Tailoring PVDF Membranes Surface Topography and Hydrophobicity by a Sustainable Two-Steps Phase Separation Process

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Supporting Information

ABSTRACT: This work validates a sustainable way to produce customized PVDF membranes, suitable for contactors applications, in which DMSO is employed as nonhazardous solvent, in place of substances of very high concern (SVHC), by a combination of vapor-induced and liquid-induced phase separation (VIPS and LIPS) stages, and without using any chemical additive as pore forming. The experimental results highlight the key role of the kinetic and thermodynamic parameters of the phase separation processes involved in the control of the surface and transport properties of the PVDF membranes. Namely, combining VIPS and LIPS techniques in a controlled way, allowed to produce symmetric porous membranes with customized rough surface topography (root-mean-square roughness up to 0.67 μm) and hydrophobicity (water contact angle up to 140°) according to a biomimetic behavior as that of lotus leaves surfaces, through an environmental friendly fabrication process. The resulting membranes are characterized by a high porosity (total porosity ≥70%, mean pore size 0.08–0.4 μm), with well interconnected pores, despite no pore former additives were included in the dope solution, making them ideal candidates for application in membrane contactors. The quality of the produced membrane (permeate flux up to 12.1 kg h⁻¹ m⁻² with salt rejection 99.8%) is assessed by MD tests and results showed comparable performance to commercial PVDF membranes having similar mean pore size, porosity and surface roughness, but produced using SVCH solvents.

KEYWORDS: PVDF membranes preparation, green solvents, liquid induced phase separation, vapor induced phase separation, DMSO

INTRODUCTION

The industrial production of membranes, mainly polymeric, has registered a considerable increase in the last decades, driven by the continuous introduction of membrane-based operations in several manufacture cycles.¹ While membranes are currently the globally dominant technology in wastewater purification and seawater desalination,² the interest now moves to convert old and inefficient traditional chemical production processes in more compact systems, which enable a better exploitation of raw materials, lower energy consumption, lower waste generation, and reduced plant size, in agreement to the Process Intensification (PI) principles.³,⁴

Polymeric membranes dominate the membrane market and they are mainly produced by phase separation (PS) processes in which, basically, a polymer is dissolved in an organic solvent or solvents mixture, and the solution is then demixed in a controlled way (e.g., by the addition of a nonsolvent).⁵ Notably, although membrane-based operations are generally considered by themselves green and sustainable, it is frequently overlooked that the membrane fabrication itself is quite far to be green.

Most of the solvents used in industrially relevant membranes productions are hazardous to human health and to the environment.⁶ They are also currently mentioned as substances of very high concern (SVHC) in different lists guides, such as CHEM 21, GHS and REACH.⁷,⁸ It has been estimated that every year more than 50 billion liters of wastewater contaminated with SVCH solvents are produced in membrane manufacture at industrial scale.⁶ Therefore, there is great attention today to develop innovative production protocols where harmful solvents are replaced by less toxic substances, to make industrial membrane production more environmental friendly.⁹,¹⁰ Obviously, in doing this, membrane performances need to be kept, or even improved, by preserving target chemical-physical-structural parameters.

Among many others, polyvinylidene fluoride (PVDF) is one of the most used polymer for the fabrication of membranes due
to its outstanding chemical, thermal and mechanical stability.\textsuperscript{11–14} Some consolidated applications of PVDF membranes can be found in microfiltration (MF), ultrafiltration (UF) and membrane bioreactors (MBR) operations for wastewaters treatment, food, and health applications.\textsuperscript{11–14} Some other emerging uses of PVDF membranes in industrially relevant processes are membrane distillation (MD) for water desalination, membrane-assisted crystallization (MCR) for the processing of pharmaceutical compounds, and nondispersive absorption in gas–liquid membrane contactors for CO\textsubscript{2} capture.\textsuperscript{15–18} Despite the several advantages afforded by the use of PVDF membranes, the main drawback is the extensive use of toxic and harmful SVHC, such as N,N-dimethylformamide (DMF), dimethylacetamide (DMA) and N-methyl-2-pyrroldione (NMP)\textsuperscript{12–14,19–24} in the production of such membranes by PS processes. Some examples of green approaches developed for PVDF membranes fabrication include the thermal induced phase separation (TIPS) using green solvents like PolarClean.\textsuperscript{25} However, in TIPS process economic and environmental issues are raised by the high temperatures used for polymer solubilization (160 °C).\textsuperscript{26} Triethyl phosphate (TEP) has also been used for membrane fabrication by liquid induced phase separation (LIPS).\textsuperscript{26,27} However, this solvent cannot be defined green because of its moderate hazard profile.\textsuperscript{7,8} In the present study, dimethyl sulfoxide (DMSO) is selected as nonhazardous solvents for PVDF membrane preparation. Up to now, the use of dimethyl sulfoxide (DMSO) as solvent for PVDF has been limited to few examples of LIPS processes\textsuperscript{27–29} for the production of asymmetric skin-type membranes. Moreover, wet freezing methods exploiting the high melting temperature of the DMSO (19 °C)\textsuperscript{30} were also reported.\textsuperscript{31–33} However, the PVDF membranes produced in the cited literature works were not suitable for MCs applications, because of their limited hydrophobicity and low liquid water entry pressure.\textsuperscript{27–29,31–33}

It is also important to note that, despite some authors reported that the DMSO/PVDF cast solution was exposed to ambient air for few seconds before LIPS\textsuperscript{27,28} this step cannot be assimilated to a VIPS process because of the short exposition times (∼30 s, while our results indicate a threshold of 5 min to have a VIPS guided process) and the lacking of control of the environmental humidity. Concerning the last point, the exposition of the cast film to air with a low relative humidity and prolonged times can favor solvent evaporation instead of water vapor diffusion with the consequent formation of a denser skin layer instead of a porous one.\textsuperscript{34}

In this work, we developed a fabrication procedure in which DMSO is employed, in a combination of vapor-induced phase separation (VIPS) and LIPS stages, and without using any chemical additive as pore forming, to produce customized PVDF membranes suitable for contactors applications. To the best of our knowledge, this is the first time that DMSO is used as solvent for PVDF membranes preparation by VIPS technique, while studying in deep the effect of humidity and exposition time on membrane properties. The results highlight the key role of the kinetic and thermodynamic parameters of the phase separation in the control of the surface and transport properties of the PVDF membranes. Namely, the specific advantages of using VIPS over LIPS technique\textsuperscript{25–24} have been exploited to produce symmetric skinless porous membranes with rough surface topography and hydrophobic biomimetic surfaces, by an environmental friendly fabrication process. These properties, in addition to a narrow pore size distribution, high porosity, excellent chemical resistance, long-term stability, low thermal conductivity, and suitable thickness, represent fundamental requirements for efficient application in membrane contactors fields, such as MD and MCR.\textsuperscript{16,35} The quality of the membrane produced is assessed by a comparison in MD application with a commercial PVDF membrane produced using SVCH solvents.

## EXPERIMENTAL SECTION

### Membranes Preparation.

PVDF Solef 6010 (Mw 300–320 kDa, M\textsubscript{w}/M\textsubscript{c} 2.1–2.6)\textsuperscript{30} is kindly supplied by Solvay Solexis. DMSO (analytical grade) is purchased from Merck.

The membranes are prepared from homogeneous solutions of PVDF (15 wt %) solubilized under magnetic stirring in DMSO (85 wt %) at 55 °C. The polymer solutions are cast with an initial thickness of 350 μm onto a nonwoven fabric (thickness 109 ± 1 μm), used to ensure a high mechanical resistance to the system, by a micrometric casting knife (Elcometer 3700). The casting is carried out inside a box with controlled temperature (30 ± 1 °C for all the samples) and relative humidity (RH). The cast film is first exposed to an atmosphere with a certain RH (34–64%) for various times (0–20 min), in order to have the VIPS process. Finally, the membrane formation is completed by LIPS, immersing the forming film in a water coagulation bath. The membranes are prepared in triplicate. All the samples are characterized and the results reported are the average of at least three measurements.

### Membranes Characterization.

The morphologies of the membranes (top and cross section) are examined by an EVO MA10 Zeiss scanning electron microscope (SEM). Cross sections are prepared by fracturing the membranes and prolonged times can favor solvent evaporation instead of water vapor diffusion with the consequent formation of a denser skin layer instead of a porous one.\textsuperscript{34}

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Membrane surface roughness is measured by a Nanoscope III atomic force microscope (AFM) (Digital Instruments, VEECO Metrology Group) in air, in contact mode imaging. The average of three different measurements on 14 × 14 μm\textsuperscript{2} squares of membrane surfaces, is reported. Roughness analysis is performed by WSxM 5.0 Develop 6.1 software (Nanotec Electronica S. L.)\textsuperscript{37} by calculating average roughness (Ra), root-mean-square roughness (RMS), and maximum height (Rmax).

The membranes surface wettability is evaluated by water contact angle (CA) measurements using a CAM 200 device (KSV Instruments, Ltd.). The mean pore diameter is measured by a capillary flow porometer (PMI, Porous Materials Inc. Ithaca, NY) using a wetting liquid (3M Fluorinert Electronic Liquid FC-40, supplied by Essegie Srl) and nitrogen as pressurizing gas. The liquid entry pressure of water (LEP\textsubscript{w}), defined as the pressure difference at which liquid water penetrates into the membranes pores, is calculated by a theoretical expression, based on Young–Laplace equation:\textsuperscript{38}

\[
\text{LEP}_{\text{w}} = \frac{-2\gamma \cos \theta}{r_{\text{mt}}} 
\]

where γ is the water surface tension (71.99 ± 0.05 mN·m at 25 °C) is \(-1^\circ\) the contact angle between the liquid and the membrane, and \(r_{\text{mt}}\) is the the maximal pore radius detected, \(B\) is a dimensionless geometrical factor which includes the irregularities of the pores (\(B = 1\) for assumed cylindrical pores).

The film total porosity is measured by gravimetric method at 25 °C, determining the weight of the wetting liquid contained in the porous part of the film. The porosity \(\varepsilon\) is calculated by the following equation:

\[
\varepsilon = \frac{(w_2 - w_1)/D_{w}}{(w_2 - w_1)/D_{p} + (w_1/D_{p})}
\]

where \(w_1\) is the weight of dry samples, \(w_2\) the weight of the wet samples, \(D_{w}\) the wetting liquid density (1.855 g/cm\textsuperscript{3} for 3M-FC-40), and \(D_{p}\) is the polymer density (1.78 g/cm\textsuperscript{3}).
Fourier transform infrared spectroscopy (FT-IR) analyses in attenuated total reflectance (ATR) are performed using a PerkinElmer Spectrum One (PerkinElmer), on the upper surface of each membrane. The $\beta$-phase content (F(β)) is quantified using the following equation:

$$F(\beta) = \frac{A_\beta}{(K_p/K_w)A_w + A_\beta}$$

(3)

where $A_w$ and $A_\beta$ are the absorbance at 763 and 840 cm$^{-1}$; (characteristic of the $\alpha$ and $\beta$ phase, respectively) $K_w$ and $K_\beta$ correspond to the absorption coefficients at the respective wave-numbers, which values are $6.1 \times 10^3$ and $7.7 \times 10^2$ cm$^2$ mol$^{-1}$, respectively.

The membrane transport properties are tested in a direct contact membrane MD/MCr plant as detailed elsewhere.22 performances are evaluated as flux and rejection to NaCl. Operating conditions are feed and distillate temperature 53 ± 2 °C and 20 ± 2 °C, respectively; feed and distillates flow rate 12 L h$^{-1}$ (axial velocity 6.1 m h$^{-1}$) membrane area $2.4 \times 10^{-3}$ m$^2$; feed composition NaCl 1 g L$^{-1}$ (0.017M), if not otherwise specified.

The flux (J) and rejection (R) are defined as follows:

$$J = \frac{M_p}{t/A}$$

(4)

$$R = 1 - \frac{C_d}{C_f} \times 100$$

(5)

where $M_p$ is the permeate mass expressed in kg; $t$ is the permeation time in hours, and $A$ is the active membrane area in square meters.

## RESULTS AND DISCUSSION

DMSO is aprotic solvent with polarity quite similar to those of DMF, DMA and NMP. However, it has a lower affinity for the PVDF than the other solvents cited, as confirmed by the calculation of the difference in solubility parameters (Supporting Information (SI) Table S1).30,36,43-45

Polymers and solvents can be represented in the so-called “Hansen three-dimensional space” in which a substance is identified by three coordinates corresponding to the solubility parameters associated with dispersion forces ($\delta_d$), polar forces ($\delta_p$), and hydrogen bonding ($\delta_h$). Nearer two substances are in the Hansen space, that is, lower are the differences in solubility parameters, more affine are each other. The distance between two points in this 3D representation can be calculated as follows:

$$\Delta \delta = (\delta_{dp} - \delta_{dh})^2 + (\delta_{hp} - \delta_{hp})^2 + (\delta_{hp} - \delta_{hp})^2)^{1/2}$$

(6)

where the second subscript $p$ or $s$ is referring to the polymer PVDF or solvent, respectively.

In general, two substances are considered mixable when the difference in total solubility parameters is $\leq 5$ MPa$^{1/2}$.43 The high difference in solubility parameters between the PVDF and water confirms that the latter is a nonsolvent for this polymer ($\Delta \delta = 31.5$ MPa$^{1/2}$, SI Table S1). DMA, DMF, NMP, and DMSO, are all good solvents for the PVDF ($\Delta \delta < 5$ MPa$^{1/2}$). However, the difference in Hansen solubility parameters is higher for DMSO, because of the larger difference in dispersion and polar components (SI Figure S1).

These results are in agreement with the wider solubility gap reported in water/solvent/PVDF ternary phase diagram for DMSO, in comparison with DMA, DMF, and NMP.44,46 This means that, from a purely thermodynamic point of view, a lower amount of water is sufficient to induce the phase separation of a PVDF solution solubilized with DMSO. However, DMSO is also characterized by a higher viscosity and a lower diffusion coefficient in water, compared to DMA, DMF, or NMP (SI Table S1).45 These properties influence heavily the kinetics of the phase separation processes of the DMSO/water system, with a more delayed diffusion solvent/nonsolvent. Accordingly, the peculiar chemical-physical properties of the DMSO have relevant influence on both thermodynamic and kinetic effects involved in PVDF membrane formation by phase separation methods.47 Therefore, it is not possible to use the already known protocols developed for the VIPS and/or LIPS methods with SVCH solvents, to the case of DMSO to prepare PVDF membranes. It is instead necessary to deeply investigate the influence of factors like the time of exposition to humid air and the relative humidity during VIPS, to develop customized PVDF membranes for membrane contactors applications.

Figure 1 shows the SEM and AFM images of PVDF membranes surfaces prepared for VIPS times ranging from 0 (i.e., no VIPS stage but only LIPS) to 20 min, while keeping constant humidity (RH 50%).

The surfaces of the membranes prepared with VIPS time ≤1 min (Figure 1 A,B) are rather smooth and apparently dense. This morphology is the results of the rapid solvent/nonsolvent exchange and polymer precipitation at the coagulation bath/polymer solution interface during the LIPS stage. When the cast polymer solution is immersed in the coagulation bath, the concentration of the nonsolvent at the film surface reaches immediately that value triggering phase separation. The phase with the higher polymer concentration forms the solid part of the membrane; the phase with the lower polymer concentration gives rise to the pores. The gradient of the polymer chemical potential resulted in a movement of the polymer perpendicularly to the surface, leading to a polymer concentration increase and the formation of a denser skin layer which hinders the solvent/nonsolvent exchange through the internal layers, with the consequent formation of an asymmetric membrane.48

A VIPS time of only 1 min is not sufficient to influence the membrane morphology in a relevant way with respect to a simple LIPS process.

A different surface topography is observed for the membranes prepared by VIPS times ≥5 min. The surfaces are porous and rough, composed of spherulitic microparticles linked together through fiber-like connections (Figure 1C–E). During the VIPS stage, the polymeric solution, initially homogeneous, demixes in two liquid phases under the effect of the diffusion of the nonsolvent vapors. The diffusion of the nonsolvent in vapor phase into the cast solution (VIPS stage), is slower than in the liquid phase (LIPS stage). The water vapors induce localized microphase separation on the membrane surface forming nucleation clusters of PVDF crystals. This leads to a uniform and flat concentration profile of the three components in the film cross-section,59-61 precipitant (water), polymer (PVDF) and solvent (DMSO), inducing the formation of a skinless membrane with a more
porous and rough surface. The formation of an interconnected porous structure in the PVDF membrane is completed by the solvent/nonsolvent exchange during the LIPS stage in which the absorbed water works also as green pore former.

In agreement with their formation mechanism, the membranes prepared with VIPS time \( \leq 1 \) min are characterized by smaller pore size than membranes prepared at higher exposition times. Notably, for VIPS time of 5 min the mean pore size is higher than for longer times (10 and 20 min, Figure 2).

It is argued that a longer exposition to humid air gives rise to water condensation on the cast film, which locally undergoes a LIPS mechanism when in contact with the nonsolvent in liquid phase, giving rise to denser regions on the membrane surface. However, all the membranes prepared are characterized by a total porosity of 70 ± 5%, indicating that the VIPS exposition time influences mainly the surface porosity while keeping the bulk porosities quite similar.

Surface topography is directly correlated to the wetting aptitude of the membrane. Artificial porous membranes with hydrophobic properties adequate for MD/MCr applications are obtained by the applied approach aiming to replicate the highly rough surface of lotus leaves through the slow diffusion of the water vapors during LIPS step, which favor the formation of spherulites on the top membrane surface. It is important to highlight that the surface of these spherulites are not smooth but characterized by several rough microprotusions that contribute further to the increase of the membrane hydrophobicity (Figure 3), giving highly hydrophobic surfaces, with water contact angle between 132° and 140° for VIPS times \( \geq 5 \) min (Figure 4). On the contrary, in the case of pure LIPS process (i.e., VIPS time 0), the contact angle decreases to 71°, leading to substantially hydrophilic membranes, in agreement with the quite smooth surface obtained. For VIPS time 1 min the surface displayed a low hydrophobic character, with a contact angle of 93°, supporting a prevalently LIPS driven membrane formation mechanism (Figure 4).

Figure 1. SEM (left) and 3D AFM height (right) images of the surface of PVDF membranes prepared at different VIPS times while keeping constant the RH at 50%. VIPS time: (A) 0 min; (B) 1 min; (C) 5 min; (D) 10 min; (E) 20 min. SEM images are taken at 10 KX magnification.

Figure 2. Pore diameter of membranes prepared at different VIPS times while keeping constant the RH at 50%.

Figure 3. SEM image of the typical spherulitic microstructures characterizing the surface of the PVDF membrane prepared at VIPS time \( \geq 5 \) min. Images taken at 30 KX magnification of a membrane cast at VIPS time min and RH 50%.

Figure 4 correlated the values of water contact angle with the surface roughness. The RMS and the contact angle of the membranes increased consistently moving from LIPS-driven (zero or 1 min of VIPS) to VIPS-driven membrane formation mechanism (VIPS time \( \geq 5 \) min).

The results are in agreement with the Cassie–Baxter’s wetting model, predicting that for a rough hydrophobic surface, a nonwetting liquid may not penetrate into surface cavities, resulting in the formation of air pockets, leading to a composite solid–liquid–air interface where hydrophobicity increases with...
the surface roughness. The highest surface root mean-square roughness (0.67 μm) and, as a consequence, the highest water contact angle, is observed at VIPS time 5 min (140°). The membrane produced has a calculated LEPw of 3 bar confirming the applicability of the sample in membrane contactors. A maximum in β phase fraction (0.92) of the PVDF crystallites is also observed for the sample produced at VIPS time 5 min and quantified by ATR-FT-IR (SI Figure S2).

The ATR-FT-IR spectra of the prepared PVDF membranes (SI Figure S3) show the signals of the α and β polymorphs, with a dominance of the latter because of the use of a polar solvent (i.e., DMSO) which favors the formation of the β phase, having the highest dipolar moment with the polar C–F bonds aligned in the same direction. On the contrary, the dipole moments of α crystallites are oriented in opposite directions, resulting in a zero net polarization. During PVDF crystallization, the α form is the kinetically favored polymorph, while the β form is the most thermodynamically stable one. Moving from VIPS time 0−5 min (i.e., from a LIPS to a VIPS driven mechanism), it is observed an increase of the β fraction. The slower VIPS membrane formation process favors the thermodynamic polymorph in comparison with the faster LIPS process. Increasing further the VIPS time (>5 min), the local LIPS phenomena, due to water vapors condensation on the membranes surface, reduces the β fraction (SI Figures S2 and S3). The PVDF polymorphism depends also from the relative humidity during the VIPS stage. Fixing the exposition time to 5 min, a reduction of the β fraction is observed with the increase of the relative humidity (SI Figures S2 and S4). Moving from RH 34 to 64%, the β fraction decreases from 1 (i.e., only β phase) to 0.78 due to the faster reaching of the solubility gap, with the consequent reduction of the content of the thermodynamic polymorph. Moreover, increasing the relative humidity, local LIPS phenomena might also occur, as suggested observing the surface of the membrane prepared at RH 65%, showing the typical morphology of a LIPS driven mechanism (Figure 5 D and Figure 1 A) and characterized by β phase fraction close to a pure LIPS process (SI Figure S2). Also, the mean pore size of the membrane prepared at RH 64% results similar to that of the membrane prepared with LIPS (0.075 vs 0.076 μm, respectively; Figures 6 and 2). These results support a LIPS driven mechanism at this high value of relative humidity (RH 64%). The high amount of humidity cannot be completely absorbed by the cast film resulting in a partial water condensation on the film surface with the formation of denser regions. Water condensation could be also furthermore reinforced by surface cooling during the exposition time, due

Figure 4. Water contact angle (CA, left axis, symbol triangle) and root mean-square roughness (RMS, right axis, filled square symbol) of membranes prepared at different VIPS times while keeping constant the RH at 50%.

Figure 5. SEM (left) and 3D AFM height (right) images of the surface of PVDF membranes prepared at different RH conditions while keeping constant the VIPS time at 5 min: (A) RH 34%; (B) RH 44%; (C) RH 50%; (D) RH 64%. SEM images are taken at 10 KX magnification.

Figure 6. Mean pore diameter for membranes prepared at different values of relative humidity (RH) during VIPS step while keeping constant the VIPS time at 5 min.
to DMSO evaporation from the liquid film to reach the equilibrium vapor pressure. Conversely, SEM images of the membranes prepared in the RH range 34−50% show open porous surface structures along with the spherulitic morphology, indicative of partial polymer crystallization during the slow phase separation process induced by the water vapors (Figure 5 A-C).

The surface roughness and hydrophobicity of all these membranes are high because of the predominant effect the vapor uptake by the cast film, with respect to the condensation phenomena (Figure 7). However, the mean pore diameter increases rising RH from 34 to 50% due to the increase of nonsolvent uptake (Figure 6).

Figure 7. Water contact angle (CA, left axis, symbol triangle) and root mean-square roughness (RMS, right axis, filled square symbols) for membranes prepared at different values of relative humidity (RH) during VIPS step while keeping constant the VIPS time at 5 min.

The performances of the PVDF membranes were tested in a lab-scale MD/MCr experimental setup and compared with a commercial UF PVDF membrane having comparable properties (Table 1).

Table 1. Selected Properties of the Commercial UF PVDF Membranes

| Property                              | Value          |
|---------------------------------------|----------------|
| mean pore size (μm)                   | 0.28 ± 0.02    |
| total porosity (%)                    | 68 ± 2         |
| thickness (μm)                        | 170 ± 3        |
| RMS (μm)                              | 0.55 ± 0.03    |
| water contact angle (deg)             | 132 ± 2        |
| calculated LEPw (bar)                 | 2.9            |

According to data reported in Figure 8, salt rejection is higher than 99% for the samples produced at VIPS time ≥5 min (RH 50%) and RH < 64% (VIPS time 5 min).

These conditions correspond to boundaries for VIPS driven PVDF membranes formation. All these membranes have a spherulitic surface morphology, elevated surface roughness, high water contact angle and appropriate LEPw (between 1.3 and 4.3), which match well with the requirements for membrane contactors. Whereas, in the case of samples formed by a LIPS guided mechanism and characterized by a higher surface wettability, would have potential applications in those processes requiring hydrophilic surfaces, like in MF, UF, or MBRs.

The best performing sample for membrane contactors applications results that prepared at 5 min of VIPS and 50% RH, having the higher mean pore size combined with elevated surface roughness and high LEPw (3 bar).

The superior performance of the PVDF membranes produced in these conditions are due to an optimal combination of water vapor uptake and negligible liquid water condensation effect on the cast liquid film during the VIPS stage. This membrane show flux and rejection comparable to the commercial PVDF sample \( J = 12.1 \text{ kg m}^{-2} \text{ h}^{-1} \), \( R = 99.8\% \) vs \( J = 12.0 \text{ kg m}^{-2} \text{ h}^{-1} \), \( R = 99.7\% \), respectively, with NaCl 1 g L\(^{-1}\), Figure 8). Using as feed a solution of NaCl 29.2 g L\(^{-1}\), as a model of seawater, the flux of both membranes decreased to 10 kg m\(^{-2}\) h\(^{-1}\) as a consequence of the higher solution activity, while keeping the salt rejection complete. These results further support the applicability of the produced membrane in membrane contactors applications.
Long-term testing of this sample indicates that no reduction of flux and/or rejection are observed reusing the same sample for 8 runs (5 h each test, the sample was washed with distilled water and then dried after each run before the reuse).

It is also worth noting that the commercial sample, used as reference, is produced using toxic solvents, like DMA and NMP, and pore forming additives in the casting solution to promote pore formation during LIPS (i.e., hydrosoluble additives like PVP). On the contrary, either toxic solvent or pore forming additives are not used in the green biomimetic approach developed in the present study.

**CONCLUSIONS**

This study demonstrates a sustainable and easily scalable two steps phase separation process for the preparation of PVDF membranes with tailored surface topography and hydrophobicity, without the use of toxic solvents and harmful additives. DMSO and water are used as green solvent and nonsolvent, respectively, in a combined VIPS and LIPS technique.

The slow and controlled diffusion of the water vapor into the cast polymer solution during VIPS stage triggered the localized nucleation clusters of PVDF crystallites prevalently in the microphase separation on the membrane surface, forming pores. Consequently, these results represent the first step toward a concrete alternative to industrially consolidated membrane preparation protocols involving SVHC solvents.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.8b01407.

Table S1. Some properties of PVDF and selected solvents. Figure S1. Three-dimensional plot of Hansen solubility parameters for PVDF, DMA, DMP, NMP and DMSO. Figure S2. Content of the β-phase (F(β)) in the membrane series prepared: (A) at different VIPS time (RH 50%) and (B) different relative humidity (VIPS time 5 min). Figure S3. ATR-FT-IR spectra of the PVDF membranes prepared at different VIPS time while keeping constant the RH at 50%. VIPS time: a) 0 min (i.e., LIPS); b) 1 min; c) 5 min; d) 10 min; e) 20 min. The lines highlight the position of the characteristic peaks of the α-phase (763, 795, 854, 975, and 1384 cm⁻¹) and β-phase (840, 1172, and 1273 cm⁻¹)). Figure S4. ATR-FT-IR spectra of the PVDF membranes prepared at different RH conditions while keeping constant the VIPS time at 5 min: a) RH 34%; b) RH 44%; c) RH 50%; d) RH 64%. Figure S5. Thickness of the membranes prepared: (A) at different VIPS time (RH 50%) and (B) different relative humidity (VIPS time 5 min). Figure S6. SEM image of the cross section of the PVDF membrane prepared at VIPS time 5 min and RH 64%.

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**REFERENCES**

(1) Ulbricht, M. State of the art and perspectives of organic materials for membrane preparation. In Comprehensive Membrane Science and Engineering, 2nd ed.; Drioli, E., Giorno, L., Fontananova, E., Eds.; Elsevier B.V.: Oxford, 2017; pp 85–119.

(2) Cucic, E.; Di Proio, G.; Fontananova, E.; Drioli, E.; Membrane technologies for seawater desalination and brackish water treatment. In Advances in Membrane Technologies for Water Treatment: Materials, Processes and Applications; Basle, A.; Cassano, A.; Rastogi, N. K., Eds.; Elsevier: Amsterdam, The Netherlands, 2015; Chapter 13, pp 411–441.

(3) Stankiewicz, A.; Moulijn, J. A. Process Intensification. Ind. Eng. Chem. Res. 2002, 41, 1920–1924.

(4) Drioli, E.; Brunetti, A.; Di Proio, G.; Barbieri, G. Process intensification strategies and membrane engineering. Green Chem. 2012, 14, 1561–1572.

(5) Strathmann, H.; Giorno, L.; Drioli, E. Basic Aspects in Polymeric Membrane Preparation. In Comprehensive Membrane; Drioli, E., Giorno, L., Eds.; Elsevier B.V.: Oxford, 2010; Vol. 1, pp 91–111.

(6) Razali, M.; Kim, J. F.; Attfield, M.; Budd, P. M.; Drioli, E.; Moo Lee, Y.; Szekely, G. Sustainable wastewater treatment and recycling in membrane manufacturing. Green Chem. 2015, 17, 5196–5205.

(7) Peat, D.; Wells, A.; Hayler, J.; Sneddon, H.; Robert Mc Elroy, C.; Abou-Shehada, S.; Dunn, P. J. CHEM21 selection guide of classical- and less classical-solvents. Green Chem. 2016, 18, 288–296.

(8) Globally Harmonized System of Classification and Labelling of Chemicals (GHS) http://www.unece.org/trans/danger/publi/ghs/welcome_e.html.

(9) Faggian, V.; Scanferla, P.; Paulussen, S.; Zuin, S. Combining the European chemicals regulation and an (eco)toxicological screening for a safer membrane development. J. Cleaner Prod. 2014, 83, 404–412.

(10) Szekely, G.; Jimenez-Solomon, M. F.; Marchetti, P.; Kim, J. F.; Livingston, A. G. Sustainability assessment of organic solvent nanofiltration: from fabrication to application. Green Chem. 2014, 16, 4440–4473.

(11) Lutz, H. Ultrafiltration: Fundamentals and Engineering. In Comprehensive Membrane; Drioli, E.; Giorno, L., Eds.; Elsevier B.V.: Oxford, 2010; Vol. 2, pp 115–139.
Liu, F.; Hashim, N. A.; Liu, Y.; Moghareh Abed, M. R.; Li, K. Progress in the production and modification of PVDF membranes. *J. Membr. Sci.* 2011, 375, 1–27.

Kang, G.-D.; Cao, Y.-M. Application and modification of poly(vinylidene fluoride) (PVDF) membranes – a review. *J. Membr. Sci.* 2014, 463, 145–165.

Fontanovana, E.; Bahattab, M. A.; Alilj, S. A.; Allowardt, M.; Rinaldi, G.; Vuento, D.; Nagy, J. B.; Diroli, E.; Di Proio, G. From hydrophobic to hydrophilic polyvinylidene fluoride (PVDF) membranes by gaining new insight into material’s properties. *RSC Adv.* 2015, 5, 56219–56231.

Diroli, E.; Di Proio, G.; Cucio, E. *Membrane-Assisted Crystallization Technology, Advances in Chemical and Process Engineering*, Eds.; Imperial College Press: London, 2015; Vol. 2.

Rahajeldeh, S.; Yoshimoto, S.; Teramoto, M.; A-Marzouqi, M.; Matsuyama, H. CO₂ absorption by using PVDF hollow fiber membrane contactors with various membrane structures. *Sep. Purif. Technol.* 2009, 69, 210–220.

Gómez-Coma, L.; Garea, A.; Ibraheem, A. Hybrid Solvent ([lemin][Ac]_2water) To Improve the CO₂ Capture efficiency in a PVDF Hollow Fiber Contactor. *ACS Sustainable Chem. Eng.* 2017, 5, 734–743.

Zhang, W.; Shi, Z.; Zhang, F.; Liu, X.; Jin, J.; Jiang, L. Superhydrophilic and Superoleophilic PVDF Membranes for Effective Separation of Water-in-oil Emulsions with High Flux. *Adv. Mater. Interfaces* 2015, 2, 2071–2076.

Park, S. Y.; Chung, J. W.; Chao, Y. K.; Kwak, S.-Y. Amphiphilic Thiol Functional Linker Mediated Sustainable Anti-Biofouling Ultrafiltration Nanocomposite Comprising a Silver Nanoparticles and Poly(vinylidene fluoride) Membrane. *ACS Appl. Mater. Interfaces* 2013, 5, 10705–10714.

Gopakumar, D. A.; Pasquini, D.; Henrique, M. A.; de Morais, L. C.; Grohens, Y.; Thomas, S. Meldrum’s Acid Modified Cellulose Nanofiber-Based Polyvinylidene Fluoride Microfiltration Membrane for Dye Water Treatment and Nanoparticle Removal. *ACS Sustainable Chem. Eng.* 2017, 5, 2026–2033.

Zhao, Q.; Xie, R.; Luo, F.; Faraj, Y.; Liu, Z.; Ju, X. J.; Wang, W.; Chou, L. Y. Preparation of high strength poly(vinylidene fluoride) porous membranes with cellular structure via vapor-induced phase separation. *J. Membr. Sci.* 2018, 549, 151–164.

Al-Marzouqi, F. A.; Bilad, M. R.; Arafat, H. A. Improving liquid entry pressure of polyvinylidene fluoride (PVDF) Membranes by exploiting the role of fabrication parameters in vapor-induced phase separation VIPS and non-solvent-induced phase separation (LIPS) processes. *Appl. Sci.* 2017, 7, 181.

Peng, Y.; Fan, H.; Dong, Y.; Song, Y.; Han, H. Effects of exposure time on variations in the structure and hydrophobicity of polyvinylidene fluoride membranes prepared via vapor-induced phase separation. *Appl. Surf. Sci.* 2012, 258, 7782–7781.

Hassankiadeh, N. T.; Cui, Z.; Kim, J. H.; Shin, D. W.; Lee, S. Y.; Sanguineti, A.; Arcella, V.; Lee, Y. M.; Diroli, E. Microporous poly(vinylidene fluoride) hollow fiber membranes fabricated with PolarClean as water-soluble green diluent and additives. *J. Membr. Sci.* 2015, 479, 204–212.

Fadhil, S.; Marino, T.; Makki, H. F.; Alsalhyy, Q. F.; Figoli, A. Novel PVDF-HFP flat sheet membranes prepared by triethyl phosphate (TEP) solvent for direct contact membrane distillation. *Chem. Eng. Process.* 2016, 102, 16–26.

Wang, Q.; Wang, Z.; Wu, Z. Effects of solvent compositions on physicochemical properties and anti-fouling ability of PVDF microfiltration membranes for wastewater treatment. *Desalination* 2012, 297, 79–86.

Bottino, A.; Camera-Roda, G.; Capannelli, G.; Munari, S. The formation of microporous polyvinylidene difluoride membranes by phase separation. *J. Membr. Sci.* 1991, 57, 1–20.

Zhang, M.; Zhang, A. Q.; Zhu, B. K.; Du, C. H.; Xu, Y. Y. Polymorphism in porous poly(vinylidene fluoride) membranes formed via immersion precipitation process. *J. Membr. Sci.* 2008, 319, 169–175.

Van Krevelen, D. W. Properties of Polymers; Elsevier: Amsterdam, 1990.

Mu, C.; Su, Y.; Sun, M.; Chen, W.; Jiang, Z. Fabrication of microporous membranes by a feasible freeze method. *J. Membr. Sci.* 2010, 361, 15–21.

Su, Y.; Liang, Y.; Mu, C.; Jiang, Z. Improved Performance of Poly(Vinylidene Fluoride) Microfiltration Membranes Prepared by Freeze and Immersion Precipitation Coupling Method. *Ind. Eng. Chem. Res.* 2011, 50, 10525–10532.

Wang, B.; Ji, J.; Li, K. Crystal nuclei templated nanostructured membranes prepared by solvent crystallization and polymer migration. *Nat. Commun.* 2016, 7, 12804.

Fontanovana, E.; Cucuto, V.; Cucio, E.; Trotta, F.; Biasizzo, M.; Diroli, E.; Barbieri, G. Influence of the preparation conditions on the properties of polymeric and hybrid cation exchange membranes. *Electrochim. Acta* 2012, 66, 164–172.

Cucio, E.; Di Proio, G.; Diroli, E. Membrane distillation and osmotic distillation. In *Comprehensive Membrane Science and Engineering*; Diroli, E.; Gionno, L., Eds.; Elsevier B.V.: Amsterdam, The Netherlands, 2010; Vol. 4, Chapter 4.01, pp 1–20.

http://www.solypastics.com (accessed October 2, 2018).

Horcas, I.; Fernandez, R.; Gomez-Rodiguez, J. M.; Colchero, J.; Gomez-Herrero, J.; Baro, A. M. WSXM: A software for scanning probe microscopy and a tool for nanotechnology. *Rev. Sci. Instrum.* 2007, 78, 013705–013705–8.

Franken, A. C. M.; Nolten, J. A. M.; Mulder, M. H. V.; Bargeman, D.; Smolders, C. A. Wetting criteria for the applicability of membrane distillation. *J. Membr. Sci.* 1987, 33 (3), 315–328.

Pallas, N. N.; Harrison, Y. An Automated Drop Shape Apparatus and the Surface Tension of Pure Water. *Colloids Surf.* 1990, 43, 169–194.

Gregorio, R.; Cestari, M. Effect of crystallization temperature on the crystalline phase content and morphology of poly(vinylidene fluoride). *J. Polym. Sci. Part B: Polym. Phys.* 1994, 32, 859–864.

Martins, P.; Lopes, A. C.; Lanceros-Mendez, S. Electroactive phases of poly(vinylidene fluoride): Determination, processing and applications. *Prog. Polym. Sci.* 2014, 39, 683–706.

Majidi Salehi, S.; Di Proio, G.; Fontanovana, E.; Nicoletta, F. P.; Cucio, E.; De Filipo, G. Membrane distillation by novel hydrogel composite membranes. *J. Membr. Sci.* 2016, 504, 220–229.

Barton, A. F. M. *CRC Handbook of Polymer-Liquid Interaction Parameters and Solubility Parameters*; CRC Press: Boca Raton, 1990.

Zao, D.; Li, H. Membrane Formation Mechanism for Water-Solvent-PVDF Systems and Membrane Structure for Ultrafiltration Application. *Adv. Mater. Res.* 2012, 576, 129–132.

Yi, K.; Fang, L. Q.; Zhang, L.; Li, N.; Zhou, Y.; Kon Ryu, S.; Guang Jin, R. Diffusion coefficients of dimethyl sulfoxide (DMSO) and H₂O in PAN wet spinning and its influence on morphology of nascent polycrylonitrile (PAN) fiber. *J. Eng. Fibr. Fabr.* 2013, 8, 107–113.

Fadaei, A.; Salimi, A.; Mirzataheri, A. Structural elucidation of morphology and performance of the PVDF/PEG membrane. *J. Polym. Res.* 2014, 21, 545–552.

Fontanovana, E.; Jansen, J. C.; Cristiano, A.; Cucio, E.; Diroli, E. Effect of additives in the casting solution on the formation of PVDF membranes. *Desalination* 2006, 192, 190–197.

Strathmann, H.; Kimerle, K. Analysis of the structure-determining process of phase inversion membranes. *Desalination* 1990, 79, 283–302.

Di Proio, G.; Fontanovana, E.; Cucio, E.; Diroli, E. From Tailored Supports to Controlled Nucleation: Exploring Material Chemistry, Surface Nanostructure, and Wetting Regime Effects in Heterogeneous Nucleation of Organic Molecule. *Cryst. Growth Des.* 2012, 12, 3749–3757.
(50) Matsuyama, H.; Teramoto, M.; Nakatani, R.; Maki, T. Membrane formation via phase separation induced by penetration of nonsolvent from vapor phase. II. Membrane morphology. *J. Appl. Polym. Sci.* 1999, 74, 171–178.

(51) Caquineau, H.; Menut, P.; Deratan, A.; Dupuy, C. Influence of the relative humidity on film formation by vapor induced phase separation. *Polym. Eng. Sci.* 2003, 43, 798–808.

(52) Gao, J.; Liu, Y.; Xu, H.; Wang, Z.; Zhang, X. Mimicking Biological Structured Surfaces by Phase-Separation Micromolding. *Langmuir* 2009, 25, 4365–4369.

(53) Liao, Y.; Wang, R.; Fane, A. G. Fabrication of Bioinspired Composite Nanofiber Membranes with Robust Superhydrophobicity for Direct Contact Membrane Distillation. *Environ. Sci. Technol.* 2014, 48, 6335–6341.

(54) Zhang, W.; Shi, Z.; Zhang, F.; Liu, X.; Jin, J.; Jiang, L. Superhydrophobic and Superoleophilic PVDF Membranes for Effective Separation of Water in Oil Emulsions with High Flux. *Adv. Mater.* 2013, 25, 2071–2076.

(55) Cassie, B. D.; Baxter, S. Wettability of porous surfaces. *Trans. Faraday Soc.* 1944, 40, 546–551.

(56) Xiang, Y.; Xue, L.; Shen, J.; Lin, H.; Liu, F. Effect of solvents on morphology and polymorphism of polyvinylidene fluoride membrane via supercritical CO2 induced phase separation. *J. Appl. Polym. Sci.* 2014, 131, 41065.

(57) Tao, M. M.; Liu, F.; Ma, B. R.; Xue, L. X. Effect of solvent power on PVDF membrane polymorphism during phase inversion. *Desalination* 2013, 316, 137–145.

(58) Cui, Z.; Hassankiadeh, N. T.; Zhang, Y.; Drioli, E.; Lee, Y. M. Crystalline polymorphism in poly(vinylidene fluoride). *Prog. Polym. Sci.* 2015, 51, 94–126.