Supporting Information

Dialkyl carbonates as green solvents for Polyvinylidene Difluoride membrane preparation

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Hansen solubility parameters (HSPs) of polymers and solvents

Table S1. HSPs predicted for each polymer and solvent tested.

Polymer	**δ_d**	**δ_p**	**δ_h**
PVDF	17.0	12.1	10.2
PES	19.6	10.8	9.2
PAN	22.4	14.1	9.1
PEEK-WC[a]	16.5	11.0	14.6
Solvent	**δ_d**	**δ_p**	**δ_h**
DMC	15.5	8.6	9.7
DEC	15.1	6.3	3.5
EC	18.0	21.7	5.1
PC	20.0	18.0	4.1
GlyMC	16.2	8.4	7.6
Gly_2C	16.2	7.6	7.5
DGlyMC	16.2	7.6	7.5
$DGly_2C$	16.1	6.9	7.6
NMP	18.0	12.3	7.2
Sulfolane	17.8	17.4	8.7
Acetone	15.5	10.4	7.0
Butyl benzoate	18.3	5.6	5.5
DMI	17.6	7.1	7.5
Cyclohexanone	17.8	8.4	5.1
Benzyl benzoate	20.0	5.1	5.2

[a] Values taken from: A. Figoli, T. Marino, S. Simone, E. Di Nicolò, X.-M. Li, T. He, S. Tornaghid, E. Drioli; Towards non-toxic solvents for membrane preparation: a review; Green Chem., **2014**, 16, 4034.

Preliminary PVDF membrane screening

Table S2. Preliminary PVDF polymers screening with commercial and synthetic DACs through NIPS technique[a].

Solvents	Polymers	
	PVDF6010	PVDF21510
DEC		
EC		
PC		
GlyMC		
Gly_2C		
DGlyMC		
$DGly_2C$		

[a] DMC was excluded since it was predicted and tested to be insoluble in all the selected polymers. Green table cells display those DAC/polymer combinations which resulted in a homogeneous solution and in the consequent membrane formation.

Hansen solubility parameters (HSPs) – 10 % wt. PVDF21510

Table S3. HSPs predicted for each solvent tested and the solubility of Solef PVDF21510 at 10 wt%.

Solvent	**δ_d**	**δ_p**	**δ_h**	**Soluble?**	**R_a /MPa^{½}**
DMC	15.5	8.6	9.7	N	8.38
DEC	15.1	6.3	3.5	Y	7.58
EC	18.0	21.7	5.1	Y	8.10
PC	20.0	18.0	4.1	Y	6.05
GlyMC	16.2	8.4	7.6	Y	6.76
Gly_2C	16.2	7.6	7.5	Y	7.37
DGlyMC	16.2	7.6	7.5	Y	7.37
$DGly_2C$	16.1	6.9	7.6	Y	8.07
NMP	18.0	12.3	7.2	Y	2.39
Sulfolane	17.8	17.4	8.7	Y	5.18
Acetone	15.5	10.4	7.0	Y	6.20
Butyl benzoate	18.3	5.6	5.5	Y	8.03
DMI	17.6	7.1	7.5	Y	6.94
Cyclohexanone	17.8	8.4	5.1	Y	5.22
Benzyl benzoate	20.0	5.1	5.2	N	9.39

[a] Values taken from: A. Figoli, T. Marino, S. Simone, E. Di Nicolò, X.-M. Li, T. He, S. Tornaghid, E. Drioli; Towards non-toxic solvents for membrane preparation: a review; Green Chem., **2014**, 16, 4034.

PVDF 21510-based membranes (10% polymer loading)

Table S4. Membrane preparation using PVDF21510 (10% wt.) with different DACs through VIPS-NIPS technique.

Membrane code	Solvent	Technique	Casting temperature (°C)	Membrane formation
EC10-0M	EC	NIPS (VIPS 0 min)	130	YES
EC10-2.5M	EC	VIPS 2.5 min	130	YES
EC10-5M	EC	VIPS 5 min	130	YES
PC10-0M-A	PC[a]	NIPS (VIPS 0 min)	60	YES
PC10-2.5M-A	PC[a,b]	VIPS 2.5 min	60	YES
PC10-5M-A	PC[a,b]	VIPS 5 min	60	YES
GlyMC10-0M	GlyMC	NIPS (VIPS 0 min)	60	NO
GlyMC10-2.5M	GlyMC	VIPS 2.5 min	60	NO
GlyMC10-5M	GlyMC	VIPS 5 min	60	NO
Gly_2C10-0M	Gly_2C	NIPS (VIPS 0 min)	60	NO
Gly_2C10-2.5M	Gly_2C	VIPS 2.5 min	60	NO
Gly_2C10-5M	Gly_2C[b]	VIPS 5 min	60	YES
DGlyMC10-0M	DGlyMC	NIPS (VIPS 0 min)	70	NO
DGlyMC10-0M	DGlyMC	VIPS 2.5 min	70	NO
DGlyMC10-2.5M	DGlyMC	VIPS 5 min	70	YES
$DGly_2C$10-0M	$DGly_2C$	NIPS (VIPS 0 min)	70	YES
$DGly_2C$10-2.5M	$DGly_2C$	VIPS 2.5 min	70	YES
$DGly_2C$10-5M	$DGly_2C$	VIPS 5 min	70	YES

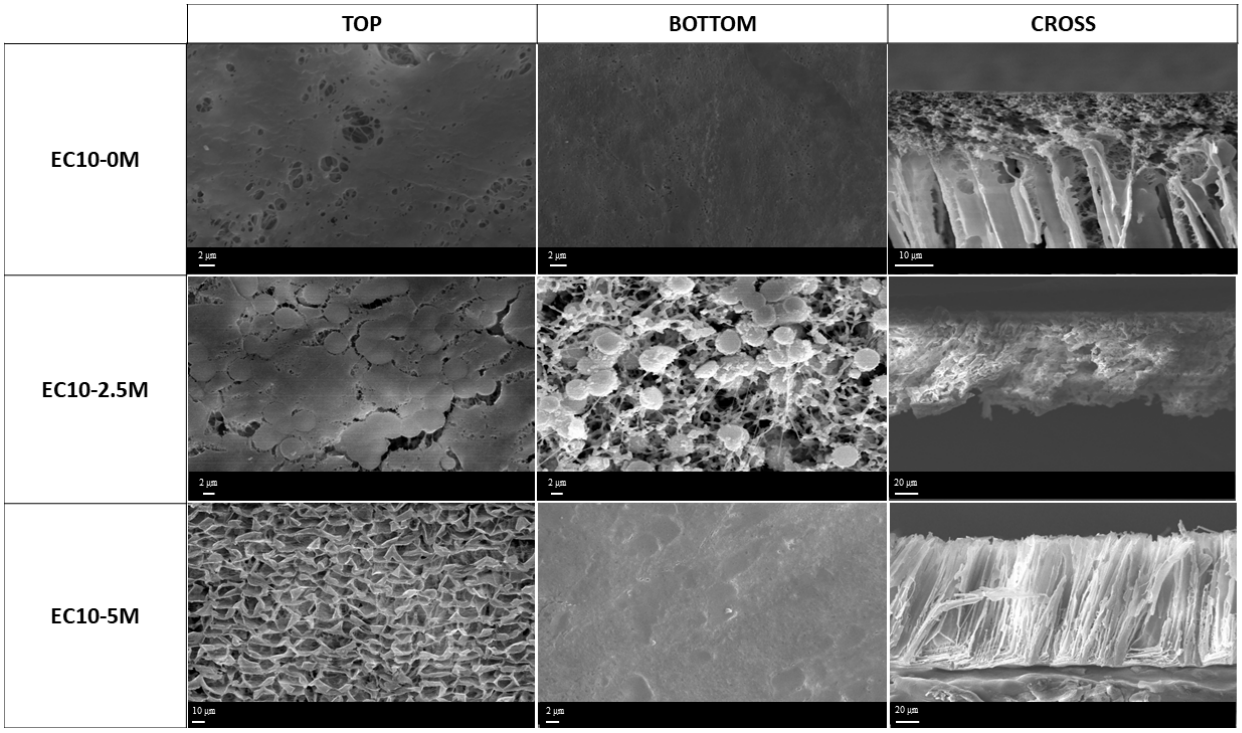
[a]Additives employed: Polyethylene glycol MW = 200 (10 wt.%) and PVP K17 (5 wt.%); [b]Surface imperfections and inhomogeneities.

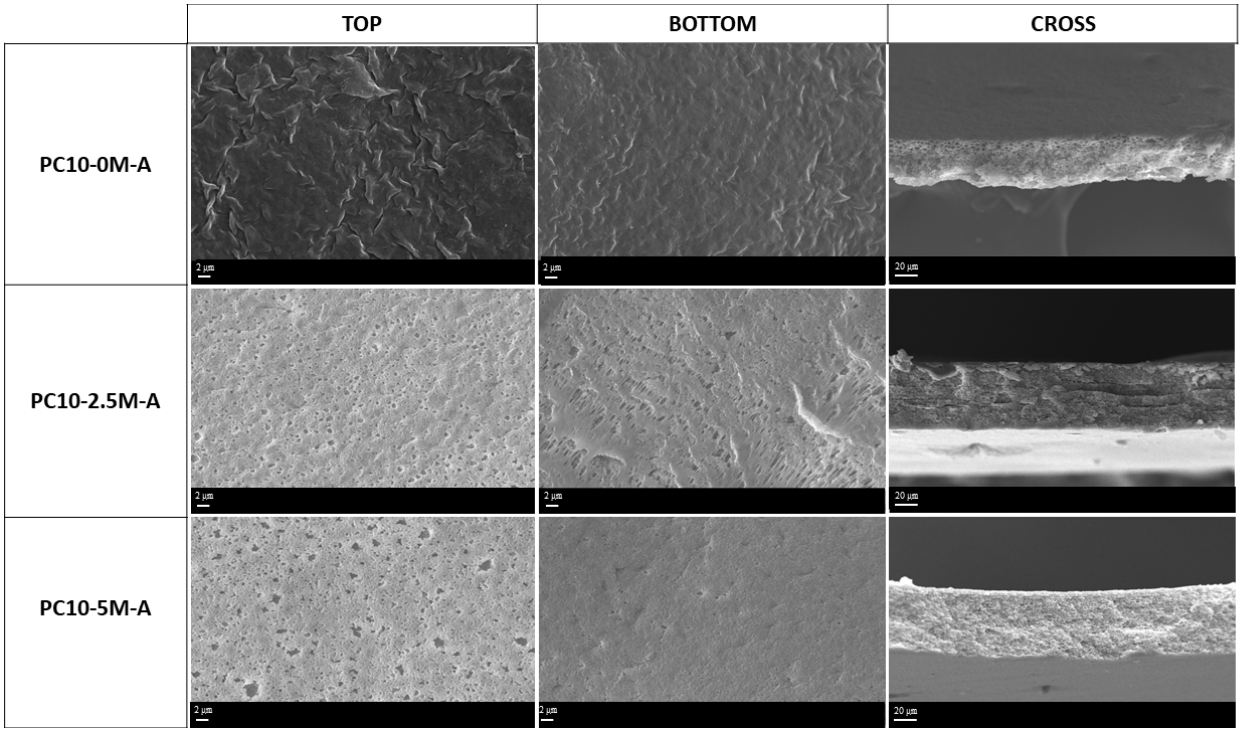
Examples of membranes with surface imperfections

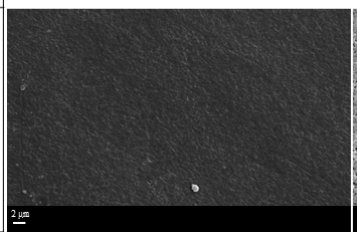
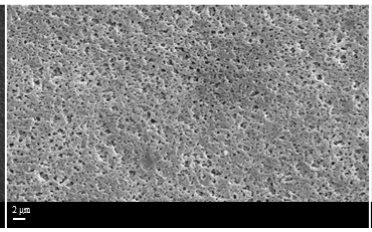
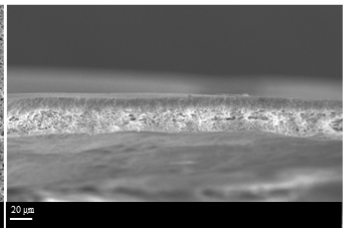
Membrane code	Surface imperfections image
PC10-2.5M-A	
PC10-5M-A	
Gly_2C10-5M	

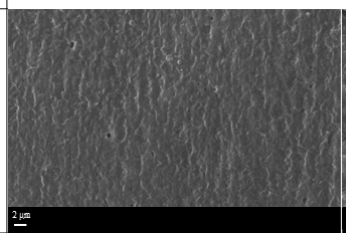
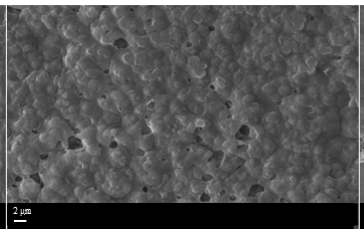
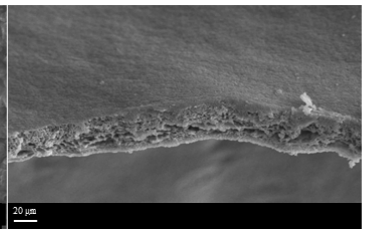
Figure S1. Examples of some DACs-derived membranes surface imperfections and inhomogeneities.

SEM analyses PVDF 21510-based membranes (10 wt.% polymer loading)





	TOP	BOTTOM	CROSS
Gly_2C10-0M	No membrane formation		
Gly_2C10-2.5M	No membrane formation		
Gly_2C10-5M			

	TOP	BOTTOM	CROSS
DGlyMC10-0M	No membrane formation		
DGlyMC10-2.5M	No membrane formation		
DGlyMC10-5M			

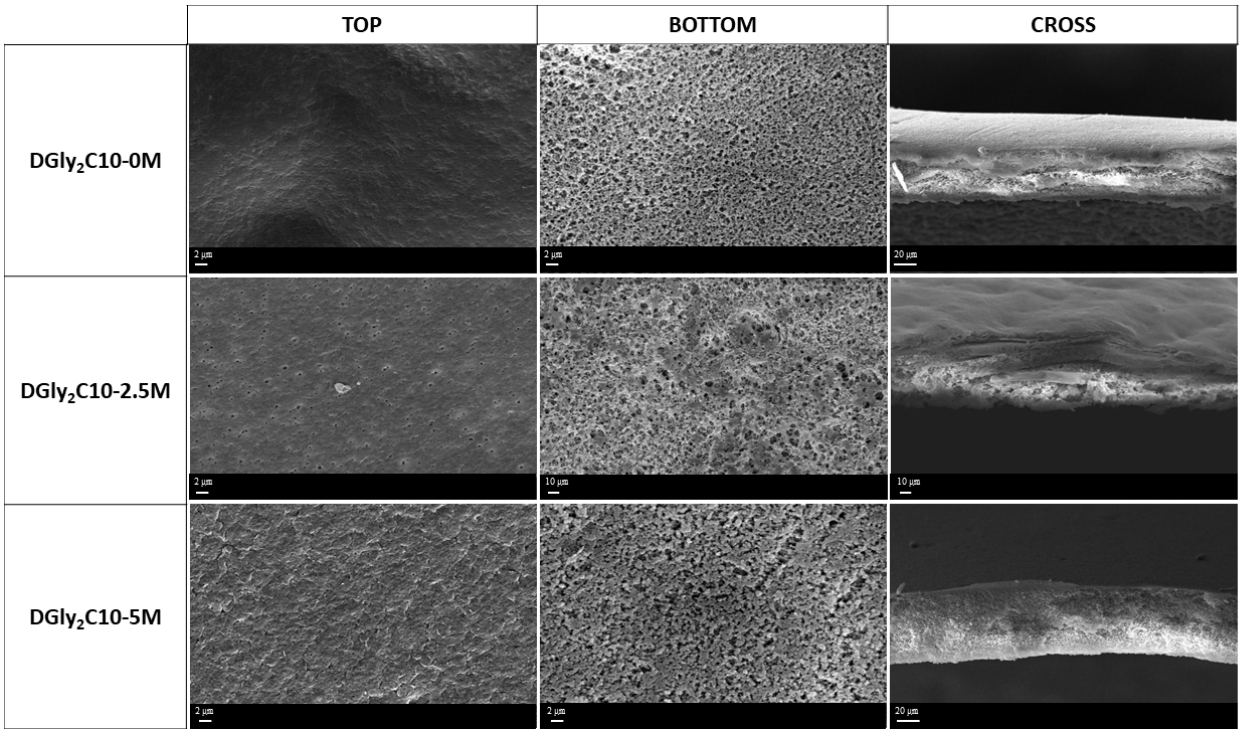
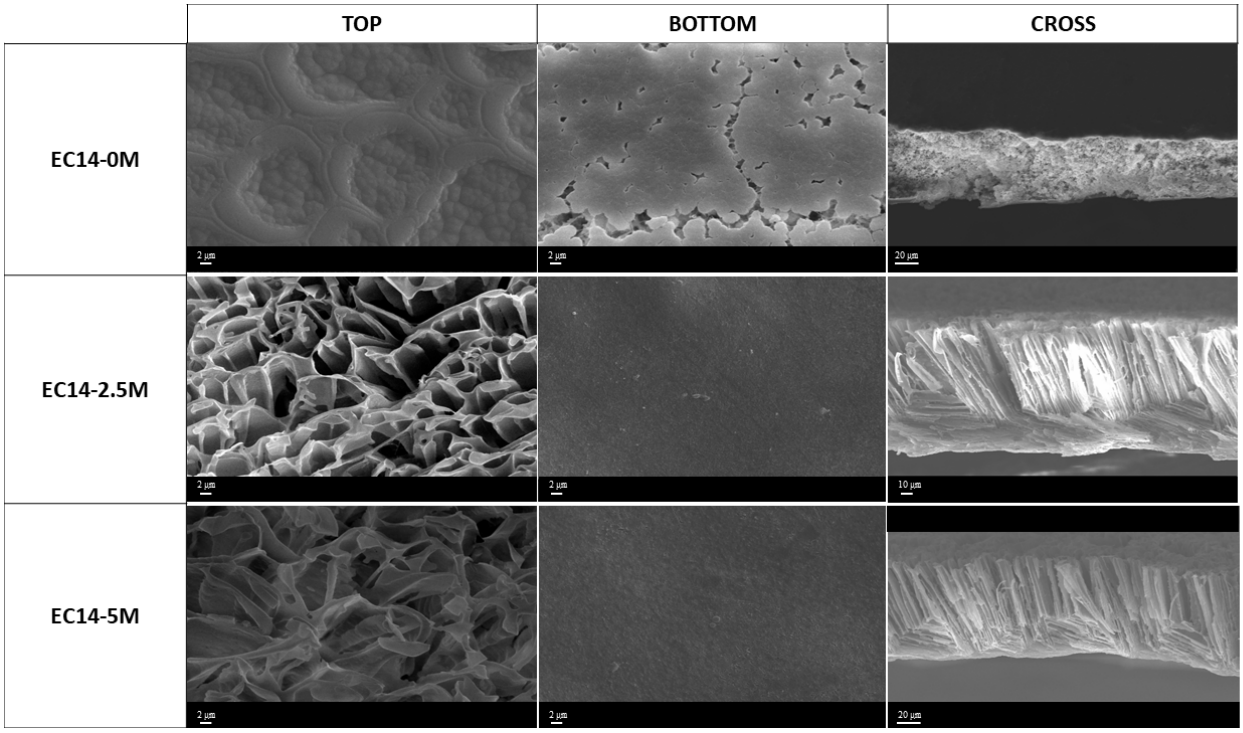
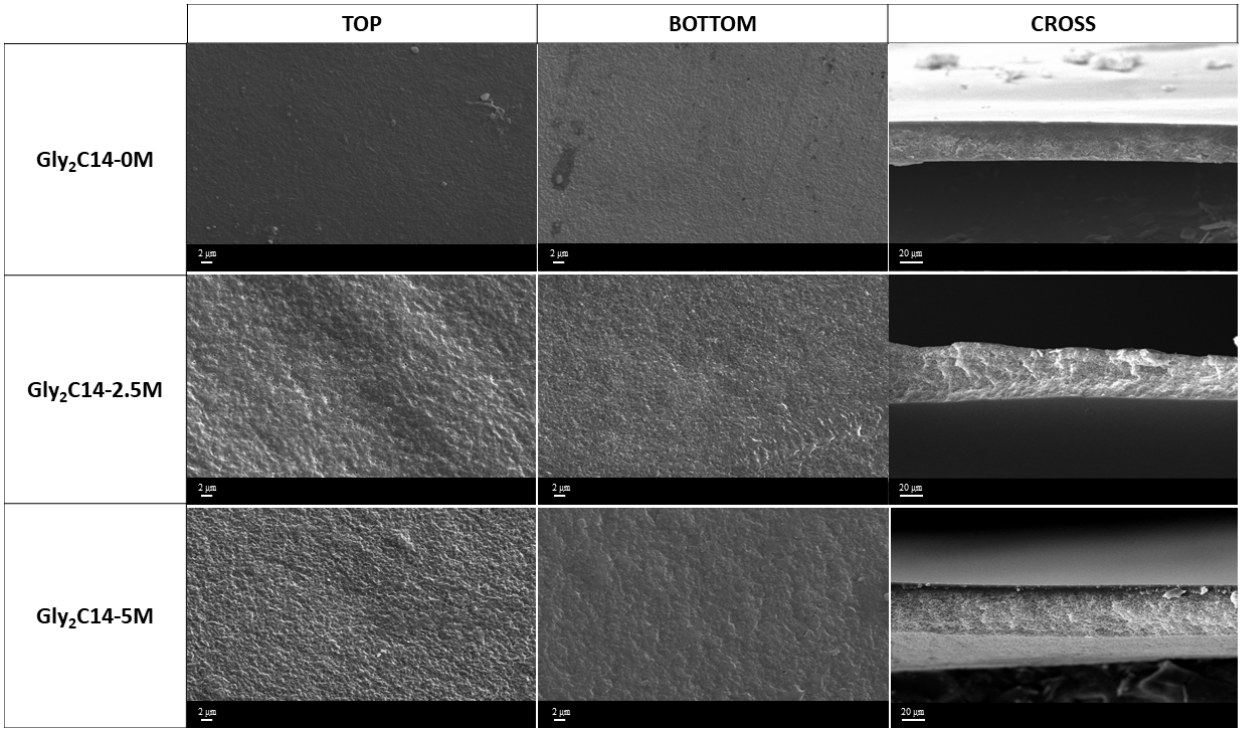


Figure S2. SEM analyses of DACs-derived membranes with 10 wt.% PVDF21510 loading obtained via NIPS and NIPS-VIPS technique: 0.0, 2.5 and 5.0 min in the climatic chamber, RH = 55%. Magnification for top and bottom surfaces: 5000 X and 1000 X for cross sections.

SEM analyses PVDF 21510-based membranes (14 wt.% polymer loading)





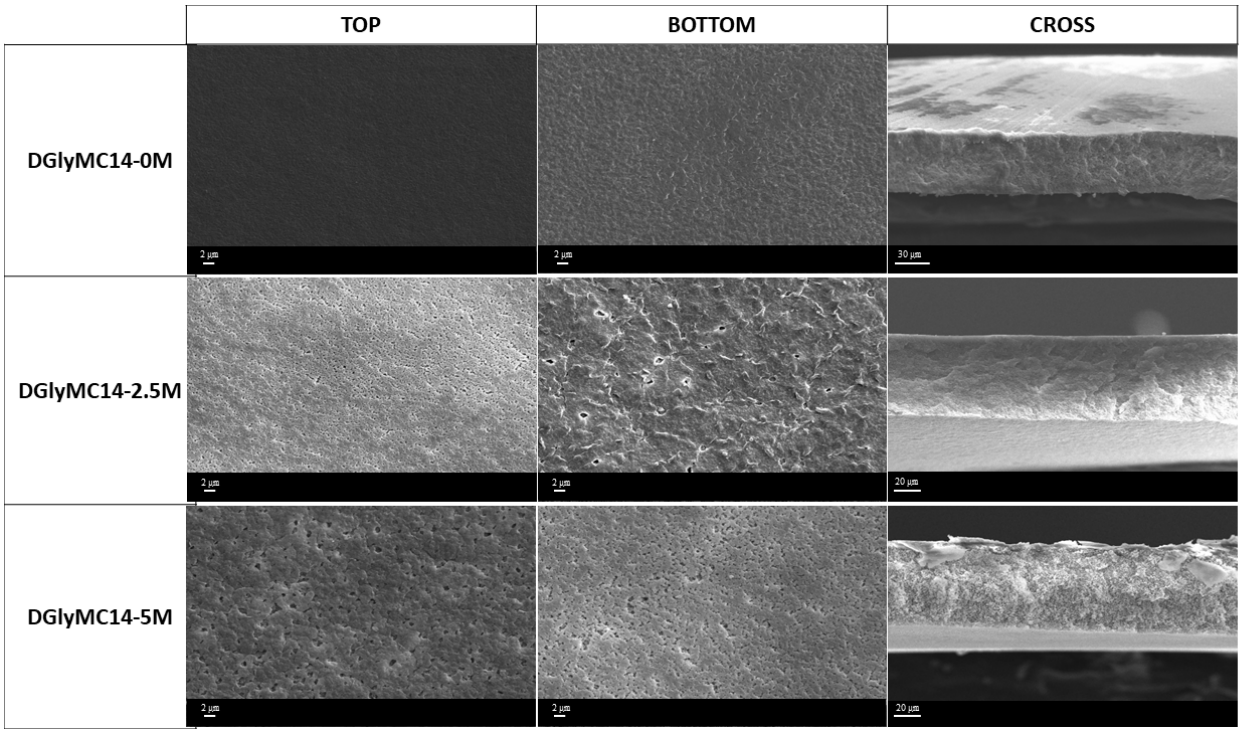


Figure S3. SEM analyses of DACs-derived membranes with 14 wt.% PVDF21510 loading obtained via NIPS and NIPS-VIPS technique: 0.0, 2.5 and 5.0 min in the climatic chamber, RH = 55%. Magnification for top and bottom surfaces: 5000 X and 1000X for cross sections. The remaining SEM pictures are displayed in Figure 5 in the main text.

Thickness and porosity of PVDF 21510-based membranes

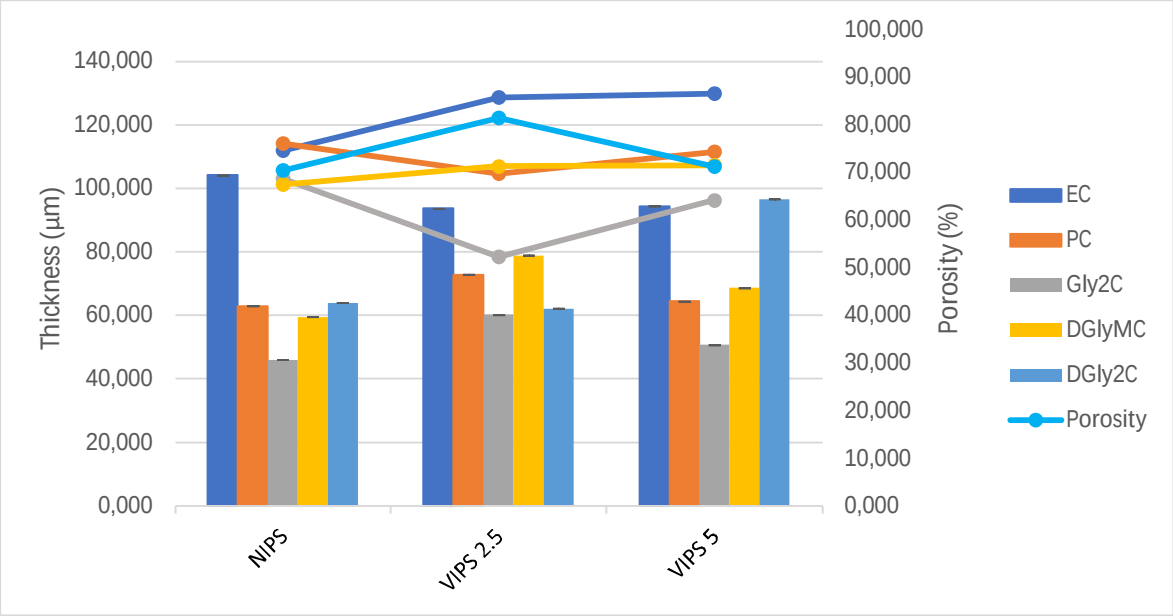


Figure S4. Thickness and porosity of PVDF21510 membranes using synthetic DACs as solvents (14% wt. polymer loading). Climatic chamber conditions: T = 25 °C, RH = 55%. For PC solvent, only trials containing additives were considered.

Emod and Ebreak PVDF 21510-based membranes

Table S5. Young's module (N/mm^2) and elongation at break (%) of the synthetized membranes (14 wt.% polymer loading) via NIPS and VIPS techniques.

Solvent	[PVDF21510] (%)	Technique	Emod (N/mm^2)	Elongation at break (%)
EC	14	NIPS	32.8±6	183.7±8
EC	14	VIPS 2.5	10.3±2	50.6±11
EC	14	VIPS 5.0	10.8±2	69.4±3
PC[a]	14	NIPS	39.7±15	39.5±8
PC[a]	14	VIPS 2.5	71.5±9	86.1±17
PC[a]	14	VIPS 5.0	52.7±13	202.4±44
DGlyMC	14	NIPS	124.6±4	138.9±21
DGlyMC	14	VIPS 2.5	55.9±6	15.8±4
DGlyMC	14	VIPS 5	14.8±2	70.1±12
Gly_2C	14	NIPS	66.5±22	352.5±63
Gly_2C	14	VIPS 2.5	92.0±2	63.2±17
Gly_2C	14	VIPS 5	94.3±6	88.5±5
$DGly_2C$	14	NIPS	37.6±2	234.9±2
$DGly_2C$	14	VIPS 2.5	10.8±1	29.8±4
$DGly_2C$	14	VIPS 5.0	49.8±2	31.3±9

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

Contact angle PVDF 21510-based membranes

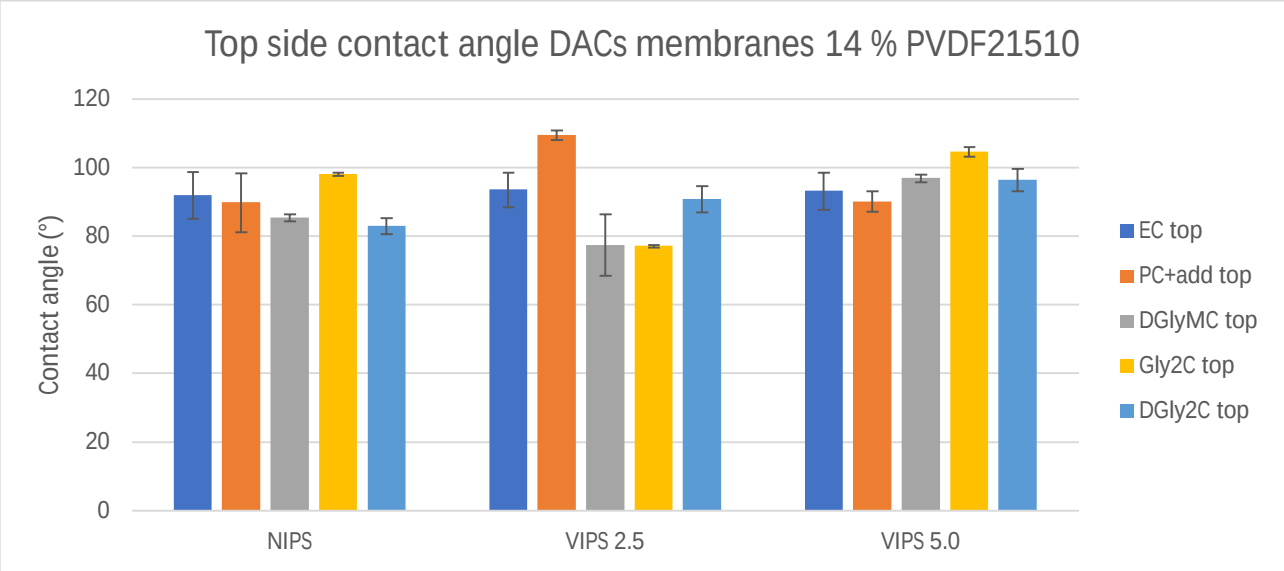


Figure S5. Top and bottom contact angle values of the synthetized membranes (14 wt.% polymer loading).

Pore size and bubble point of PVDF 21510-based membranes

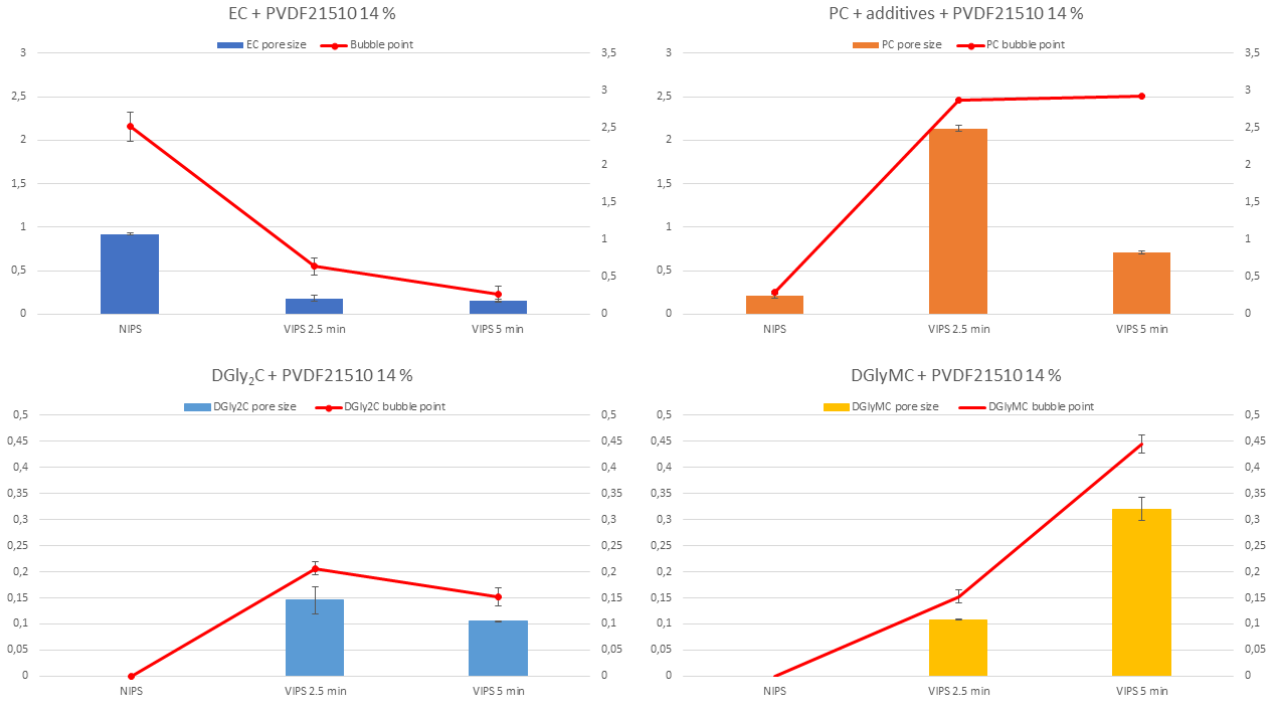


Figure S6. Pore size and bubble point of PVDF21510 (14 wt.%) membranes using DACs as solvents.