

University of Groningen

Applicability of organic carbonates as green solvents for membrane preparation

Rasool, Muhammad Azam; Pescarmona, Paolo P.; Vankelecom, Ivo F. J.

Published in:
ACS Sustainable Chemistry & Engineering

DOI:
[10.1021/acssuschemeng.9b01507](https://doi.org/10.1021/acssuschemeng.9b01507)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2019

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Rasool, M. A., Pescarmona, P. P., & Vankelecom, I. F. J. (2019). Applicability of organic carbonates as green solvents for membrane preparation. *ACS Sustainable Chemistry & Engineering*, 7(16), 13774-13785. <https://doi.org/10.1021/acssuschemeng.9b01507>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

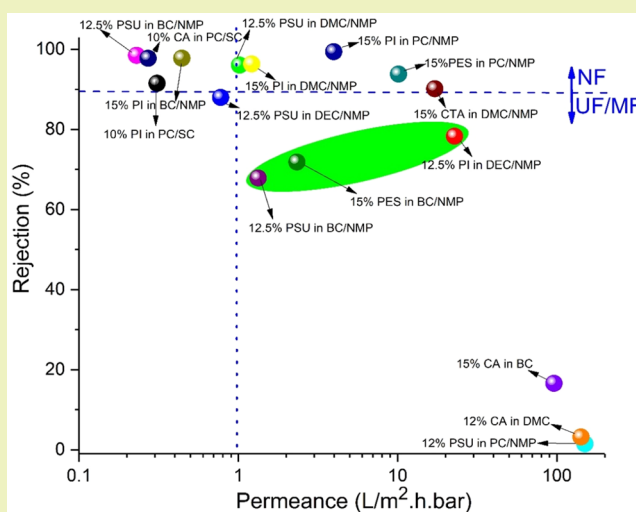
Applicability of Organic Carbonates as Green Solvents for Membrane Preparation

Muhammad Azam Rasool,[†] Paolo P. Pescarmona,[‡] and Ivo F. J. Vankelecom^{*,†}[†]cMACS - Centre for Membrane Separations, Adsorption, Catalysis, and Spectroscopy for Sustainable Solutions, Faculty of Biosciences Engineering, KU Leuven, Celestijnenlaan 200F, P.O. Box 2454, 3001 Leuven, Belgium[‡]Chemical Engineering Group, Engineering and Technology Institute Groningen (ENTEG), University of Groningen, Nijenborgh 4, 9749 AG, Groningen, Netherlands

Supporting Information

ABSTRACT: Common polar aprotic solvents, like *N,N*-dimethylformamide (DMF), 1,4-dioxane, *N,N*-dimethylacetamide (DMA) and tetrahydrofuran (THF), are excellent for membrane preparation. However, due to their toxicity or volatile nature, it would be useful to replace them by “greener” solvents for environmental and health reasons. In this work, organic carbonates, obtainable through carbon dioxide fixation, were selected as green solvents to find possible use in membrane preparation. Polymer solubility experiments were performed to screen their applicability in the phase inversion process to create porous membrane with appropriate structures and selectivities. Hansen solubility parameters were used to rationalize the solubility results. Membrane morphology and pore structure were characterized using scanning electron microscopy (SEM), while the performance of the membrane was determined by applying a 35 μ M aqueous feed solution of rose bengal (RB, MW = 1017 Da) to screen the potential of these polymer/organic carbonate systems toward nanofiltration application.

KEYWORDS: Green solvents, Organic carbonates, Solubility parameters, Phase inversion, Polymeric membranes, Nanofiltration



INTRODUCTION

Due to their toxic or volatile nature and their environmental persistence, traditional solvents often have a considerable impact on human health and the environment. In addition to this, these solvents are commonly considered as waste after use since their recycling is difficult or noneconomical.^{1,2} Moreover, about all common solvents are based on nonrenewable crude oil resources. The trend to use green solvents^{3,4} is therefore growing.³

Current technologies used for separation purposes are often waste generating and energy consuming, e.g., extractions or distillations. As sustainable alternative to these more conventional separation processes, membrane technology has been gaining interest, especially in gas separation^{5,6} and wastewater or solvent treatment.^{7,8} As the use of membranes is growing rapidly, concerns about sustainability are also growing. Use of sustainable solvents during the preparation of the membranes has thus become much more important.

Polymer solubility in a solvent plays a crucial role for membranes preparation, particularly in the nonsolvent induced phase separation (NIPS) process to form asymmetric porous membranes, as currently used for preparation of the large

majority of commercial membranes.^{9–12} In the NIPS process, a cast film is immersed in a water bath (nonsolvent) where solvent and nonsolvent demix, resulting in cast film coagulation in the form of porous membrane.^{13–18}

Organic carbonates are esters of carbonic acid, which consist of a carbonyl functional group attached to two alkoxy groups. The general structure is $R_1-O(C=O)O-R_2$. A large number of organic carbonates is used as solvents. Organic carbonates in general are environmentally friendly, have low eco-toxicity, and show good biodegradability.^{19–21} The most common carbonate solvents are propylene carbonate, glycerol 1,2-carbonate, and butylene carbonate. These cyclic carbonates have a high boiling point and low toxicity. Their synthesis in supercritical CO_2 can be considered as environmentally friendly.^{19–21} Although acyclic carbonates are not considered green due to flammability, cyclic carbonates fulfill all conditions of being green solvents. In addition to this, organic carbonates have a low viscosity as

Received: March 18, 2019

Revised: July 16, 2019

Published: July 21, 2019

Table 1. Polymers with Their Structures and Molecular Weights (MW) Used in This Work

| Polymer | Structure | MW (kDa) |
|--------------------------------|-----------|----------|
| Polyethersulphone (PES) | | ~35 |
| Polysulfone (PSU) | | 21 |
| Polyacrylonitrile (PAN) | | 100 |
| Polyvinyl alcohol (PVA) | | 13-23 |
| Polyvinylidene fluoride (PVDF) | | 534 |
| Chitosan | | 50-190 |
| Polyimide (PI) | | 90-134 |
| Cellulose triacetate (CTA) | | 278-282 |
| Cellulose acetate (CA) | | ~30 |

compared to most other biobased solvents, which is generally favorable in preparation of membranes.

Numerous applications of organic carbonates have been published exploiting the polar nature of these solvents.²¹⁻²⁵ Use of organic carbonates in membrane preparation has been much

less explored. Only two attempts have been reported to prepare polymeric membranes using propylene carbonate (PC):^{26,27} in thermally induced phase separation (TIPS) of polyvinylidene fluoride membranes²⁶ and of polyether imide (PEI) for ultrafiltration (UF) or microfiltration (MF).²⁷ No attempt has

Table 2. Structures of Solvents^a

| Chemical name | Structure | Supplier | Purity (%) |
|------------------------|-----------|------------------|------------|
| Dimethyl carbonate | | TCI | ≥99 |
| Diethyl carbonate | | TCI | >98 |
| Propylene carbonate | | TCI | ≥98 |
| 1,2-Butylene carbonate | | TCI | >98 |
| Glycerol 1,2-carbonate | | TCI | >90 |
| 1,2-Hexylene carbonate | | synthetic source | 99 |
| Styrene carbonate | | synthetic source | 99 |

^a1,2-Hexylene carbonate has a boiling point of 262 °C (CAS No. 66675-43-2). Styrene carbonate has a melting point around 56 °C (CAS No. 9927-92-3). (CAS Registry Numbers are provided by the author.)

been made so far to apply these solvents in membrane preparation via NIPS.^{28–30} Also none of these syntheses have so far allowed to prepare membranes suitable for nanofiltration (NF), which is more challenging as higher polymer concentrations have to be generally realized to obtain such denser membrane structures, i.e. a high solvent–polymer compatibility is required.

EXPERIMENTAL SECTION

Materials. Most polymers (CA, PVDF, PES, PAN, PVA, and chitosan) used in this work were purchased from Sigma-Aldrich (Belgium), while polysulfone (Udel P-1700 LCD) was provided by Solvay (Belgium), PI (Matrimid 5218) by Huntsman (Switzerland), and CTA by Eastman (USA). Molecular weights and chemical structures of these polymers are given in Table 1. Polymers were dried at 100 °C for 24 h. All solvents were purchased from Sigma-Aldrich (Belgium) or TCI fine chemicals (Belgium). Their structures and molecular weights (MW) are given in Table 2. 1,2-Hexylene carbonate and styrene carbonate, which were prepared by cycloaddition of CO₂ to 1,2-epoxyhexane and styrene oxide, respectively, in the presence of a catalytic system consisting of Bu₄Ni/H₂O.³¹

Solubility Parameters Determination. Hildebrand and Hansen Solubility Parameters (HSP). The Hildebrand and the Hansen theories are based on the “like dissolves like” principle.^{32,33} Hansen plotted the heat of vaporization of a material in a 3-dimensional space as a vector (Figure 1), representing the following components in each dimension:

- dispersive interaction (δ_D)
- polar interaction (δ_P)

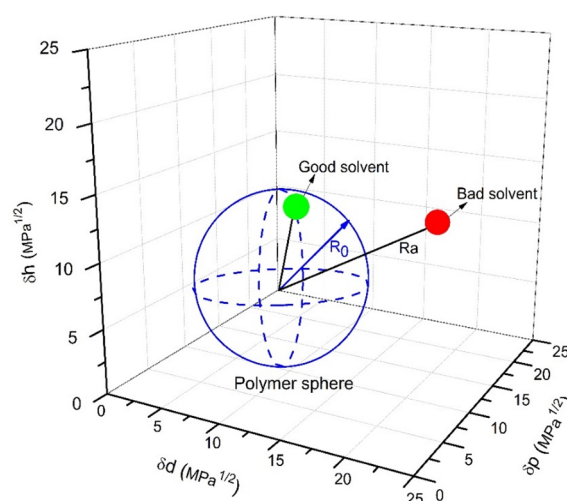


Figure 1. Graph representing the radius of the Hansen solubility sphere and exemplifying the position of a good and a bad solvent for this specific polymer.¹¹

- hydrogen bonding (δ_H)

The Hildebrand parameter (δ_t) is the geometric means of the three components of the HSP, calculated by eq 1.

Similar δ_t values of polymer and solvent indicate that they are compatible to form homogeneous solution.^{32,34–43}

$$\delta_t = \sqrt{\delta_D^2 + \delta_p^2 + \delta_H^2} \quad (1)$$

Hildebrand and HSP values of each polymer and organic carbonate based solvent are given in the Supporting Information (Table S2).^{32,34} Hansen solubility parameter values for diethyl carbonate, styrene carbonate, glycerol 1,2-carbonate CTA and chitosan, were calculated with the help of Table S1 (Supporting Information).^{40,41,36,35} Hansen solubility parameters (HSPs) values for each substance (polymer or solvent) were calculated using the following eqs (eqs 2–4);

$$\delta_D = \frac{\sum F_{di}}{V} \quad (2)$$

$$\delta_p = \frac{\sum F_{pi}}{V} \quad (3)$$

$$\delta_H = \sqrt{\frac{\sum E_{hi}}{V}} \quad (4)$$

where F_{di} , F_{dpi} , and E_{hi} are the parameters of dispersion forces, polar forces, and hydrogen bonding, respectively, as described by the Hoftzyer Van Krevelen method (see Supporting Information).^{40,41,36,35}

Equation 5 is used to calculate the R_a value (interaction distance), reflecting the polymer solvent affinity. A small R_a value indicates a good polymer–solvent compatibility, and the polymer will most probably be soluble in that solvent.

$$R_a = [\sqrt{4(\delta_{D2} - \delta_{D1})^2 + (\delta_{p2} - \delta_{p1})^2 + (\delta_{H2} - \delta_{H1})^2}] \quad (5)$$

In the case of polymer solutions, R_a is a measure of the affinity between polymer and solvent represented by (1 and 2, respectively).

Polymer Solubility and Membrane Preparation. For polymer solubility determination, 0.15 g of polymer (moisture free) was initially weighed in a glass vial for 15 wt % polymer solution preparation. Magnetic stirring was used continuously to stir the samples at room temperature for 2 days.

The homogeneous polymer solution (15 wt % in most cases) was used to cast polymer films with a wet thickness of 0.250 mm at room temperature with a speed of 1.0 m/min casting on a polypropylene nonwoven fabric soaked with respective solvent, prior to casting. Deionized water as nonsolvent was used in the coagulation bath for phase inversion.

Membrane Morphology. For membrane morphology and internal structure characterization, a scanning electron microscope (SEM, JEOL JSM 6010LV) was used to get cross-section images. Membrane samples were freeze-cracked using liquid nitrogen to get cross sections. Sample charging under the electron beam was reduced by coating the samples with a conductive gold/palladium layer of about 8 nm thickness using a high-resolution sputter coater (Cressington HR208).

Filtrations. To evaluate the membrane performance, filtration experiments were performed in dead-end mode with a high-throughput setup (HTML, Belgium),^{44,45} allowing the filtrations of 16 membrane coupons simultaneously, at 23 °C under pressure ranging from 5 to 16 bar. The active surface area for each membrane coupon was 0.000172 m². A 35 μ M rose bengal (1017 Da, Figure 2) solution in Milli-Q water was used as feed.

The aqueous feed solution (RB) was stirred magnetically at 325 rpm to minimize concentration polarization. Permeance was calculated with the help of eq 6 by gravimetrically weighing the collected permeate, while RB-rejection (R in %) was calculated by using eq 7 in which C_F and C_P are the initial feed and permeate concentrations, respectively. Dye concentrations in the feed and permeate were recorded at a wavelength (λ) of 548 nm on a PerkinElmer Lambda 12 UV–vis spectrophotometer.

$$\begin{aligned} \text{permeance (L/m}^2 \cdot \text{h} \cdot \text{bar)} \\ &= \frac{\text{Vol [L]}}{\text{membrane area [m}^2 \cdot \Delta p \text{ [bar]} \cdot \text{time (h)}} \end{aligned} \quad (6)$$

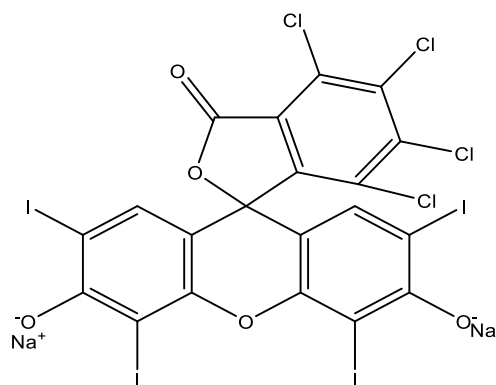


Figure 2. Structure of rose bengal (RB), used as the probe molecule.¹¹

$$\text{retention (R)} = \left(1 - \frac{C_p}{C_f}\right) \times 100 [\%] \quad (7)$$

RESULTS AND DISCUSSION

Polymer/Solvent Compatibility Determination. HSPs for all polymers and organic carbonates are plotted in Figure 3.

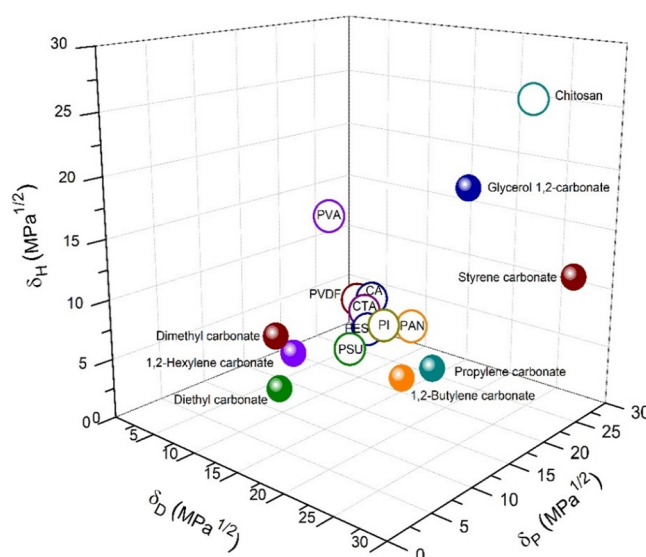


Figure 3. Representation of Hansen solubility parameters (HSPs) in a three-dimensional box, filled balls representing organic carbonates (solvents) and empty balls representing polymers.

Empty balls represent polymers, while filled balls represent organic carbonates (solvents). If the HSP values of the polymer are similar or near the HSPs values of the organic carbonate, the polymer/solvent system is expected to be compatible to form a homogeneous solution; hence, the polymer would most probably be well soluble in the corresponding solvent. Polymer/solvent interaction distances were calculated by using eq 5 and reported in Table 3. R_a quantitatively measures how alike polymer and solvents are; the smaller the R_a value, the greater the chances for polymer solubility. Polymers, which were experimentally found to be actually soluble in a given solvent, are highlighted in green. In some cases, solubility was theoretically expected by the low R_a values but not found experimentally (highlighted in yellow). CA is the only polymer that actually dissolved in two carbonates, i.e., 1,2-butylene carbonate and dimethyl carbonate. In some cases, CA, PVDF, PES, PSU, and

Table 3. Polymer/Carbonates Systems with Their R_a (Interaction Distance) Values

| Solvents | CA | PAN | PES | CTA | PSU | Chitosan | PVA | PI | PVDF |
|------------------------|------|------|------|------|------|----------|------|------|------|
| Dimethyl carbonate | 5.3 | 16.1 | 10.7 | 9.5 | 9.6 | 34.7 | 17.6 | 13.1 | 9.3 |
| Diethyl carbonate | 8.7 | 15.3 | 10.2 | 10.1 | 8.4 | 36.4 | 16.6 | 12.4 | 10.6 |
| Propylene carbonate | 16.2 | 7.2 | 8.9 | 9.3 | 10.6 | 25.4 | 16.7 | 8.9 | 10.2 |
| Glycerol 1,2-carbonate | 18.7 | 16.0 | 17.2 | 15.4 | 19.8 | 12.9 | 11.9 | 17.3 | 14.7 |
| 1,2-Butylene carbonate | 6.8 | 11.2 | 7.0 | 3.4 | 10.2 | 28.3 | 10.2 | 9.5 | 2.7 |
| 1,2-Hexylene carbonate | 5.9 | 13.9 | 8.6 | 8.0 | 7.2 | 33.9 | 10.5 | 10.9 | 8.3 |
| *Styrene carbonate | 32.2 | 19.1 | 24.3 | 26.3 | 25.8 | 21.0 | 30.0 | 21.9 | 27.6 |

^aAs styrene carbonate is solid at room temperature, solubility could not be verified experimentally. Only the R_a values are shown.

PAN had low R_a values for some solvents but no solubility was experimentally found in such solvents. Sometimes, only swelling of the polymer powder was observed instead of actual solubility, even after warming up the solutions to 60 °C. In the cases of PVDF and CTA in 1,2-butylene carbonate, gel formation was seen. This only happened after having solubilized the polymer at a higher temperature, followed by cooling.

Solvent Mixtures. Since only two cases were found from this broad screening in which the polymer became dissolved really well, a conventional solvent was added to find the capability of carbonates for membrane preparation. Using eq 8, HSP values of these mixtures were calculated, as shown in Table 4. HSP and R_a values for all mixtures are given in the Supporting Information (Tables S11–S20).

$$(S1 \times X\% + S2 \times X\%) / 100 \quad (8)$$

Table 4. HSP Values for Two Carbonates and Their Respective Mixtures

| solvents | δ_D (MPa ^{1/2}) | δ_P (MPa ^{1/2}) | δ_H (MPa ^{1/2}) | δ (MPa ^{1/2}) |
|---|-------------------------------------|-------------------------------------|-------------------------------------|-----------------------------------|
| S1 = solvent 1 (styrene carbonate) | 29.5 | 24.7 | 12.3 | 40.4 |
| S2 = solvent 2 (propylene carbonate) | 20.0 | 18.0 | 4.1 | 27.2 |
| 30% S1 70% S2 | 22.8 | 20.0 | 6.6 | 31.1 |
| 25% S1 75% S2 | 22.4 | 19.7 | 6.2 | 30.4 |

Table 5. R_a Interaction Distances between Polymers and (PC/SC) Solvent Mixtures

| Polymer | R_a |
|---------------|-------|
| PI (Matrimid) | 9.6 |
| CA | 19.6 |
| CTA | 12.2 |
| PVDF | 13.4 |
| PSU | 12.7 |
| Chitosan | 22.5 |
| PES | 10.9 |
| PAN | 6.4 |
| PVA | 19.2 |

Since styrene carbonate (SC) is a solid at room temperature, solvent mixtures were made with propylene carbonate (PC). In order to check the ideal ratio of SC and PC (maximum amount of SC solubility in PC), SC was added to a fixed concentration (wt %) of PC until saturation was obtained at room temperature. This maximum SC solubility in PC was found to be around 30 wt %. A 30 wt % SC/PC mixture was thus used in further solubility screening and membrane preparation. For PC/SC mixtures, R_a values were calculated for given polymers by using eq 5. Green values in Table 5 represent the cases where the polymer actually dissolved in the PC/SC mixture (i.e., PI and CA). Yellow highlights represent cases where the solubility in the PC/SC mixture was theoretically expected (i.e., PAN), but not experimentally confirmed. In the case of CA, the R_a value is high, but nevertheless, CA was soluble in the PC/SC mixture. For all other polymers, no solubility was expected theoretically due to the R_a values higher than 10, which was also confirmed experimentally.

For PSU, PVDF, PAN, PES, CTA, and PI, *N*-methyl-2-pyrrolidone (NMP) was added to the organic carbonate in a 2:1 ratio. NMP was selected due to its well-known compatibility with these polymers. NMP is considered nongreen/non-renewable, but using it in a dilute form in the membrane preparation process can already significantly reduce the total volume of this solvent in the overall process. In some cases, solvent mixtures were found suitable for polymer solubility (highlighted in green). Polymers whose solubility was expected in these mixtures (due to R_a values lower than 8) but which were insoluble experimentally are highlighted in yellow in Table 6.

Table 6. R_a Values between Polymers and Organic Carbonate/NMP Solvent Mixtures

| Solvent mixture (2:1 ratio) | PSU | PVDF | CTA | PI | PAN | PES |
|-----------------------------|------|------|-----|------|------|------|
| Dimethyl carbonate/NMP | 6.8 | 6.2 | 6.2 | 10.1 | 12.9 | 7.6 |
| Diethyl carbonate/NMP | 5.9 | 7.5 | 6.9 | 9.6 | 12.3 | 7.2 |
| Propylene carbonate/NMP | 8.3 | 7.8 | 6.8 | 7.3 | 6.5 | 6.6 |
| Glycerol 1,2-carbonate/NMP | 14.3 | 9.1 | 9.8 | 12.1 | 11.3 | 11.7 |
| 1,2-Butylene carbonate/NMP | 8.4 | 6.7 | 6.2 | 8.6 | 8.7 | 7.0 |
| 1,2-Hexylene carbonate/NMP | 5.3 | 5.8 | 5.3 | 8.7 | 11.4 | 6.2 |

Table 7. R_a Values between CA and Organic Carbonate/Methyl Lactate Solvent Mixtures

| Solvent mixture (2:1 ratio) | R_a values for CA |
|--------------------------------------|---------------------|
| Diethyl carbonate/Methyl lactate | 10.5 |
| Glycerol 1,2- carbonate/Me l lactate | 7.6 |
| 1,2-Hexylene carbonate/Me lactate | 9.0 |

Table 8. R_a Values between Chitosan, PVA, and Organic Carbonate/Water Solvent Mixtures

| Solvent mixture (2:1 ratio) | R_a values for chitosan | R_a values PVA |
|---|---------------------------|------------------|
| Dimethyl carbonate/ H ₂ O | 27.8 | 4.4 |
| Diethyl carbonate/ H ₂ O | 28.0 | 2.3 |
| Propylene carbonate/ H ₂ O | 18.2 | 8.8 |
| Glycerol 1,2-carbonate/ H ₂ O | 14.2 | 15.5 |
| 1,2- Butylene carbonate/ H ₂ O | 20.4 | 7.4 |
| 1,2- Hexylene carbonate/ H ₂ O | 26.8 | 2.8 |

Other solvent mixtures had high R_a values and the experimental solubility for corresponding polymers was neither expected nor found.

For PSU, the R_a values are lower than 9, except for glycerol 1,2-carbonate/NMP. Theoretically, it was thus expected for these solvent mixtures to dissolve PSU, which turned out not to be the case only for 1,2-hexylene carbonate. For PVDF, all R_a values were below 9. Solubility was thus theoretically expected in all cases, but only swelling was experimentally found and even then only in three cases (highlighted in yellow). Possibly, PVDF would become more soluble when heating above 60 °C. For CTA, all R_a values were below 9 and solubility was thus theoretically expected in all cases.

However, actual solubility was found only in dimethyl carbonate/NMP and diethyl carbonate/NMP mixtures. R_a values for PI were lower than 10 in most cases. PI was experimentally soluble in most solvent mixtures, except for glycerol 1,2-carbonate and 1,2-hexylene carbonate. For PAN, R_a values of solvent mixtures in most cases were higher than 10, so no solubility was expected, which was also confirmed experimentally. R_a values of PES with the solvent mixtures were below 9 in all cases, except for glycerol 1,2-carbonate/NMP mixture. Despite these low R_a values, actual solubility was only found in propylene carbonate/NMP and 1,2-butylene carbonate/NMP mixtures. For CA, organic carbonates were mixed with methyl lactate (which is also a green solvent) due to good solubility of CA in methyl lactate.⁴⁶ Nevertheless, in 1,2-hexylene carbonate/methyl lactate and diethyl carbonate/

methyl lactate mixtures, only suspensions were observed (Table 7).

For chitosan and PVA, organic carbonates were mixed with water (a highly green solvent) in a 1:2 ratio, due to the good compatibility PVA and chitosan with water. To increase the solubility of these polymers in water, 1% acetic acid was added to water in small amounts.⁴⁷ Due to the similarity in Hildebrand values of chitosan and water, solubility was anticipated. However, chitosan was found only partially soluble. Although only R_a values for PVA with glycerol 1,2-carbonate/water mixtures were higher than 10 (Table 8), no actual solubility was observed. Some compatibility was seen with PVA for the combinations highlighted in yellow (dimethyl carbonate/H₂O diethyl carbonate/H₂O and 1,2-hexylene carbonate/H₂O) in Table 8. While chitosan was only soluble in water containing few drops of organic acid (acetic acid 1 wt %).

General Considerations on Solubility Limitations. For the reported systems, theoretically obtained solubility parameters seem a rather rough approximation of the actual behavior, as also found elsewhere.^{11,48,49} Interaction distances (R_a) or affinities between polymers and solvents are more complex than HSPs. In addition to this, molecular shape, size, and geometry play a vital role:⁴⁸ smaller and linear molecules dissolve more quickly than larger molecules. For the cases in which interaction distance of polymer and solvent is small but the polymer is still not soluble, probably due to the high molecular weight of the polymers, that might create steric hindrance in dissolution. Additionally, intermolecular interactions in semicrystalline polymers, e.g., in PVDF, or abundant

Table 9. Solvents or Solvent Mixtures, Polymers, and Nonsolvents Used in the Phase Inversion Process and the Cross-Sectional SEM Images of the Resulting Membranes Cast from 10–15 wt % Solutions^a

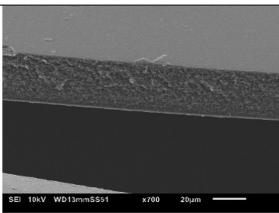
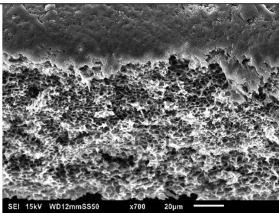
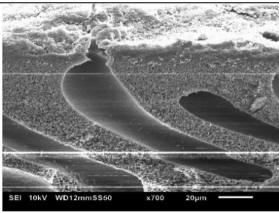
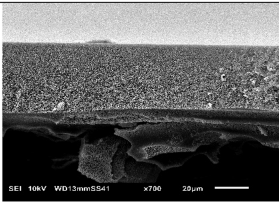
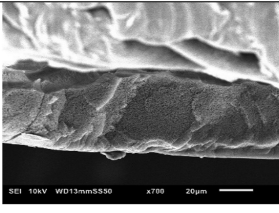
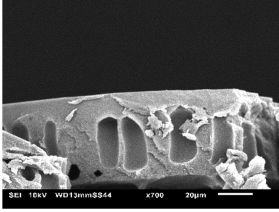
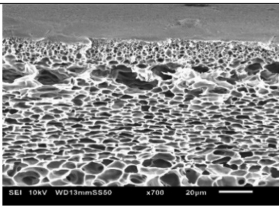
| Solvent or solvent mixture | Polymer conc. (wt%) | Non-solvent | Membrane cross section |
|-------------------------------------|---------------------|-------------|--|
| Dimethyl carbonate (DMC) | 12wt%CA | water |  |
| 1,2-Butylene carbonate (BC) | 15wt%CA | water | No membrane |
| | | ethanol |  |
| Dimethyl carbonate/NMP (DMC/NMP) | 15wt%PI | water |  |
| Diethyl carbonate/NMP (DEC/NMP) | 15wt%PI | water |  |
| Propylene carbonate/NMP (PC/NMP) | 15wt%PI | water |  |
| 1,2-Butylene carbonate/NMP (BC/NMP) | 15wt%PI | water |  |
| Dimethyl carbonate/NMP (DMC/NMP) | 15wt%PSU | water |  |

Table 9. continued

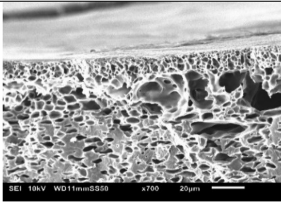
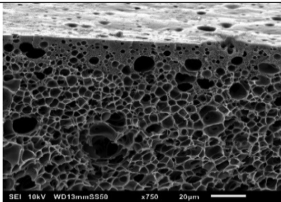
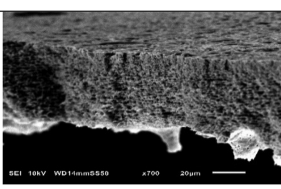
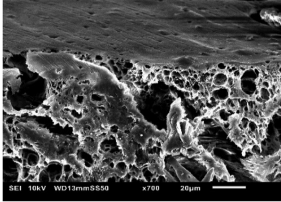
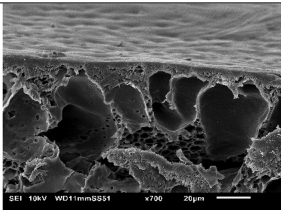
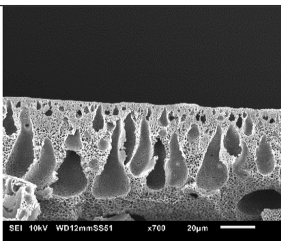
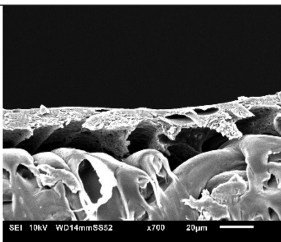
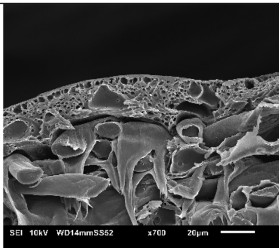
| Solvent or solvent mixture | Polymer conc. (wt%) | Non-solvent | Membrane cross section |
|--|---------------------|-------------|--|
| Diethyl carbonate/NMP (DEC/NMP) | 12.5wt%PSU | water |  |
| Propylene carbonate/NMP (PC/NMP) | 12.5wt%PSU | water |  |
| 1,2-Butylene carbonate/NMP (BC/NMP) | 12.5wt%PSU | water |  |
| Propylene carbonate/NMP (PC/NMP) | 15wt%PES | water |  |
| 1,2-Butylene carbonate/NMP (BC/NMP) | 15wt%PES | water | (No membrane) |
| | | ethanol |  |
| Dimethyl carbonate/NMP (DMC/NMP) | 15wt%CTA | water |  |
| Propylene carbonate/styrene carbonate (PC/SC) | 10wt%CA | water |  |

Table 9. continued

| Solvent or solvent mixture | Polymer conc. (wt%) | Non-solvent | Membrane cross section |
|---|---------------------|-------------|--|
| Propylene carbonate/styrene carbonate (PC/SC) | 10wt%PI | water |  |

^aPure ethanol (commercial grade) was used as nonsolvent, when water was not suitable for phase inversion.

H-bonding, as in, e.g., PVA or chitosan, can prevent polymers from dissolution in the absence of strong mixing or heating.^{32,50,48}

Phase Inversion. The identified combinations of solvents and polymers that were found to lead to complete solubility were exploited for preparing membranes by phase inversion (Table 9). In the NIPS process, the cast polymer film is immersed in a nonsolvent bath. This induces liquid–liquid demixing, resulting after a certain time in a polymer-rich and a polymer-lean phase. The polymer-rich phase solidifies and creates the membrane matrix via gel formation, crystallization, or vitrification.⁵¹ The polymer-lean phase creates the pores in this solidified material. Depending on the solvent/nonsolvent exchange rate and the strength of the nonsolvent to phase-separate the polymer, two types of demixing can be distinguished. So-called “instantaneous demixing” creates a porous skin-layer, often with macrovoids (finger or oval-like structure), while so-called “delayed demixing” creates a denser skin layer with a more spongy substructure.^{52,53} The time span for instantaneous and delayed demixing is not exactly defined in the literature. In phase inversion, both thermodynamic and kinetic aspects thus play a role to finalize the membrane structure, which makes it complicated to be fully understood.¹³

After casting the polymer solutions into films, these cast films were immersed in water as nonsolvent (NS), or in ethanol when water as NS was not appropriate for phase inversion (Table 9).^{13,54,52} After membrane preparation, SEM was used to study the membranes morphology (images are also given in Table 9). From Figure 4, it is clear that it is hard to rationalize the appearance of macrovoids from the calculations of affinities between nonsolvents and polymers or solvents and nonsolvents. On the contrary, addition of ethanol to the NS system clearly lowered the affinity or interaction distance (R_a) between the nonsolvent mixture and the polymer (NS-P) drastically, which was needed to create the pores in the 1,2-butylene carbonate/CA system (leading to a well-defined asymmetric cross-section, as shown in Table 9) and for PES in BC/NMP (where macrovoids were formed).

Membranes prepared from CTA from DMC/NMP had porous structures with finger-like macrovoids. Similar structures were formed for PI membranes prepared from DMC/NMP and BC/NMP systems. While in the case of PI membranes prepared from DEC/NMP and PC/NMP, dense sponge-like structures are obtained.

The membrane prepared from PES, using the PC/NMP mixture, has a structure with irregular tear-shaped macrovoids, while CA and PI membranes cast from PC/SC mixture have a structure with small tear-shaped macrovoids. Possibly, this small

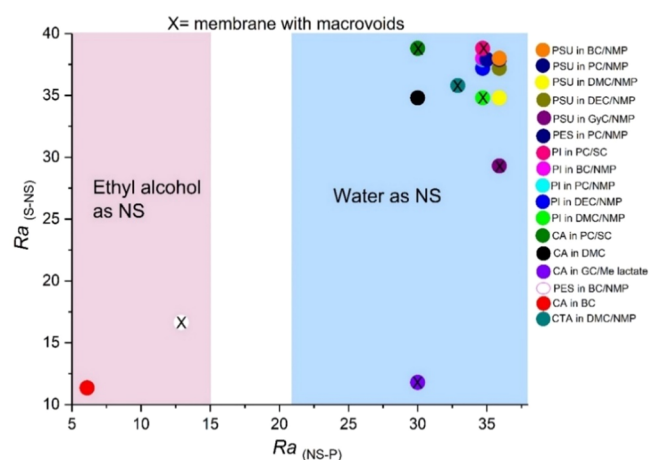


Figure 4. Interaction distances between solvent nonsolvent vs nonsolvent polymer interaction (X = membrane with macrovoids structure).

size of the macrovoids can be linked to the penetration of the polymer solution into the polypropylene layer (used as support), which significantly decreased the overall thickness of the cast film. The CA membrane was more dense with few macrovoids, as compared to the PI membrane cast from same PC/SC mixture. All membranes prepared from PSU, regardless of the solvents used in the casting solution, have sponge-like structure. In contrast, in the literature PSU membranes prepared from common solvents like NMP or DMF contain macrovoids.^{52,54} The interaction distance between solvent and nonsolvent (water) for NMP and DMF (35.5 and 31.4, respectively) is smaller than with organic carbonates (except for glycerol 1,2-carbonate; see the Supporting Information). Due to the smaller R_a between NMP and water, they mix better with water as compared to organic carbonates, which results in a higher driving force for mixing, thus inducing faster demixing during the phase inversion process. Membranes with macrovoid structures are then formed. However, organic carbonates have a larger interaction distance with the nonsolvent (water), which leads to poor interaction and less miscibility. As a result, demixing in phase inversion is delayed and membranes with spongy structures are produced. For NF or when used as a support for denser layers in pressure-driven membrane applications, spongy structures are generally desirable due to the expected enhanced pressure stability.⁵¹

Filtration Experiments. Membranes prepared via the NIPS process can be used for different kinds of separations, depending on the size of the pores in the selective skin layer. Even though

the main aim of this study was to find polymer/organic carbonate systems that formed homogeneous solutions that could be turned into porous structures, nanofiltration (NF) experiments were performed on these nonoptimized membranes. As the molecular weight of rose bengal (RB) is 1017 Da, NF membranes should reject this dye for at least 90%. Membranes with NF-level separations are more challenging to obtain by NIPS, as such membranes usually require high polymer concentrations in the casting solution, hence necessitating decent solvents to dissolve the desired polymer very well. Results obtained from these preliminary filtration experiments are given in Figure 5.

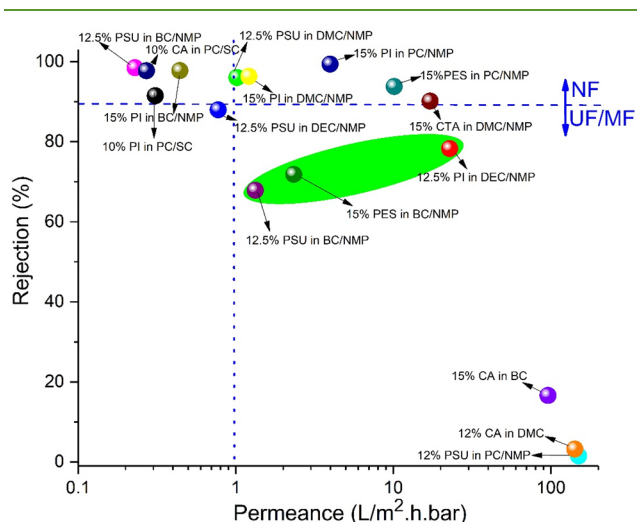


Figure 5. Permeance versus rejection of membranes prepared from carbonate-based solvents or solvent mixtures, categorizing them as either NF or MF/UF membranes.

It is well-known that permeance decreases while solute rejection increases by casting the membranes with high polymer concentration.^{52,54} Although membranes were cast in this work from low polymer concentrations (below 15 wt %), many membranes still reached the NF-criterion with RB rejections higher than 90%. Membranes prepared with 15% CTA in DMC/NMP, 15% PES in PC/NMP, 15% PI in DMC/NMP, 15% PI in PC/NMP, and 12.5% PSU in DEC/NMP all have RB rejections above 90% with decent permeances above 1.0 L·m⁻²·h⁻¹·bar⁻¹. With RB rejections above 90%, the best membranes were obtained from the 15% CTA in DMC/NMP membrane system with a permeance around 17.2 L·m⁻²·h⁻¹·bar⁻¹ and from 15% PES in PC/NMP with a permeance of 10.8 L·m⁻²·h⁻¹·bar⁻¹.

The membranes prepared from 10% CA in PC/SC, 10% PI in PC/SC, 12.5% PSU in BC/NMP, and 12.5% PI in BC/NMP systems had RB rejections higher than 90% but permeances lower than 1.0 L·m⁻²·h⁻¹·bar⁻¹. Probably these membranes could achieve permeances higher than 1.0 L·m⁻²·h⁻¹·bar⁻¹ by using more dilute casting solutions.

Other membrane systems, 12.5% PI in DEC/NMP, 15% PES in BC/NMP, and 12.5% PSU in BC/NMP (green-oval like circle zone in Figure 5), have RB rejections lower than 90% but above 60%. The potential to reach NF performance clearly exists in these systems just by casting the membranes with high polymer concentration, as dissolution visually still proceeded easily and quickly.^{52,53} Other membrane systems (12% CA in dimethyl carbonate or 12% PSU in PC/NMP) could be useful

for MF/UF depending on the molecular weight cutoff (MWCO) of the membranes or as support material for other more selective layers.

CONCLUSIONS

Polymer solubility tests were performed to find the possible use of organic carbonates as green alternatives in membrane preparation, either by using these solvents as such or by mixing with less sustainable solvents conventionally used to decrease the volumes of the latter solvents in the membrane fabrication. In most cases, solvent mixtures indeed had to be made to dissolve the polymers commonly used in membrane technology. For CA, this could be done by adding another green solvent (i.e., methyl lactate) to the carbonates, while styrene carbonate was mixed with propylene carbonate. For other polymer systems, NMP was added in small amounts. Solubility results could be partially rationalized by using Hansen and Hildebrand solubility parameters. Membranes with either spongy or macrovoid structure were successfully prepared via the NIPS process. Most membranes qualified for NF, sometimes already showing excellent selectivity/permeance combinations. Further investigation and optimization of these systems is likely to lead to improvements in the performance of this class of membranes. Membranes obtained from other polymer/organic carbonate systems still have the capacity to reach NF-selectivities, e.g., by casting the membranes from solutions high polymer concentrations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.9b01507.

Examples of ecofriendly synthesis of organic carbonates (Scheme S1) and tables of solubility parameter component group distribution (Table S1), Hansen solubility parameters (HSP) and Hildebrand values for polymers and solvents (Table S2), relative energy differences (RED) and solubility parameters (R_s) of each polymer for responding solvent or solvent mixture (Tables S3–S20), and R_s values of solvents and nonsolvents (water and ethyl alcohol) (Tables S21 and S22) (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: ivo.vankelecom@kuleuven.be. Fax: +32 1632 1998. Tel: +32 1632 1594.

ORCID

Muhammad Azam Rasool: 0000-0002-6504-2311

Paolo P. Pescarmona: 0000-0003-3608-6400

Ivo F. J. Vankelecom: 0000-0002-0104-9493

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Yasser Alassmy is acknowledged from Engineering and Technology Institute Groningen (ENTEG), University of Groningen, Nijenborgh 4, 9749 AG Groningen, Netherlands, currently working at King Abdulaziz City for Science and Technology (KACST), Riyadh, Saudi Arabia, for providing

styrene carbonate and 1,2-hexylene carbonate. Muhammad Azam Rasool acknowledges the European Commission - Education, Audiovisual and Culture Executive Agency (EACEA) for providing a scholarship under the Erasmus Mundus Doctorate in Membrane Engineering (EUDIME) program (<http://eudime.unical.it/>). Also KU Leuven (C16/17/005), Vlarlo (AIO/150474/SBO), and the Belgian Federal Government through an I.A.P.-P.A.I. grant (IAP 7/05 FS2) are acknowledged for funding.

REFERENCES

- (1) Capello, C.; Hellweg, S.; Hungerbühler, K. Environmental Assessment of Waste-Solvent Treatment Options. *J. Ind. Ecol.* **2008**, *12* (1), 111–127.
- (2) Amelio, A.; Genduso, G.; Vreysen, S.; Luis, P.; Van der Bruggen, B. Guidelines Based on Life Cycle Assessment for Solvent Selection during the Process Design and Evaluation of Treatment Alternatives. *Green Chem.* **2014**, *16* (6), 3045–3063.
- (3) Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press, 1998.
- (4) Anastas, P. T. Green Chemistry as Applied to Solvents. *Clean Solvents* **2002**, *819* (3), 1–9.
- (5) Basu, S.; Khan, A. L.; Cano-Odena, A.; Liu, C.; Vankelecom, I. F. J. Membrane-Based Technologies for Biogas Separations. *Chem. Soc. Rev.* **2010**, *39* (2), 750–768.
- (6) Jeon, Y.; Lee, D. Gas Membranes for CO₂/CH₄ (Biogas) Separation: A Review. *Environ. Eng. Sci.* **2015**, *32* (2), 71–85.
- (7) Marchetti, P.; Solomon, M. F. J.; Szekeley, G.; Livingston, A. G. Molecular Separation with Organic Solvent Nano Filtration: A Critical Review. *Chem. Rev.* **2014**, *114*, 10735–10806.
- (8) Vandezande, P.; Gevers, L. E. M.; Vankelecom, I. F. J. Solvent Resistant Nanofiltration: Separating on a Molecular Level. *Chem. Soc. Rev.* **2008**, *37* (2), 365–405.
- (9) Capello, C.; Fischer, U.; Hungerbühler, K. What Is a Green Solvent? A Comprehensive Framework for the Environmental Assessment of Solvents. *Green Chem.* **2007**, *9* (9), 927–934.
- (10) Nelson, W. M. *Green Solvents for Chemistry: Perspectives and Practice*; Oxford University Press: Oxford; New York, 2003.
- (11) Rasool, M. A.; Vankelecom, I. F. J. Use of γ -Valerolactone and Glycerol Derivatives as Bio-Based Renewable Solvents for Membrane Preparation. *Green Chem.* **2019**, *21*, 1054.
- (12) Abdel-Fatah, M. A. Nanofiltration Systems and Applications in Wastewater Treatment: Review Article. *Ain Shams Eng. J.* **2018**, *9* (4), 3077–3092.
- (13) Holda, A. K.; Vankelecom, I. F. J. Understanding and Guiding the Phase Inversion Process for Synthesis of Solvent Resistant Nanofiltration Membranes. *J. Appl. Polym. Sci.* **2015**, *132* (27), 1–17.
- (14) Kim, D.; Moreno, N.; Nunes, S. P. Fabrication of Polyacrylonitrile Hollow Fiber Membranes from Ionic Liquid Solutions. *Polym. Chem.* **2016**, *7* (1), 113–124.
- (15) Hendrix, K.; Koeckelberghs, G.; Vankelecom, I. F. J. Study of Phase Inversion Parameters for PEEK-Based Nano Filtration Membranes. *J. Membr. Sci.* **2014**, *452*, 241–252.
- (16) Tao, M. mi; Liu, F.; Ma, B. rong; Xue, L. xin. Effect of Solvent Power on PVDF Membrane Polymorphism during Phase Inversion. *Desalination* **2013**, *316*, 137–145.
- (17) Mohamed, M. H.; Wilson, L. D. Porous Copolymer Resins: Tuning Pore Structure and Surface Area with Non Reactive Porogens. *Nanomaterials* **2012**, *2* (2), 163–186.
- (18) Matsuyama, H.; Yamamoto, A.; Yano, H.; Maki, T.; Teramoto, M.; Mishima, K.; Matsuyama, K. Effect of Organic Solvents on Membrane Formation by Phase Separation with Supercritical CO₂. *J. Membr. Sci.* **2002**, *204* (1–2), 81–87.
- (19) Sakakura, T.; Kohno, K. The Synthesis of Organic Carbonates from Carbon Dioxide. *Chem. Commun.* **2009**, *11*, 1312–1330.
- (20) Mikami, K. *Green Reaction Media in Organic Synthesis*; John Wiley & Sons, 2008.
- (21) Schäffner, B.; Schäffner, F.; Verevkin, S. P.; Börner, A. Organic Carbonates as Solvents in Synthesis and Catalysis. *Chem. Rev.* **2010**, *110* (8), 4554–4581.
- (22) Taherimehr, M.; Decortes, A.; Al-Amsyar, S. M.; Lueangchaichaweng, W.; Whiteoak, C. J.; Escudero-Adán, E. C.; Kleij, A. W.; Pescarmona, P. P. A Highly Active Zn(Salphen) Catalyst for Production of Organic Carbonates in a Green CO₂ Medium. *Catal. Sci. Technol.* **2012**, *2* (11), 2231–2237.
- (23) Agrigento, P.; Al-Amsyar, S. M.; Sorée, B.; Taherimehr, M.; Gruttadauria, M.; Aprile, C.; Pescarmona, P. P. Synthesis and High-Throughput Testing of Multilayered Supported Ionic Liquid Catalysts for the Conversion of CO₂ and Epoxides into Cyclic Carbonates. *Catal. Sci. Technol.* **2014**, *4* (6), 1598–1607.
- (24) Taherimehr, M.; Al-Amsyar, S. M.; Whiteoak, C. J.; Kleij, A. W.; Pescarmona, P. P. High Activity and Switchable Selectivity in the Synthesis of Cyclic and Polymeric Cyclohexene Carbonates with Iron Amino Triphenolate Catalysts. *Green Chem.* **2013**, *15* (11), 3083.
- (25) Kamphuis, A. J.; Picchioni, F.; Pescarmona, P. P. CO₂-Fixation into Cyclic and Polymeric Carbonates: Principles and Applications. *Green Chem.* **2019**, *21* (3), 406–448.
- (26) Benzinger, W. D.; Robinson, D. N. Porous Vinylidene Fluoride Polymer Membrane and Process for Its Preparation. US4384047A, 1983.
- (27) Muller, H.-J.; Wechs, F. Process for Producing Microporous Powders and Membranes. 4968733, 1990.
- (28) Nederberg, F.; Lohmeijer, B. G. G.; Leibfarth, F.; Pratt, R. C.; Choi, J.; Dove, A. P.; Waymouth, R. M.; Hedrick, J. L. Organocatalytic Ring Opening Polymerization of Trimethylene Carbonate. *Biomacromolecules* **2007**, *8* (1), 153–160.
- (29) Haynes, W. M. *CRC Handbook of Chemistry and Physics*; CRC Press, 2014.
- (30) Jörnè, J.; Tobias, C. W. Electrodeposition of the Alkali Metals from Propylene Carbonate. *J. Appl. Electrochem.* **1975**, *5* (4), 279–290.
- (31) Alassmy, Y.; Pescarmona, P. P. The role of water revisited and enhanced: a sustainable, affordable catalytic system for the conversion of CO₂ into cyclic carbonates under mild conditions. *ChemSusChem* **2019**, DOI: 10.1002/cssc.201901124.
- (32) Hansen, C. M. *Hansen Solubility Parameters: A User's Handbook*; CRC Press, 2002.
- (33) Hansen, C. M. *Hansen Solubility Parameters*; CRC Press, 2013; Vol. 53.
- (34) Hansen, C. M. Polymer Additives and Solubility Parameters. *Prog. Org. Coat.* **2004**, *51* (2), 109–112.
- (35) Barton, A. F. M. *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*; CRC Press, 1991.
- (36) Barton, A. F. M. *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*; Routledge, 2017.
- (37) Barton, A. M. *Handbook of Polymer-Liquid Interaction Parameters and Solubility Parameters*; Routledge, 2018.
- (38) Kwok, A. Y.; Qiao, G. G.; Solomon, D. H. Synthetic Hydrogels 3. Solvent Effects on Poly(2-Hydroxyethyl Methacrylate) Networks. *Polymer* **2004**, *45* (12), 4017–4027.
- (39) Van Krevelen, D. W.; Te Nijenhuis, K. Cohesive Properties and Solubility. In *Properties of Polymers*, 4th ed.; Van Krevelen, D. W., Te Nijenhuis, K., Eds.; Elsevier: Amsterdam, 2009; Chapter 7, pp 189–227.
- (40) Van Krevelen, D. W.; Hoftyzer, P. J. Practical Evaluation of the $[\eta]$ -M Relationship. III. Estimation of the Exponent A. *J. Appl. Polym. Sci.* **1967**, *11* (11), 2189–2200.
- (41) Van Krevelen, D. W.; Te Nijenhuis, K. *Properties of Polymers: Their Correlation with Chemical Structure; Their Numerical Estimation and Prediction from Additive Group Contributions*; Elsevier, 2009.
- (42) Brown, G. H. Regular Solutions. By Joel H. Hildebrand and Robert L. Scott. *Inorg. Chem.* **1963**, *2* (2), 431–432.
- (43) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press, 1953.
- (44) Li, X.; Vandezande, P.; Vankelecom, I. F. J. Polypyrrole Modified Solvent Resistant Nanofiltration Membranes. *J. Membr. Sci.* **2008**, *320* (1–2), 143–150.

- (45) Vandezande, P.; Li, X.; Gevers, L. E. M.; Vankelecom, I. F. J. High Throughput Study of Phase Inversion Parameters for Polyimide-Based SRNF Membranes. *J. Membr. Sci.* **2009**, *330* (1–2), 307–318.
- (46) Medina-Gonzalez, Y.; Aimar, P.; Lahitte, J.-F.; Remigy, J.-C. Towards Green Membranes: Preparation of Cellulose Acetate Ultrafiltration Membranes Using Methyl Lactate as a Biosolvent. *Int. J. Sustainable Eng.* **2011**, *4* (1), 75–83.
- (47) Qin, C.; Li, H.; Xiao, Q.; Liu, Y.; Zhu, J.; Du, Y. Water-Solubility of Chitosan and Its Antimicrobial Activity. *Carbohydr. Polym.* **2006**, *63* (3), 367–374.
- (48) Stefanis, E.; Panayiotou, C. Prediction of Hansen Solubility Parameters with a New Group-Contribution Method. *Int. J. Thermophys.* **2008**, *29* (2), 568–585.
- (49) Bottino, A.; Capannelli, G.; Munari, S.; Turturro, A. Solubility Parameters of Poly(Vinylidene Fluoride). *J. Polym. Sci., Part B: Polym. Phys.* **1988**, *26* (4), 785–794.
- (50) Hansen, C. M. Polymer Additives and Solubility Parameters. *Prog. Org. Coat.* **2004**, *51* (2), 109–112.
- (51) Mulder, J. *Basic Principles of Membrane Technology*; Springer Science & Business Media, 2012.
- (52) Holda, A. K.; Vankelecom, I. F. J. Integrally Skinned PSf-Based SRNF-Membranes Prepared via Phase Inversion-Part B: Influence of Low Molecular Weight Additives. *J. Membr. Sci.* **2014**, *450*, 499–511.
- (53) Tsay, C. S.; Mchugh, A. J. Mass Transfer Modeling of Asymmetric Membrane Formation by Phase Inversion. *J. Polym. Sci., Part B: Polym. Phys.* **1990**, *28* (8), 1327–1365.
- (54) Holda, A. K.; Aernouts, B.; Saeys, W.; Vankelecom, I. F. J. Study of Polymer Concentration and Evaporation Time as Phase Inversion Parameters for Polysulfone-Based SRNF Membranes. *J. Membr. Sci.* **2013**, *442*, 196–205.