s). The final membrane structure is determined by phenomena occurring on each of these different scales. As reviewed in the above section, considering a large number of variables, process speed, and complexity of the interactions, the membrane formation process via TIPS is difficult to observe and characterize via experiment methods alone. Therefore, modeling is a particularly useful tool to significantly increase our understanding of membrane formation. Since the 1980s, many models on different scales, including macroscopic transport models, mesoscopic phase-field (PF) models, and molecular-scale simulations, have been proposed to describe the transfer phenomena and membrane formation in the evaporation and precipitation steps of the TIPS process [200]. Nevertheless, only a few of them were focused on the PVDF/diluent systems. The macroscopic transport models and the PF models represent "top-down" approaches, while the molecular-scale simulations are "bottom-up" in the sense that the system behavior is emergent from a set of first-principles particle interactions. In the following part of this section, a brief review of the model research of the membrane formation via TIPS is given according to the three spatiotemporal scales.

Fig. 10 displays a schematic representation of the casting polymer solution and the surrounding "bath" for the TIPS processes. As shown in the figure, the polymer/diluent (or called solvent) solution at a high temperature is immersed into a cooling bath after short evaporation of the diluent to induce a polymer concentration gradient in the casting solution; however, the concentration gradient normally only exists near the surface of the polymer solution. On the macroscale, one can easily understand that the membrane formation via TIPS should involve three closely related transport phenomena: fluid dynamics, heat transfer, and mass transfer. In physics and engineering science, these three transport phenomena normally occur simultaneously and the mathematical tools needed for describing them are similar [201]. The bases for these mathematical models are the fundamental physical and chemical laws, such as the laws of conservation of mass, energy, and momentum, and they are normally expressed by different kinds of continuity equations that can be regarded as a stronger, local form of conservation laws [202]. Since 1998, several transport modeling works have been conducted to describe the heat transfer and calculate the concentration profiles of different components during the TIPS process, to predict the morphology and properties of the membranes [200,203]. Lloyd et al. conducted a series of theoretical, modeling, and experimental work to investigate the effects of different process parameters on the membrane structure, focusing on PP/diluent systems [200,203–206]. The casting film and bath were treated as finite and infinite domains, corresponding to the different parts of Fig. 10. The variable l(t) denotes the (moving) position of the interface between them, continuity equations of the system can be written as

$$\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial z}(\rho v) \tag{7}$$

$$\frac{\partial \rho_2}{\partial t} + \frac{\partial}{\partial z}(\rho_2 v) = \frac{\partial}{\partial z}\left(\rho D_{23}\frac{\partial \omega_2}{\partial z}\right) \tag{8}$$

Here, subscripts refer to the diluent (2) and polymer (3), D_{23} refers to the mutual diffusion coefficient of the diluent, ρ and ρ_i are the mass densities of the membrane solution and Component *i*, respectively. ω_i denote the weight fraction of component *i*, respectively, and v is the mass average velocity. As shown in Eqs. (1) and (2), the evaporation model was based on Fick's diffusion law, and the quenching model employed Fourier's Law within the casting solution, as described by

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial z^2} \tag{9}$$

The component volume concentration and temperature profile evolution were calculated and proven to agree with the membrane microstructure and membrane thickness obtained from the corresponding experimental observation. At the same time, Barton and McHugh calculated the evolution of pore size gradients in the casting solution via a combination of the simple heat transport and kinetics of the droplet growth rate, which was the first TIPS modeling work to predict the membrane pore morphologies [207]. In 2006, Li and Krantz et al. incorporated Lloyd's model [203] with the polymer crystallization Avrami theory to predict spherulite sizes prepared by TIPS solid-liquid phase separation process as shown in Path (C) of Fig. 6 [208,209]. In

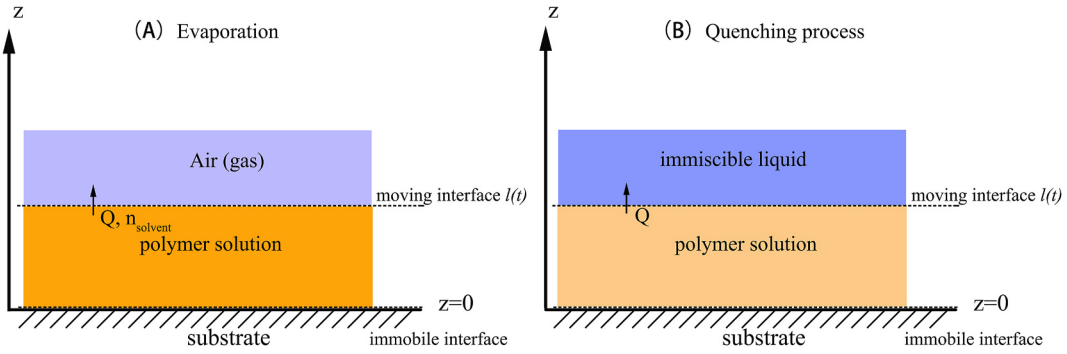


Fig. 10. Schematic of the casting polymer solution and the surrounding "bath" for the TIPS processes. A and B represent the evaporation during the quenching period, respectively.

2016, our group established a modified Maxwell-Stefan model to describe the mass and heat transfer in the air gap and coagulation bath stages of the TIPS process, taking into account a cylindrical configuration [210]. The model form was like Eqs. (5)–(7), and temperature and concentration fields of the system during the TIPS process were calculated to disclose the governing factor that determines the membrane asymmetry. In 2017, based on the Flory-Huggins theory, a specific diffusion formalism for dilute systems, and external mass transfer in free convection, a numerical model were developed by Bouyer et al. to investigate optimized operating conditions for the polyvinyl alcohol (PVA)/water system, because of an interest to use water as a solvent instead of traditional organic solvents [211].

On the mesoscale, the PF approach is a powerful tool for modeling membrane formation processes due to its ability to predict morphological and structural evolution during the phase separation, on time and length scales commensurate with the phase domains and their evolution [212]. PF approach evolves continuous field variables that represent volume-averaged molecular concentrations. Such field variables provide information such as the local composition within a particular phase at any location, as well as the positions of interfaces between unique phase domains, where concentration transiting from one value to another. Cahn-Hilliard (CH) equation to evolve conserved field variables represents a basic pillar of the PF technique. The CH equation is essentially a diffusion equation for multi-component mixtures that are informed by an assumed thermodynamic model for the free energy of mixing [213] as

$$\frac{\partial \varphi}{\partial t} = \nabla \cdot \left(M \nabla \left(\frac{\partial f_{mix}(\varphi)}{\partial \varphi} - 2\kappa \nabla^2 \varphi \right) \right) \tag{10}$$

Here, φ is a conserved field variable which, for polymer membrane formation research, is typically used to represent the local volume fraction of polymer in a polymer-solvent solution. The mobility of the field variable is represented by M, and the interfacial energy of the hetero-phase interfaces is scaled by the parameter κ. The thermodynamic energy of mixing f_{mix} can be chosen from a quantitative theoretical model (such as the FH model, in which $f_{mix}(\varphi) = \Delta G_m$), or based on a simpler, qualitative polynomial equation. The earliest application of the CH equation to specifically simulate the polymer membrane formation process via TIPS can be attributed to Caneba and Soong in 1985 [214]. They focused on a hypothetical polymer/diluent system and conducted one-dimensional simulations of the TIPS process in a polymer-solvent system at various locations relative to a cooling surface. Their results estimated pore sizes as a function of membrane depth away from the cooling surface and demonstrated the versatility of this approach. After that, Chan et al. conducted two-dimensional simulations and investigated the temperature-induced spinodal decomposition of polymer-solvent systems quenched into the unstable region of the phase diagram [215,216]. The studies assumed isotropic quenches and focused on the growth and coarsening rates of the hypothetical polymer-rich and polymer-poor phases. Later, Lee et al. applied PF techniques to understand the effect of temperature gradients (or anisotropic quenches) on the phase morphology, with one-dimension and two-dimensions [217,218]. Anisotropic domain morphologies were found to depend on the rate of quenching in both the lower and higher temperature regions. Kukadiya and Chan et al. conducted simulations to understand how thermal diffusion influences the non-uniform temperature fields during the spinodal decomposition [219,220]. In 2015, based on the polymethyl methacrylate/cyclohexanol system, Matsuyama's group conducted three-dimensional simulations of the TIPS process, including the effects of a polymer concentration gradient that leads to an anisotropic structure [221]. Recently, Millett et al. conducted large-scale three-dimensional computer simulations based on phase field theory to investigate the TIPS process for the PVDF/DPC system and predict the complex networks of porosity. The effect of different heat transfer situations including isotropic and anisotropic quenches on the phase separation process was studied to understand how gradients in the characteristic domain size develop for varying conditions. Although the domain size is an order of magnitude smaller than typical polymer sheet membranes, this work demonstrated the simulation tool is fast becoming a valuable tool to predict pore structure throughout an entire membrane cross-section [222].

Thirdly, because the molecular structure of the systems has a significant effect on the membrane formation and the aforementioned two methods (transfer and PF models) treat atoms and molecules implicitly, some microscale molecular-scale simulation method, which includes molecular dynamics (MD) and dissipative particle dynamics (DPD), has particular superiority in simulating the membrane formation due to trajectories of these individuals and the molecular structure information can be directly involved. Outputs of molecular simulations are representations of structures, which can be analyzed in the context of phenomena of interest, such as membrane structure and pore size. Among the two simulation methods, the MD method was firstly proposed in 1953 [223], and now has a practical limit of ~10 ns on the time scale and ~10 nm on the length scale of the phenomena that may be studied, even with an advanced and powerful computer. Considering that a complete phase inversion membrane formation process normally involves time scales on the order of seconds and length scales on the order of microns, it's clear that an MD simulation will not be able to follow a complete process. Therefore, people don't adopt the MD method to simulate the phase separation due to its limitation in Spatio-temporal scales but tend to use it to reveal the interaction between the system components and calculate some key thermodynamic parameters such as solubility parameters [224], to assist and verify the experimental results to optimize the membrane preparation parameters. For example, Matsuyama's group employed a combination of experimental results and MD simulations to investigate the mass transfer between the extruded solvent propylene carbonate (PC) and PVDF/DPC solution by using a triple-orifice spinneret in the TIPS process, because the MD system employed the full atomistic potential field [225]. The MD calculation results elucidated the mutual penetration of PC and the PVDF solution from the contacting interface occurred and increased as increasing the contacting time, which subsequently affected the phase separation mechanism of the PVDF solution near the contact interface and the resultant membrane structure.

From 2009 to 2020, our group has firstly established a simulation methodology based on a simulation method dissipative particle dynamics (DPD) and published a series of papers on the investigation of the membrane formation process via TIPS [226–228]. The DPD can be regarded as a coarse-grained molecular dynamic simulation method and based on it, different membrane preparation conditions, including quenching temperature, initial polymer concentration, additives, have all been covered to get a full understanding of the PVDF membrane formation process via the TIPS process. We then focused on the PVDF/DPC system to study the effect of the interface mass transfer between the casting film and the coagulation bath on the TIPS process. Detailed information such as phase separation morphologies, domain size evolution, and pore size distribution that could be connected to experimental observation was provided. We found that membrane formation is a complex multiscale process because the temperature gradient governed by the heat transfer on the macroscale determines the phase separation period, and the compatibility between the components, which actually is resulted from the atomistic force field on the microscale, also identify the phase separation rate and morphology evolution kinetics on the mesoscale. The final membrane structure, as well as performance, was determined by phenomena occurring on different scales. Afterward as mentioned above, we established a modified MS model to obtain the concentration and temperature field of the casting solution in the air gap and coagulation bath stages [229]. Subsequently, a multiscale methodology that based on (DPD) simulation and the results of macroscopic mathematical models were established to obtain a multiscale understanding of the membrane formation process

via TIPS, also considering the PVDF/DPC system [230]. The simulation results indicated that the temperature gradient in the polymer solution resulted from the heat transfer across the interface had a significant influence on the phase separation process, whereby different parts of the polymer solution possessed different cooling rates and coarsen time, which resulted in a microporous membrane with anisotropic structure.

Fig. 11 displays a summary of the modeling research reviewed in this section. As shown in the figure, the external field of the polymer solution was changed, which brought a series of changes, including temperature and concentration change, phase separation, and phase inversion (polymer solidification), which determines the membrane structure. The aforementioned three models have their advantages in describing phenomena on different scales. Firstly, a combination of the phase diagrams and transport models can provide a relatively accurate concentration and temperature field as well as the transport path which can be depicted by plotting the temperature and concentration onto the phase diagrams. Whereas, this model is limited in directly reproducing the phase separation structure. In contrast, PF methods are very powerful in displaying the phase separation evolution and can reach the real scales. Nevertheless, molecular structure information cannot be involved. Finally, molecular simulation (a representative is DPD) is intrinsically different and assumptions are made about the forces or energetic interactions between segments of matter, which means theoretically, the membrane formation process can be reproduced in computers. However, due to the limitation of the computational power, the scales of the molecular simulations are still far from the real membrane. Based on the progress of the latest modeling research, it can be predicted that in the future, appropriate multiscale modeling with efficient coarse-grained potentials obtained from the molecular tools and covering advantages of large-scale modeling methods may be developed to reproduce the pore structures on certain systems of industrial interest.

4.5. Hydrophilic modification

Due to its excellent chemical, thermal, and mechanical stabilities, PVDF has become an attractive material for preparing polymeric membranes. However, when applied in the filtration processes such as biological effluent treatment, protein purification, and bacteria filtration, *etc.*, the PVDF membranes prepared via TIPS probably suffer from membrane protein-fouling due to the low surface energy and hydrophobic characteristics, thereby, decreasing the membranes' effective lifetime and causing more operation costs of the replacement and maintenance of the membrane modules. It is generally believed that an increase in hydrophilicity results in better membrane fouling resistance. Different modification ways have been explored to tailor the surface engineering of the PVDF membrane in recent years. Two commonly applied ways are post-treatment (surface modification) and hydrophilic modification by blending.

4.5.1. Post-treatment

Surface post-treatment is usually achieved by coating or grafting a functional layer on the prepared membrane surface, in which most of the modified sites occur on the top and/or bottom surface of the membranes. It should be noted that the surface modification methods can be applied to PVDF membranes with various structures obtained via different methods, including TIPS and NIPS. However, since this section only focuses on the PVDF membranes prepared via TIPS, herein we only summarize the surface modification to the PVDF membranes fabricated via TIPS.

Surface coating is a cost-effective, energy-efficient, and relatively simple way to improve the surface hydrophilicity of the PVDF membranes through coating or depositing a thin functional hydrophilic layer onto the membrane surface, and can be used in large-scale industrial applications. Table 5 lists a summary of the key results of the hydrophilic modification research work adopting the surface modification method. Among the various hydrophilic materials, cholic acid [231], polydopamine [155], and TA-PVP (tannic acid (TA)-polyvinylpyrrolidone (PVP)) [232] were coated on the PVDF membranes by immersing the pristine PVDF membranes into the solutions and the interaction between the membrane surface and the coating layers was physical adsorption interaction. For example, deposition of polydopamine is a typical surface hydrophilic method, and the interaction between the polydopamine layer and the membrane surface is normally attributed to adhesion derived from amino, imino, hydroxyl and catechol functional groups and π–π interactions [155]. For poly (vinyl alcohol) (PVA) [178,233] and polyethyleneimine (PEI) [234], the modification process evolved cross-linking reactions between the coating components while the binding to the PVDF membranes were still physical forces. For block copolymers (BCPs), our group constructed a BCP (poly(styrene-b-4-vinylpyridine), denoted as PS4VP)) PS4VP on the surface layer

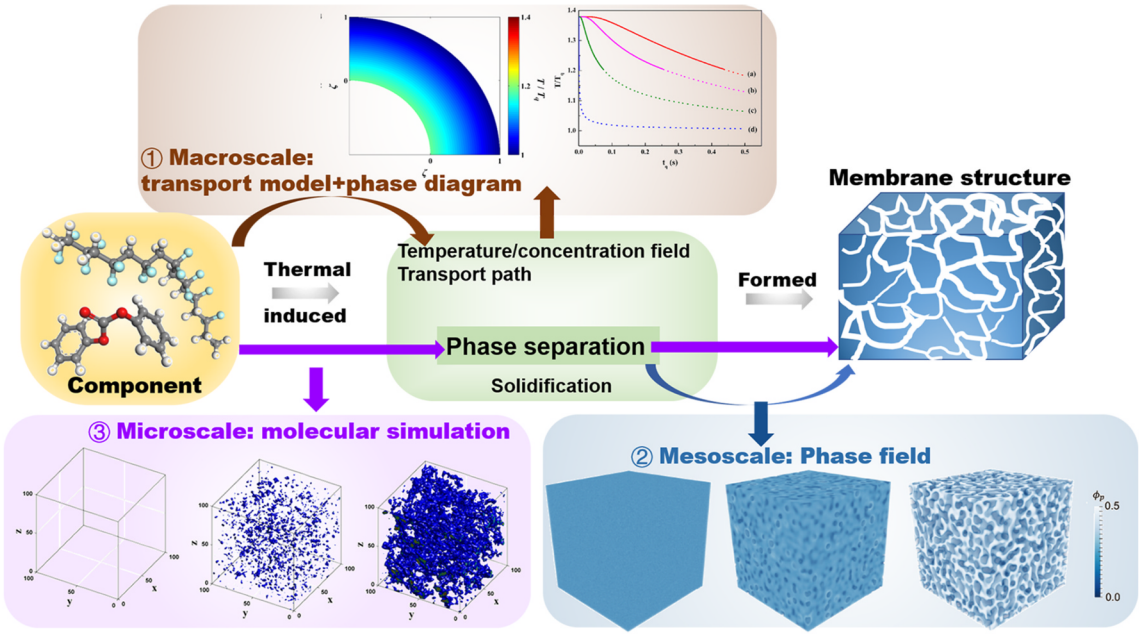


Fig. 11. A summary of the modeling research on the membrane formation via TIPS.

of a porous PVDF membrane support via a dip-coating and SNIPS (a method combining the BCP self-assembly and NIPS) process [235]. Several indices were mostly applied to reflect the effect of the hydrophilic modification, such as the minimum static contact angle, pure water flux (PWF), operation flux, and the flux recovery ratio, as listed in Table 5, although obvious diversities exist in the data of the indices for the different surface coating modifications. Considering the differences of the cost and treating systems, it is hard to easily say which material is better. However, it was indicated that the main problem of the surface coating was the instability of the coated layer which could be washed away along with the operation and cleaning process due to the relatively weak physical adsorption interaction between the PVDF membranes and coating layers [16]. As a result, stability tests were conducted in most of the works mentioned above to prove the coating's durability [231,232,234].

Compared to the coating procedure, surface grafting has been more applied to modify the PVDF membrane surfaces through covalent bonding interactions between the grafted chains and the membrane. Covalent attachment of graft chains on the membrane surface avoids their delamination and offers long-term chemical stability of grafted chains, in contrast with the physical surface coating method [243]. Surface grafting can be achieved by versatile means, including "grafting from polymerization" and "grafting to method". The first means monomers are polymerized onto the membrane surface through an initiation process, while the second indicates that polymers are directly immobilized on the membrane surface through coupling reactions [244,245].

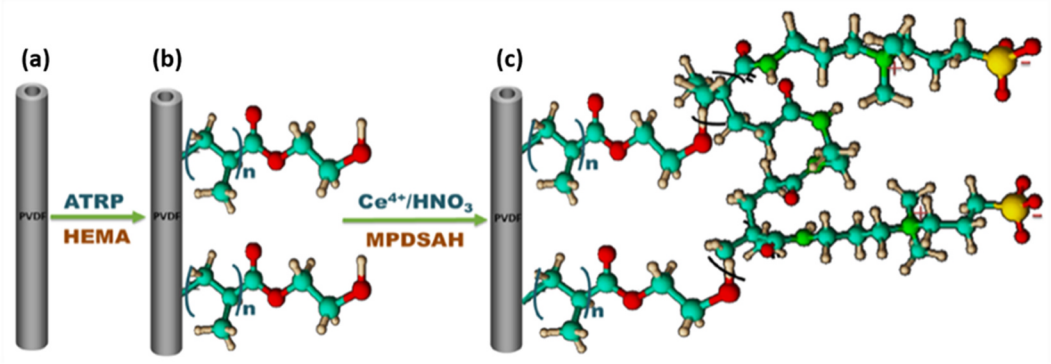
"Grafting to" methods possess an obvious advantage that the grafting polymer can be synthesized previously before grafting. However, the grafting degree on the membrane surface might be limited due to the well-known low reactivity of the coupling reaction, which is not always enough for industrial applications despite the precise control of the graft chain structure. Table 5 also summarized the materials adopted to modify the PVDF membranes via the "grafting to" method.

Rather than the "grafting to" method, more people applied the "grafting from polymerization" to modify the PVDF membranes prepared via TIPS. The process of "grafting from" polymerization consists of two steps: (1) attachment of initiators onto surfaces and (2) polymer growth from initiator sites [246]. Versatile initiation methods for "grafting from" polymerization of monomers onto the surface of a membrane include free radical graft polymerization, "high energy irradiation"-induced graft polymerization, plasma-induced graft polymerization, and combined methods [244]. "Grafting from" has more choices to control the grafting degree, chain lengths, and structure by varying different initiating means, monomer, concentration, temperature, solvent, additive, and other reaction conditions.

According to Table 5, poly (acrylic acid) (PAAc) was widely applied to grafted onto the PVDF membranes by a free radical graft polymerization by an alkaline pretreatment [238] or exposed in Co^{60} irradiation [247], and then PEG or a Ni layer was immobilized onto the PVDF-PAAc membranes through different reactions. The modified membranes presented 100% flux recovery and reduced fouling propensity when filtrating 0.1 g/L sodium alginate solution. It should be noted that our group has conducted intense studies on the hydrophilic modification of PVDF membranes via the "grafting from polymerization" method. Firstly, hollow fiber PVDF membranes prepared via the TIPS process were modified via a surface alkaline treatment initiated-ATRP (atom transfer radical polymerization) with zwitterionic sulfobetaine to improve the hydrophilic and anti-fouling properties since there is strong hydration existing between zwitterionic monomers and water molecules [239,240]. Whereas the alkaline treatment degrades the PVDF membrane and lowers its original mechanical strength, as a result, a two-step graft polymerization method, which can be seen in Fig. 12, was proposed to enhance the mechanical property of the PVDF hollow fiber MF membrane and increase the surface grafting amount of sulfobetaine polymer simultaneously. The reaction kinetics of the two-step graft polymerization was investigated further and the conditions of the preparation process were adjusted to elucidate the internal relationship between kinetic chain length and grafting amount of the sulfobetaine polymer. As a result, the modified PVDF membrane showed stable anti-fouling, permeating, and hydrophilicity performance, as listed in Table 5. Subsequently, we found that based on our previous work [236], the PVP immobilized on/in the PVDF membrane attracted more sulfobetaine monomer into the membrane interior for subsequent graft polymerization onto the membrane surface and subsurface, and then a thick poly(sulfobetaine) grafting layer was able to be formed [248,249]. The shielding effect of type 1-1 electrolyte on the intra- and/or inter-chain associations of poly(sulfobetaine) chains was superior to that of other electrolytes, which contributed to the completely stretched structure of sulfobetaine polymer chains and a thick poly(sulfobetaine) layer with a thickness of 4.8 ± 0.2 μm, which resulted in a novel hollow fiber UF membrane with good performance. Protein separation by the novel membrane could be effectively achieved by isoelectric focusing of one component, as shown in Fig. 13.

Table 5
A summary of key results of the hydrophilic modification research work adopting the surface modification method.

Modification method	Reagents	Hydrophilic modification effects			
		Pure water flux (L/(m^2·h·bar))	Minimum static contact angle (°)	Operation flux (L/(m^2·h·bar))	Flux recovery ratio
Surface coating	cholic acid [231]	8500	82	–	–
	TA-PVP [236]	15000–16000	52	2819 (oil/water emulsion)	96.5%
	Polyethyleneimine (PEI) [234]	10782	16	–	–
	poly (vinyl alcohol) (PVA) [178,233]	~1400	64	20–40 (100 ppm of BSA solution)	–
	polydopamine [155]	3855.6	62	2600–2900 (1000 ppm of BSA solution)	≥88%
	PS4VP [235]	90.8 (MWCO = 74 kDa)	70	–	–
Surface grafting to	PVP [236]	650	77	–	≥85% (100 ppm of BSA solution)
	poly (ethylene glycol) dimethacrylate (PEGDMA) [237]	≥1400	52	≥1200 (2000 ppm of BSA solution)	–
Surface grafting from	poly (acrylic acid) (PAAc)-PEG [238]	~1200	~80	~1100 (2000 ppm of BSA solution)	>95%
	PAAc-Ni	–	47.1	(100 ppm sodium alginate solution)	100%
	zwitterionic sulfobetaine [239–242]	~1350	22.1	~1300 (1000 ppm sodium alginate solution)	~98%



Radical formation:
$ROH + Ce(IV) \rightarrow RO\cdot + Ce(III) + H^+$
Initiation:
$RO\cdot + A \rightarrow RO\text{-}A\cdot$
Propagation:
$RO\text{-}A\cdot + A \rightarrow RO\text{-}A\text{-}A\cdot$
$RO\text{-}A\text{-}A\cdot + A \rightarrow RO\text{-}A_2\text{-}A\cdot$
$RO\text{-}A_{n-1}\text{-}A\cdot + A \rightarrow RO\text{-}A_n\text{-}A\cdot$
Termination:
$RO\text{-}A_n\text{-}A\cdot + \cdot A\text{-}A_n\text{-}OR \rightarrow RO\text{-}A_n\text{-}A\text{-}A\text{-}A_n\text{-}OR$
Oxidative termination:
$RO\cdot + Ce(IV) \rightarrow$ Oxidative product$+ Ce(III) + H^+$

ROH: PVDF-polyHEMA A: MPDSAH

Fig. 12. Schematic diagram for the modification of PVDF MF membrane with sulfobetaine 3-(methacryloylamino) propyl-dimethyl- (3-sulfopropyl) ammonium hydroxide via a two-step graft polymerization [239].

4.5.2. Hydrophilic modification by blending

Hydrophilic modification by blending is usually used to achieve the desired functional properties along with the membrane preparation, therefore the preparation and modification process can be accomplished in a single step. Compared with surface post-treatment, blending modification is a more practical way that can be applied to industrial-scale production [6,21]. Polymer materials and inorganic nanoparticles are unusually used for blending modification, which will be summarized in Table 6.

As shown in Table 6, some common hydrophilic polymers such as PVA and EVOH have all been adopted to blend with PVDF to improve the resultant membrane performance. Although sometimes the water flux was increased and the contact angle was decreased, the mechanical properties of the blend membranes were worse than that of the pristine PVDF membrane due to the poor compatibility between the hydrophilic polymers and PVDF, which demonstrated that the compatibility between PVDF solution and the hydrophilic polymer is the key issue for the modification, and the diluent also plays a significant role. To overcome this issue, some amphiphilic copolymers such as p(MMA-MPDSAH) have been synthesized to replace linear hydrophilic polymers. The hydrophobic chain segments of the polymer provided good compatibility with the PVDF matrix while the hydrophilic chain segments extended on the

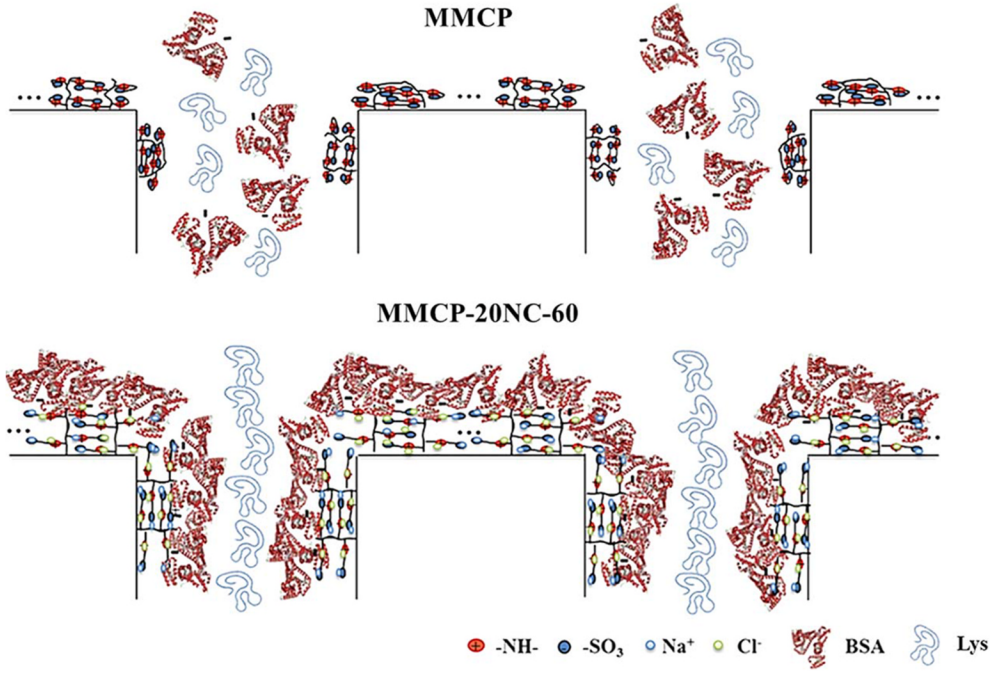


Fig. 13. Schematic models of BSA and lysozyme (Lys) transport through the MF membrane (MMCP) and UF membrane (MMCP-20NC-60) at pH = 10 [244,248].

surfaces and inner channels of the porous membrane which bring long-term hydrophilicity.

Recently, nanomaterials have been very popular for blending into the polymer matrix to bring in some magical effects. As listed in Table 6, nanoparticles such as TiO_2 [254], SiO_2 [255], ZnO [39] et al. have all been employed to distributed in the PVDF matrix and improve the membrane performance. Similar to the hydrophilic polymers, the addition of the nanoparticles cannot only alter the phase separation mechanism but also affect the dispersibility of the polymeric matrix due to the compatibility issue. Thus some people developed modification methods to lower the huge surface energy difference of two phases [150,175]. Besides, oxidized multi-wall carbon nanotubes (O-MWCNT) have also been used to prepare hybrid membranes [153]. Fig. 14 shows that the oxygen-containing groups in O-MWCNTs benefited them to form hydrogen bonds with water molecules, and the surface hydrophilicity of the resultant membranes was improved. In addition, the derivative of graphene oxide (GO), SiO_2@GO nanohybrid, was fabricated and employed to synthesize PVDF/SiO_2@GO nanohybrid membranes via TIPS for the first time also with DBP as the diluent [154]. With the addition of PVDF/SiO_2@GO nanohybrid, the resultant membranes exhibited improved surface hydrophilicity and antifouling ability, even better than that with O-MWCNT as the addition.

In summary, during the past two decades, different hydrophilic modification methods have been proposed to enhance the hydrophilicity of the membranes, so as to improve the anti-fouling performance. Some properties including the PWF, water contact angle, protein adsorption capacity, flux, and flux recovery ratio were often employed to characterize the hydrophilicity. Whereas for industrialization, people care more about the anti-fouling property and long-term stability rather than the hydrophilicity, and it is clear that they are not completely equivalent. However, the long-term stability test and flux recovery ratio have been neglected by some of the previous researches, and this should be paid attention to in future research work. Also, the relation between the anti-fouling property and the membrane structure should be figured out in the future.

5. Advanced manufacturing of PVDF membrane via TIPS and its applications

Since the 1990s, PVDF membranes and membrane modules have gradually been realized in industrial production and applied in the water treatment of industrial wastewater and municipal sewage. In contrast to the lab-scale research, the development of commercial membrane fabrication cannot be fully obtained due to commercial consideration. The available information mainly includes membrane preparation procedure, membrane performance as well as some successful applications. This section mainly introduces typical advanced membrane performance. In addition, taking the situation of Beijing Scinor Membrane Technology Co. Ltd. (BSMT) as a typical representative, advanced manufacture of the PVDF membranes fabricated via TIPS and the corresponding applications have also been introduced.

5.1. Advanced manufacture of PVDF membrane prepared via TIPS

At present, fabricating PVDF membranes via the TIPS process has been successfully industrialized and commercialized by different manufacturers, including Asahi Kasei Group (Japan) [113,114,256], Toray Membrane (Japan) [257], Memstar (Singapore) [258] and Beijing Scinor Membrane Technology Co. Ltd. (China) [259,260]. The main parameters of their MF/UF membrane products have been summarized in Table 7. As listed in Table 7, hollow fiber membranes are more popular for practical water treatment since the productivity and the efficiency of the separation process can be largely improved due to the large surface area per unit volume of the fiber module [22,261]. Different membrane modules including pressurized, submerged, and MBR (membrane bioreactor) have been developed and widely applied in drinking water production, industrial usage, wastewater treatment, and pretreatment of desalination [262,263].

Limited information can be obtained based on the patents published by Asahi Kasei Group (Japan) [113,114,256], Toray Membrane (Japan) [257], and Memstar (Singapore) [258]. Firstly, for Asahi Kasei Group, it was reported that they produced PVDF membranes with refined three-dimensional network structure by adding silica nanoparticles which would be dissolved by NaOH solution later into PVDF-DBP system [114]; secondly, Toray Membrane adopted a method to prepare hollow fiber PVDF membranes that comprised extruding PVDF resin solution into a cooling bath and solidifying the extruded solution, wherein the casting solution contained PVDF whose fraction was around 20–60 wt%, a hydrophilic porosity-giving agent such as PVP whose fraction was 1–30 wt%, and a solvent of PVDF such as γ-butanediol or NMP. The temperature of the casting solution had a range of 80–175 °C [257]. Thirdly, as for Memstar, the casting solution that consisted of PVDF, ZnO nanoparticles, and an organic solvent mixture that contained DOP, DBP, and DMAc was formed at 180 °C and then put into a water bath at 20 °C

Table 6
A summary of key results of the hydrophilic modification research work adopting the blending modification method.

Blending material species	Reagent	Hydrophilic modification effects			
		Pure water flux (L/(m^2·h·bar))	Minimum static contact angle (°)	Operation flux (L/(m^2·h·bar))	Flux recovery ratio
Polymer materials	PVA [250]	1600	57	–	91.1% (1000 ppm of BSA solution)
	A zwitterionic copolymer of p(MMA-MPDSAH)[a] [251]	–	<50	–	–
	poly(ethylene-co-vinyl alcohol) (EVOH) [252]	449.11	43		87.3% (1000 ppm of BSA solution)
	TD-A [253]	1944	56.8		~85% (500 ppm of BSA solution)
Inorganic nanoparticles	TiO_2 [254]	105.1	>100	–	–
	SiO_2 [255]	120	–	–	–
	SiO_2+3-aminopropyltriethoxysilane (APTES) [175]	320	–	160 (500 ppm of BSA solution)	93.8%
	oxidized multi-wall carbon nanotube (O-MWCNT) [153]	230.7	100	160 (500 ppm of BSA solution)	82.7%
	SiO_2@GO nanohybrid [154]	182.6	86	100 (500 ppm of BSA solution)	~80%
	SiO_2 [150]	920.6	101	–	–
	ZnO [39]	70.9	68.3	–	94.9% (300 ppm ovalbumin solution)

Note: Superscript '[a]' is the abbreviation of poly(methyl methacrylate [3-(methacryloylamino)propyl]dimethyl(3-sulfopropyl) ammonium-hydroxide).

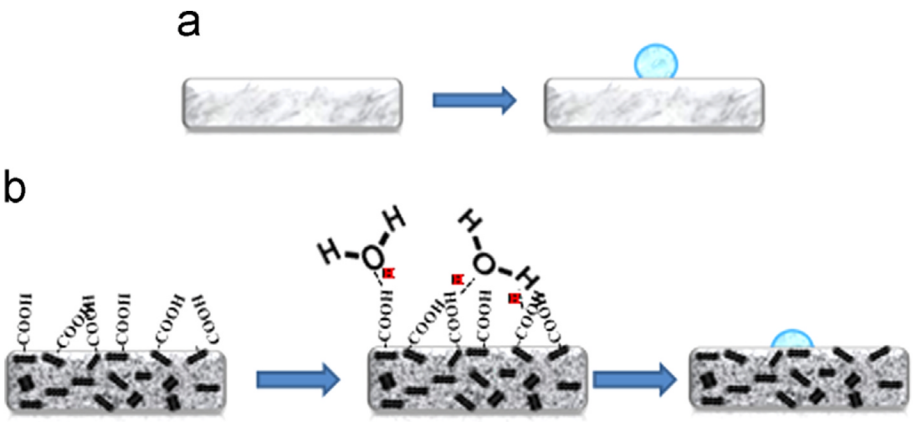


Fig. 14. The schematic diagram of O-MWCNTs' effect on PVDF/O-MWCNT membranes: (a) without O-MWCNTs and (b) with O-MWCNTs [153].

Table 7
A manufacturer and parameter summary of commercially available PVDF membrane fabricated via TIPS.

Manufacturer		Asahi Kasei	Toray	Memstar	Scinor
Membrane properties	Nominal pore size (μm)	0.1–1	0.01	0.01–0.6	0.1
	Shape	Hollow fiber	Hollow fiber	Hollow fiber	Hollow fiber
Operating Limits	Operating temperature range (°C)	0–40 °C	0–40 °C	5–45 °C	1–40 °C
	Normal operating TMP/(kPa)	<300	<300	≤120	≤300
	Operating pH range	1–10	1–10	1–12	1–11
	Cleaning pH range	1–14	0–12	1–14	1–13

to get solidified. Afterward, the organic solvents and nanoparticles were removed by ethanol and sulfuric acid solution, respectively. The membranes have three-dimensional porous structure, the tensile strength can attain 11 MPa, while the pure water flux reached 2000 L/(m^2·hr·bar). However, more information about the membrane production of the three companies is hardly obtained based on the web due to some commercial considerations. In the following part, progress about membrane fabrication and membrane module development conducted by BSMT will be introduced and described as a typical representative for the PVDF membrane industrialization. This is because that our group who are from Beijing Key Laboratory of Membrane Materials and Engineering of Tsinghua University have paid lots of effort to prepare PVDF membranes with desirable performance via TIPS since 2008, and some of the accomplishments, as well as key results, have been underlined in Section 3. In addition, in 2009, BSMT has established cooperation with us and succeeded to fabricate a PVDF hollow fiber membrane with good performance in full-scale, based on our previous research achievement of the TIPS (L-L) process and hydrophilic modification.

Fig. 15 shows a schematic diagram of the PVDF hollow fiber membranes preparation process developed by BSMT. As shown in the figure, the powder of polymer and diluents were mixed and then added into a twin-screw extruder by a single screw combined with an electronic balance. After heated and mixed in the twin-screw extruder for 2–3 min, the mixture of PVDF and diluents were spun into hollow fiber through a spinning nozzle and then entered into the water to seduce an L-L phase separation. And then the diluent was extracted from fiber with solvent (ethanol) which would be later collected, purified, and recycled (more than 98.5%) back into the process. Due to the adoption of Soxhlet extraction - cooling crystallization - distillation purification cycle process, the diluents could be almost fully recycled, which realized 'zero liquid discharged to the environment to make the whole manufacturing process more environmentally friendly [264]. The structure of the fabricated PVDF hollow fiber membrane product was presented in Fig. 16, which shows a bi-continuous structure without any skin layers. The permeability in pure water and tensile strength are higher than 1200 L/(m^2·hr·bar) and 6.0 MPa, respectively. Moreover, the PVDF hollow fiber membrane product shows excellent rejection of bacteria and viruses. Based on our experience in the industrialization of the PVDF membrane fabrication and module development, it has been found that a membrane process that is possible to industrialize must have these features: (1) Process control of the preparation should be easy to realize and be stable; (2) On the premise of ensuring the quality of the products, the process should be as simplest as possible; (3) Standards for the product quality much be identified and developed.

5.2. Applications of the PVDF membranes prepared via TIPS

Variable characteristics of the membrane would be required by different industries, such as the higher flux requirement of municipal wastewater advanced treatment, the higher chemical tolerance requirement of industrial wastewater treatment, the safety and the intercept performance requirement against bacteria and viruses of drinking water purification or even some special requirements like ozone tolerance of the membrane for some technical processes. Based on the unique adhesive formula and innovative technology of encapsulating, different membrane modules, including pressurized UF modules, submerged UF modules, and MBR modules, have been designed and assembled by BSMT according to the characteristics of the prepared PVDF membrane and different application situations. During the last 10 years, the PVDF hollow fiber membranes fabricated via TIPS (L-L) have been applied in several applications that cover almost all industries due to their excellent performance, and the total treated water has been achieved 5,000,000 tons per day. Table 8 lists the latest and typical application of the membrane modules from BSMT applied in different water treatment projects during the recent decade. This table shows that the TIPS UF membranes have a wide range of applications for different conditions, and they can be operated with a relatively higher flux even under poor feed quality.

As the core material of the MF/UF technology application introduced by Section 1, PVDF membranes have been widely applied in wastewater treatment and have almost occupied half of the whole MF/UF membrane market. According to reports from Asahi Kasei Group [265] and BSMT [266], the PVDF membranes prepared via the TIPS (L-L) process are quite resilient on the whole, with lifetimes potentially spanning over a decade. However, it is reported that normally service lives of the PVDF plat and hollow fiber membranes are around 5–7 years and 3–5 years long, which means that in the next few years, a huge number of waste

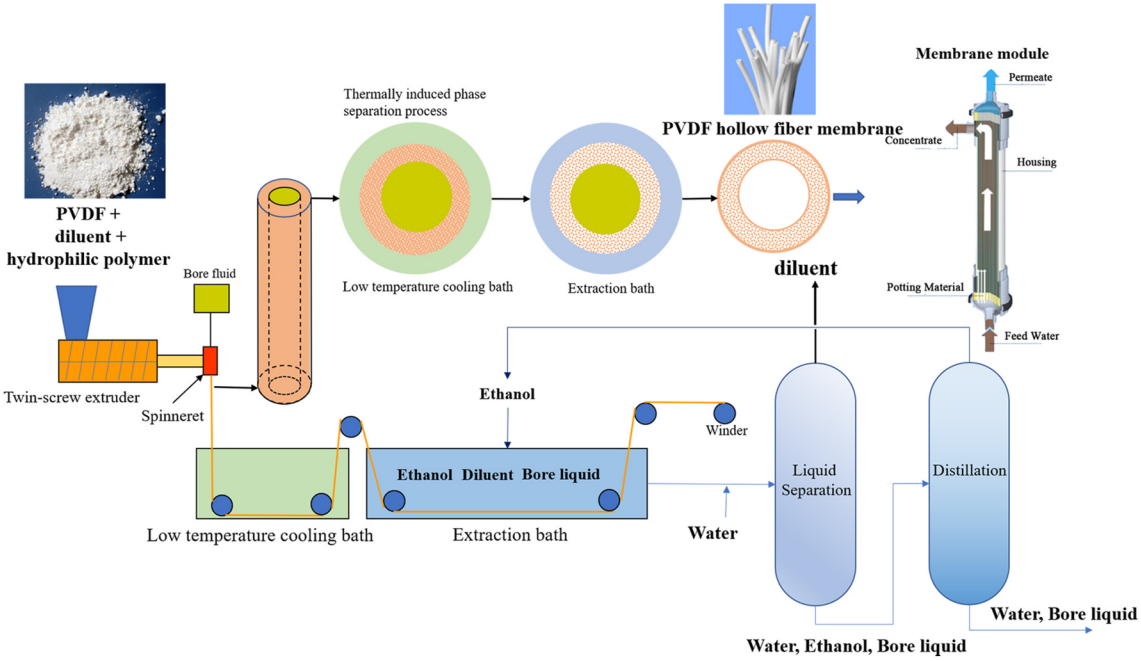


Fig. 15. A schematic diagram of the PVDF hollow fiber membranes preparation process developed by BSMT.

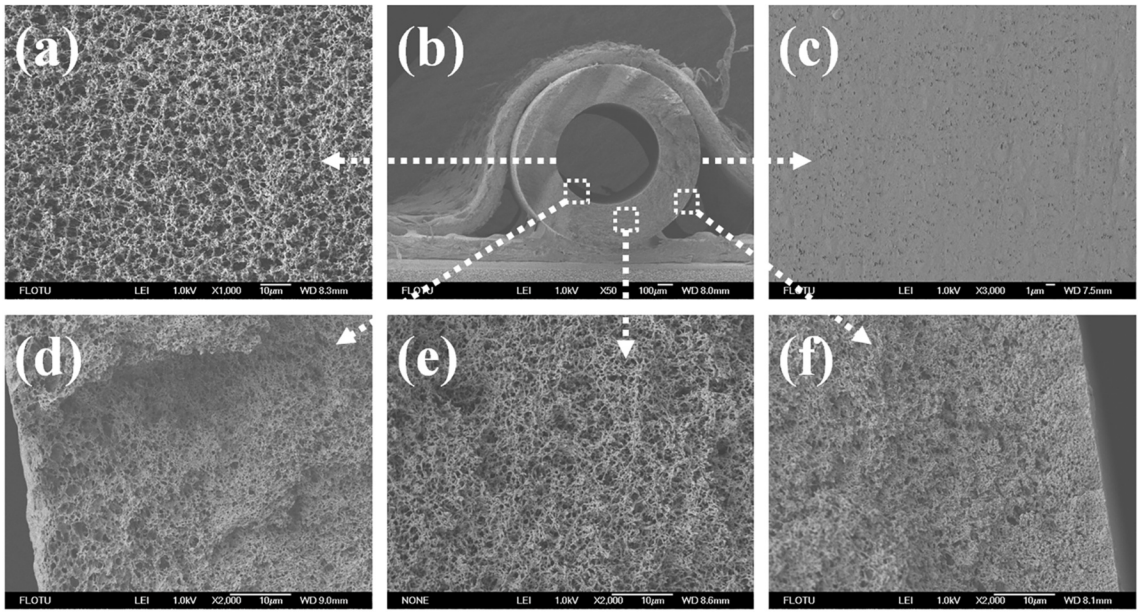


Fig. 16. SEM photographs of PVDF hollow fiber membrane fabricated via TIPS (L–L) process: (a) Inner surface; (b)Whole cross-section; (c) Outer surface; (d) Cross-section near the inner surface; (e) Enlarged cross-section; and (f) Cross-section near the outer surface.

PVDF membranes will accumulate in the industry because there are no more physical or chemical methods that can be available to clean the PVDF membranes for further use [267]. In recent years, some people are already trying to propose appropriate methods to realize the disposal and recycling of the waste PVDF membranes. At present, a feasible way that has been more published is to prepare recycled membranes using the waste PVDF membranes which have run in the membrane bioreactor (MBR) system [267–269]. The results showed that the PVDF molecular weight decreased with the increase of the running time, which also led recycled PVDF hollow fiber membranes to have higher porosity and better permeability. Also, the mechanical properties and protein rejection may be different from that of the new membranes. Some patents have proposed new pre-treating methods for the waste PVDF membranes for their recycling [270,271]. Although until recently, there are not many research works published, we think more attention and efforts will be focused on this topic in response to the concept of global sustainable development and recycling economy.

6. Emerging advanced techniques based on TIPS

It can be seen that during the past decades, extensive progress has been made both in the research and industrial fields. Nowadays, PVDF membranes fabricated via TIPS have attained both high permeability and good mechanical properties. People have mastered how to prepare PVDF membranes with a bi-continuous porous cross-section, and the surface pore size of which is normally around 0.1 μm. Recently, much

Table 8
Lists of typical application cases used PVDF hollow fiber membrane fabricated via TIPS (L-L).

Project category	Commissioning time	Project/module type	Source	Capacity (ton per day)	Water quality	Operation flux (L/(m^2·h))
Drinking water purification	Jun-2019	Tianjin Yixianyuan Drinking Water Plant Expansion and Reconstruction Projects, China/Pressurized	Surface water	30,000	COD: 5 mg/L Turbidity: 5 NTU	61
Municipal waster water treatment	Nov-2017	Phase IV Membranes Replacement at Edward C. Little Water Recycling Facility of West Basin MWD, USA/ Submerged	Municipal Wastewater	45,000	SS: 15 mg/L Turbidity: 5 NTU	30
Industrial wastewater treatment	May-2017	Luxi Chemical Group Co., Ltd. Power Branch Tuichengjinyuan Chemical Wastewater Project, China/ Pressurized	Industrial Wastewater	44,400	COD: 15 mg/L Turbidity: 3 NTU	70.4
Seawater desalination pretreatment	May-2018	Seawater Desalination Phase I Project at Bohai New Area Industrial Zone, China/Pressurized	Sea Water	100,000	SS: 10 mg/L	47.7

attention has been paid to improve the PVDF membrane structure and performance further. An important direction is to care more about the membrane surface to make it can have a much smaller pore size that is below 0.1 μm or even near 1 nm, so as to decrease the molecular weight cut-off (MWCO) of the membranes to dozens of kDa, and further increase the anti-fouling property and extend the application. As mentioned above, the process kinetics such as cooling rates affects the surface morphology and may help to decrease the surface pore size. Nevertheless, the influence is that strong enough to decrease the pore size to a new level. In the recent decade, people are searching for some new techniques to improve the membrane surface morphology.

Considering that the mass transfer across the interface between the casting solution and the coagulation of the NIPS process normally forms membrane structure with a thin and dense surface layer located on a porous sublayer. Therefore, recently some people are trying to introduce a mass transfer across the polymer solution-coagulation interface to further improve the membrane structure and performance. The new method has been named as 'nonsolvent TIPS' [272], nonsolvent assisted TIPS [273], complex thermally induced phase separation (c-TIPS) [274], or combined NIPS-TIPS (*N*-TIPS) method [145]. The idea of this combination should be traced back to the work conducted by Matsuyama's group who prepared PMMA porous membrane by the combined use of thermally induced phase separation (TIPS) and immersion precipitation [275]. They found that near the top surface contacted with the nonsolvent, a thin dense layer with much smaller pores was formed due to the outflow of the diluent. Fig. 17 shows a simplified schematic diagram of mass transfer of the different membrane preparation processes. Because the mass transfer across the interface was induced in the membrane formation processes and the rate of the diluent outflow was often higher than that of the coagulation inflow, the membrane prepared usually would have dense surface layers. In addition, since the heat transfer is normally faster than the mass transfer process, the inner cross-section and surface structures would not be altered a lot. For PVDF, people introduced the mass transfer to the original TIPS process through different ways including altering the composition of the coagulation [179], adopting water-soluble diluents when water was the coagulation [125,165,274], or changing the compatibility between the diluent and extruded solvent [40,162]. However, the mass transfer across the interface between the casting solution and coagulation is very complicated and strongly influenced by the viscosity, additives, flow rate et al., various membrane structures and properties would be formed. For example, Matsuyama's group confirmed by experiments and simulations that when using a triple-orifice spinneret to prepare hollow fiber membranes, extruding solvents with good compatibility with the diluent that dissolved the polymer in the dope solution, the movement of the diluent towards the surface between the polymeric dope solution and extruded solvent from the bulk dope solution decreases the polymer surface concentration, which provided a membrane surface with a large pore size and high porosity. Whereas, some people also found that adopting a water-soluble diluent can lead to the inter-diffuse between the diluent and water, which is beneficial for the formation of a membrane surface with a small pore size and low porosity. Therefore, it should be pointed out that concerning the addition of additives such as hydrophilic polymers, now the combined process is very complicated and allows delicate regulations in the casting solution and coagulation to realize precise control both in the main structure and the surface morphology [40,162]. At present, although lots of experimental experience has been accumulated during the several years, the thermodynamics and kinetics of the combined phase separation remain unclear. Whereas, the emphasis of the review paper is more focused on the PVDF membranes prepared via TIPS, a detailed review and discussion about the combined process should be figured out in the next few years for people to control the membrane formation better.

7. Conclusions and outlook challenges

In this review, the latest progress of the production and hydrophilic modifications of PVDF membranes prepared via the TIPS process was

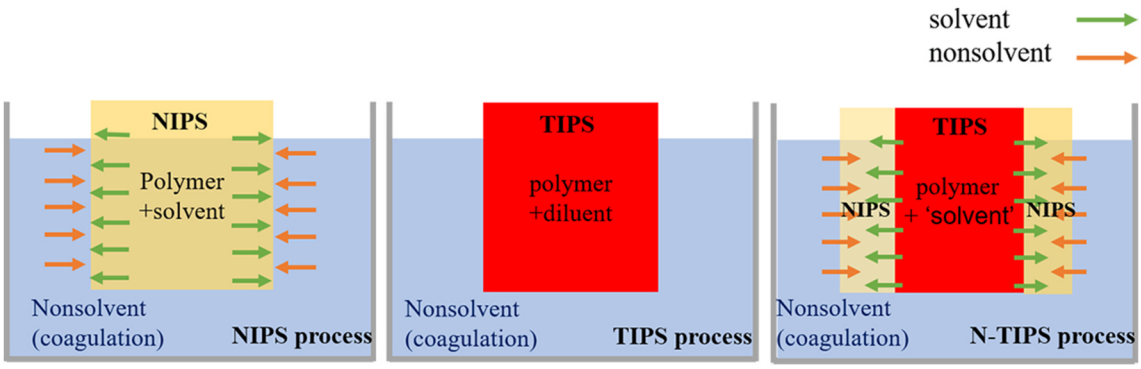


Fig. 17. A schematic diagram of the mass transfer of the different membrane preparation processes.

comprehensively reviewed. In the beginning, we summarized the properties and performances of PVDF as a membrane material such as crystallization, thermal stability, and chemical resistance from a perspective of membrane manufacture. Then the development of PVDF microporous membranes preparation around 2005 was recalled when NIPS dominated the PVDF preparation. Meanwhile, a comparison between NIPS and TIPS was made to show that TIPS was a flexible and controllable method for membrane preparation. Then a comprehensive summary was made to illustrate how to successfully realize the preparation of PVDF membranes via TIPS in the lab-scale for the water treatment, including the diluent selection, the criterions proposed to estimate the interaction between the polymer and diluents, the membrane formation kinetics study, and the dynamic analysis of the membrane formation based on modeling and simulation methods as well as the hydrophilic membrane modification. Subsequently, taking the membrane production and module development of BSMT PVDF membrane manufacture as a typical example, key issues to realize industrialization for membrane preparation and application via TIPS were summarized. Besides, disposal and recycling of the waste PVDF membranes were also mentioned. Finally, because people have realized that membranes fabricated by TIPS and NIPS all possess their advantages and limitations, this work proposed emerging advanced techniques based on TIPS to improve the PVDF membranes with better performance, and a successful example is combining TIPS and NIPS to regulate the membrane structure.

In the future, in order to realize controllable membrane fabrication with better performance, fundamental evolution will emerge both on the thermodynamic research and membrane formation procedure. For the thermodynamic aspect, although at least three criteria that have been introduced in this manuscript can be followed to find new diluent systems, sometimes people still feel confused due to a lack of basic physical parameters such as HSP. In addition, the membrane formation procedure is crucial for improving the membrane structure and a slight change may have a great positive effect on the membrane performance. In the next step, Also, more effort will be paid in developing new methods and processes to further realize development and industrialization, which would also comply with the research routine proposed by this article. Therefore, this paper would be a useful reference for researchers focusing on the manufacture and development of polymeric membrane modules via TIPS.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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