Imidazolium-based co-poly(ionic liquid) membranes for CO_2/N_2 separation

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ABSTRACT

The development of efficient carbon dioxide capture and separation technologies is at the fore front of the priorities in the climate change policies. Poly(ionic liquid)s (PILs) have been emerging as extremely promising materials for the fabrication of membranes for CO_2 separation. This work is a step forward to evaluate the performance of PIL-based copolymers in the preparation of membranes for CO_2/N_2 separation. In particular, imidazolium-based homo and copolymers were synthesized by RAFT co-polymerization of different imidazolium salts and characterized by nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) analysis. The membrane forming ability of the synthesized PILs, as well as the influence of different side chain groups (ethyl, pentyl, benzyl and napthyl) at imidazolium ring, were evaluated using the solvent casting technique. In order to improve membrane forming ability and CO_2 separation performance, different amounts of free ionic liquid (IL), $[C_2mim][NTf_2]$, were added into the synthesized homo and copolymers, and PIL–IL composite membranes were prepared. The CO_2 and N_2 permeation properties of the obtained free standing PIL–IL membranes were measured at 20 $^{\circ}$C and 100 kPa and the results obtained compared through the Robeson plot.

KEYWORDS

Poly(ionic liquid)s; PIL-based copolymers; PIL–IL composite membranes; Gas transport; CO_2/N_2 separation.

1. INTRODUCTION

The development of new materials for carbon dioxide (CO_2) capture is becoming of vital importance as concerns on the growing concentration of anthropogenic CO_2, associated to global warming and unpredictable climate changes are being widely expressed. In particular, considerable attention has been paid to ionic liquids (ILs), due to the unique tunability of their properties[1-2] and superior CO_2 affinity in comparison with light gases, such as N_2 and CH_4.[3-4] Several approaches have been proposed: from mixtures of ILs with other solvents, such as amines[5] and glycols,[6] to functionalization of ILs with diverse chemical groups,[7-12] to other more sophisticated methodologies, as for instance ILs impregnation on different porous supports, such as polymeric membranes,[13-14] zeolites,[15] silica gel,[16] metal-organic frameworks.[17]

In what concerns the use of ILs in membranes, two strategies deserve special attention: the use of an inert porous membrane to support ILs and the incorporation of ILs in a polymeric matrix. Supported ionic liquid membranes (SILMs) have been widely studied for CO_2 separation as they offer a facile preparation methodology.[18] Results using a large number of ILs show that SILMs is a very promising strategy since high CO_2 permeabilities and attractive permselectivities can be obtained. However, SILMs present a major drawback: their low stability under high trans-membrane pressures and high temperatures, due to the weak capillary forces that hold the ILs within the pores. On the other hand, the incorporation of ILs in polymeric membranes, in which the IL is entrapped in the tight spaces between the polymer chains, has proved to be a successful approach, providing membranes with increased mechanical strength compared to SILMs. A large variety of common polymers has been used to prepare polymer–IL composites,[19-21] but the most successful approach lays on the use of poly(ionic liquid)s (PILs),[22-23] since they allow the incorporation of higher amounts of ILs, due to the large degree of strong ionic interactions between the IL and the PIL components.

On top of that, neat PIL membranes possess higher CO_2 sorption capacities than their corresponding IL monomers,[24] and present CO_2/CH_4 and CO_2/N_2 on par or greater than those observed for SILMs.[23, 25-27]

The gas permeation properties of PIL membranes are strongly influenced by the structures of the polymer backbone and/or polycation,[28-30] the substituent at the quaternized atom,[22-23, 25, 27, 30-34] and the anion.[23, 35-37] Gas permeation properties through PIL–IL composite membranes based on PILs bearing different cation functionalities, such as imidazolium, pyridinium, pyrrolidinium, ammonium and cholinium, have been investigated. The results showed that although PIL–IL membranes based on pyridinium-based PIL exhibited the highest CO_2 permeability (20.4 Barrer), the greatest CO_2/CH_4 (43.0) and CO_2/N_2 (34.7) permselectivities were found for membranes comprising the PIL cholinium.[30] Moreover, PIL–IL membranes containing different anions, such as dicyanamide ($[N(CN)_2]^-$), tricyanomethane ($[C(CN)_3]^-$), tetracyanoborate ($[B(CN)_4]^-$) and bis(trifluoromethylsulfonyl) imide ($[NTf_2]^-$), were studied and it was concluded that the anion also influences both CO_2 permeabilities and CO_2/N_2 permselectivities [23, 35, 36, 38].[23, 35-36, 38]

Most of the PIL-based membranes developed for CO_2 separation use imidazolium-based PILs as polymer matrices,[39] due to the simplicity of the base ion, ease of modification and wide variety of chemistries available. Noble's group has developed numerous membranes using imidazolium-based PILs, ranging from neat PILs, to gemini and polar-substituted PILs. These solid dense membranes showed CO_2 permeability values from 4 to 30 Barrer and CO_2/N_2 permselectivities between 30 and 40.[25-27] In order to improve the CO_2 separation performance of PIL imidazolium-based membranes, several strategies have been proposed being the use of composite structures containing both PILs and ILs the most successful one. It has been shown that the incorporation of 20 wt% of a free IL into an imidazolium-based PIL can lead to an enhancement in permeability up to 400 %.[22] In order to increase the amount of

free IL without severely compromising mechanical stability, IL-based cross-linkers can be used. For example, Li *et al.* incorporated up to 60 wt% of free IL into poly(vinylimidazolium) membrane materials,[40] while Carlisle et al. made cross-linked poly(vinylimidazolium) membranes with 75 wt% of free IL.[41]

The design of membranes with PIL copolymers is an alternative strategy for CO_2 separation. The structures of PIL copolymers, which have been developed for this purpose, are given in Figure 1.

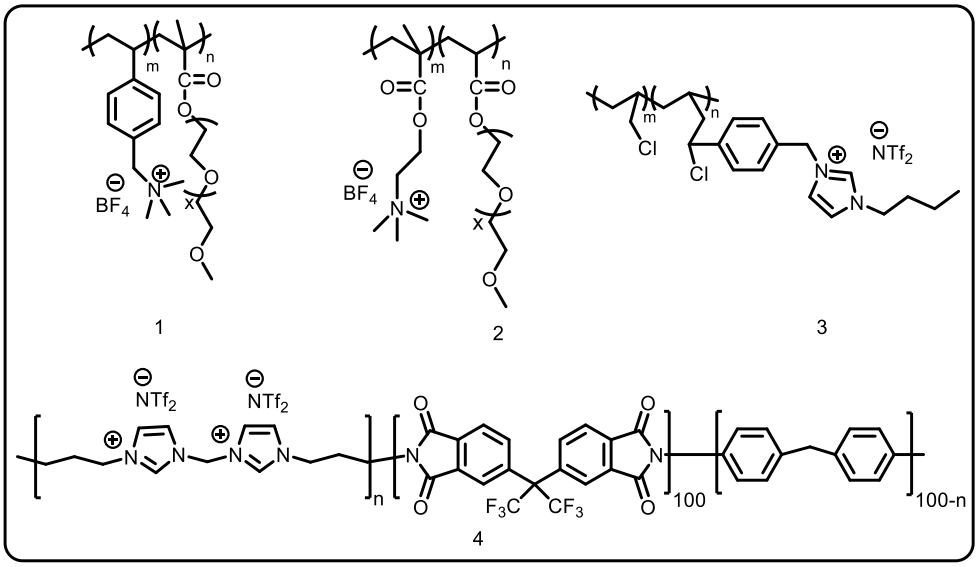


Figure 1 Different PIL copolymers structures which have been used to develop CO_2 separation membranes.

Radosz and his co-workers developed membranes with PIL copolymers made by grafting of poly(ethylene glycol) onto ammonium-based PILs.[42] The obtained membranes were found to be chemically and mechanically stable and shown CO_2 permeabilities as high as 40 Barrer (at 351 ºC) with CO_2/N_2 permselectivities up to 70.[42] Later, Li *et al.* prepared different random copolyimides using di-amino functional ILs and made free standing membranes by solvent casting technique. The influence of free volume raised by aromatic groups in polyimides on gas sorption and diffusion behavior was investigated. The incorporation of IL moieties into polyimide backbone decreased the availability of free volume in copolyimides

resulting in a significant decrease of the gas permeabilities compared to those of the pure polyimides.[43] Chi *et al.* proposed CO_2 separation membranes with different graft copolymers, consisting of poly(vinyl chloride) in main chains and imidazolium-based PIL in side chains. In sum, increasing the PIL content in copolymer results increased the CO_2 permeabilities. Nevertheless, a slight decrease in CO_2/N_2 permselectivities was also observed.[44]

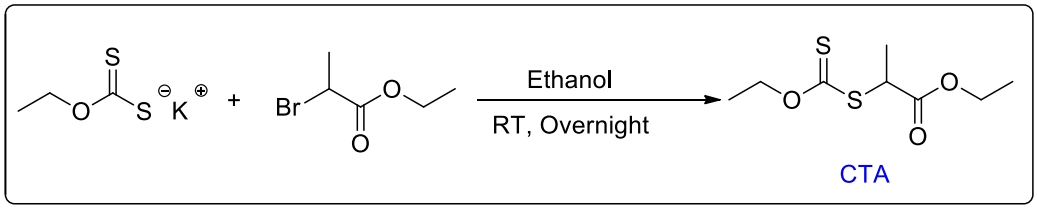
In this work, imidazolium-based homo and co-PILs having different side chain groups (ethyl, pentyl, benzyl and napthyl) at imidazolium ring were synthetized through RAFT polymerization and characterized. The membrane forming ability of the synthesized PILs and PIL–IL composites, containing different amounts of free $[C_2mim][NTf_2]$ IL, was evaluated using the solvent casting technique. The CO_2 and N_2 permeation properties of the obtained free standing PIL–IL membranes were measured using a time lag apparatus and the CO_2/N_2 separation performance discussed. The goal of this work is to understand the influence of using co-PILs, having different side chain groups (ethyl, pentyl, benzyl and napthyl) at imidazolium ring, on the stability and gas separation properties of PIL–IL composite membranes.

2. EXPERIMENTAL SECTION

2.1. Materials. 1-Vinylimidazole (>99%), *n*-bromoethane (98%), *n*-bromopentane (98%), benzyl bromide (98%), styrene, ethyl-2-bromopropionate (99%), 1-(chloromethyl)naphthalene (97%), potassium ethyl xanthogenate (96%) and lithium bis(trifluoromethylsulfonyl)imide salt ($LiNTf_2$, 99%) were purchased from Sigma-Aldrich Chemicals (India) and used as received. The 2, 2'-Azo-bis isobutyronitrile (AIBN) was obtained from AVRA Chemicals (India) and recrystallized in methanol before further use. In order that, 3 g of AIBN were taken in 15 mL of methanol and slowly heated until the solid was completely dissolved. Then, the solution was allowed to cool slowly on insulated

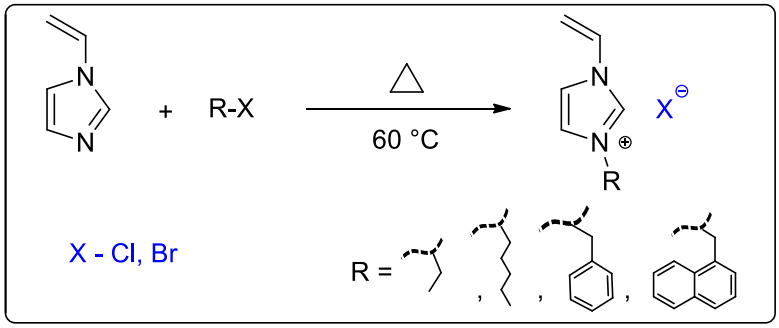
surface. The obtained crystals were filtered and dried under vacuum. All the solvents used were purchased from Rankem Chemicals (India) and distilled prior usage.

2.2. Synthesis. The chain transfer agent (CTA), potassium ethyl xanthogenate 1.06 g (6.62 mmol), was first dissolved in ethanol in a round bottom flask, and 1 g of ethyl-2-bromopropionate (5.52 mmol) was added. The mixture was stirred at room temperature (RT) overnight, as depicted in Scheme 1. At the end of the reaction, the 2-ethoxythiocarbonylsulfanyl-propionic acid ethyl ester was obtained (1.13 g, 92% yield).[45]



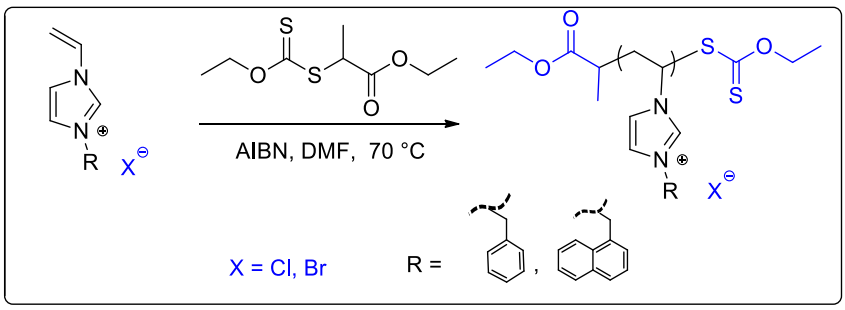
Scheme 1. Synthesis of CTA.

The vinylimidazolium-based monomers having different side chains, namely ethyl, pentyl, benzyl and napthyl were synthesized as described elsewhere.[46] Briefly, the monomer 1-vinyl-3-pentyl imidazolium bromide, (ViPenIm)Br was prepared in quantitative yields by mixing 3 g of 1-vinylimidazole (31.8 mmol) with 7.22 g of *n*-bromopentane (47.81 mmol) in a round bottom flask. The mixture was then allowed to react at 60 °C, in an oil bath for 3 h. The other vinyl monomers were synthesized following the same procedure, as shown in Scheme 2. Nevertheless, in the synthesis of the (ViBenIm)Br monomer, 1-vinylimidazole was initially dissolved in 10 mL of methanol and bromobenzene was added slowly in dropwise portions. This mixture was heated at 60 °C for 3 h and the 1-vinyl-3-benzylimidazolium bromide (ViBenIm)Br was produced in quantitative yield .



Scheme 2. Synthesis of vinylimidazolium monomers.

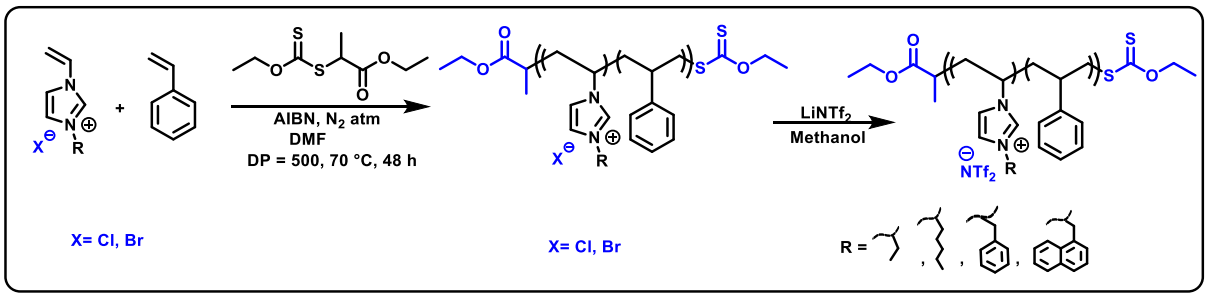
The prepared ionic monomers were polymerized by RAFT polymerization using xanthate-based CTA as shown in Scheme 3. In a typical procedure, 3 g of 1-vinyl-3-benzyl imidazolium bromide (11.29 mmol), 50.21 mg of CTA (0.226 mmol) and 7.42 mg AIBN (0.045 mmol) were taken in a flame dried Schlenk flask and dissolved in 10 mL of dimethylformamide. In order to eliminate any dissolved gases, three freeze thaw cycles were performed. Then, the reaction mixture was heated at 70 °C for 24 h. The obtained white colour poly(ViBenIm)Br was purified by precipitation in cold chloroform and dried under vacuum (2.56 g, 85% yield). The other ionic monomers were polymerized following the same procedure.



Scheme 3. RAFT polymerization of vinylimidazolium monomers.

The poly(vinylimidazolium)-polystyrene copolymers were synthesized by RAFT co-polymerization of vinyl monomers with styrene, as shown in Scheme 4. In a typical procedure, 3.2 g (13.05 mmol) of 1-vinyl-3-pentylimidazolium bromide, 1.36 g (13.05 mmol)

of styrene, 11.59 mg of CTA (0.0521 mmol) and 1.7 mg of AIBN (0.059 mmol) were taken in a flame dried Schlenk flask and dissolved in 10 mL of dimethylformamide. In order to eliminate any dissolved gases, three freeze thaw cycles were performed. Then, the reaction mixture was heated at 70 °C for 48 h. The obtained brown colour poly(ViPenIm)(Sty)Br was purified by precipitation in cold chloroform and dried under vacuum (4.52 g, 89% yield). The remaining poly(vinylimidazolium)-polystyrene copolymers were synthesized following the same procedure used for poly(ViPenIm)(Sty)Br [46]. To prepare the poly(ViPenIm)(Sty)NTf_2, a simple anion metathesis reaction was carried out. Three grams (7.62 mmol) of poly(ViPenIm)(Sty)Br were dissolved in methanol and then an aqueous solution of lithium bis(trifluoromethylsulfonyl)imide (4.37 g, 15.24 mmol) was dropwise added. The mixture was kept for stirring at room temperature for 24 h. The obtained product was washed with an excess amount of water, filtered and dried under vacuum (4.21 g, 93% yield). The anion metathesis reaction of the remaining poly(vinylimidazolium)-polystyrene copolymers were carried out following the same procedure.[46]



Scheme 4. Synthesis of the co-poly(ionic liquid)s [ViRIm](Sty)X.

2.3. Polymer characterization. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AC-400 spectrometer in appropriate deuterated solvents. Differential scanning calorimetry (DSC) experiments were performed using a DSC Q200 instrument from TA. Samples were crimped in non-recyclable aluminium hermetic pans and analysed under nitrogen atmosphere by heating and cooling cycles at a rate of 10 ºC min^{-1}. Thermal gravimetric analyses (TGA) were carried out using a TGA Q50 instrument from TA. Samples

were heated at a constant rate of 10 ºC min^{-1}, from room temperature to 600 ºC, under a nitrogen atmosphere.

2.4. Membranes preparation. The membrane forming ability of the pure PILs and different PIL–IL combinations was evaluated using solvent casting technique, as previously reported [38]. In the case of pure PILs, 12 (w/v)% of PIL solutions were prepared by dissolving an appropriate amount of PIL in acetone. The PIL solutions were stirred at room temperature until complete dissolution of the polymers. The PIL–IL composite solutions in acetone were prepared in a vial by combining appropriate amounts of homo PILs (Scheme 3) or PIL-based copolymers (Scheme 4) with the commercially available $[C_2mim][NTf_2]$ IL. Then, the solutions were stirred until both PIL and IL were completely dissolved and a homogeneous solution was obtained. All the prepared PIL and PIL–IL solutions were then poured into Petri dishes and left for acetone evaporation during 2 days at room temperature. The solvent evaporation took place slowly and in a saturated solvent environment in order to obtain homogeneous membranes. Finally, to ensure that the solvent was completely evaporated, the membranes were dried at 45 ºC overnight, before gas permeation experiments.

2.5. Gas permeation experiments. Ideal gas (CO_2 and N_2) permeabilities and diffusivities through the prepared membranes were measured, at 20 ºC with a trans-membrane pressure differential of 100 kPa, using the time lag apparatus, which is fully described elsewhere.[47] First, each membrane was degassed under vacuum inside the permeation cell for 12 h. All the permeation data were measured at least in triplicate on a single membrane sample. The permeation cell and lines were evacuated until the pressure was below 0.1 kPa before each run. No residual IL was found inside the permeation cell at the end of the experiments. The membranes thickness (202 to 231 μm) were measured using a digital micrometer (Mitutoyo,

model MDE-25PJ, Japan). Average thickness was calculated from six measurements taken at different locations of each membrane sample.

Gas transport through the prepared PIL–IL dense membranes was assumed to follow a solution-diffusion mass transfer mechanism,[48] where the permeability (P) is related to diffusivity (D) and solubility (S) as follows:

$$P = D \times S \tag{1}$$

The permeate flux of each gas (J_i) was determined experimentally using Eq. (2),[49] where V^p is the permeate volume, Δp_d the variation of downstream pressure, A the effective membrane surface area, t the experimental time, R the gas constant and T the temperature.

$$J_i = \frac{V^p \Delta p_d}{AtRT} \tag{2}$$

Ideal gas permeability (P_i) was then determined from the steady-state gas flux (J_i), the membrane thickness (ℓ) and the trans-membrane pressure difference (Δp_i), as shown in Eq. (3).[50]

$$P_i = \frac{J_i}{\Delta p_i / \ell} \tag{3}$$

Gas diffusivity (D_i) was determined according Eq. (4). The time lag parameter (θ) was calculated by extrapolating the slope of the linear portion of the p_d vs. t curve back to the time axis, where the intercept is equal to θ.[50]

$$D_i = \frac{\ell^2}{6\theta} \tag{4}$$

After P_i and D_i were known, the gas solubility (S_i) was calculated using the relationship shown in Eq. (1). The ideal permeability selectivity (or permselectivity), $\alpha_{i/j}$, was obtained by

dividing the permeability of the more permeable specie *i* to the permeability of the less permeable specie *j*. As shown in Eq. (5), the permselectivity can also be expressed as the product of the diffusivity selectivity and the solubility selectivity:

$$\alpha_{i/j} = \frac{P_i}{P_j} = \left(\frac{D_i}{D_j}\right) \times \left(\frac{S_i}{S_j}\right) \tag{5}$$

3. RESULTS AND DISCUSSION

3.1. Synthesis and characterization of imidazolium-based homo and co-PILs. Imidazolium-based homo and co-PILs were synthesized by RAFT polymerization using CTA as chain transfer agent. The copolymers were synthesized by taking styrene and vinyl imidazolium-based monomers in 1:1 ratio. Even though both monomers were taken in 1:1 ratio, different amount of imidazolium block have seen in copolymer composition probably due to its lower reactivity over styrene. From the ^{1}H NMR studies (see Figures S7 to S10 in Supporting Information for further details), the amount of imidazolium block present in the co-PILs was found to be in between 83 and 96% (Table 1). The synthesized polymers bearing Br/Cl as counter-anions were then subjected to anion exchange using $LiNTf_2$ salt.

The thermal stability of the homo and co-PILs was evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements and the data obtained depicted in Table 1. From the DSC results, it can be observed that the two homo PILs, poly(ViBenIm)NTf_2 and poly(ViNapIm)NTf_2 exhibit T_g values around -19.8 and 8.6 °C, respectively (Figures. S11 and S12). On the other hand, the four copolymers, poly(ViEIm)(Sty)NTf_2, poly(ViPenIm)(Sty)NTf_2, poly(ViBenIm)(Sty)NTf_2 and poly(ViNapIm)(Sty)NTf_2 showed T_g values of -26.3, 59.4, 97.2 and 95.0°C, respectively (Figures S13 to S16). It can be observed that T_g is strongly depend on chemical structure of the backbone and side groups. The presence of stiff backbones and bulky side groups in the structure hinders the activation of the backbone segmental motion resulting in a rise in T_g

values.[51] Homo and co-PILs having napthyl groups in the side chain shown higher T_g values than those of homo and co-PILs presenting benzyl groups (see Table 1). In the case of co-PIL having pentyl group in the side chain, an higher T_g value was also found in comparison to that of the co-PIL bearing ethyl group (see Table 1).

Regarding the TGA analysis, the two homo PILs displayed two step decomposition pattern and showed thermal stabilities up to 260 ºC, as it can be observed in Figures S17 and S18, respectively. Conversely, the four co-PILs showed one step decomposition pattern with decomposition temperatures between 274 and 304 ºC (Figures S19 to S22).

Table 1 Thermal properties of the prepared homo and co-PILs: decomposition (T_{dec}) and glass transition (T_g) temperatures.

PILs	% of Imidazolium block[a]	% of styrene block[a]	T_g (ºC)[b]	T_{dec} (ºC)[c]
Poly(ViBenIm)NTf_2	100	0	-19.8	266.6
Poly(ViNapIm)NTf_2	100	0	8.6	259.1
Poly(ViEIm)(Sty)NTf_2	83	100	-26.3	304.4
Poly(ViBenIm)(Sty)NTf_2	86	100	97.2	274.0
Poly(ViNapIm)(Sty)NTf_2	96	100	95.0	283.1
Poly(ViPenIm)(Sty)NTf_2	95	100	59.4	291.6

[a] Relative percentage of styrene and imidazolium in co-PILs calculated from NMR data.
[b] T_{dec} defined as the temperature at which the polymer starts fragmentation into smaller molecules.
[c] T_g defined as the temperature at the middle point of the glass transition region.

3.2. Membrane forming ability. Our attempts to prepare free standing membranes with the two synthesized pure homo PILs, namely poly(ViBenIm)NTf_2 and poly(ViNapIm)NTf_2, were unsuccessful, since they became very brittle and broke even before being peeled out of the Petri dishes. Although the prepared poly(vinylimidazolium)-polystyrene copolymers

showed better film forming ability than the homo PILs, the obtained co-PIL membranes were not flexible enough to be peeled out of the Petri dishes and handled without breaking. Therefore, the incorporation of different amounts of free $[C_2mim][NTf_2]$ IL was tested as a strategy to enhance the film forming ability of the homo and poly(vinylimidazolium)-polystyrene copolymers. Also, it is well documented in literature that a large amount of IL incorporated into the PIL leads to higher the CO_2 permeability and diffusivity through the PIL–IL membrane.

Table 2 Composition of the prepared PIL–IL materials and their ability to be processed into stable and homogenous free standing solid membranes.

PIL	**wt% of $[C_2mim][NTf_2]$ (IL)**						
	-	**10**	**20**	**25**	**30**	**40**	**60**
Poly(ViBenIm)NTf_2	✖	γ	γ	-	-	♯	-
Poly(ViNapIm) NTf_2	✖	δ	δ	-	-	δ	♯
Poly(ViEIm)(Sty) NTf_2	✖	♯	♯	-	-	-	-
Poly(ViPenIm)(Sty) NTf_2	✖	✓	♯	♯	♯	♯	♯
Poly(ViBenIm)(Sty) NTf_2	✖	-	δ	✓	♯	♯	♯
Poly(ViNapIm)(Sty) NTf_2	✖	-	δ	Δ	✓	♯	♯

(✖) Brittle, **(γ)** Sticky, **(♯)** Jelly, **(δ)** Breaks in to pieces, **(✓)** Membrane obtained,
(-) not performed

Table 2 summarizes the results obtained regarding the ability of PIL-IL combinations to be processed into mechanically stable flat form membranes. As it can be observed, only the PIL–IL materials containing the random copolymers poly(ViPIm)(Sty)NTf_2, poly(ViBenIm)(Sty)NTf_2 and poly(ViNapIm)(Sty)NTf_2, combined with 10, 25 and 30 wt% of

IL [C_2mim][NTf_2], respectively, resulted in stable and homogenous free standing membranes. The amount of IL needed to obtain stable composite membranes seems to be greatly depend of the co-PIL structure, which can promote different polymer chain arrangements. Table 2 also shows that the synthesized copolymers are in general not able to sustain or accommodate higher amounts of free IL, since the resulting composites turn into gel like-materials. No membrane could be obtained using poly(ViEIm)(Sty)NTf_2 and higher amounts of free IL lead to leaching of the IL from the membrane. Pictures of the co-PIL–IL composite membranes are shown in Figure 2.

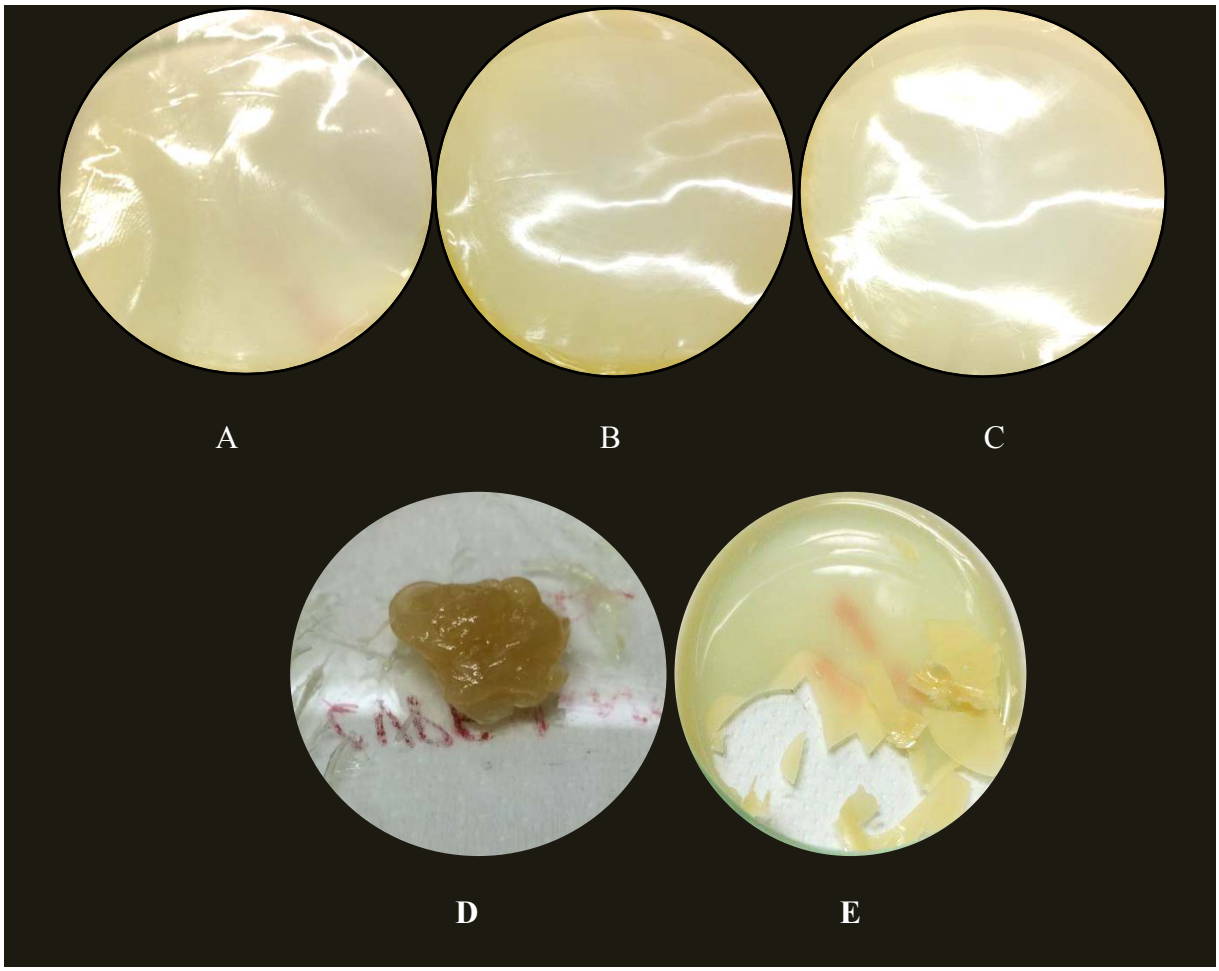


Figure 2 Pictures of the PIL–IL membranes: (A) poly(ViPenIm)(Sty)NTf_2 with 10 wt% IL, (B) poly(ViBenIm)(Sty)NTf_2 with 25 wt% IL, (C) poly(ViPenIm)(Sty)NTf_2 with 30 wt% IL (D) poly(ViBenIm) NTf_2 with 20 wt% IL (E) poly(ViNapIm) NTf_2 with 20 wt% IL.

3.3. Gas permeability, diffusivity and solubility. The gas (CO_2 and N_2) permeability and diffusivity values, determined using a time lag apparatus, in the co-PIL–IL composite membranes are illustrated in Figures 3 (A) and (B), respectively, while the gas solubility values calculated using Eq. (1) are shown in Figure 3 (C). The CO_2 permeability values were found to be two orders of magnitude higher than those of N_2 in the three co-PIL–IL composite membranes. This observation confirms the membranes' aptitude to separate CO_2 from N_2. On the other hand, and as expected, the N_2 diffusivities are always higher than those of CO_2, due to smaller size of the former gas. Regarding gas solubility, a similar behavior to that of gas permeability is observed, since the N_2 solubility values obtained were significantly lower than those of CO_2 amongst the co-PIL–IL composite membranes. Thus, the high CO_2 permeability compared to that of N_2 can be essentially attributed to the high levels of CO_2 solubility relative to N_2. These findings are in agreement with several studies for CO_2 separation using other PIL–IL composites.[30, 33-35]

The results presented in Figure 3 (A) show that the three co-PIL–IL membranes studied possess similar gas permeabilities. However, and bearing in mind that generally gas permeabilities increase with the free IL content into polymer membranes,[30,37-41] an odd behavior was observed in the present work: the highest gas permeabilities was obtained for the Poly(ViNapIm)(Sty)NTf_2–30%IL membrane which also has the highest amount of free IL incorporated (30 wt%), while the lowest gas permeabilities were observed for Poly(ViBenIm)(Sty)NTf_2–25%IL, although Poly(ViPenIm)(Sty)NTf_2–10%IL is the membrane that contains the lowest amount of free. This behavior suggests that the poly(vinylimidazolium)-polystyrene copolymers structural features have a strong influence on the gas permeation properties of the prepared co-PIL–IL membranes. For instance, the co-PIL having pendant napthyl group at the imidazolium ring allowed the preparation of a composite membrane with 30 wt% of free IL that has similar CO_2 permeability (~ 24 Barrer)

to that of the composite made with the co-PIL bearing the pentyl as the side chain group (~ 22 Barrer) and only 10 wt% of free IL. In other words, the presence of either the napthyl or the benzyl group, instead of the pentyl group at the imidazolium ring of the PIL backbone seems to contribute to increase linear chain packing, certainly through π-π interactions, contributing for more packed membranes. This large influence of the PIL structural features in the gas permeation properties is probably more marked in these composites that have small amount of IL incorporated that it would be if a large amount of IL could be incorporated.

Another interesting point is that the typical behavior obtained for dense membranes, where the gas permeability is controlled by the gas diffusion is not observed in the present case. Despite the fact that membranes with different poly(vinylimidazolium)-polystyrene copolymers are here compared, it can be seen that gas diffusion follows the order of the IL amount presented in the composite (Figure 3 (B)), thus allowing the conclusion that the liquid like state of the membrane seems to play a more dominant role in gas diffusion. Also to be remarked is the influence of the polycation backbone in the gas solubility results, with the poly(ViPIm)(Sty)NTf_2 exhibiting the highest gas solubility results. In fact, the solubility profile (Figure 3 (C)) obtained for the three studied membranes is similar to the gas permeability (Figure 3 (A)).

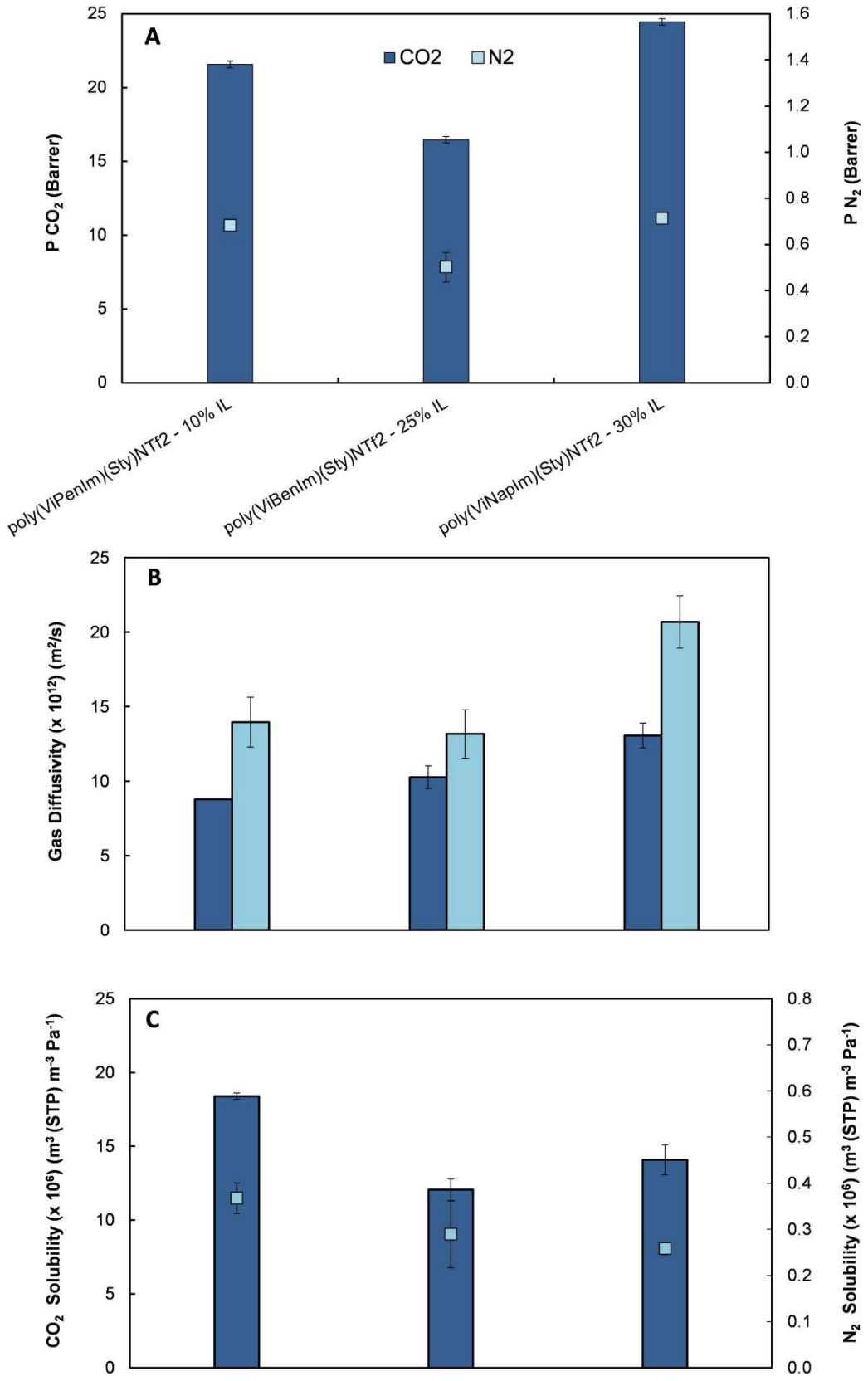


Figure 3 Gas permeabilities (A), diffusivities (B) and solubilities (C) through the prepared imidazolium-based co-PIL–IL membranes. Error bars represent standard deviations based on three experimental replicas.

3.4. CO_2/N_2 separation performance. The ideal CO_2 permeability and CO_2/N_2 permselectivity of the co-PIL–IL membranes obtained are listed in Table 3. As it can be seen, the CO_2/N_2 permselectivities of these membranes are quite similar, with values ranging from 31.7 to 34. Although different poly(vinylimidazolium)-polystyrene copolymers were used, the incorporation of higher amount of free $[C_2mim][NTf_2]$ IL slightly increased the CO_2/N_2 permselectivity of the co-PIL–IL composite membranes by 3.9% and 4.4% in Poly(ViBenIm)(Sty)NTf_2–25%IL and Poly(ViNapIm)(Sty)NTf_2–30%IL, respectively, compared to that of the Poly(ViPenIm)(Sty)NTf_2–10%IL. This is in agreement with the results previously reported for other PIL–IL composite membranes.[33, 36-38, 40, 52]

A comparison of CO_2/N_2 separation performance between the results obtained in this work and the recently published data for other PIL–IL composite membranes is illustrated in the so-called Robeson plot (Figure 4),[53] which is widely used to evaluate the performance of membrane materials. This plot displays a solid black line, the empirical 2008 upper bound for CO_2/N_2 gas pair, which is based on a large amount of experimental data for known polymeric membrane materials and illustrates the trade-off between permeability and permselectivity. From Figure 4, it can be observed that the three membranes studied in this work are placed in middle of the Robeson plot. Unfortunately, the results obtained for the co-PIL–IL composite membranes lie below the CO_2/N_2 upper bound, close to available literature data for other PIL–IL composite membranes made of homo PILs having imidazolium-based backbones and 20 wt% of free IL.

Table 3 CO_2 permeability (P) and CO_2/N_2 permselectivity (α) values of the prepared co-PIL–IL composite membranes. The listed uncertainties represent the standard deviations, based on three experiments.

PIL–IL composite Membranes	Thickness (µm)	P CO_2 (Barrer)	α CO_2/N_2
Poly(ViPenIm)(Sty)NTf_2 – 10% IL	217	21.6 ± 0.2	31.7
Poly(ViBenIm)(Sty)NTf_2 – 25% IL	231	16.5 ± 0.2	32.9
Poly(ViNapIm)(Sty)NTf_2 – 30% IL	202	24.5 ± 0.2	34.4

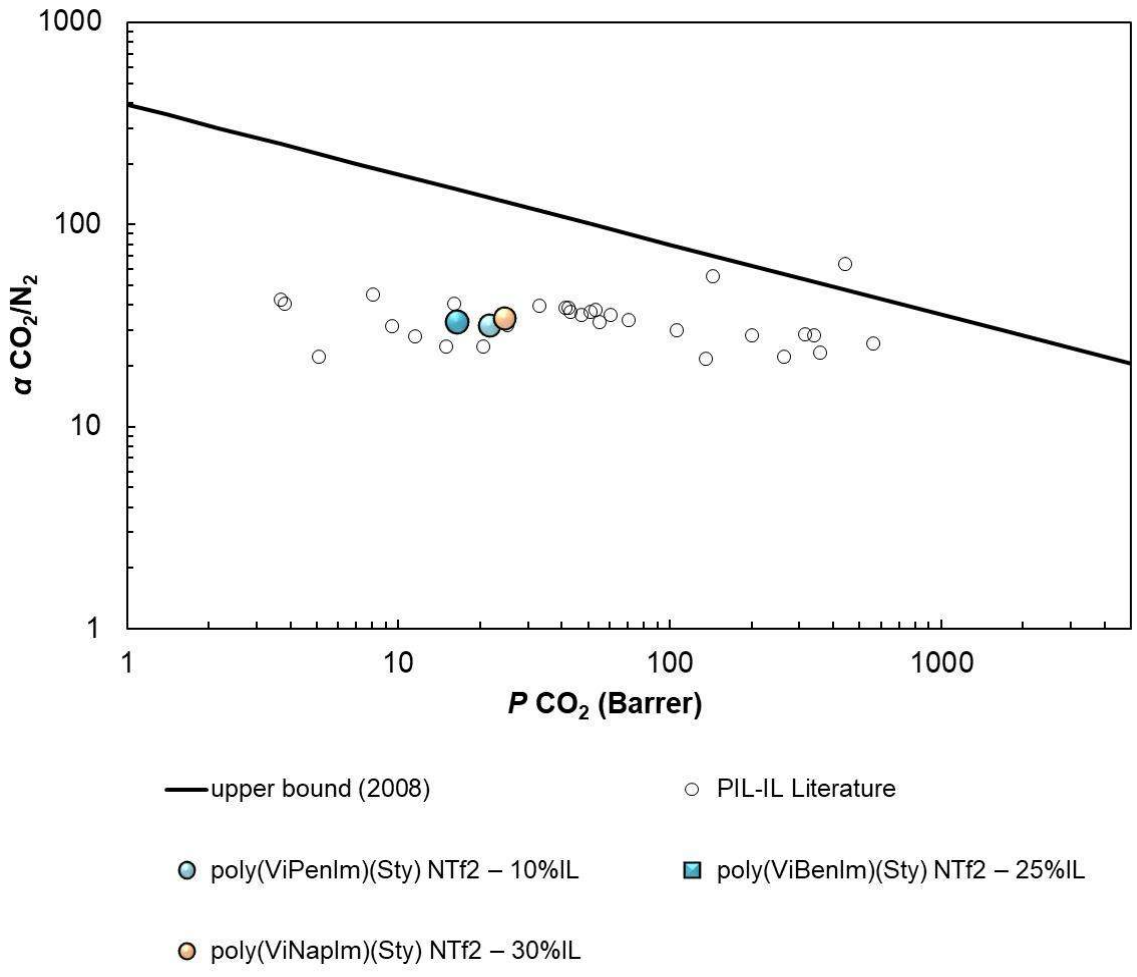


Figure 4 CO_2/N_2 separation performance of the co-PIL–IL composite membranes obtained in this work. Data is plotted on a log-log scale and the upper bound is adapted from Robeson.[53] Literature values of other PIL–IL composite membranes previously reported are also illustrated for comparison.[23, 30, 32, 38, 40, 47, 54]

4. CONCLUSIONS

RAFT derived imidazolium-based homo and co-poly(ionic liquid)s were successfully synthesized and anion metathesis reactions were performed. The prepared polymers were characterized by nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The results showed that the synthesized poly(vinylimidazolium)-polystyrene copolymers have high thermal stabilities (up to 300 ºC) and are thus suitable for post-combustion CO_2 separation. The membrane forming ability of the prepared imidazolium-based homo and co-poly(ionic liquid)s was evaluated using the solvent casting technique. It was found that the synthesized homo and poly(vinylimidazolium)-polystyrene copolymers were unable to be processed into mechanically stable flat form membranes due to their brittle nature. Consequently, the homo and poly(vinylimidazolium)-polystyrene copolymers were blended with different amounts (10, 20, 25, 30, 40 and 60 wt%) of free $[C_2mim][NTf_2]$ IL. Only the random copolymers poly(ViPIm)(Sty)NTf_2, poly(ViBenIm)(Sty)NTf_2 and poly(ViNapIm)(Sty)NTf_2, combined with 10, 25 and 30 wt% of $[C_2mim][NTf_2]$, respectively, resulted in stable and homogenous free standing solid membranes. The membranes exhibited CO_2 permeabilities ranging from 16.5 to 24.5 and CO_2/N_2 permselectivities from 31.7 to 34.4, thus falling in a region of the Robeson plot below the 2008 upper bound, where other PILs bearing similar amount of IL also are. Curiously, and due to the small amount of IL incorporated in the co-PIL–IL composites, the effect of the polymer backbone structure in the gas diffusion and solubility can be observed.

ASSOCIATED CONTENT

Supporting Information. The NMR, DSC and TGA spectra of the synthesized homo and poly(vinylimidazolium)-polystyrene copolymers are given in Supplementary Information, which is available free of charge online.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

Δp_d	Variation of downstream pressure
Δp_i	Pressure driving force
A	Effective membrane surface area
CO_2	Carbon Dioxide
D	Diffusivity
ILs	Ionic Liquids
J_i	Steady-state gas flux
ℓ	Membrane thickness
N_2	Nitrogen
P	Permeability
PILs	Poly(ionic liquid)s
R	Ideal Gas Law constant
S	Solubility
t	Time
T	Temperature
V^p	Permeate Volume
$\alpha_{i/j}$	Permselectivity
θ	Time lag parameter

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Imidazolium-based co-poly(ionic liquid) membranes for CO_2/N_2 separation

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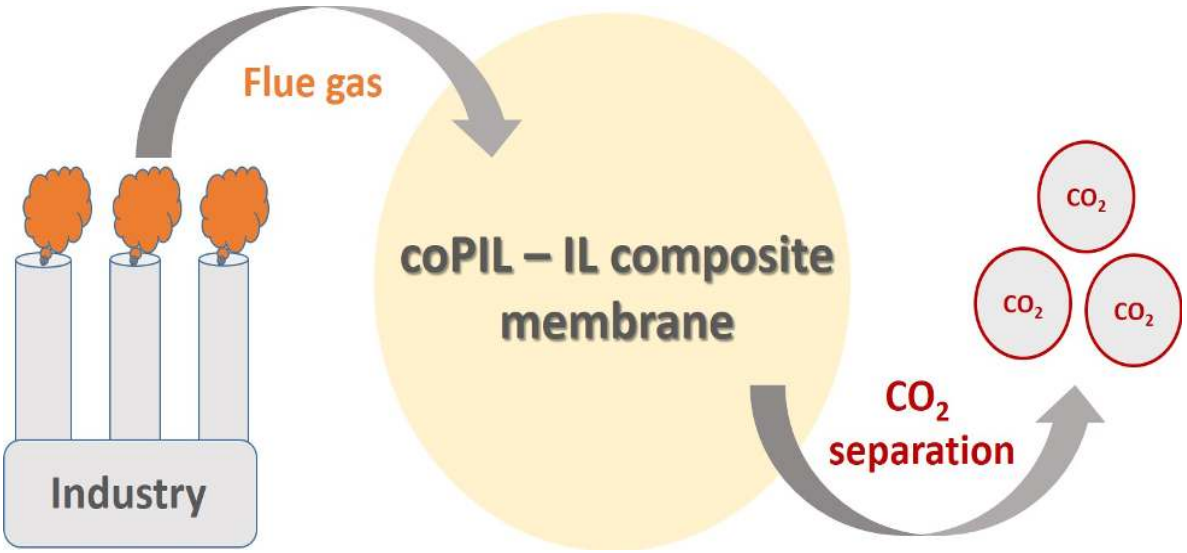

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