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Research Article

Dialkyl Carbonates as Green Solvents for Polyvinylidene Difluoride Membrane Preparation

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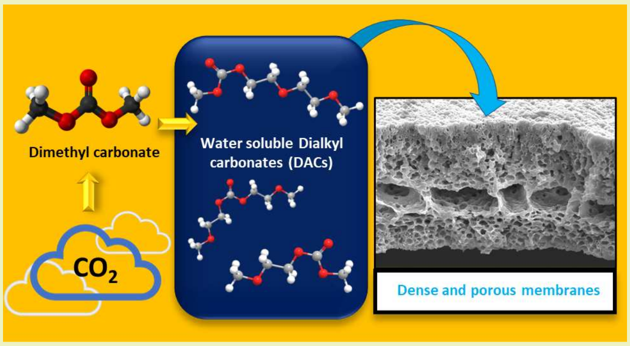
ABSTRACT: Membrane processes are employed in a wide variety of industrial applications such as separation of complex mixtures, hydrogen isolation, CO_2 removal, wastewater treatment, etc. Their use allows energy savings on the production cost compared to other traditional separation technologies. Nevertheless, the preparation of membranes not always fulfills sustainability obligations, especially when considering the commonly employed solvents, i.e., *N*-methyl-2-pyrrolidone and *N*,*N*-dimethylformamide, to mention just a few. Dialkyl carbonates (DACs) are well-known green solvents and reagents that have been extensively investigated as safe alternatives to chlorine-based compounds and media such as alkyl halides, phosgene, and chlorinated solvents. Following our recent study on a scale-up procedure to non-commercially available or expensive DACs, herein we report for the first time the application of organic carbonates as green media for membrane preparation. Theoretical thermodynamic studies were first carried out to predict the solubilities in DACs of different polymers commonly employed for membranes preparation. As a result, the use of selected organic carbonates as media for polyvinylidene difluoride membrane preparation was investigated by nonsolvent-induced phase separation (NIPS) and a combination of vapor-induced phase separation (VIPS)-NIPS techniques. Membranes obtained with custom-made DACs displayed greater structural resistances and smaller pore sizes compared to the ones achieved using commercially available cyclic organic carbonates. Data collected showed that it was possible to achieve a wide variety of dense and porous membranes by using a single family of compounds, highlighting once again the great versatility of DACs as green solvents.



KEYWORDS: *Dialkyl carbonates, Green solvents, Polyvinylidene difluoride, Membranes*

■ INTRODUCTION

The intrinsic proprieties of membrane-based processes make them a simple, flexible, selective, and environmentally friendly technology which requires low energy consumption as well as simple scale-up and operational conditions.[1−3] Membrane processes are effectively employed in a wide variety of industrial applications including the separation of complex mixtures, hydrogen isolation and CO_2 removal,[4] wastewater treatment,[5] and water desalination,[6,7] allowing up to 50% of energy savings on the production cost compared to other traditional separation technologies.[4]

Nevertheless, to completely fulfill sustainability obligations, as highlighted in the recent European Green Deal (EGD),[8,9] attention must be given to membrane preparation procedures and, in particular, to solvent selection. In fact, most of the commonly employed solvents in this field (namely, *N*-methyl-2-pyrrolidone, NMP; *N*,*N*-dimethylformamide, DMF; and *N*,*N*-dimethylacetamide, DMAC) display cancerogenic and teratogenic effects,[10] thus representing a threat to the ecosystem and human beings.[11,12]

However, replacing traditional organic solvents with greener alternatives is not an easy task, since they have a particular set of properties that play a crucial role in determining the final membrane morphology and performance. Solvent properties such as viscosity, dielectric constant, polarity, and boiling point greatly affect membrane characteristics imparted in their formation.[12]

In the last 20 years, the number of scientific publications concerning toxic solvent replacement in membrane preparation grew sharply.[13] Different green solvent categories have been proposed for membrane preparation, mostly using NIPS and TIPS techniques: (i) biobased solvents such as Cyrene and its derivatives,[14−16] dimethyl isosorbide (DMI),[12] methyl

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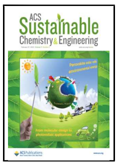

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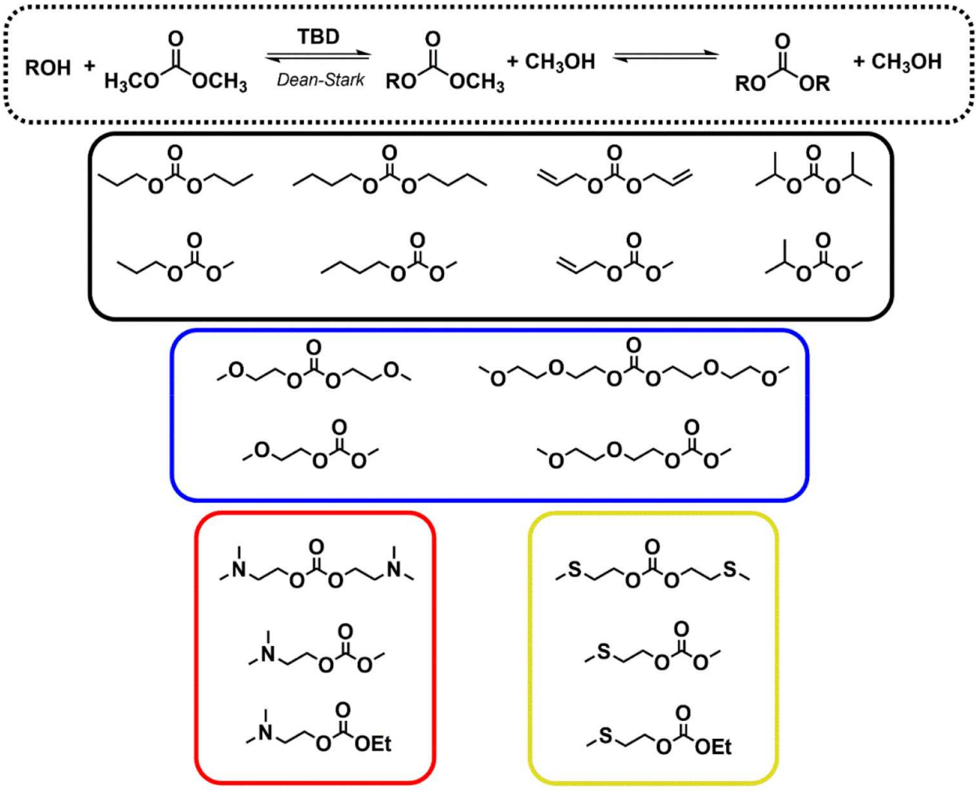

Figure 1. Library of DACs synthesized via TBD-catalyzed transcarbonylation reactions: alkyl-based DACs (black frame), alkoxyalkyl-based DACs (blue frame), alkylamino-based DACs (red frame), and alkylthio-based DACs (yellow frame).

lactate,[17] *N*,*N*-dimethyl lactamide and succindiamide,[18] γ-valerolactone,[13,19] γ-butyrolactone,[20] glycerol derivatives,[21−23] 2-methyl tetrahydrofuran (2-Me THF),[17] (ii) nonionic synthetic organic solvents (Rhodiasolv and PolarClean),[24−27] (iii) ionic liquids (IL),[28−34] (iv) deep eutectic solvents (DES),[35,36] and (v) dialkyl carbonates (DACs).[11,37,38]

DACs are widely known to be safe alternatives to chlorine-based reagents and solvents. They have been extensively employed as green replacements to alkyl halides and dimethyl sulfate in alkylation procedures and phosgene-derived compounds in carbonylation and alkoxycarbonylation reactions.[39] In addition, organic carbonates can be employed both as solvents and reagents for the synthesis and upgrading of various biobased platform chemicals such as isosorbide,[40,41] 5-(hydroxymethyl)furfural (HMF), 2,5-furandicarboxylic acid (FDCA), and its esters.[42−47]

Compared to chlorine-based compounds, organic carbonates offer different benefits, among which are (i) low toxicity, (ii) non-persistence in the environment, and (iii) absence of dangerous wastes and side products.[48] Due to these characteristics, these compounds can be securely used and handled without any particular safety precautions for the operator.[49] Nevertheless, because of their lower reactivity compared to chlorinated compounds, reactions involving DACs usually require higher temperatures (60−200 °C) and longer reaction times.

Among DACs, several studies reported the use of commercially available cyclic carbonates, namely, ethylene carbonate (EC), propylene carbonate (PC), and butylene carbonate (BC) as green solvents for membrane preparation,[11,37,38] while applications of acyclic DACs in this field is almost unexplored apart from some tests involving dimethyl carbonate (DMC) and diethyl carbonate (DEC).[38,50−52] Although the aforementioned cyclic carbonates are produced industrially at low cost, the lack of diversity across their chemical structures means they can only be used to solubilize a limited number of polymers. Furthermore, in some cases, high temperatures (up to 130 °C) are required to achieve homogeneous polymer solutions.[53,54] To overcome these issues, DACs possessing different functional groups could be employed, but this usually means low scale industrial production and a higher market price.[11,55]

Recently, we have developed a high yielding scale-up synthesis of noncommercially available or expensive DACs (both symmetric and asymmetric) via a transcarbonylation reaction of an alcohol with DMC, promoted by the nitrogen-based organocatalyst 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD). DACs were obtained at a 100 mL scale (yields up to 97%) without time-consuming purifications, using inexpensive reagents and recycling up to 90% of the starting compounds (Figure 1).

The majority of DACs obtained was demonstrated to partially or completely biodegrade in the environment, and—except for amino and thio-based carbonates—they did not display any cytotoxicity in animal cells.[49]

Starting from these premises, the present work focuses on the use of both custom-made and commercially available DACs as non-toxic and biodegradable solvents for the preparation of polymeric membranes with dense and porous morphologies. Preliminary theoretical thermodynamic studies were conducted to predict the solubilities of different polymers in DACs. As a result, a polyvinylidene difluoride (PVDF) co-polymer was selected as the most suitable material for membrane preparation using non-solvent-induced phase separation (NIPS) and vapor-induced phase separation (VIPS) techniques. The influence of polymer concentration and additives on membrane properties and performances was evaluated. In addition, a comparison between commercially available organic carbonates and DACs synthesized via DMC transcarbonylation was conducted, highlighting their relative performances in polymer solubility and efficiency in membrane preparation.

■ EXPERIMENTAL SECTION

Materials. The PVDF Solef 21510 (polyvinylidene fluoride-co-hexafluoropropylene, MW = 290−310 kDa) polymer was supplied by Solvay Specialty Polymers (Bollate (MI), Italy). Ethylene carbonate (EC, 98%) and propylene carbonate (PC, 99.7%) were purchased by Sigma-Merck and used without any further purification. Polyvinylpyrrolidone K17 (PVP) MW = 38 kDa, supplied by BASF, and polyethylene glycol (PEG) MW = 200, supplied by Sigma-Aldrich, were employed as additives.

Thermodynamics: Hansen Solubility Parameters. Hansen solubility parameters (HSPs)[56] describe the different intermolecular interactions of a solvent arising from dispersive forces, δ_d; polar (dipole−dipole) forces, δ_p; and hydrogen bonding, δ_h. HSPs represent the components of the total cohesive energy density of a liquid, the square of the Hildebrand solubility parameter (δ_T), as given by eq 1.

$$\delta_T = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2} \qquad (1)$$

The three HSPs are represented as the x, y, z coordinates in the Hansen sphere model, used to compare solvent polarities for the purpose of understanding the solubility of polymers.[57,58] In this work, HSPs were obtained using Hansen Solubility Parameters in Practice (HSPiP, fourth edition, 5.3.08).[59,60] HSPiP can generate the 3D Hansen space and calculate the interaction distance (R_a) value between different solvents (s) and a solute (x) (eq 2). Thus, it assists users in the comparison of target solvents with traditional ones.[59]

$$R_a = \sqrt{4 \times [(\delta_{ds} - \delta_{dx})^2 + (\delta_{ps} - \delta_{px})^2 + (\delta_{hs} - \delta_{hx})^2]} \qquad (2)$$

Synthesis of Linear Dialkyl Carbonates (DACs). Symmetrical and asymmetrical DACs were synthesized in large scale according to the procedure previously reported in the literature.[49]

Membrane Preparation Using PVDF Solef 21510. A dope solution (10 or 14 wt %) of PVDF Solef 21510 in each of the selected DACs was prepared and heated at a temperature between 40 and 130 °C until complete dissolution was achieved. The compositions of the investigated membranes and the preparation conditions are summarized in Table 1. In the case of membranes prepared in the presence of additives, PVP K17 and PEG were initially dissolved in the selected DAC under stirring at 30 °C. After the complete dissolution of the additives, the Solef 21510 polymer was added, and the temperature was raised until a homogeneous solution was achieved. The solution was left for 2 h without stirring before casting to remove possible air bubbles. Then, the polymer solution was cast on a glass support using a casting knife with a gap set of 250 μm.

VIPS trials were conducted within a climatic chamber at 25 °C and with 55% relative humidity (RH). Cast solutions were exposed to humidity for 0.0, 2.5, or 5.0 min before immersion in a distilled water coagulation bath (20 °C). Once formed, membranes were kept in fresh water overnight. Afterward, membranes were washed three times in hot water (at 60 °C) to remove any residual solvent. Membranes were finally dried at room temperature for 24 h.

Table 1. PVDF21510 Membranes Prepared via NIPS and VIPS Techniques[a]

Membrane code	Solvent	PVDF21510 (wt %)	T (°C)[b]	Time (min)[c]
EC10−0M	EC	10	110	0.0
EC10−2.5M	EC	10	110	2.5
EC10−5M	EC	10	110	5.0
PC10−0M-A	PC	10	60	0.0
PC10−2.5M-A	PC	10	60	2.5
PC10−5M-A	PC	10	60	5.0
GlyMC10−0M	GlyMC	10	60	0.0
GlyMC10−2.5M	GlyMC	10	60	2.5
GlyMC10−5M	GlyMC	10	60	5.0
Gly_2C10−5M	Gly_2C	10	60	5.0
DGlyMC10−5M	DGlyMC	10	70	5.0
$DGly_2C10$−0M	$DGly_2C$	10	70	0.0
$DGly_2C10$−2.5M	$DGly_2C$	10	70	2.5
$DGly_2C10$−5M	$DGly_2C$	10	70	5.0
EC14−0M	EC	14	130[d]	0.0
EC14−2.5M	EC	14	130[d]	2.5
EC14−5M	EC	14	130[d]	5.0
PC14−0M-A	PC	14	80	0.0
PC14−2.5M-A	PC	14	80	2.5
PC14−5M-A	PC	14	80	5.0
GlyMC14−0M	GlyMC	14	70	0.0
GlyMC14−2.5M	GlyMC	14	70	0.0
GlyMC14−5M	GlyMC	14	70	0.0
Gly_2C14−0M	Gly_2C	14	70	0.0
Gly_2C14−2.5M	Gly_2C	14	70	2.5
Gly_2C14−5M	Gly_2C	14	70	5.0
DGlyMC14−0M	DGlyMC	14	90	0.0
DGlyMC14−2.5M	DGlyMC	14	90	2.5
DGlyMC14−5M	DGlyMC	14	90	5.0
$DGly_2C14$−0M	$DGly_2C$	14	70	0.0
$DGly_2C14$−2.5M	$DGly_2C$	14	70	2.5
$DGly_2C14$−5M	$DGly_2C$	14	70	5.0

[a] Code meaning: abbreviation of the solvent−polymer concentration (10 or 14 wt %)−minutes of exposure in the climatic chamber (0.0, 2.5, or 5 min). The letter "A" in the membrane codes indicates the presence of both PEG MW = 200 (10 wt %) and PVP K17 (5 wt %) as additives. Gly_2C, bis(2-methoxyethyl) carbonate; GlyMC, 2-methoxyethyl methyl carbonate; DGlyMC, 2-(2-methoxyethoxy)ethyl methyl carbonate; $DGly_2C$, bis(2-(2-methoxyethoxy)ethyl) carbonate. Distilled water was used as the nonsolvent in the coagulation bath. [b] Solubilization temperature. [c] Time in the climatic chamber. [d] PVDF melting point.

Characterization. Membranes surfaces and cross sections were observed by using a scanning electron microscope (SEM, Zeiss EVO, MA10). In case of cross sections, they were fractured, after freezing, in liquid nitrogen. All the samples were sputtered with gold (Quorum Q 150R S) before analyses. Bubble point and pore size were determined using a Porolux 1000 porometer using Fluorinert as a wetting liquid. The porosity of the membranes was calculated by eq 3

$$\text{Porosity}(\%) = \frac{\frac{wt_w - wt_d}{\rho_k}}{\frac{wt_w - wt_d}{\rho_k} + \frac{wt_d}{\rho_p}} \times 100 \qquad (3)$$

where wt_w is the membrane wet weight, wt_d is the membrane dry weight, ρ_k is the kerosene density (0.786 g/cm^3), and ρ_p is the polymer density (PVDF: 1.77 g/cm^3).

Membranes mechanical properties were determined using a Zwick Roell Z 2.5 testing unit where the membrane samples were stretched unidirectionally at a steady velocity of 5 mm min^{-1}.

The thicknesses of the membranes were evaluated by a digimatic micrometer (Mitutoyo 543-561D; metric dial indicator, 0 → 30 mm; measurement range, 0.0005 mm−0.001 mm; resolution, 1.5 μm).

Contact angle measurements were performed using a CAM 200 instrument (CAM200, KSV instruments, Finland) using ultrapure water.

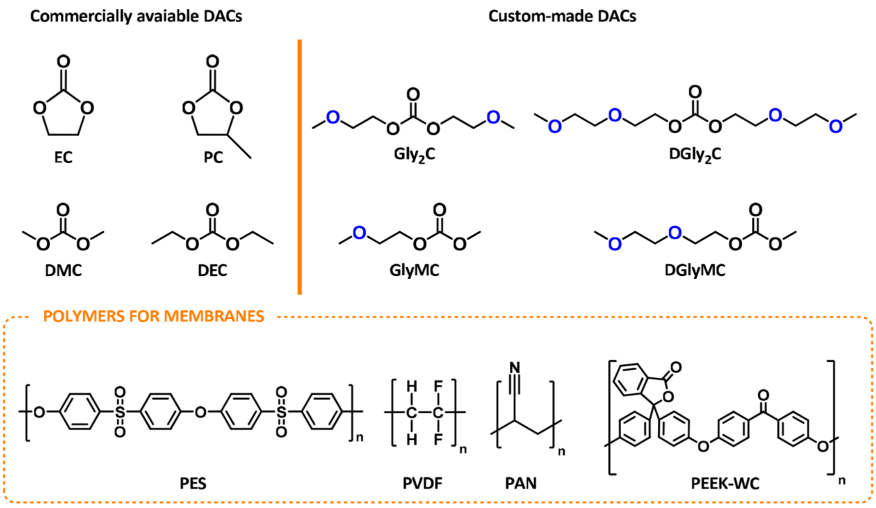

Figure 2. Chemical structure of the selected water-soluble DACs and polymers.

ATR-FTIR spectra were analyzed using a UATR crystal Diamond/ZnSe, Spectrum One System, by PerkinElmer Instruments. Spectra were recorded at a resolution of 4 cm^{-1}.

Pure water permeability (PWP) was measured using a lab-scale cross-flow cell. Water was pumped by means of a peristaltic pump (Tuthill Pump Co., California) through the membrane (area of 0.0008 m^2). The PWP was determined by using eq 4

$$\mathrm{PWP} = \frac{Q}{(A^{\times}t^{\times}\Delta p)} \quad (4)$$

where Q is the permeate volume (liters), A is the membrane area (m^2), t is the time (hours), and p is the pressure (bar).

Rejection tests were performed on the membranes prepared at 5.0 min of evaporation time (since they resulted permeable to water for all the investigated solvents except that for Gly_2C) using a dead-end filtration cell (Millipore Stirred Ultra-filtration Cell 8010) with an active area of 0.00038 m^2 and applying a pressure of 2.2 bar. A methylene blue (MB) aqueous solution (10 mg/L) was fed and filtered through the membranes for 60 min. The rejection (R) toward the dye MB was calculated by eq 5

$$R\% = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (5)$$

where C_f is the concentration of MB in the feed and C_p is the concentration of MB in the permeate. The MB concentration was determined via a spectrophotometer (ShimadzuUV-160A, Kyoto, Japan) at the wavelength of 664 nm.

■ RESULTS AND DISCUSSION

For this study several commonly used polymers for membranes were selected, i.e., polyether sulfone (PES), polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN), and amorphous polyetheretherketone called PEEK-WC or poly(oxa-p-phenylene-3,3-phthalido-p-phenylene-oxa-p-phenylene-oxy-phenylene) (Figure 2).

Solubility in water for a solvent is crucial for allowing the solvent/nonsolvent exchange during the phase separation process in membrane preparation. Thus, we selected as green media DACs that—according to previous investigations—displayed good water solubility (Figure 2 custom-made DACs, Table 2).[49] Commercially available carbonates, namely, ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), and diethyl carbonate (DEC), were also investigated as a comparison (Figure 2, Table 2).

Table 2. Physical–Chemical Properties of Commercial and Synthetic DACs[49]

DACs	bp (°C)	H_2O sol. (g/L)	(A)logP
DMC[a]	90	114.7	0.3
DEC[a]	126	18.8	1.2
EC[a]	248	778.0	0.1
PC[a]	242	200.0	−0.41
GlyMC	197	121.7[b]	0.5[b]
DGlyMC	214	194.4[b]	0.4[b]
Gly_2C	231	194.4[b]	0.4[b]
$DGly_2C$	329	420.2[b]	0.2[b]

[a]Values taken from https://echa.europa.eu/information-on-chemicals/registered-substances. [b]Computational predictions.

In Table 2 are displayed the boiling point, water solubility (H_2O sol. g/L) and the octanol–water partition coefficient (K_{OW} or P) of both custom-made and commercially available organic carbonates. All the DACs have high affinity to water (values from 194 to 778 g/L), excluding DMC, DEC, and GlyMC which display lower water solubilities (values from 19 to 122 g/L). DACs can be defined as high boiling VOCs except for $DGly_2C$ because its boiling point of 329 °C is higher than the VOC threshold temperature of 250 °C.[61]

Hansen Solubility Parameters (HSPs) Prediction and Solubility Tests. Hansen solubility parameters (HSPs) describe polymer solubility using a thermodynamic basis to quantify empirical "like dissolves like" observations. Dispersion forces (δ_d), dipoles (δ_p), and hydrogen bonding (δ_h) parameters measure the intermolecular interactions between solvents and solutes. When represented visually, a short distance between the plotted HSPs of the solvent and polymer in the 3D Hansen space indicates similarity between the two components. Polymers are generally soluble only in solvents with similar HSPs values.

HSPs for the selected polymers, i.e., PVDF, PES, PAN, and PEEK-WC, and solvents comprising commercial and synthetic DACs, are plotted in Figure 3, while HSP values are reported in the Supporting Information (Table S1). Solvents able to solubilize the polymer are represented as blue balls and fall within the Hansen solubility sphere (green), while those which are not are displayed as red cubes.

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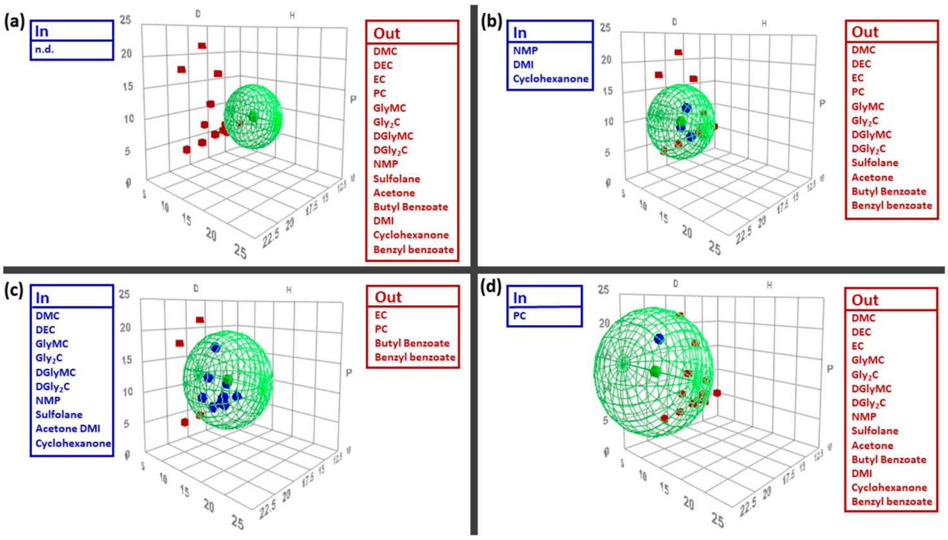

Figure 3. Hansen sphere of each of the polymers tested: (a) PEEK-WC, (b) PES, (c) PVDF, and (d) PAN. Compounds able (inside the sphere, blue color) and unable (outside the sphere, red color) to solubilize each polymer are listed on the sides.

According to its HSPs values, PVDF showed to be soluble in most of the synthetic and commercial carbonates and PAN only in PC, while none of the DACs are predicted to dissolve PES and PEEK-WC. Indeed, solvents displayed inside the PES Hansen sphere as blue balls (Figure 3b) correspond to compounds not belonging to the DACs family (namely, DMI, cyclohexanone, and NMP).

Considering these results, two types of PVDF polymers available in our laboratory, namely, Solef PVDF6010 and the copolymer Solef PVDF21510, were further investigated. In particular, the latter one showed to be the most soluble in the DACs selected for this study. In fact, in a preliminary screening, we were able to obtain stable membranes with a higher number of DACs (Table S2, Supporting Information). Thus, PVDF21510 was selected as the most suitable material for membrane preparation employing organic carbonates.

The solubility of the PVDF copolymer in each solvent was then experimentally investigated to confirm the predictions, and the data collected are plotted using HSP software (Figure 4). A solution of Solef PVDF21510 (10 wt %) was prepared employing different solvents (DACs and representative conventional solvents) and heated at a temperature between 60 and 110 °C until complete dissolution was achieved (if soluble at all). In Figure 4, the center of the sphere (green ball) represents the calculated HSPs of the polymer: δ_d = 17.8 MPa$^{1/2}$, δ_p = 13.6 MPa$^{1/2}$, δ_h = 5.2 MPa$^{1/2}$ (see also Table S3, Supporting Information).

PVDF21510 was solubilized by all the synthetic and commercial DACs except for DMC (Figure 4). In the case of EC, the high temperatures (110−130 °C) required to achieve complete polymer solubilization indicate that the actual polarities of the solvents under experimentation may be significantly different to what they are calculated to be at room temperature with HSPs.[11] EC is at the very edge of the solubility sphere, thus requiring temperatures close to the melting point of the polymer. As a result, the polymer solubilization may be closer to a hot melt liquid−liquid interaction than a true dissolution. Nevertheless, the range of solvent polarities that are complementary to dissolving Solef PVDF21510 (green sphere, Figure 4) is occupied by DACs. Most probably, increasing the number of ether moieties in the DACs also increases the interaction radius with the solute. GlyMC, with a single ether moiety, has the closest HSPs to PVDF21510 of the synthesized DACs. GlyMC also has the lowest boiling point and lowest water solubility from this set of novel solvents.

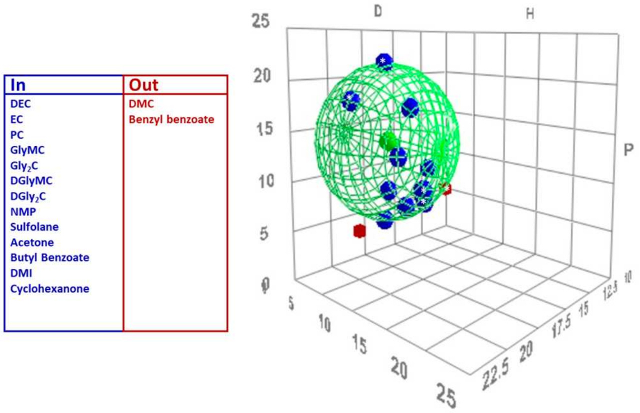

Figure 4. Hansen solubility sphere. Solvents able to solubilize the polymer are represented as blue balls and fall within the Hansen solubility sphere (green), while those which are not are displayed as red cubes. DACs visible in the image have been highlighted with a white asterisk. The center of the sphere (represented as a green ball) shows the optimum HSP for good solvency (namely, [17.8, 13.6, 5.2] MPa$^{1/2}$).

It was demonstrated experimentally that the solubility limit of PVDF 21510 in the different DACs investigated (for obtaining a clear and stable solution) ranged from 28% of polymer concentration (when EC was used as a solvent) to 38% (when PC was used as a solvent), and it is inherently related to the applied temperature.

Membrane Preparation Employing DACs as Green Solvents. Studies on membrane production were performed employing the PVDF21510 polymer and different DACs. For all the trials reported in Table 3, both non-solvent-induced phase separation (NIPS) and vapor-induced phase separation (VIPS) techniques were used. The dope solution containing the dissolved polymer and the selected DAC was gradually

Table 3. Membrane Preparation Using PVDF21510 (14 wt %) with Different DACs

Membrane code	Solvent	Technique	Casting temp. (°C)	Membrane formation
EC14-0M	EC	NIPS (VIPS 0 min)	130	YES
EC14-2.5M	EC	VIPS 2.5 min	130	YES
EC14-5M	EC	VIPS 5 min	130	YES
PC14-0M	PC[b]	NIPS (VIPS 0 min)	70	YES
PC14-0M-A	PC[a]	NIPS (VIPS 0 min)	80	YES
PC14-2.5M-A	PC[a]	VIPS 2.5 min	80	YES
PC14-5M-A	PC[a]	VIPS 5 min	80	YES
GlyMC14-0M	GlyMC	NIPS (VIPS 0 min)	70	NO
GlyMC14-2.5M	GlyMC	VIPS 2.5 min	70	NO
GlyMC14-5M	GlyMC	VIPS 5 min	70	NO
Gly$_2$C14-0M	Gly$_2$C	NIPS (VIPS 0 min)	70	YES
Gly$_2$C14-2.5M	Gly$_2$C	VIPS 2.5 min	70	YES
Gly$_2$C14-5M	Gly$_2$C[b]	VIPS 5 min	70	YES
DGlyMC14-0M	DGlyMC	NIPS (VIPS 0 min)	90	YES
DGlyMC14-2.5M	DGlyMC	VIPS 2.5 min	90	YES
DGlyMC14-5M	DGlyMC	VIPS 5 min	90	YES
DGly$_2$C14-0M	DGly$_2$C	NIPS (VIPS 0 min)	70	YES
DGly$_2$C14-2.5M	DGly$_2$C	VIPS 2.5 min	70	YES
DGly$_2$C14-5M	DGly$_2$C	VIPS 5 min	70	YES

[a] Additives employed: Polyethylene glycol MW = 200 (10 wt %) and PVP K17 (5 wt %). [b] Surface imperfections and inhomogeneities (yellow table cells, see also Figure S1). Code meaning: abbreviation of the solvent−polymer concentration (14 wt %)−minutes of exposure in the climatic chamber (0.0, 2.5, or 5 min). The letter "A" at in the membrane codes highlight the presence of additives (namely, PEG MW = 200 (10 wt %) and PVP K17 (5 wt %)).

heated until a homogeneous solution was achieved; homogeneous solutions were obtained at a temperature between 60 and 130 °C, depending on the solvent employed. The solution was then left for 2 h without stirring before casting, in order to remove possible air bubbles. Afterward, the hot polymer solution was cast on a glass support using a casting knife (gap set of 250 μm) and it was directly submerged in a water bath at 20 °C (NIPS technique) and inserted in the climatic chamber for 2.5 or 5 min (relative humidity, RH, of 55% at 25 °C) and then submerged in a water bath at 20 °C (VIPS-NIPS technique).

In Table 3, green table cells represent polymer/DAC combinations which led to the formation of a polymeric membrane. Those in red caused the disruption of the membrane immediately after the immersion into the coagulation bath, while in yellow are depicted those membranes which formed with surface imperfections (examples can be found in Figure S1, Supporting Information).

Initial trials were conducted employing a 10 wt % polymer loading, leading to fragile and non-reproducible membranes (see also SEM analyses in Figure S2, Supporting Information), particularly when EC was used as a solvent (see Table S4, Supporting Information). A higher PVDF21510 concentration (14 wt %) led to more stable membranes, and therefore, it was employed in the experiments with all the selected DACs. In fact, a superior structural resistance given by a greater polymer concentration most likely avoided membrane disruption during the immersion in the coagulation bath. Moreover, it must be mentioned that EC required high temperature to solubilize the polymer (at both 10 and 14 wt %); thus, the casting via NIPS technique was problematic. In fact, the dope solution, once removed from the oil bath, rapidly solidified, in some cases adhering the casting knife to the glass surface. Therefore, the TIPS technique could be more suitable to prepare membranes with this cyclic carbonate as previously reported in the literature.[11]

PC14−0M displayed many surface imperfections (Table 3), so PEG (10 wt %) and PVP (5 wt %) were used as additives. Previous investigations showed that the combined use of PVP and PEG increases the dope solution viscosity affecting the kinetics of the phase inversion process by decreasing the solvent/nonsolvent exchange rate[62] contributing to the formation of membranes with less defects. This was also confirmed in our case study when casting the PVDF copolymer at 80 °C in the presence of these additives (PC14−0M-A, PC14−2.5M-A, PC14−5M-A).

No membrane could be obtained with GlyMC independently of the polymer concentration (Table 3; Table S4, Supporting Information). This result contradicts the HSP modeling that indicated GlyMC had the most complementary polarity for the polymer of all the synthesized DACs. The poor membrane formation is most likely due to the poor water miscibility of GlyMC (Table 2). In order to form a membrane via NIPS, instantaneous solvent−nonsolvent demixing during

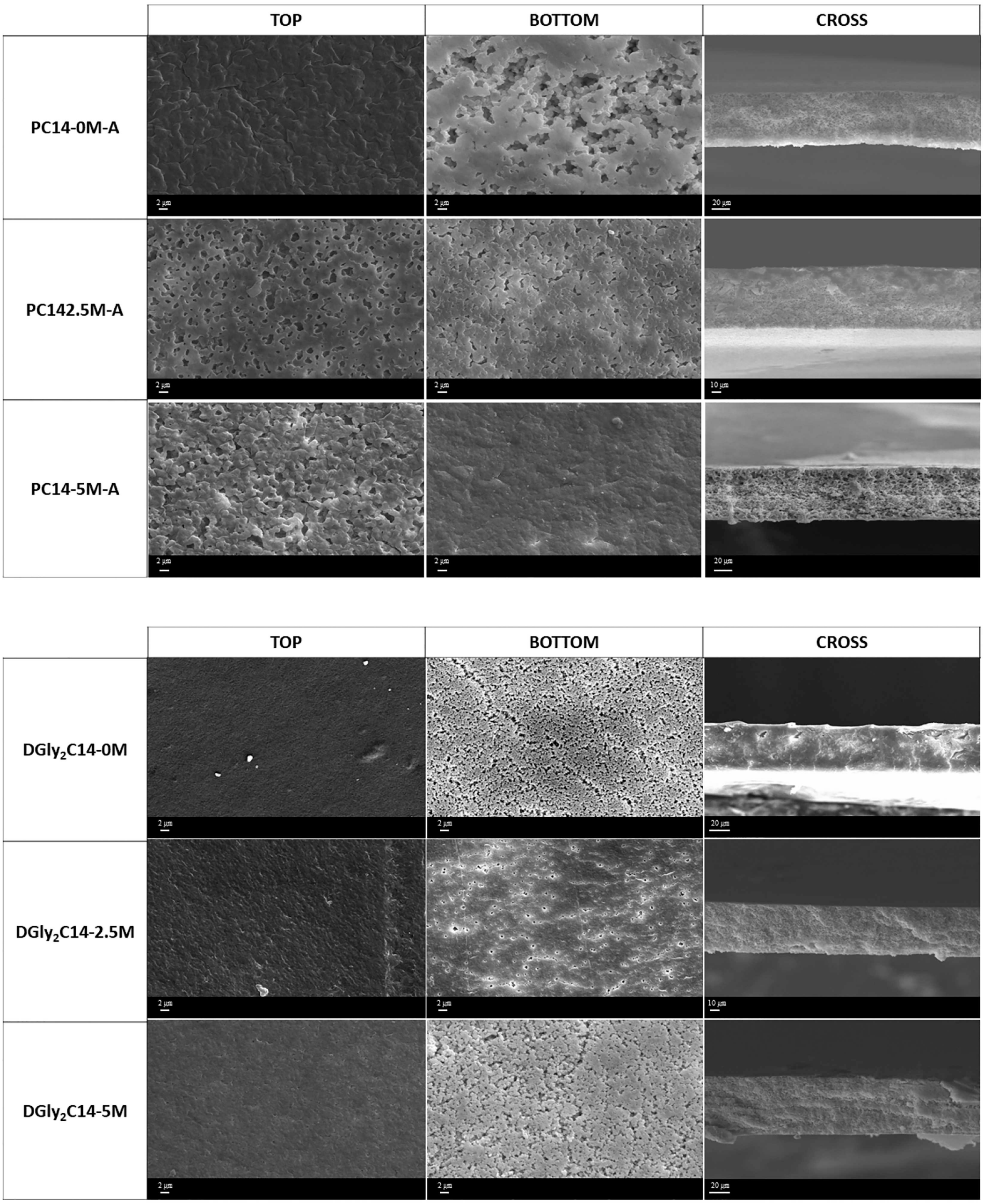

Figure 5. SEM analyses of PC- and DGly$_2$C-derived membranes with 14 wt % PVDF21510 loading obtained via NIPS and NIPS-VIPS techniques: 0.0, 2.5, and 5.0 min in the climatic chamber, RH = 55%. Magnification for top and bottom surfaces: 5000X and 1000X for cross sections. Remaining SEM pictures are displayed in Figure S3 in the Supporting Information.

the phase inversion needs to occur. Similarly, VIPS requires condensation of water vapor on the surface of the membrane resulting in localized phase separation through solvent/nonsolvent interactions.[63]

Gly$_2$C, DGlyMC, and DGly$_2$C can be efficiently used for membrane preparation independently by the exposure time in the climatic chamber. The only exception was for the membrane casted with Gly$_2$C after 5 min in the climatic chamber that showed some surface imperfections.

In conclusion data reported in Table 3 clearly show that PVDF21510-based membranes can be easily formed with custom-made linear DACs compared to commercially available cyclic carbonates that required either high temperatures or the use of additives to avoid surface imperfections.

It should be mentioned that the temperature used for solubilizing the polymer in the selected custom-made DACs ranged from 70 to 90 °C. This dissolution temperature was similar, or even lower, with respect to the temperature required for solubilizing PVDF polymers using other green solvents (e.g., Cyrene, 70 °C;[16] DMI, 120 °C;[12] DES, 120 °C;[64] Tamisolve, 80 °C[65]) or using traditional solvents (e.g., NMP, 80 °C;[66] DMF, 80 °C[67]).

Membrane Characterizations: Morphology. Figure 5 and Figure S3 (Supporting Information) report SEM pictures of PVDF21510 membranes prepared via VIPS with different DACs at different evaporation times (Table 3, at 0.0, 2.5, and 5.0 min). Obtained membranes revealed different structures depending on the solvent employed for their preparation. In general, membranes prepared by the NIPS technique showed a more compact and denser layer, which was replaced by more porous structures when the cast film was exposed to humidity (VIPS) before coagulation in water (NIPS), as also confirmed by pore size measurements. As widely recognized, humidity has, in fact, a porogen effect on membrane surfaces. The adsorption, by the cast film, of water molecules from humid air delays the phase inversion process favoring the formation of more porous structures.[68,69]

Almost all the membranes showed sponge-like morphologies visible along their cross-sections as an indication of a lower demixing rate. However, EC14−0M, EC14−2.5M, and EC14−5M membranes represent the exception, being characterized by columnar cross-sectional structures (Figure S3). This is probably related to the higher solubility of EC in water with respect to the other investigated DACs, favoring a faster solvent/nonsolvent exchange rate. In fact, among the investigated DACs, EC is the solvent with the highest solubility in water (see Table 2) which makes it more likely to diffuse from the cast film to the water bath during the phase inversion process. Generally, fast demixing rates lead to the formation of membranes characterized by finger-like or macrovoid structures.[70,71]

Cross sections of PC14−0M-A, PC14−2.5M-A, and PC14−5M-A, on the contrary, were more compact and characterized by sponge-like architectures (Figure 5). This can be related to the presence of additives (PEG and PVP). These additives are generally employed as pore forming agents, improving membrane pore size and porosity thanks to their affinity with water. Moreover, their hydrophilic nature induces a faster demixing rate of the dope solution in the coagulation bath, fostering the formation of very open structures characterized by fingers and macrovoids.[65]

In this case study, it was observed that the addition of PVP and PEG led to the formation of membranes with a sponge-like morphology. This result may be due to the fact that the concomitant addition of PVP and PEG led to an increase in dope solution viscosity which slowed down the solvent/nonsolvent exchange rate during membrane formation, an effect already reported in the literature.[72] Therefore, it is reasonable to assume that the kinetic factors (e.g., viscosity), entering into play during the coagulation of these membranes, were dominant with respect to thermodynamic factors.

Membranes prepared with solvents Gly$_2$C, DGlyMC, and DGly$_2$C showed similar morphologies characterized by compact and dense structures visible along their cross sections (Figure 5, Figure S3). This can be related to the same R_a values (7.37) of these solvents, as reported in Table S3 (Supporting Information), which is lower compared to EC (8.10). The lower the R_a value is, the higher the polymer−solvent affinity is, thus resulting in a lower demixing rate leading to the formation of membranes with sponge-like architecture structures.[70,71,73,74]

Thickness, Porosity, and Contact Angle. Table 4 represents thickness, porosity, and contact angle values of membranes obtained with the synthetic DACs as solvents (graphical representation available in the Supporting Information, Figure S4). Since GlyMC did not lead to the formation of any membrane even after 5 min in the climatic chamber, it was not included in the results.

Table 4. Thicknesses, Porosities, and Contact Angles of Novel PVDF21510-Based Membranes[a]

Membrane code	Technique	Thickness (μm)	Porosity (%)	Contact angle (deg)
EC14−0M	NIPS	93 ± 3	75 ± 1	92 ± 7
EC14−2.5M	VIPS 2.5	94 ± 1	86 ± 1	94 ± 5
EC14−5M	VIPS 5	94 ± 1	87 ± 1	93 ± 5
PC14−0M-A[b]	NIPS	63 ± 1	76 ± 1	90 ± 9
PC14−2.5M-A[b]	VIPS 2.5	73 ± 1	70 ± 1	110 ± 1
PC14−5M-A[b]	VIPS 5	64 ± 1	74 ± 1	90 ± 3
GlyMC14−0M	NIPS	n.d.[c]	n.d.[c]	n.d.[c]
GlyMC14−2.5M	VIPS 2.5	n.d.[c]	n.d.[c]	n.d.[c]
GlyMC14−5M	VIPS 5	n.d.[c]	n.d.[c]	n.d.[c]
Gly$_2$C14−0M	NIPS	46 ± 1	69 ± 1	98 ± 1
Gly$_2$C14−2.5M	VIPS 2.5	60 ± 1	52 ± 1	77 ± 1
Gly$_2$C14−5M	VIPS 5	51 ± 1	64 ± 1	105 ± 1
DGlyMC14−0M	NIPS	59 ± 1	67 ± 1	85 ± 1
DGlyMC14−2.5M	VIPS 2.5	79 ± 1	71 ± 1	77 ± 9
DGlyMC14−5M	VIPS 5	69 ± 1	72 ± 1	97 ± 1
DGly$_2$C14−0M	NIPS	64 ± 1	70 ± 1	83 ± 2
DGly$_2$C14−2.5M	VIPS 2.5	62 ± 1	81 ± 1	91 ± 4
DGly$_2$C14−5M	VIPS 5	97 ± 1	71 ± 1	96 ± 3

[a] Membranes were prepared using 14 wt % polymer concentration after 0.0, 2.5, and 5.0 min in the climatic chamber at $T = 25$ °C and RH = 55%. For the PC solvent, only trials containing additives were considered. [b] Additives employed: Polyethylene glycol MW = 200 (10 wt %) and PVP K17 (5 wt %). [c] No membrane formed.

Different trends in porosity and thickness can be observed according to the solvent employed. EC14 membranes displayed a sharp increase in porosity when exposed to humidity for 2.5 min, which then remained constant even after doubling the evaporation period. This behavior can be easily justified by the morphologies exhibited by the membranes as shown in Figure 5. As the exposure time to humidity was introduced before NIPS, the morphologies of the membranes changed from compact structures to lamellar porous architectures.

PC14-A and Gly$_2$C14 membranes had similar porosity trends, reaching their minimum after 2.5 min in the climatic chamber. In both cases after an exposure period of 5.0 min, their porosity increased to 74% and 64% respectively. The cross-section morphology of the membrane was, in fact, quite similar (Figure 5) independently from the preparation procedure employed.

DGly$_2$C14 membranes showed the highest porosity degree after 2.5 min in the climatic chamber, while porosity values of the corresponding membrane via NIPS and VIPS 5.0 min were comparable.

For DGlyMC14 membranes, the degree of porosity grew mildly upon increasing the exposure time to humidity. As visible from SEM images (Figure 5), the exposure to humidity led to the formation of surface pores responsible of the overall membrane porosity increase.

In general, the membranes did not always show a clear and linear trend in porosity. A potential explanation could be the variation of the closed porosity microstructure within these membranes.

The porosity measurement technique employed in this work, in fact, cannot provide measurements of the closed cells which may be present in the membrane structure, as also observed elsewhere in the literature.[75] Indeed, since the closed cells cannot be measured with the porosity technique employed here, it is possible that the closed porosities among these membranes are different, this is what would impact the membrane porosity values.

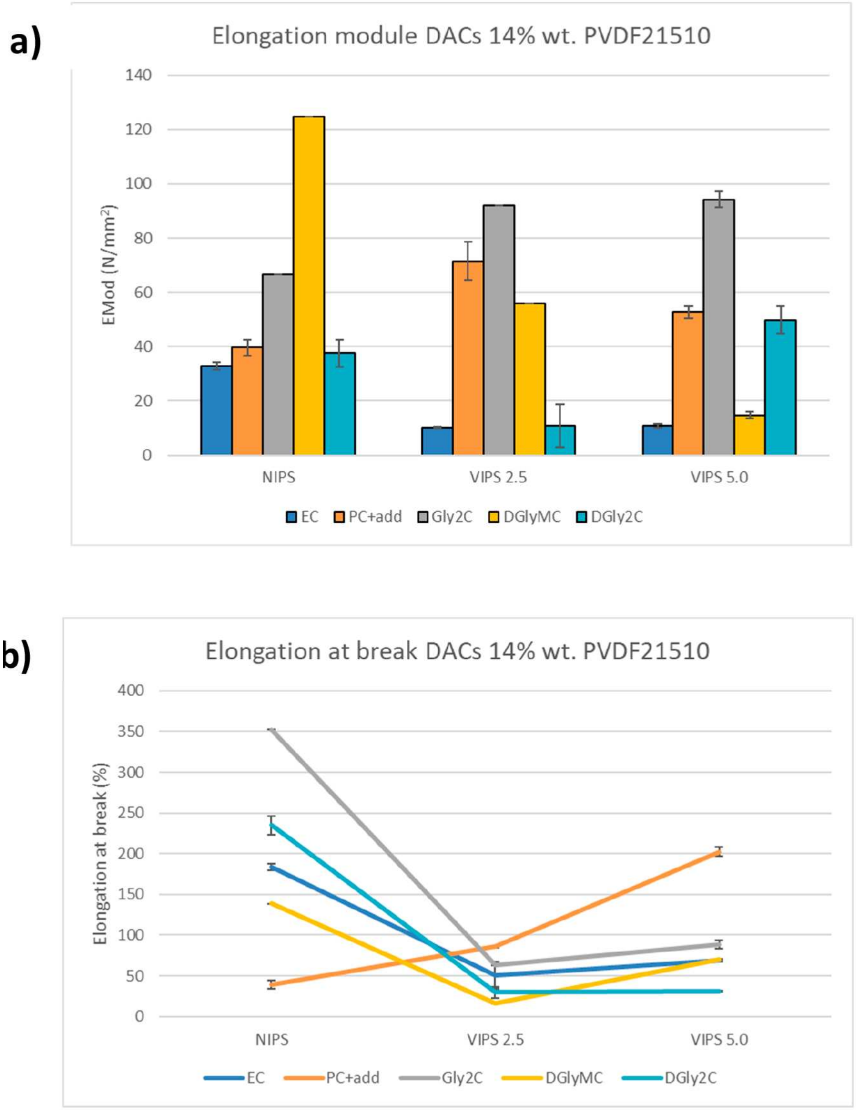

Figure 6. (a) Young's modulus (N/mm^2) and (b) elongation at break (%) of the prepared membranes (14 wt % polymer loading). Membranes have been divided according to their exposure time to humidity (namely, 0.0, 2.5, and 5.0 min).

The thickness of the membranes, although cast at the same gap set of 250 μm, was variable and dependent on the solvent employed (Table 4). For most of the membranes, the thickness increased when exposed to lower evaporation times (2.5 min) and then decreased at higher evaporation times (5 min). This can be due to a shrinkage phenomenon occurring to the membranes. It was observed, in fact, that as the exposure time of the cast film was prolonged; the membranes were subjected to a surface and vertical shrinkage which can occur during different moments of membrane preparation: in the climatic chamber, in the coagulation bath, and after drying. As also already observed in the literature, higher evaporation times lead to an increased shrinking phenomenon.[75] However, this phenomenon was not observed for the membranes prepared with EC and DGly$_2$C. The reason can be ascribed to the different solubility capacities of these solvents respect to the other DACs. Generally, the higher the solubility parameter of the solvent, the higher the shrinking degree of the membrane prepared with it.[76] This is related to the fact that solvents with higher solubility establish more and stronger interactions with the polymer chains, creating more stress between them. The stress would be then released during the preparation of the membrane and, in particular, during the drying process when the temperature is raised.[76]

As can be seen from Table 4, among the investigated DACs, EC and DGly$_2$C are the solvents with the highest R_a values (therefore lower solubility for the polymer). This lower affinity could be the reason why the shrinking phenomenon in the related membranes was less pronounced. and the decrease in the overall thickness, once exposed for longer time to humidity, was not observed.

The wettabilities of the produced membranes were analyzed through the determination of their contact angles. Data are reported in the last column of Table 4 (see also Figure S5, Supporting Information).

Contact angle analyses give an indication of the wettability of the produced membranes, ranging from 77° to 110°. The presence of residual PVP or PEG within the membrane would impact on contact angle due to their polar natures. This was discarded as no improvement in hydrophilicity was observed when comparing PVP/PEG/PVDF systems to pure PVDF. Since the membrane surfaces must all be made by the same material (PVDF copolymer), the discrepancies observed can be related to the differences in surface roughness of each membrane. In this regard, Wenzel[77] proposed a phenomenological model relating membrane roughness and wetting. In particular, the measured contact angle (θ_m) is related to the surface roughness by eq 6

$$\cos\theta_m = r\cos\theta_y \tag{6}$$

where r is the ratio of the projected surface area to the real surface area ($r = 1$ for a smooth surface and $r > 1$ for a rough surface), and θ_y is the Young contact angle, which is equal to θ_m if $r = 1$.[78] According to this equation, the higher the surface roughness, the higher the contact angle of a membrane.[79]

In this case, the membranes prepared by the VIPS technique generally presented contact angle values higher than the membranes produced by NIPS. This effect has been already observed in other studies where PVDF membranes were produced by NIPS and VIPS techniques.[16] The phenomenon is related to the fact that the VIPS process induces the formation of a higher surface porosity and larger surface pore size. This causes the formation of air pockets beneath the surface which hamper the penetration of the liquid leading to an improvement in the measured contact angle values.[80−82]

Mechanical Properties. Mechanical proprieties of the newly prepared membranes were evaluated in terms of Young's modulus (EMod, expressed in N/mm^2) and the elongation at break (expressed in %). Data are reported in Figure 6a and b and in Table S5 (Supporting Information).

EC14 and DGlyMC14 membranes' mechanical resistances (EMod) decreased as the exposure time to humidity increased (Figure 6a). This can be due to the fact that when the exposure time to humidity was increased also the porosity increased (Table 4). It is widely accepted, in fact, that a higher overall void fraction represents structural weak points in the membrane, causing a sharp drop in membrane mechanical resistance.[69,83,84] Conversely, Gly$_2$C14 membranes' EMod raised as the evaporation time increased, probably due to the absence of a porous structure as noticed in the morphology analyses (Figure 5) and in agreement with porosity values. All membranes displayed similar trends in terms of Ebreak, reaching their minimum after 2.5 min in the climatic chamber. PC14 membranes once again showed a different tendency with the maximum EBreak value reached with VIPS 5.0 min (Figure 6b).

Overall, membranes prepared with synthetic DACs displayed higher mechanical resistances compared to commercial ones, as proved by a higher EMod. The only exception was given by PC14 membranes which showed good EMod values and great elasticities. This can be ascribed to the presence of additives which led to a higher membrane stability and therefore to enhanced mechanical performances. The suppression of finger structures in the membranes prepared with PC, with respect to the membranes prepared with EC, certainly contributed to the improvement of their mechanical properties.

Pore Size and Pure Water Permeability (PWP). The pore sizes of the new membranes were next investigated (Table 5). Graphical representations were displayed in the Supporting Information (Figure S6). Larger pore sizes were detected upon increasing the exposure time to humidity. The solvent employed played a major role, strongly affecting membranes' pore sizes. However, in all cases, the membranes presented pore sizes in the microfiltration (MF) range.

Table 5. Pore Sizes and Bubble Points of PVDF21510 (14 wt %) Membranes Using DACs as Solvents[a]

Membrane code	Technique	Pore size (μm)	Bubble point (μm)
EC14−0M	NIPS	0.12 ± 0.01	0.65 ± 0.19
EC14−2.5M	VIPS 2.5	0.18 ± 0.04	0.64 ± 0.12
EC14−5M	VIPS 5.0	0.16 ± 0.01	0.27 ± 0.10
PC14−0M-A[b]	NIPS	0.21 ± 0.03	0.29 ± 0.02
PC14−2.5M-A[b]	VIPS 2.5	0.3 ± 0.01	0.45 ± 0.01
PC14−5M-A[b]	VIPS 5.0	0.71 ± 0.01	0.5 ± 0.01
Gly$_2$C14−0M	NIPS	n.m.[c]	n.m.[c]
Gly$_2$C14−2.5M	VIPS 2.5	n.m.[c]	n.m.[c]
Gly$_2$C14−5M	VIPS 5	n.m.[c]	n.m.[c]
DGlyMC14−0M	NIPS	n.m.[c]	n.m.[c]
DGlyMC14−2.5M	VIPS 2.5	0.11 ± 0.01	0.15 ± 0.01
DGlyMC14−5M	VIPS 5	0.32 ± 0.02	0.44 ± 0.01
DGly$_2$C14−0M	NIPS	n.m.[c]	n.m.[c]
DGly$_2$C14−2.5M	VIPS 2.5	0.14 ± 0.03	0.21 ± 0.01
DGly$_2$C14−5M	VIPS 5.0	0.10 ± 0.01	0.15 ± 0.02

[a] No membranes were formed with GlyMC, so it was not considered. [b] Additives employed: Polyethylene glycol MW = 200 (10 wt %) and PVP K17 (5 wt %). [c] Values not measurable.

Overall, two of the synthetic DACs (DGlyMC and DGly$_2$C) resulted in membranes having smaller pores (ranging between 0.32 and 0.10 μm) compared to commercially available organic carbonates (EC and PC, pore sizes between 0.7 and 0.12 μm). For both bespoke solvents, dense membranes were formed when the NIPS technique was employed. Gly$_2$C14 membranes resulted in dense surface layers with no measurable pores, as also visible in SEM images (Figure 5).

In general, cyclic and more bulky molecules (like the commercial EC and PC) diffuse through polymers more slowly than linear molecules (like synthetic DACs) even though there is complete miscibility between the polymer and solvent and the molecular volumes do not differ significantly.[85] This could be the reason why EC needed higher temperatures (130 °C) to solubilize the polymer, while PC required the presence of additives (PVP and PEG) to get stable and uniform membranes. The higher casting temperature and the presence of additives can be both responsible of the formation of membranes with larger pore sizes as a consequence of the faster demixing rate of the dope solution.

The role of VIPS, before coagulation in water (NIPS), in fostering the formation of more porous surfaces is widely accepted.[86] For membranes prepared with EC and DGly$_2$C, the pore size first increased (at 2.5 min) and then decreased (at 5.0 min). This phenomenon has been already observed and reported in the literature for PES membranes and related to thermodynamic and kinetic factors.[16] The exposure of a polymeric cast film to humidity causes, in fact, a delay in the phase-inversion process favoring the formation of more porous surfaces as a consequence of the creation of larger pore-lean phases. However, it can happen that a prolonged exposure time to humidity can cause the coarsening of the polymer-lean phase resulting in a reduction of the interconnectivity of membrane pores, finally leading to a smaller pore size. Water permeability (PWP) followed the same trend of pore size for almost all membranes (Table 6). All membranes prepared with Gly$_2$C and those prepared by NIPS with DGlyMC and DGly$_2$C were found not permeable to water as also confirmed by pore size measurements (no measurable pore size). Membranes prepared using PC as a solvent were found to

Table 6. Water Permeability of New Membranes with 14 wt % of PVDF 21510 Loading

Membrane code	Technique	PWP (L m^{-2} h^{-1} bar^{-1})
EC14−0M	NIPS	84 ± 8
EC14−2.5M	VIPS 2.5 min	16 ± 2
EC14−5M	VIPS 5 min	350 ± 35
PC14−0M-A[a]	NIPS	40 ± 4
PC14−2.5M-A[a]	VIPS 2.5 min	106 ± 20
PC14−5M-A[a]	VIPS 5 min	156 ± 20
Gly_2C14−0M	NIPS	0
Gly_2C14−2.5M	VIPS 2.5 min	0
Gly_2C14−5M	VIPS 5 min	0
DGlyMC14−0M	NIPS	0
DGlyMC14−2.5M	VIPS 2.5 min	0
DGlyMC14−5M	VIPS 5 min	59 ± 6
$DGly_2C14$−0M	NIPS	0
$DGly_2C14$−2.5M	VIPS 2.5 min	24 ± 2
$DGly_2C14$−5M	VIPS 5 min	180 ± 20

[a] Additives employed: Polyethylene glycol MW = 200 (10 wt %) and PVP K17 (5 wt %).

be among the most permeable (PWP up to 156 L/m^2 h bar) and in line with the high values of pore size data found for these membranes. These results can be ascribed to the use of pore forming additives (PVP and PEG) that were necessary to prepare these membranes.

The performances of the membranes prepared at the evaporation time of 5.0 min were investigated in terms of rejection (%) toward the dye MB. The highest rejection (80%) was found for the membrane $DGly_2C14$−5M as a consequence of its lower pore size (0.10 μm), while the lowest rejection value (9%) was found for the membrane PC14−5M-A related to its higher pore size (0.71 μm). The MB rejection was 67% for the membrane EC14−5M (pore size of 0.16 μm) and 14% for the membrane DGlyMC14−5M (pore size of 0.32 μm).

FT-IR Analyses. According to the polymorphs displayed by the PVDF polymer (namely, α, β, γ, δ, and ε), the resulting membranes can exhibit different morphologies and performances.[51,52,87] The α phase represents the nonpolar form, kinetically stable, and predominant, where nonpolar solvents are employed for PVDF processing. The β phase is the polar form, thermodynamically stable, occurring when polar solvents are employed.[88] FT-IR spectra (Figure 7) evidence the presence of both crystalline phases.

The α phase was visible in the peaks at 1402 and 1176 cm^{-1}, common to all membranes, and at 762 cm^{-1} for Gly_2C14, PC14-A, and DGlyMC14 membranes. The peaks at 840, 874, 1070, and 1274 cm^{-1} (this latter one just for EC14, $DGly_2C14$, and DGlyMC14 membranes) are ascribable to the β phase.[16,65] The peak at 840 cm^{-1}, detectable for all membranes, is common for both β and γ phases.[89] For Gly_2C14 and PC14-A membranes, α and β phases were present in equal measure. For all the other membranes, the β polymorphism was dominant suggesting that, in these cases, thermodynamic factors played the major role during PVDF crystallization process. The β phase is, generally, the result of the interactions of water nonsolvent molecules and PVDF polymers through strong and weak hydrogen bonds which lead to the growth of PVDF crystals.[64,90]

Moreover, the prevalence of the β phase can be related to the use, in all cases, of solvents with a polar nature (as evidenced by the values of (A)logP reported in Table 2).

Possible Applications of Newly Produced Membranes. According to the data collected, it is evident that the family of DACs allowed to produce a wide variety of membranes. These compounds were easily synthesizable in large scale in a sustainable way.[49] Despite the chemical similarities between the selected DACs, the nascent membranes displayed different proprieties, as highlighted by the characterization analyses carried out in the previous paragraphs. To underline their applicability, membranes were divided according to their pore size range, adding insights on their possible exploitations in diverse fields (Table 7).

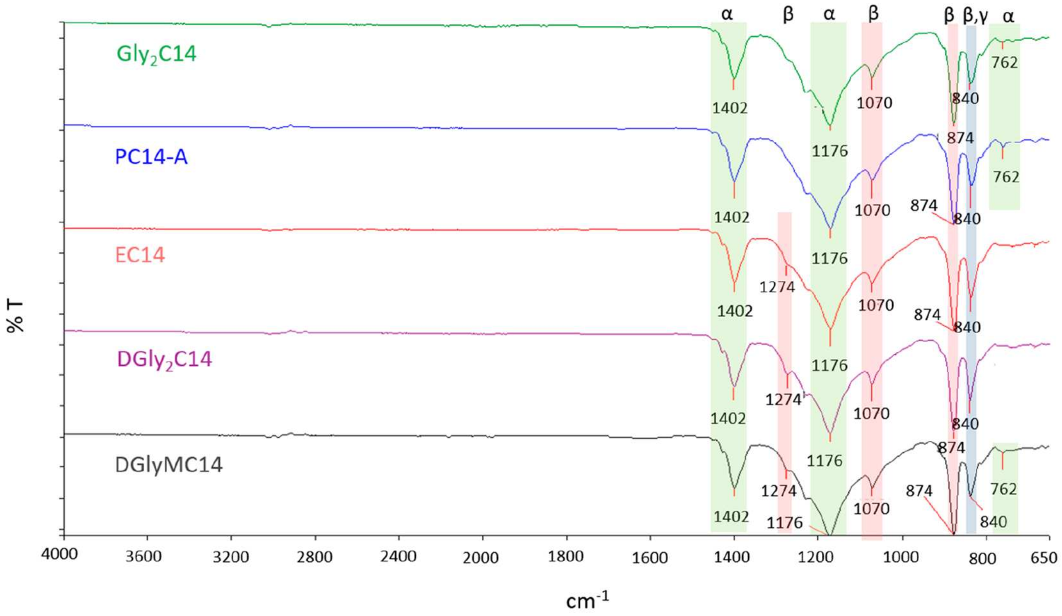

Figure 7. FT-IR spectra of DACs + PVDF21510 membranes.

Table 7. Possible Membrane Applications Based on Their Pore Size Ranges

Membrane code	Pore size (μm)	Field of separation	Possible applications
$Gly_2C14-0M$	n.m.[b]	**Gas separation/Pervaporation**	•CO_2 separation from other gases
$Gly_2C14-2.5M$	n.m.[b]		•Separation of liquid azeotropic mixtures
$Gly_2C14-5M$	n.m.[b]		•Aroma recovery
DGlyMC14−0M	n.m.		
$DGly_2C14-0M$	n.m.[b]		
EC14−0M	0.12 ± 0.01	**Microfiltration**[91]	•Harvesting of bacterial and yeast cells
EC14−2.5M	0.18 ± 0.04		•Recovery of latex pigments from paints
EC14−5M	0.16 ± 0.01		•Water purification
PC14−0M-A[a]	0.21 ± 0.03		•Clarification of juices, beer, and wine
PC14−2.5M-A[a]	0.3 ± 0.01		•Bacterial removal from milk
PC14−5M-A[a]	0.71 ± 0.01		•Dye removal from textile wastewater
DGlyMC14−2.5M	0.11 ± 0.01		•Protein purification
DGlyMC14−5M	0.32 ± 0.02		•Chromatographical separation
$DGly_2C14-2.5M$	0.14 ± 0.03		
$DGly_2C14-5M$	0.10 ± 0.01	**Microfiltration/Ultrafiltration**[92]	•Colloidal dispersion separation
			•Purification of biological macromolecules
			•Hemodialysis
			•Ultrapure water production

[a]Additives employed: Polyethylene glycol MW = 200 (10 wt %) and PVP K17 (5 wt %). [b]Values not measurable.

■ CONCLUSIONS

In the present work, different easy-to-synthesize dialkyl carbonates (DACs) containing alkoxyalkyl groups were applied as green solvents for the preparation of poly(vinylidene fluoride) copolymer (PVDF21510) membranes. Their proprieties and characteristics were analyzed and compared to commercially available cyclic carbonates (namely, EC and PC). Polymer solubility predictions and experiments were performed using different polymer/DACs combinations and employing Hansen solubility parameters. Membranes were prepared both by nonsolvent-induced phase separation (NIPS) and by a combination of vapor-induced phase separation (VIPS)-NIPS techniques varying the exposure time to humidity (0.0, 2.5, and 5.0 min). This preliminary study shows that membranes obtained with synthetic DACs display greater structural resistances and smaller pore sizes (between 0.32 and 0.10 μm) compared to their cyclic counterparts. Moreover, the addition of additives was not necessary, while it was required for membranes obtained with PC as the solvent.

In conclusion, these preliminary data showed the yet unexplored capacities of DACs as green solvents. In fact, from a single family of compounds having very similar chemical structures, it was possible to produce a wide variety of dense and porous membranes having different characteristics and morphologies. Most of the membranes produced displayed pore sizes in the microfiltration (MF) range (which has the largest industrial market and widest applications), while some others showed dense structures. On this matter, future work is required to deeply test the possible applications of these newly reported membranes, possibly comparing them with other PVDF membranes obtained with traditional toxic solvents.

Considering the data herein discussed, other DACs having different functional groups might be applied in a similar fashion, producing even more membrane structures whose performances and characteristics can be tuned according to the organic carbonate employed as the solvent.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.2c06578.

> Hansen solubility parameters (HSPs) of polymers and solvents, preliminary PVDF membrane screening, Hansen solubility parameters (HSPs) 10 wt % PVDF21510, PVDF 21510-based membranes (10 wt % polymer loading), examples of membranes with surface imperfections, SEM analyses PVDF 21510-based membranes (10 wt % polymer loading), SEM analyses PVDF 21510-based membranes (14 wt % polymer loading), thickness and porosity of PVDF 21510-based membranes, Emod and Ebreak PVDF 21510-based membranes, contact angle PVDF 21510-based membranes, pore size and bubble point of PVDF 21510-based membranes (PDF)

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Giacomo Trapasso: investigation, data curation, some conceptualization, and writing (original draft preparation). Francesca Russo: investigation, data curation, and some conceptualization. Francesco Galiano: data curation and writing (original draft preparation). Con Rob McElroy and James Sherwood: investigation on HSP, some data curation, and writing (original draft preparation). Alberto Figoli and Fabio Aricò: conceptualization, data curation, supervision, and writing (review and editing).

Notes

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