

Supplementary Information

Experimental and theoretical studies on the formation of pure β -phase polymorphs during fabrication of polyvinylidene fluoride membranes by cyclic carbonate solvents

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Table S.1. Crystal size of the α and β -phases of PVDF.

Phase	a(Å)	b(Å)	c(Å)
β -PVDF	19.72	25.80	23.85
α -PVDF	23.10	19.84	27.72

Table S.1. presents the crystal size assembled to create a supercell for α and β -phases of PVDF.

Table S.2. Simulation box details of both α and β -phases of PVDF in contact with the solvents ethylene carbonate (EC), propylene carbonate (PC), and butylene carbonate (BC).

Solvents	β -PVDF				α -PVDF			
	a(Å)	b(Å)	c(Å)	Number of solvent molecules	a(Å)	b(Å)	c(Å)	Number of solvent molecules
EC	19.72	25.80	62.98	135	23.10	19.84	65.12	117
PC	19.72	25.80	62.98	105	23.10	19.84	65.12	91
BC	19.72	25.80	62.98	88	23.10	19.84	65.12	77

Table S.2. presents the details of the simulation box setup for the α and β PVDF phases in contact with cyclic carbonate solvents.

Table S.3. Thermodynamic constants of the examined solvents in this study.

Solvent	A	B	C	D	T_c (K)	P_c (kPa)	Equation/ method	Ref.
EC					805	6140	STAT6 and STAT8 apparatus	1, 2
PC	17.034	6202.612	-10.289	-	-	-	Antoine	3
BC	-5.6078	-4.8868	6.7442	-23.7328	778.5	4440	Wagner	1
DMF	36.48688	-68.6743	62.2708	-229.006	596.6	5220	Wagner	4
NMP	14.65738	411.28	-68.866	-	-	-	Antoine	5
DMAC	14.621	3759.913	-63.3707	-	-	-	Antoine	3

Table S.3. presents the constant variables used to calculate the vapor pressure of different solvents. All measurements were performed within the temperature interval (273 - 473 K). In case of EC, the measurements were taken by STAT6 and STAT8 apparatus.

Wagner equation for BC:

$$\ln\left(\frac{P}{P_c}\right) = \frac{T_c}{T} \left(A \left(1 - \frac{T}{T_c} \right) + B \left(1 - \frac{T}{T_c} \right)^{1.5} + C \left(1 - \frac{T}{T_c} \right)^3 + D \left(1 - \frac{T}{T_c} \right)^6 \right) \quad \text{Eq. S1}$$

Wagner equation for DMF:

$$\ln\left(\frac{P}{P_c}\right) = \frac{T_c}{T} \left(A \left(1 - \frac{T}{T_c} \right) + B \left(1 - \frac{T}{T_c} \right)^{1.25} + C \left(1 - \frac{T}{T_c} \right)^3 + D \left(1 - \frac{T}{T_c} \right)^7 \right) \quad \text{Eq. S2}$$

Antoine equation:

$$\ln P(\text{kPa}) = A - \frac{B}{T(\text{K}) + C}$$

Eq. S3

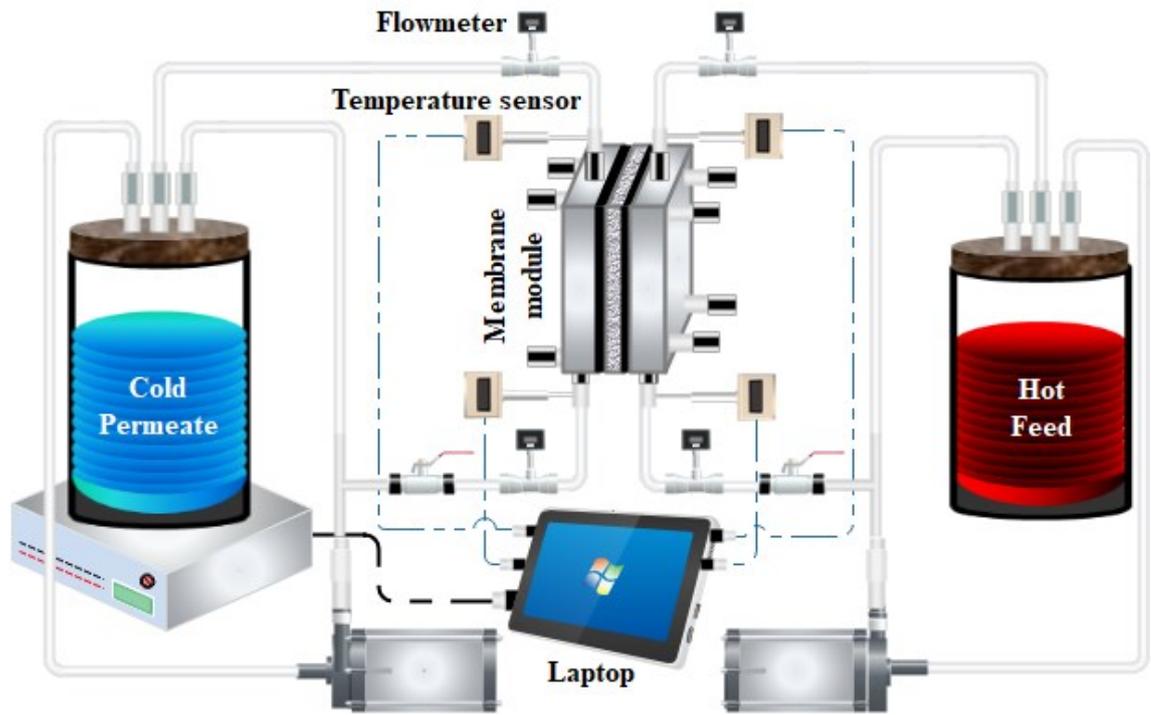


Figure S.1. DCMD lab-scale set-up

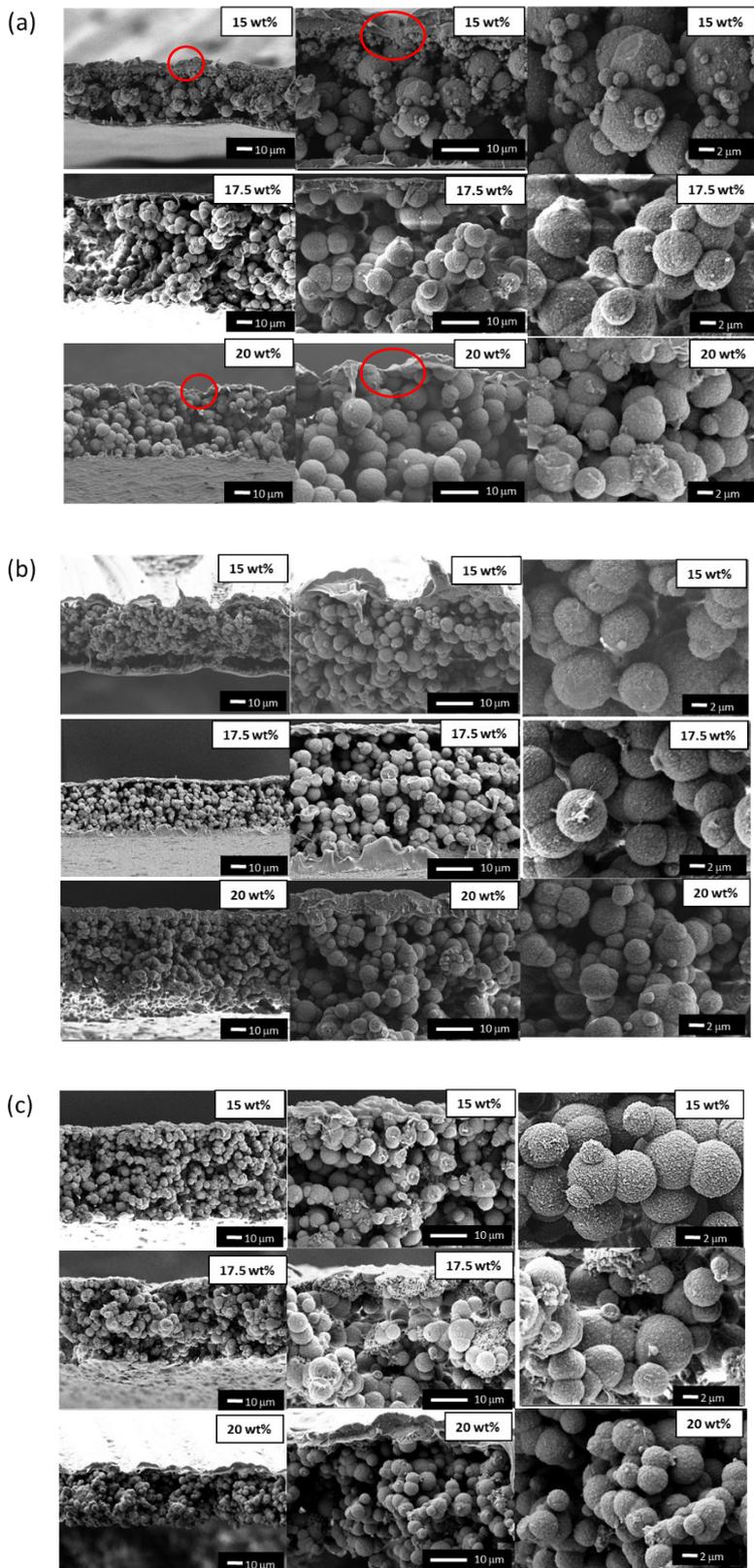


Figure S.2. SEM images of (a) PVDF/EC, (b) PVDF/PC and (c) PVDF/BC membranes prepared with different polymer concentrations.

As it is stated in the manuscript, the increasing of *PWP* of PVDF/EC-20wt% is due to the thinner skin-layer (red circle) which lower the membrane resistance towards water vapor transport resulting in a higher permeate flux.

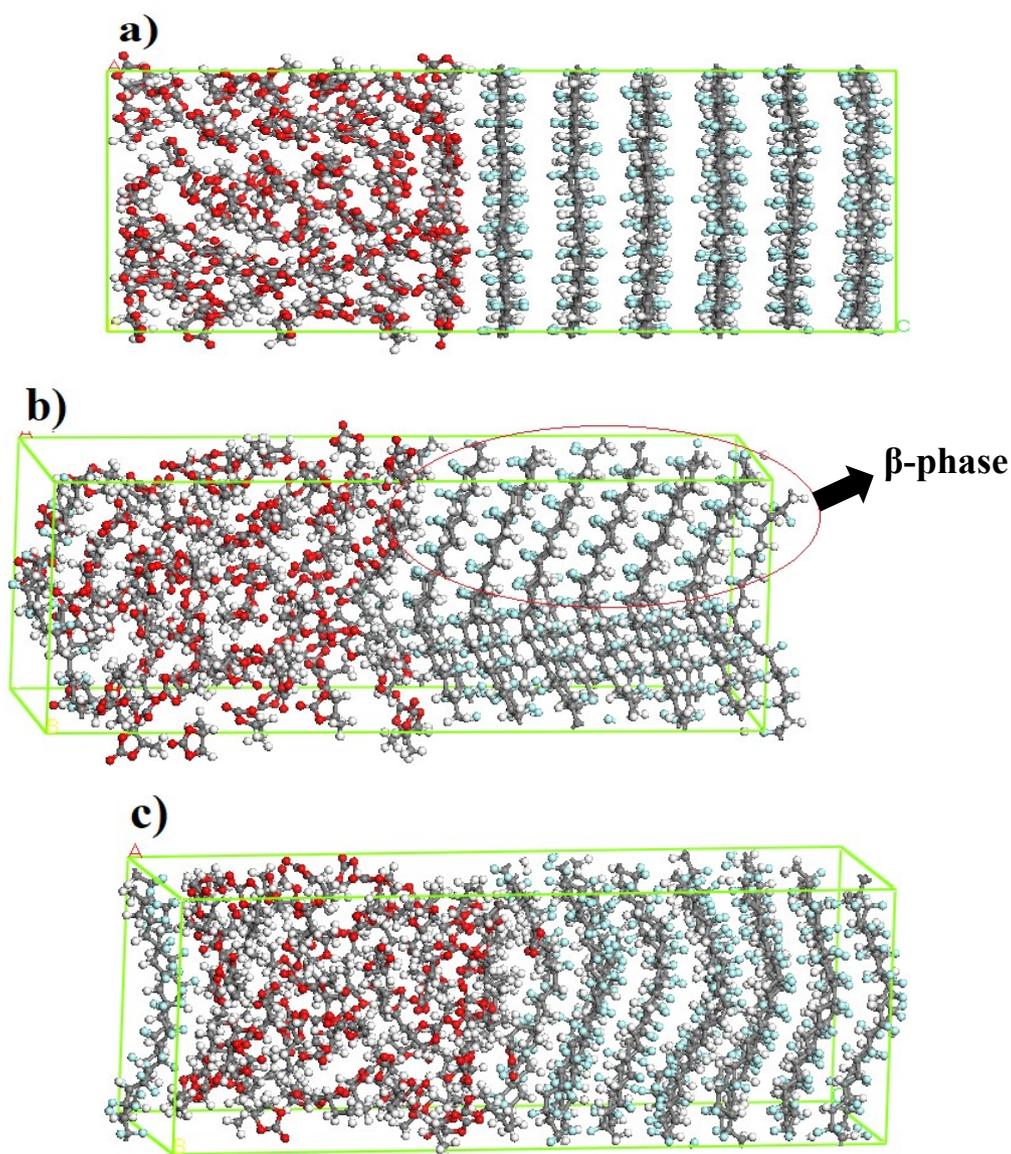


Figure S.3. Schematic of the simulation box related to a) EC, b) PC and c) BC in contact with α -PVDF surface at the end of simulation.

Figure S.3. shows the simulation boxes of α -PVDF surface in contact with cyclic carbonate solvents. The figure clearly indicates that the α -phase of PVDF is converted into β -phase as it solvated in EC solvent and formed the stable state throughout the simulation. Depressions and changes in the structure of the α -phase PVDF surface were found in PC and BC solvents. This figure has also shown that the PVDF polymer chain in contact with EC always adopts the β -phase formation, while the stability of β -phase decreases as the solvent alkyl side chain length increases.

References

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