polymers

MDPI

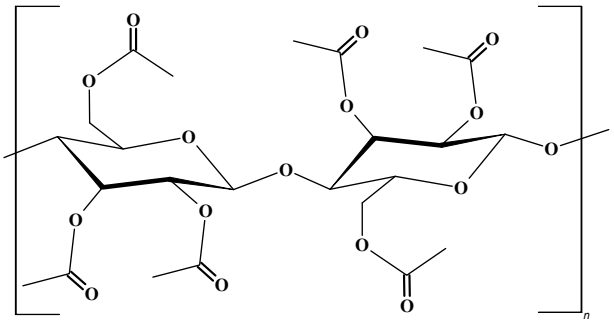
Supplementary Information for

Cellulose Acetate-Ionic Liquid Blends as Membranes for Efficient CO_2 Separation

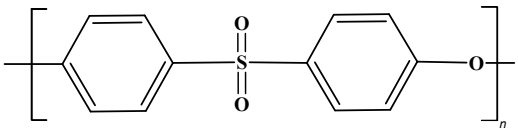
Giannis Kontos[1], Costas Tsioptsias[1,2]* and Ioannis Tsivintzelis[1,]*

[1] Department of Chemical Engineering, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece
[2] Department of Chemical Engineering, University of Western Macedonia, 50132, Kozani, Greece
* Correspondence: ktsiopts@gmail.com (C.T.), tioannis@cheng.auth.gr (I.T.)

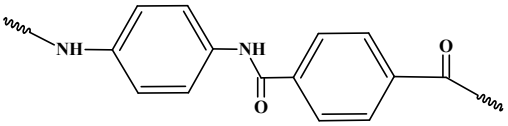
S1. Commercial polymeric membranes used in industrial CO_2 separation processes



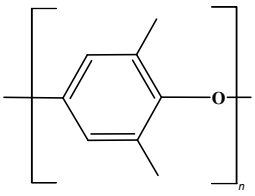
Cellulose triacetate, CTA



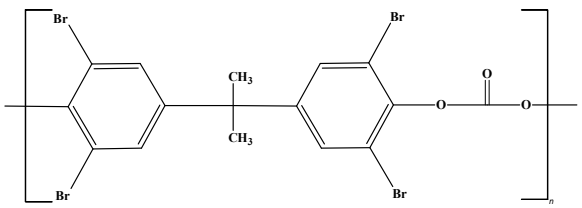
Victrex®, Ultrason® E



Kevlar®



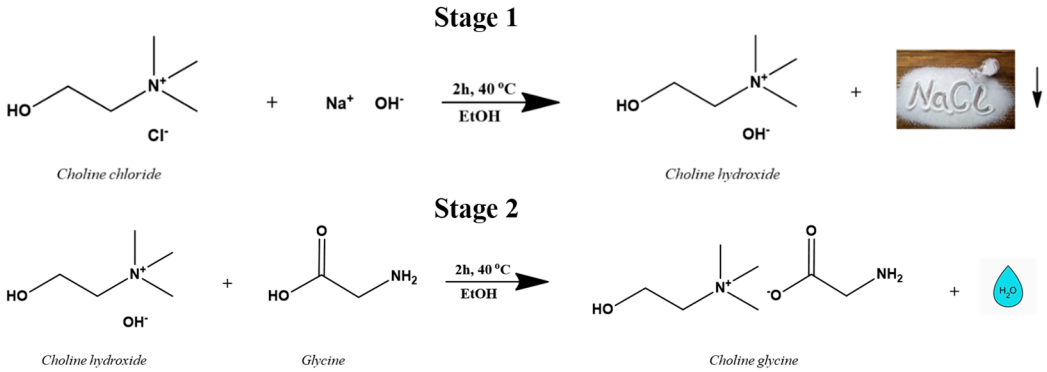
Poly (2,6-dimethyl-1,4-phenylene oxide), PPO



Tetrabromobisphenol A

Figure S1. Commercial polymeric membranes used in industrial CO_2 separation processes.

S2. [Ch][Gly] synthesis



Scheme 1. Metathesis reaction between choline chloride, [Ch^+][Cl^-], and sodium hydroxide, NaOH, in ethanol under stirring for 2 hours (Stage 1) and neutralization reaction between choline hydroxide, [Ch^+][OH^-], and glycine, to form the desirable [Ch^+][Gly^-] IL and water as by-product (Stage 2).

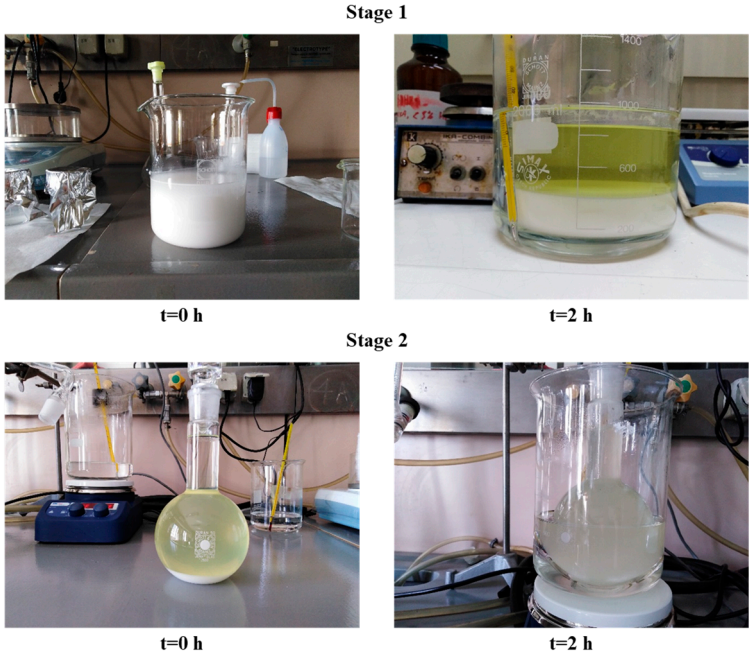


Figure S2. Choline chloride and sodium hydroxide in EtOH at t=0h and t=2h, note that NaCl precipitated as white powder (Stage 1) and choline hydroxide and glycine in EtOH at t=0h and t=2h (Stage 2).

^1H and ^{13}C NMR of the synthesized [Ch^+][Cl^-] was carried out at room temperature on a Varian 600 MHz spectrometer in D_2O with tetramethylsilane as internal standard. NMR data is reported as s = singlet, d = doublet, t = triplet, q = quatriplet and m = multiplet or unresolved, while chemical shifts (δ) values are given in ppm. The chemical shifts at 3.49-3.56 ppm (2H, m, CH_2OH), 4.03-4.10 ppm (2H, m, CH_2CH_2N) and 3.21 ppm (9H, s, $(CH_3)_3N$) originate from choline cation, whereas the signal at 3.26 ppm (2H, s, CH_2NH_2) from glycine anion (Figure S3). These results are consistent with literature findings [1-3]. Similar information can also be obtained from ^{13}C NMR analysis. The signals at 56.71 ppm (CH_2OH), 70.33 ppm (CH_2CH_2N) and 58.44 ppm (($CH_3)_3N$) are attributed to the carbon atoms of the choline cation, while those at 46.80 ppm (CH_2NH_2) and 182.82 ppm (C=O) to

carbons atoms of the glycine anion (Figure S4). These results are, also, in good agreement with the literature [2].

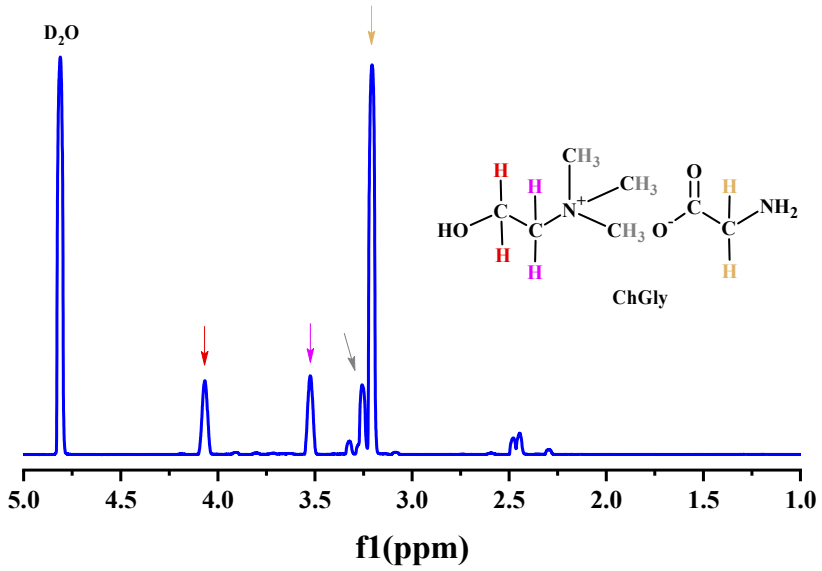


Figure S3. ^{1}H NMR spectra of the synthesized [Ch^{+}][Gly^{-}] in D_2O.

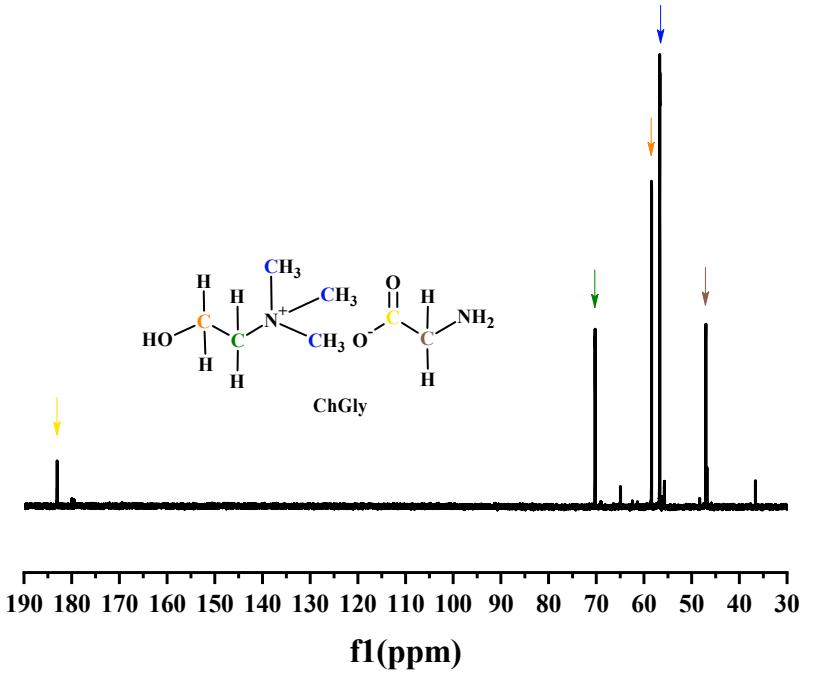


Figure S4. ^{13}C NMR spectra of the synthesized [Ch^{+}][Gly^{-}] in D_2O.

S3. CA-IL films preparation

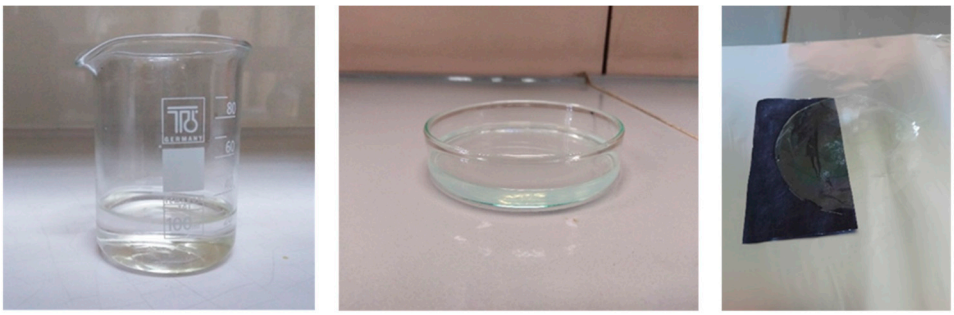


Figure S5. Composite membrane films preparation using the solution casting method.

S4. CO_2 and N_2 sorption measurements using mass loss analysis (MLA)

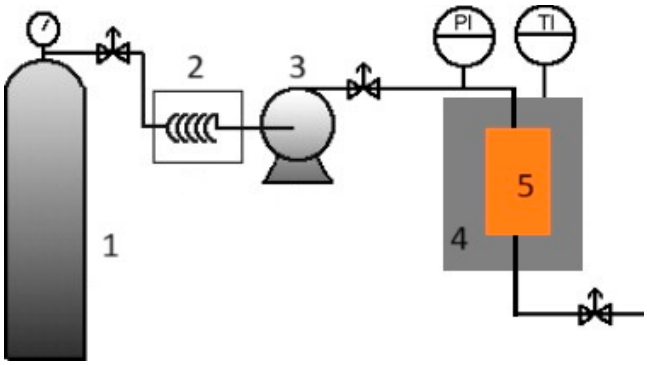
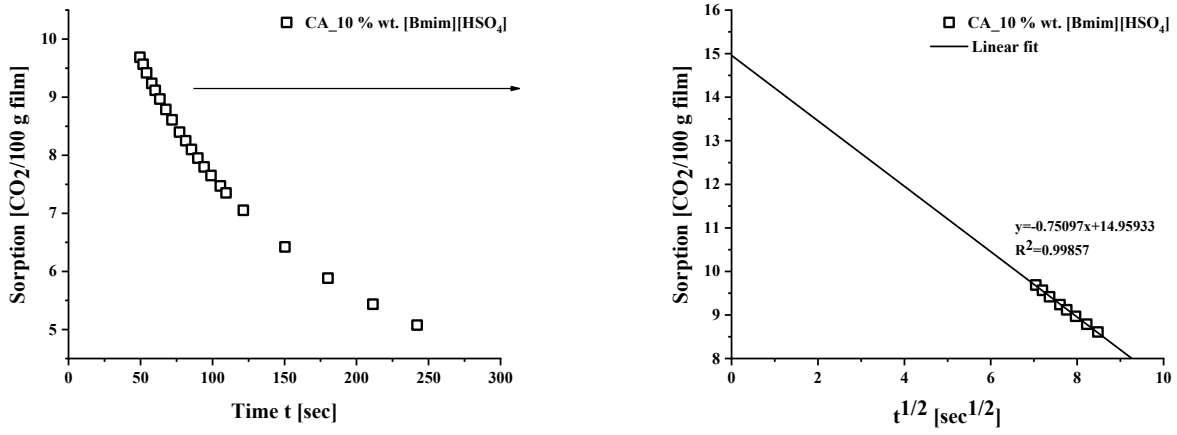


Figure S6. Sketch of the experimental setup that was used for the sorption measurements. 1: High pressure gas tank; 2: cooler; 3: syringe pump; 4: oven; 5: high pressure cell.



(**a**) (**b**)

Figure S7. CO_2 desorption from CA doped with 10% wt. [$Bmim^+$][HSO_4^-] at 25°C and atmospheric pressure after exposure at a CO_2 atmosphere at 35°C and 40 bar (a) and extrapolation to time zero using the FD model (b).

S5. Degree of crystallinity calculation of the CA-IL films using XRD analysis

After subtraction of a linear background, the experimental diffraction curve was resolved into a crystalline peak and an amorphous halo by fitting a theoretical curve. Both the crystalline peak and the amorphous halo were represented by a Gaussian distribution (Figure

S8). The degree of crystallinity was calculated as the ratio of the area of the crystalline peak to the total area [5,6].

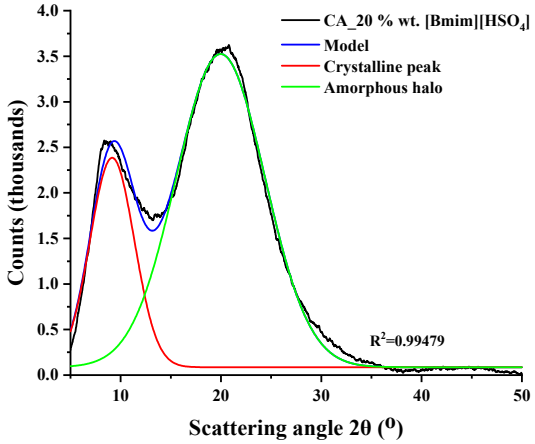


Figure S8. Degree of crystallinity calculation of the CA doped with 20% wt. [$Bmim^+$][HSO_4^-] using Gaussian function to determine the crystalline peak and the amorphous halo.

References

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