# Tailored $CO_2$-philic Anionic Poly(ionic liquid) Composite Membranes: Synthesis, Characterization and Gas Transport Properties

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# ABSTRACT

Polymeric membranes either containing, or built from, ionic liquids (ILs) are of great interest for enhanced $CO_2$/light gas separation due to the stronger affinity of ILs toward quadrupolar $CO_2$ molecules, and hence, high $CO_2$ solubility selectivity. Herein, we report the development of a series of four novel anionic poly(IL)-IL composite membranes via a photopolymerization method for effective $CO_2$ separation. Interestingly, these are the first examples of anionic poly(IL)-IL composite systems, in which the poly(IL) component has delocalized sulfonimide anions pendant from the polymer backbone with imidazolium cations as "free" counterions. Two types of photopolymerizable methacryloxy-based IL monomers (MILs) with highly delocalized anions ($–SO_2–N^{(-)}–SO_2–CF_3$ and $–SO_2–N^{(-)}–SO_2–C_7H_7$) and mobile imidazolium ($[C_2mim]^+$) counter cations were successfully synthesized and photopolymerized with two distinct amounts of free IL containing the same structural cation ($[C_2mim][Tf_2N]$) and 20 wt% PEGDA crosslinker, to serve as a composite matrix. The structure-property relationships of the four newly developed anionic poly(IL)-IL composite membranes were extensively characterized by TGA, DSC, and XRD analysis. All of the newly developed anionic poly(IL)-IL composite membranes exhibited superior $CO_2/CH_4$ and $CO_2/N_2$ selectivities together with moderate $CO_2/H_2$ selectivity and reasonable $CO_2$ permeabilities. The membrane with an optimal composition and polymer architecture ($MIL\text{-}C_7H_7/PEGDA_{(20\%)}/IL_{(1eq.)}$) reaches the 2008 Robeson upper bound limit of $CO_2/CH_4$, due to the simultaneous improvement in permeability and selectivity ($CO_2$ permeability ~ 20 barrer and $\alpha CO_2/CH_4$ ~119). This study provides a promising strategy to explore the benefits of anionic poly(IL)-IL composites to separate $CO_2$ from flue gas, natural gas, and syngas streams and open up new possibilities in the polymer membrane design with strong candidate materials for practical applications.

**Keywords:** Anionic Poly(IL)s; Photopolymerization; Composite Membranes; Gas Separation; $CO_2$ Selectivity.

## INTRODUCTION

The steady increase in atmospheric $CO_2$ has been a major concern in 21st Century as it leads to climate change-derived environmental and economic threats such as global warming, increase in hurricanes, sea-level rise, ocean acidification, glacial melting, and occupational heat stress, etc.[1-3] The development of efficient and economical technologies is important to separate $CO_2$ for geological sequestration or utilization as a chemical feedstock. $CO_2$ capture and storage (CCS), a technology for isolating and collecting $CO_2$ emissions from point sources and storing them in underground reservoirs at a depth of approximately 1500 m has emerged as central research project in many countries.[4, 5] Over the past century, several types of separation processes including absorption,[6, 7] pressure swing adsorption,[8, 9] cryogenic distillation,[10] and membrane-based separation[11, 12] have been scaled to separate $CO_2$ from gas mixtures at various pressures and compositions such as $CO_2/N_2$ (flue gas streams),[13, 14] $CO_2/CH_4$ (natural gas/biogas streams)[15, 16] and $CO_2/H_2$ (fuel gas or syngas).[17]

Membrane-based gas separation utilizing polymeric materials has been one of the promising technologies because of a low capital cost, operational simplicity, energy efficiency, modular nature (easy to scale up), and most importantly, environmental benignity (relying on physical separation mechanisms).[11, 18, 19] In the gas separation membrane process, a high-performance membrane ideally needs to exhibit a high permeability and a high selectivity as high permeability reduces the membrane area required to treat a given amount of gas, while high selectivity increases the purity of the product gas, thereby offering a cost-effective separation process. To prepare $CO_2$-selective separation membranes, polymers with high permeability and strong $CO_2$ affinity should be designed. $CO_2$ is a polar gas with a quadrupole moment and due to its' critical properties ($T_c$ = 31.1 °C, $P_c$ = 72.9 atm) is more easily condensed and is much more soluble in common polymers than other light gases ($H_2$, $N_2$, and $CH_4$). Further, the $CO_2$/light gas selectivity of polymer membranes can often be improved by the introduction of more polar functional groups, such as ionic liquids (ILs),[20] amines,[21] or poly(ethylene oxide)s.[22, 23]

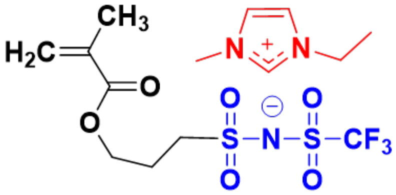
ILs, a class of low temperature molten salts with large and asymmetric organic cations and organic or inorganic anions have emerged as promising separation materials that rival conventional absorption technologies due to their large $CO_2$ solubility, excellent chemical, thermal, and electrochemical stability, and lack of volatility.[24-26] Furthermore, the tunable properties of ILs which are controlled by selection from a large array of functional groups and possible cation/anion types, bestows a greater utility for the design of $CO_2$ separation membranes. This combination of ILs with membrane technology (i.e., polymeric membranes either containing or built from ILs) is a more advanced approach and has been the subject of numerous investigations for enhanced $CO_2$ separation over the past two decades.[27-33]

Supported ionic liquid membranes (SILMs), in which ILs are impregnated into microporous polymers, were the earliest form of IL-containing membranes with ideal $CO_2$ permeabilities > 1000 barrer and $CO_2/N_2$ permselectivity > 20.[28] Despite the auspicious $CO_2$ separation performance, the leaching (or "blow-out") of immobilized ILs under even moderate transmembrane pressure differentials limited the practical use of SILMs in industrial applications. Including our previous works, membranes prepared via the polymerization of ILs which contain styrene, acrylate or vinyl groups appended to imidazolium cations, also known as poly(IL)s, have become of greater interest than SILMs for $CO_2$ separation because of moderate gas separation properties and superior mechanical properties.[30, 31, 34]

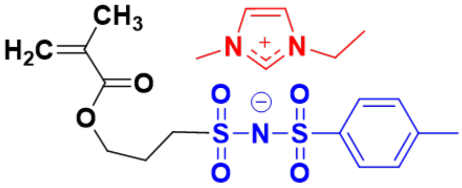
Research in poly(IL)s is driven by the desire to combine the characteristic properties and functions of ILs and classic polymers to enhance the overall performance of the material. Specifically, poly(IL)s are a subset of polyelectrolytes that share many features with ILs, such as their high $CO_2$ solubility and designer nature. On the other hand, it has been proved that the introduction of “free” ILs into neat poly(IL)s increases $CO_2$ permeability dramatically, and poly(IL)-IL composite membrane properties can also be tuned with respect to the IL content.[35-37] Nevertheless, the polymer structures used to prepare poly(IL)s have largely been limited to polycations (i.e., polymer-bound cations), particularly imidazolium groups, as they garnered the most expected common properties of ILs. There have not been any studies on poly(ILs), where anions are covalently bound to the polymer chain rather than serving as mobile counterions in poly(IL)-IL systems. Comprehensive studies on macromolecular structures and the structure-property relationships are still significant to design more poly(IL)s in membrane-based gas separation applications.

Herein, we report the development of, to the best of our knowledge, the first *anionic* poly(IL) membranes via a photopolymerization for enhanced $CO_2$ separation, in which the poly(IL) component has delocalized sulfonimide anions pendant from the polymer backbone and imidazolium cations as mobile counterions. As depicted in Chart 1, two types of methacryloxy-based IL monomers (MILs) with negatively charged trifluoromethanesulfonimide (MIL–$CF_3$)

and *para*-toluenesulfonimide (MIL–$C_7H_7$) groups having 1-ethyl-3-methylimidazolium ($[C_2mim]^+$) counterions have been designed and prepared for the synthesis of photopolymerized anionic poly(IL) membranes. The reactive methacrylate functional group and the delocalized anions ($–SO_2–N^{(-)}–SO_2–CF_3$ and $–SO_2–N^{(-)}–SO_2–C_7H_7$) were separated by a flexible $–(CH_2)_3–$ spacer. The main goal of this work is to report the benefits of abovementioned poly(IL)-IL composite membranes utilizing the possibilities of anionic poly(IL)s, for the first time. Therefore, we have selected a widely used free IL similar to the counterion of the newly designed MILs, 1-ethyl-3-methylimidazolium bistriflimide ($[C_2mim][Tf_2N]$) for effective $CO_2$ separation. On the other hand, according to our previous investigations, it has been substantiated that a porous polymer membrane support is required for imidazolium poly(IL)s as they are too brittle/fragile to form free-standing membranes.[30, 38] In this work, we anticipate a promising strategy of introduction of a crosslinking structure into the poly(IL) macrostructure for achieving better mechanical stability as well as high free IL loadings. Further interest turned out to the utilization of crosslinking network structures into anionic poly(IL)-ILs, where by choosing an appropriate crosslinker such as poly(ethylene glycol) diacrylate (PEGDA) which may also enhance separation performance. PEGDA contains ethylene oxide (EO) (i.e., $-(CH_2CH_2O)_n-$) units in its backbone, which often increases the $CO_2$ sorption concentration and improves $CO_2$ permeability and selectivity over other light gases, particularly for $CO_2/H_2$ separation.[23, 39] However, we have not considered a comparative study on PEGDA contents as the present work exclusively focused on anionic poly(IL)-IL composites. To this end, the $CO_2$ separation properties, together with physical properties of the novel anionic poly(IL)-IL composite membranes containing a minimal amount (i.e., 20 wt%) of crosslinked PEO content were reported.



**($MIL\text{-}CF_3$)**
**1-Ethyl-3-methylimidazolium 1-[3-(methacryloyloxy) propylsulfonyl]-(trifluoromethane-sulfonyl)imide**



**($MIL\text{-}C_7H_7$)**
**1-Ethyl-3-methylimidazolium 1-[3-(methacryloyloxy) propylsulfonyl]-(*p*-toluene-sulfonyl)imide**

**Chart 1.** Structures of the anionic methacryloxy-based IL monomers (MILs) used in this study.

## MATERIALS AND METHODS

**Materials.** Potassium 3-(methacryloyloxy) propane-1-sulfonate (PMAS, 98%) and poly(ethylene glycol) diacrylate (PEGDA, Mw= 575 g mol$^{-1}$) was purchased from Aldrich (St. Louis, MO, USA). Lithium hydride (LiH, >97%), trifluoromethanesulfonamide (>98%), and p-toluenesulfonamide (>98%) were purchased from Alfa Aesar (Tewksbury, MA, USA). Triethylamine ($Et_3N$) was purchased from Oakwood Chemical (Estill, SC, USA). Ethanol (EtOH, 200 proof), *N,N*-dimethylformamide (DMF, ACS grade), diethyl ether ($Et_2O$, anhydrous) and toluene (anhydrous) were purchased from VWR (Atlanta, GA, USA). Thionyl chloride ($SOCl_2$, >99%, Aldrich) was distilled over linseed oil prior to use. Tetrahydrofuran (THF, 99+%, Acros) was dehydrated by distillation over sodium and benzophenone radical anion.

The ILs [$C_2$mim][Br] and [$C_2$mim][$Tf_2N$] were prepared from 1-methylimidazole (99%, Aldrich) (St. Louis, MO, USA), 1-bromoethane (99%, Aldrich) (St. Louis, MO, USA), and $LiTf_2N$ (99%, 3M) (Minneapolis, MN, USA) according to our previously reported work.[40] Their $^1$H NMR spectra are provided in the Supporting Information (Figure S1 and S2). All other chemicals, unless otherwise noted, were obtained from commercial sources and used as received.

**Synthesis of polymerizable anionic methacryloxy-based ionic liquid monomers (MILs).** Two types of methacryloxy-based IL monomers (MILs) with negatively charged trifluoromethanesulfonimide (MIL–$CF_3$) and *para*-toluenesulfonimide (MIL–$C_7H_7$) groups having $[C_2mim]^+$ counterions were synthesized according to the developed procedures of previously reported works.[41, 42]

***Synthesis of 3-(chlorosulfonyl)propyl methacrylate (I).*** Freshly dried PMAS (30 g, 121.79 mmol) was suspended with 50 mL of anhydrous THF in 1000 mL round-bottom flask equipped with a magnetic stir bar under inert atmosphere and 3.4 mL of DMF as a catalyst was injected via syringe. The reaction mixture was cooled to 0–1 $^{O}$C and an excess amount of $SOCl_2$ (79.69 g, 669.8 mmol) was added dropwise while stirring. The reaction was set to stir at 0–1 $^{O}$C for 1 h, and then at r.t. for 12 h. After the reaction time, the obtained suspension was carefully quenched by pouring into crushed ice (600 g) and the upper aqueous layer was decanted, and the lower organic oily layer was diluted with DCM (160 mL). The DCM solution was washed with water (6 × 35 mL) and then dried over anhydrous $MgSO_4$, and the solvent was evaporated under reduced pressure at temperature $\leq 30$ $^{O}$C. The residual colorless or slightly yellow transparent oil was finally dried under vacuum at 25 $^{O}$C for 12 h. Yield: 24.5 g (88%); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$= 6.15 (s, 1H, $CH_2$=C($CH_3$)–), 5.65 (s, 1H, $CH_2$=C($CH_3$)–), 4.35 (t, 2H, CO–O– $CH_2$–), 3.81 (m, 2H, –$CH_2$–$SO_2Cl$), 2.48-2.46 (m, 2H, $CH_2$–$CH_2$– $CH_2$–), 1.96 (s, 3H,$CH_2$ = C($CH_3$)–) ; (FT-IR)/cm$^{-1}$ 1720, 1638, 1512, 1454, 1375, 1298, 1162, 1065, 947, 894, 816, 770 and 655.

***Synthesis of triethyl ammonium 1-[3-(methacryloyloxy) propylsulfonyl]-(trifluoromethane-sulfonyl)imide (IIa) and triethyl ammonium 1-[3-(methacryloyloxy) propylsulfonyl]-(p-toluene-sulfonyl)imide (IIb).*** For preparing 'trifluoromethanesulfonimide' derivative (**IIa**), trifluoromethanesulfonamide (6.58 g, 44.12 mmol) was loaded into a 500 mL round-bottom-flask with a magnetic stir bar under inert atmosphere and freshly distilled anhydrous $Et_3N$ (9.82 g, 97.06 mmol) was added under stirring. The reaction mixture was diluted with 40 mL of anhydrous THF and was cooled down to 0 $^{O}$C. The solution of **I** (10 g, 44.12 mmol) in 15 mL of anhydrous THF was added dropwise under inert atmosphere to the obtained cooled colorless THF solution of trifluoromethanesulfonamide and $Et_3N$. The reaction was set to stir at 0–1 $^{O}$C for 1 h, and then at r.t. for 1 h. After the reaction time, the resulted mixture was filtered, and the filtrate was gently evaporated at r.t. The residual slightly yellow oil was collected and dissolved in 90 mL of DCM. The DCM solution was washed with water (4 × 35 mL) and then dried over anhydrous $MgSO_4$. Solid $MgSO_4$ was removed by filtration and a catalytic amount of inhibitor (4-methoxyphenol) was added to the filtrate. The solvent was evaporated under reduced pressure at temperature ≤ 30 $^{O}$C and the residual slightly yellow transparent oil was finally dried at under vacuum at 25 $^{O}$C for 6 h. Yield: 16.6 g (85%); $^1$H NMR (500 MHz, $CDCl_3$) δ= 7.80 (bs, 1H, $H$–N($C_2H_5$)$_3$), 6.11 (s, 1H, $CH_2$=C($CH_3$)–), 5.58 (t, 1H, $CH_2$=C($CH_3$)–), 4.27 (t, 2H, CO–O–$CH_2$–), 3.29-3.18 (m, 8H, H–N ($CH_2CH_3$)$_3$ + –$CH_2$–$SO_2$–N–), 2.27-2.17 (m, 2H, $CH_2$–$CH_2$– $CH_2$–), 1.94 (s, 3H,$CH_2$ = C($CH_3$)–), 1.38-1.36 (t, 9H, H–N($CH_2CH_3$)$_3$); (FT-IR)/cm$^{-1}$ 2985, 2958, 1718, 1637, 1475, 1456, 1298, 1180, 1058, 945, 835, 816, 702 and 625.

The 'para-toluenesulfonimide' derivative (**IIb**) was synthesized by the same method from 40 mL solution of anhydrous THF with *para*-toluenesulfonamide (7.55 g, 44.12 mmol) and $Et_3N$ (9.82

g, 97.06 mmol), and the solution of **I** (10 g, 44.12 mmol) in 15 mL anhydrous THF. The purified product as slightly yellow transparent oil was collected and dried at under vacuum at 25 $^{O}$C for 6 h. Yield: 17.1 g (84%); $^{1}$H NMR (500 MHz, $CDCl_3$) δ= 9.1 (bs, 1H, $H$–$N(C_2H_5)_3$), 7.84 (bs 2H, 2×Ar$H$), 7.29-7.23 (bs 2H, 2×Ar$H$), 6.12 (s, 1H, $CH_2$=$C(CH_3)$–), 5.58 (t, 1H, $CH_2$=$C(CH_3)$–), 4.22 (t, 2H, CO–O–$CH_2$–), 3.27-3.20 (m, 8H, H–N $(CH_2CH_3)_3$ + –$CH_2$–$SO_2$–N–), 2.4 (bs 3H, Ar$CH_3$), 2.22-2.17 (m, 2H, $CH_2$–$CH_2$– $CH_2$–), 1.97 (s, 3H,$CH_2$ = $C(CH_3)$–), 1.46-1.34 (t, 9H, H–$N(CH_2CH_3)_3$); (FT-IR)/cm$^{-1}$ 2985, 2958, 2860, 1720, 1638, 1475, 1456, 1298, 1180, 1055, 948, 835, 816, 705 and 620.

***Synthesis of 1-ethyl-3-methylimidazolium 1-[3-(methacryloyloxy) propylsulfonyl]-(trifluoromethane-sulfonyl)imide (MIL-$CF_3$) and 1-ethyl-3-methylimidazolium1-[3-(methacryloyloxy) propylsulfonyl]-(p-toluene-sulfonyl)imide (MIL-$C_7H_7$).*** For preparing **MIL-$CF_3$**, a solution of **IIa** (10 g, 22.7 mmol) in 30 mL of anhydrous THF was cooled to 0 $^{O}$C in a 250 mL round-bottom-flask equipped with a magnetic stir bar under inert atmosphere. To this, a suspension of LiH (0.27 g, 34.05 mmol) in 15 mL of anhydrous THF was added dropwise with vigorous stirring. Later, the reaction mixture was allowed to warm up to room temperature and continued to stir for 2 h. After the reaction time, the resulted mixture was filtered to remove unreacted LiH. The residual filtrate was concentrated under reduced pressure and the obtained oil was washed with hexane (3 × 20 mL) under vigorous stirring. After decanting the last portion of hexane, the obtained slightly yellow very viscous oil was vacuum dried at 25 $^{O}$C for 1 h in order to yield an intermediate product **IIIa**. Further on the **IIIa** (7.45 g, 21.58 mmol) was dissolved in 50 mL of distilled water and added dropwise to the solution of $[C_2mim][Br]$ (5.77 g, 30.21 mmol) in 20 mL of distilled water at ambient temperature. The mixture was stirred 1 h at 25 $^{O}$C until precipitation of an oil was observed and thus the upper aqueous layer was decanted, and the residual oil was dissolved in 50 mL of DCM. Later, the DCM solution was washed with water (3 × 30 mL) and dried over anhydrous $MgSO_4$. The resultant solution was filtered and a catalytic amount of 4-methoxyphenol was added as an inhibitor, and the solvent was evaporated under reduced pressure at temperature $\leq 30\ ^{O}C$. The colorless transparent fluid oil was vacuum dried at 30 $^{O}$C for 1 h to obtain the final product **MIL-CF$_3$**. Yield: 7.15 g (70%); $^1$H NMR (500 MHz, $CDCl_3$) δ= 9.05 (s, 1H, N=C*H*–N), 7.38 (s, 2H, N–C*H*=C*H*-N), 6.10 (s, 1H, C$\mathit{H}_2$=C(CH$_3$)–), 5.57 (s, 1H, C$\mathit{H}_2$=C(CH$_3$)–), 4.27 (t, 4H, CO–O–C$\mathit{H}_2$– + –CH$_3$–C$\mathit{H}_2$–N–), 3.97 (s, 3H, C$\mathit{H}_3$-N) 3.27-3.23 (m, 2H, –C$\mathit{H}_2$–SO$_2$–N–), 2.27-2.17 (m, 2H, CH$_2$–C$\mathit{H}_2$–CH$_2$–), 1.93 (s, 3H,CH$_2$ = C(C$\mathit{H}_3$)–), 1.54 (t, 3H, –C$\mathit{H}_3$–CH$_2$–N–); (FT-IR)/cm$^{-1}$ 2985, 2958, 1718, 1637, 1475, 1456, 1320, 1298, 1180, 1058, 945, 835, 814, 705 and 625.

The ‘para-toluenesulfonimide’ containing **MIL-C$_7$H$_7$** was synthesized by the same method from a solution of **IIb** (10 g, 21.6 mmol) in 30 mL of anhydrous THF 40 mL and a suspension of LiH (0.26 g, 32.42 mol) in 15 mL of anhydrous THF, followed by cation exchange from an intermediate product **IIIb** (7.5 g, 20.42 mmol) with [C$_2$mim][Tf$_2$N] (5.85 g, 30.6 mmol) in total amount of 70 mL distilled water. A slightly yellow high viscous oil was collected upon DCM extraction and dried at under vacuum at 30 $^{O}$C for 1 h to obtain the final product **MIL- C$_7$H$_7$**. Yield: 6.9 g (72%);$^1$H NMR (500 MHz, $CDCl_3$) δ= 9.40 (s, 1H, N=C*H*–N), 7.78 (m, 2H, N–C*H*=C*H*-N), 7.34 (bs 2H, 2×Ar*H*), 7.16 (bs 2H, 2×Ar*H*), 6.06 (s, 1H, C$\mathit{H}_2$=C(CH$_3$)–), 5.53 (s, 1H, C$\mathit{H}_2$=C(CH$_3$)–), 4.26-4.15 (t, 4H, CO–O–C$\mathit{H}_2$– + –CH$_3$–C$\mathit{H}_2$–N–), 3.89 (s, 3H, C$\mathit{H}_3$-N) 3.14-3.07 (m, 2H, –C$\mathit{H}_2$–SO$_2$–N–), 2.38-2.34 (bs 3H, ArC$\mathit{H}_3$), 2.16-2.10 (m, 2H, CH$_2$–C$\mathit{H}_2$–CH$_2$–), 1.90 (s, 3H,CH$_2$ = C(C$\mathit{H}_3$)–), 1.45 (t, 3H, –C$\mathit{H}_3$–CH$_2$–N–); (FT-IR)/cm$^{-1}$ 2980, 2955, 2850, 1720, 1637, 1470, 1455, 1320, 1298, 1180, 1058, 945, 835, 816, 702 and 620.

**Preparation of anionic poly(IL)-IL composite membranes.** The newly synthesized polymerizable anionic methacryloxy-based IL monomer (either MIL-$CF_3$ or MIL-$C_7H_7$) and the desired amount of free IL [$C_2$mim][$Tf_2$N] (0.5 or 1 molar equivalent) were mixed with a 20 wt% of PEGDA crosslinker in a glass vial at room temperature (r.t.). Then a commercially available photoinitiator (2-hydroxy-2-methylpropiophenone) was added into the mixture at 1 wt% and magnetically stirred at r.t. The resultant homogeneous solution was degassed to remove the possible bubbles by ultrasonication for 10 min at r.t. The mixture was then poured onto a clean Rain-X® coated quartz plate and sandwiched by using a second identical quartz plate on the top. The plates were separated by aluminum tapes as spacers to control the membrane thickness. The plates were then placed under a 365 nm UV lamp (0.8 mW/cm$^2$ at 4 cm distance) for 30 min. Post-irradiation, the plates were separated easily using a clean razor blade because of spacers and the crosslinked anionic poly(IL)-IL composite membrane was peeled off. The membrane thickness of newly developed anionic poly(IL)-IL composite membranes was controlled to be 90 - 150 µm. These membranes were evaluated by various characterization methods and permeation tests.

**Characterization.** $^1$H NMR spectra were obtained on a Bruker Avance (500 MHz) instrument using d6-DMSO as a reference or internal deuterium lock. FT-IR spectra of the materials were recorded using a Perkin-Elmer Spectrum 2 in the range of 4000–400 cm$^{-1}$. Thermogravimetric analysis (TGA) of the polymer materials was conducted using Seiko TG-DTA 7300 by heating samples from r.t. to 700°C at a heating rate of 10°C/min under $N_2$ flow. The glass transition temperature ($T_g$) of each polymer material was measured using a DSC (TA Instruments, DSC

Q20) from 20°C to 300°C with a scan rate of 10°C min-1 under $N_2$. The Wide-angle X-ray diffraction (WAXD) patterns of the membranes were measured using a Bruker D8 Discover diffractometer by employing a scanning rate of 4°/min in a 2θ range from 5° to 60° with a Co Kα1 X-ray source (λ = 0.17886). The d-spacings values were calculated using Bragg's Law (d = λ/2 sinθ).

**Gas separation measurements.** The pure gas permeation measurements of newly developed anionic poly(IL)-IL composite membranes were performed using a high-vacuum time lag apparatus based on the constant-volume/variable-pressure method, as described in our previous works.[43] All measurements were conducted at 20 °C and the feed pressure was ~3 atm (~45 psia) against initial downstream vacuum (<0.01 psia). Pressures and temperatures were measured and recorded using most recent version of LabVIEW software (National Instruments). Before each permeation measurement, both the feed and the permeate sides were thoroughly evacuated to remove any residual gases. The pressure rises versus time transient of the permeate side, equipped with a pressure transducer, was recorded and passed to a desktop computer through a shield data cable. The permeability coefficient was determined from the linear slope of the downstream pressure rise versus time plot (dp/d*t*) according to the following equation:

$$P = \frac{273}{76} \times \frac{Vl}{ATp_\circ} \times \frac{dp}{dt} \qquad (1)$$

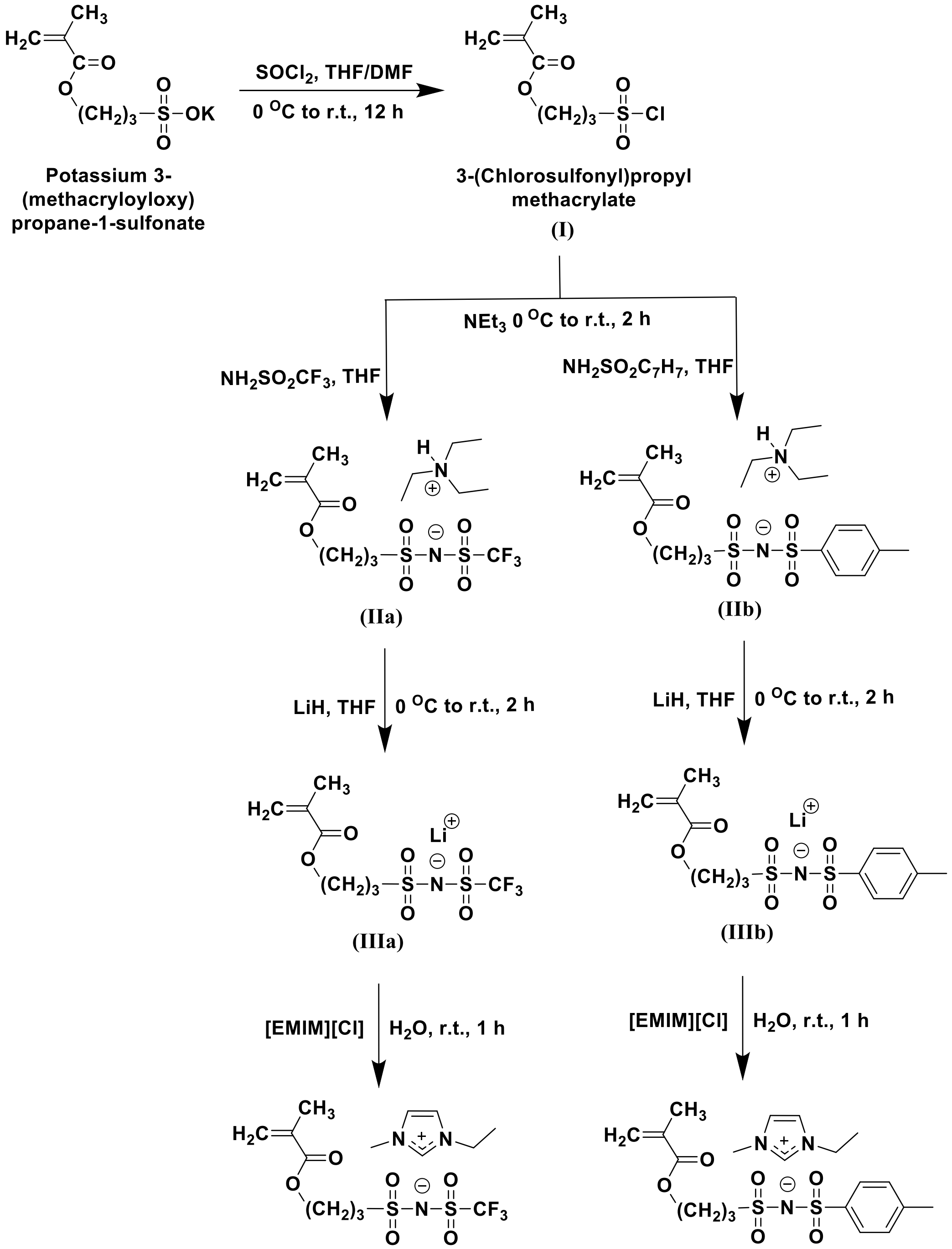
where $P$ is the permeability expressed in Barrer (1 barrer = $10^{-10}$ cm$^3$(STP)cm cm$^{-2}$ s$^{-1}$ cmHg$^{-1}$); $V$ (cm$^3$) is the downstream volume; $l$ (cm) is the membrane thickness; $A$ (cm$^2$) is the effective area of the membrane; $T$ (K) is the temperature of measurement; $p_0$ (Torr) is the pressure of the feed gas in the upstream chamber and d*p*/d*t* is the rate of the pressure rise under the steady state. The ideal permselectivity, $\alpha_{A/B}$, of the membrane for a pair of gases (*A* and *B*) was calculated from the ratio of the individual gas permeability coefficients as, $P_A/P_B$.

## RESULTS AND DISCUSSION

### Synthesis and structural characterization of polymerizable anionic methacryloxy-based ionic liquid monomers (MILs)

As outlined in Scheme 1, the synthesis of polymerizable anionic ILs with two distinct negatively charged substituents ($–SO_2–N^{(-)}–SO_2–CF_3$ and $–SO_2–N^{(-)}–SO_2–C_7H_7$) having similar $[C_2mim]^+$ counterion were conducted in four steps: (i) conversion of PMAS into the sulfonyl chloride derivative (**I**) by reacting with $SOCl_2$ in the presence of DMF as a catalyst, (ii) the coupling reaction of **I** with trifluoromethanesulfonamide or p-toluenesulfonamide (Scheme 1, **IIa** and **IIb** respectively) in the presence of a 2.2 molar amount of $Et_3N$, (iii) triethylammonium exchange reaction with LiH in the anhydrous THF (Scheme 1, **IIIa** and **IIIb**), and (iv) a metathesis reaction between the lithium salts of the desired monomers and the respective imidazolium bromide ionic liquid (Scheme 1, **MIL-CF$_3$** and **MIL-C$_7$H$_7$**). The structural characterization of newly developed MILs was further analyzed by $^1H$ NMR (Figure 1) and FTIR spectroscopic measurements (discussed later in Figure 3). The $^1H$ NMR spectra of both MILs were unambiguously consistent with their proposed chemical structures. $^1H$ NMR spectra of MILs (Figure 1) showed all the characteristic signals of imidazolium ring protons (at δ 9.4 and 7.78 ppm) and vinyl protons (at δ 6.06 and 5.53 ppm) along with the well resolved signals at δ 4.26, 3.89, 3.27, 2.27, 1.93, and 1.54 ppm for alkyl chains, indicating the successful synthesis of newly developed polymerizable anionic IL monomers. In addition, aromatic protons ($H_a$ and $H_b$ at 7.34

and 7.16, respectively) of **MIL-$C_7H_7$** were further confirmed the negatively charged $–SO_2–N^{(-)}–SO_2–C_7H_7$ substituent, proving the structural variation of newly developed MILs (Figure 1(b)).



**Scheme 1.** Schematic representation of the preparation of polymerizable anionic methacryloxy-based ionic liquid monomers (MILs).

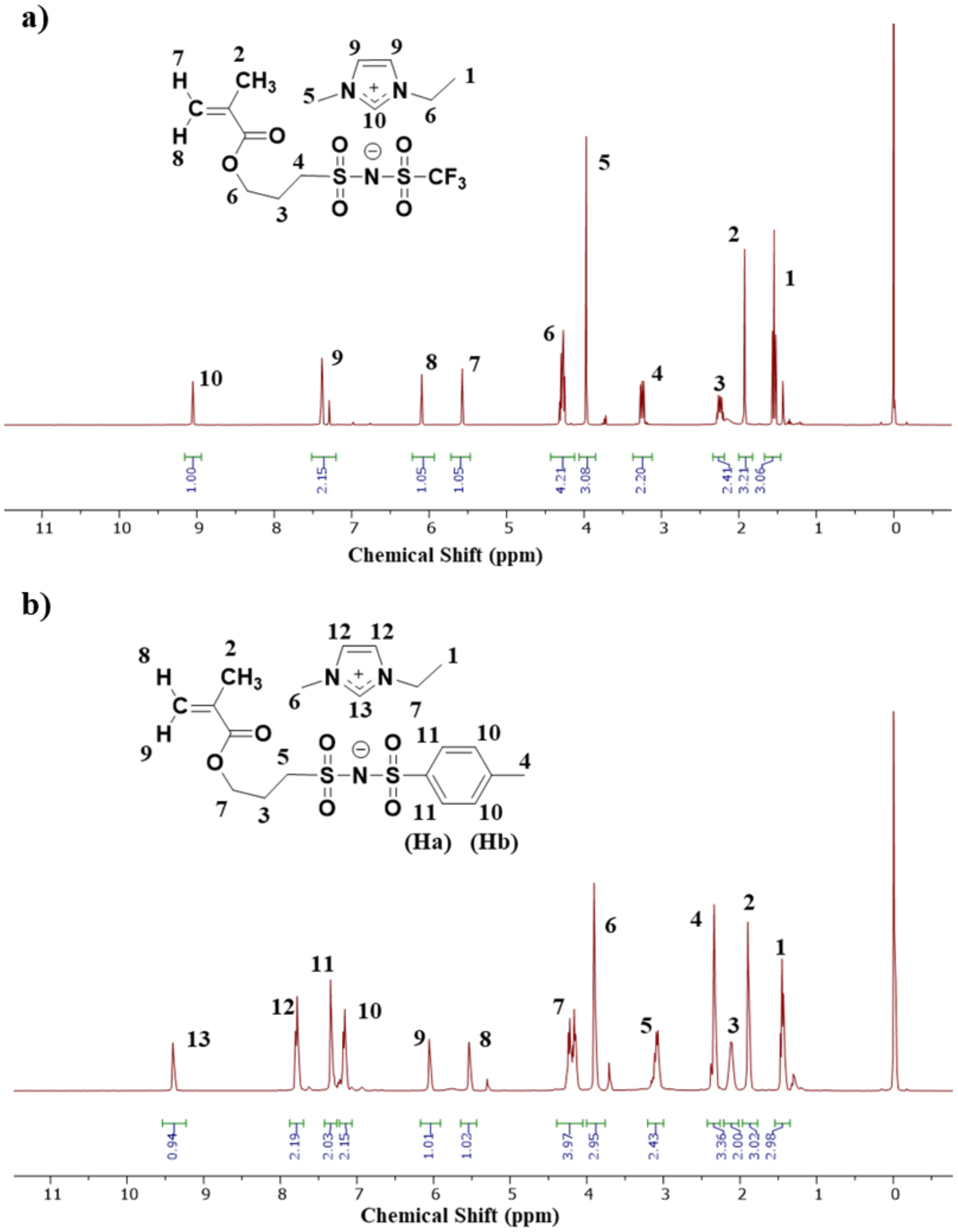


**Figure 1.** $^{1}$H NMR spectra of newly developed polymerizable anionic monomers (a) MIL-$CF_3$ and (b) MIL-$C_7H_7$.

**Preparation and characterization of anionic poly(IL)-IL composite membranes with crosslinked PEGDA network (MIL/PEGDA$_{(20\%)}$/IL).** The selection of a technique for polymer membrane fabrication is always depended on the choice of polymer and the desired application of the membrane. For the potential practical applications in gas separation, poly(IL)-IL composite membranes are usually prepare via a UV-photopolymerization method.[37, 44] In this work, an equimolar ratio was considered to incorporate non-polymerizable ILs (i.e., free ILs) into anionic poly(IL) matrix in order to equilibrate the number of free cations. As depicted in Figure 2, four blend solutions were prepared from the two newly designed polymerizable anionic MILs (MIL-$CF_3$ and MIL-$C_7H_7$) with 0.5 and 1 eq. amount of free IL ([$C_2$mim] [$Tf_2N$]). PEGDA was added at 20 wt.% to each blend solution as a crosslinker and cast into composite membranes under UV irradiation to yield MIL-$CF_3$/PEGDA$_{(20\%)}$/IL$_{(0.5eq.)}$, MIL-$CF_3$/PEGDA$_{(20\%)}$/IL$_{(1eq.)}$, MIL-$C_7H_7$/PEGDA$_{(20\%)}$/IL$_{(0.5eq.)}$, and MIL-$C_7H_7$/PEGDA$_{(20\%)}$/IL$_{(1eq.)}$. Here, it also should be mentioned that, the objective of grafting polyethylene glycol (PEG) network was to make the anionic poly(IL)-IL membranes less brittle rather than utilizing PEG contents for separation requirements as reported elsewhere.[39] All the anionic poly(IL)-IL composites were obtained as soft, flexible, and free-standing membranes, which were adequate for gas permeation testing (Figure 2).

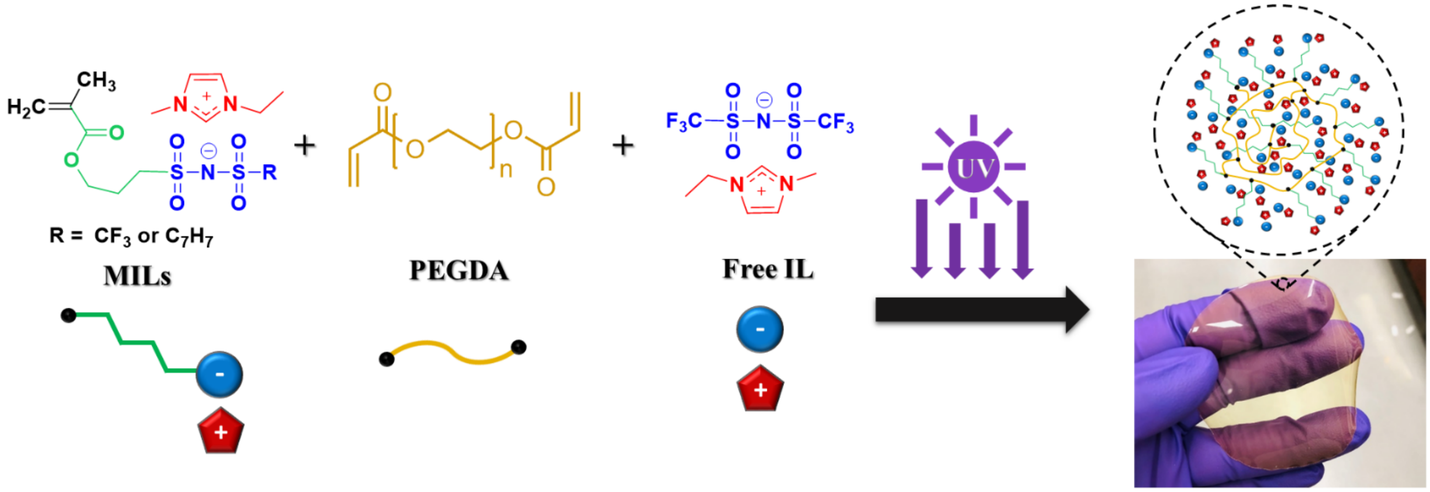


**Figure 2.** Schematic diagram for the preparation of anionic poly(IL)-IL composite membranes with crosslinked PEGDA network.

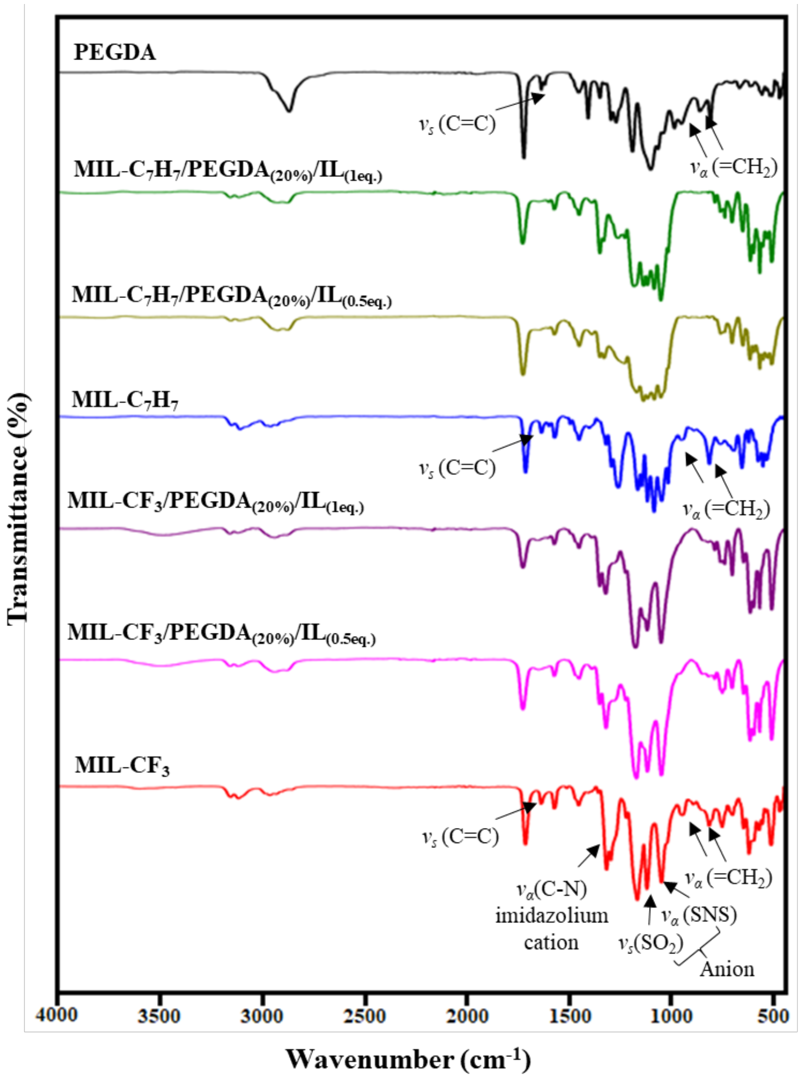


**Figure 3.** FT-IR spectra of newly developed anionic methacryloxy IL monomers (MIL-$CF_3$ and MIL-$C_7H_7$) and corresponding anionic poly(IL)-IL composite membranes together with PEGDA crosslinker.

As depicted in Figure 3, the extent of crosslinking was supported by the FT-IR spectra, which revealed that the characteristic peaks corresponding to the C=C stretching (at 1635 $cm^{-1}$), =$CH_2$ bending (at 940 $cm^{-1}$ and 815 $cm^{-1}$) of anionic methacrylate (MILs) and PEGDA crosslinker completely disappeared after UV-irradiation, indicating that the crosslinking was complete.[45] At the same time, the peaks corresponding to the C-N vibrations of the imidazolium cation (at 1320 $cm^{-1}$) and $SO_2$ and SNS stretching vibrations (at 1190 $cm^{-1}$ and 1050 $cm^{-1}$, respectively) of –$SO_2$–N–$SO_2$– anions further proved that newly developed anionic poly(IL)-IL composite matrix were successfully formed (Figure 3).

TGA analysis of the newly developed anionic poly(IL)-IL composite membranes displayed very similar thermograms with three-stage degradations and showed thermal stabilities up to 280°C, as it can be seen in Figure 4. The first stage of weight loss is observed between 280 and 380 °C corresponding to the decomposition of the crosslinker and the acrylate part of the polymer backbone. The second shoulder degradation between 380 and 450 °C is attributed to the decomposition of the anions and imidazole ring, as observed in other IL systems.[46] Finally, the third degradation at an elevated temperature between 450 °C is attributed to the degradation of the residual oligo(ethylene oxide) segments.[45] Overall, the crosslinked anionic poly(IL)-IL composite membranes were found to have a high thermal stability, which is desirable for membrane-based gas separation. In $CO_2$ separation processes, high performance membranes essentially need to display high thermal stability, particularly for $CO_2/N_2$ separations in flue gas streams.[14, 47]

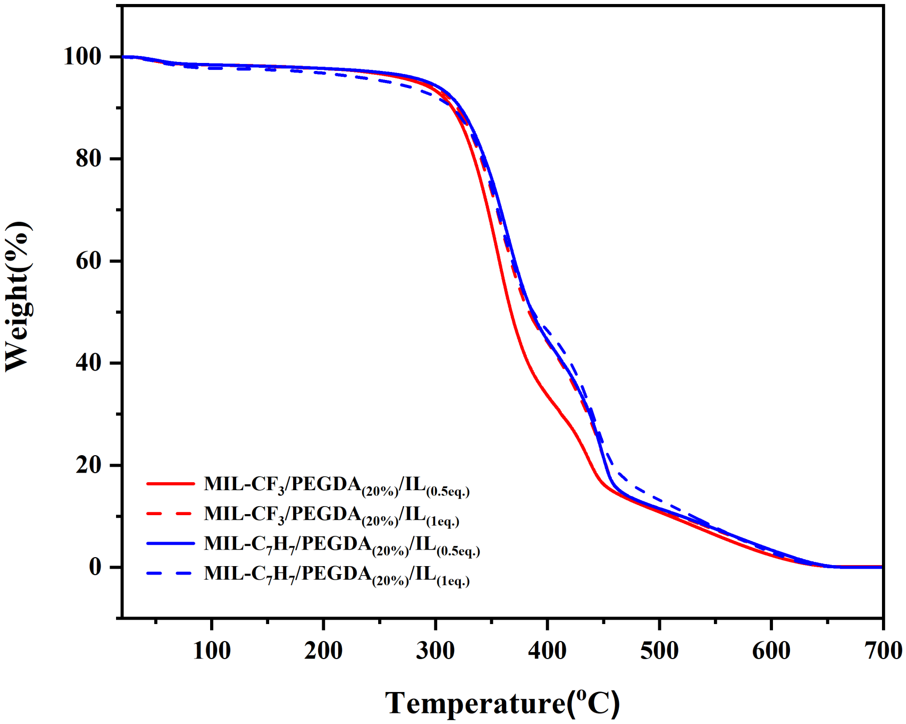


**Figure 4.** TGA curves of anionic poly(IL)-IL composite membranes with crosslinked PEGDA network (MIL/PEGDA$_{(20\%)}$/IL).

**Physical properties of anionic poly(IL)-IL composite membranes.** The polymer chain packing conditions of crosslinked anionic poly(IL)-IL composite membranes were examined by wide angle X-ray diffraction (WAXD). As depicted in Figure 5, two distinct peak distributions were found for the anionic poly(IL)-IL composite membranes based on the different free IL contents. While a bimodal diffraction peak was observed in the XRD patterns of composite membranes contain 0.5 equivalent amount of free ILs (MIL-$CF_3$/PEGDA$_{(20\%)}$/IL$_{(0.5eq.)}$ and $C_7H_7$/PEGDA$_{(20\%)}$/IL$_{(0.5eq.)}$), a single-peak distribution was obtained for 1 equivalent IL containing membranes (MIL-$CF_3$/PEGDA$_{(20\%)}$/IL$_{(1eq.)}$ and MIL-$C_7H_7$/PEGDA$_{(20\%)}$/IL$_{(1eq.)}$). These results imply that the average inter-chain distance diminishes in the 0.5 eq. free IL blends and non-uniformly packed structure is yielded for both MIL-$CF_3$/PEGDA$_{(20\%)}$/IL$_{(0.5eq.)}$ and $C_7H_7$/PEGDA$_{(20\%)}$/IL$_{(0.5eq.)}$ membranes. The inter-chain spacing values of all the four composite membranes are calculated from the main halo and summarized in the Table 1, according to the Bragg equation. It was surprisingly observed that a high d-spacing of 6.63 Å found for MIL-$C_7H_7$/PEGDA$_{(20\%)}$/IL$_{(1eq.)}$, plausible because of bulky aromatic rings disruptions. On the other hand, the XRD results also revealed that the interpenetrating crosslinked networks are amorphous, there were no sharp peaks exhibited in all XRD patterns, and the tendency to crystallize due to PEG contents has not been observed. This further proved that the barely minimum amount of PEGDA contents in the newly developed anionic poly(IL)-IL composite membranes are apparently appropriate to form flexible free standing membranes.

The thermal transition properties of anionic poly(IL)-IL composite membranes as a function of their chemical structures and chain packing architectures were further investigated using a DSC analysis (Table 1, Figure 6). A single $T_g$ of below 0 °C was observed for all anionic poly(IL)-IL composite membranes, supplementing the XRD results that the membranes were not crystalline and that the newly developed MILs and free ILs were miscible with the PEO network. The MIL-$CF_3$/PEGDA$_{(20\%)}$/IL$_{(0.5eq.)}$, MIL-$CF_3$/PEGDA$_{(20\%)}$/IL$_{(1eq.)}$, and MIL-$C_7H_7$/PEGDA$_{(20\%)}$/IL$_{(0.5eq.)}$, membranes exhibited similar $T_g$ values, around -20 °C, whereas a substantially lower value (-35 °C) was observed for the MIL-$C_7H_7$/PEGDA$_{(20\%)}$/IL$_{(1eq.)}$. The lower $T_g$ value obtained for MIL-$C_7H_7$/PEGDA$_{(20\%)}$/IL$_{(1eq.)}$ was attributed to a looser packing of the ionic groups within the crosslinked network at this composition ratio, suggesting that chain mobility of the delocalized anions (i.e., $–SO_2–N^{(-)}–SO_2–C_7H_7$) separated by the flexible spacer groups (i.e., $-(CH_2)_3-$) within the crosslinked acrylates and PEO were high and hence an enhanced gas permeability was expected for the membrane with this composition.

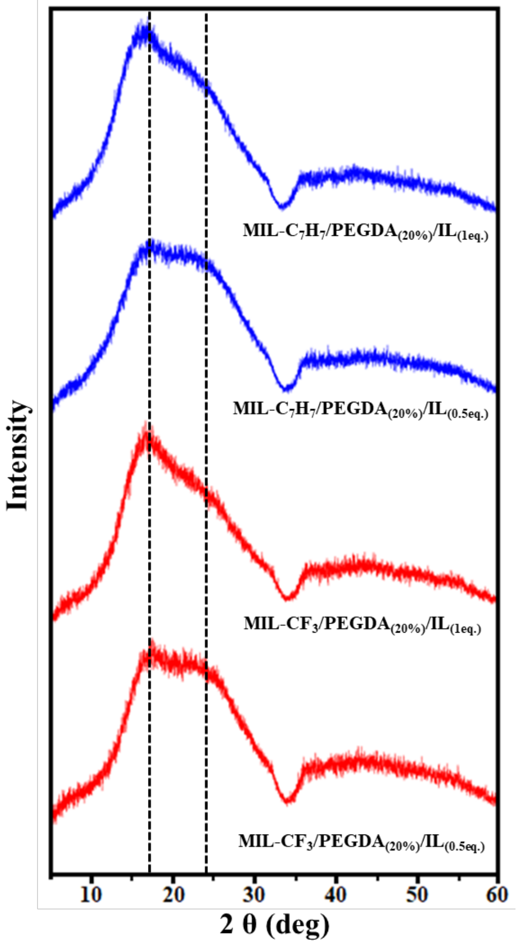


**Figure 5.** Wide-angle X-ray diffraction plots obtained from anionic poly(IL)-IL composite membranes with crosslinked PEGDA network (MIL/PEGDA$_{(20\%)}$/IL).

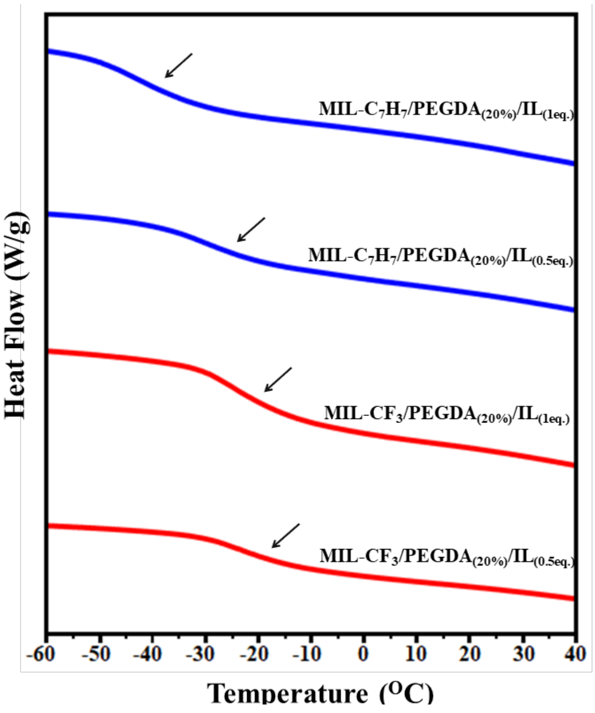


**Figure 6.** DSC curves of anionic poly(IL)-IL composite membranes with crosslinked PEGDA network (MIL/PEGDA$_{(20\%)}$/IL).

**Table 1.** Physical parameters that characterized the anionic poly(IL)-IL composite membranes

| Membrane | $T_g$ ($^{O}$C) | d-spacing (Å) |
|---|---|---|
| **MIL-CF$_3$/PEGDA$_{(20\%)}$/IL$_{(0.5eq.)}$** | -18.8 | 6.12 |
| **MIL-CF$_3$/PEGDA$_{(20\%)}$/IL$_{(1eq.)}$** | -20.6 | 6.09 |
| **MIL-C$_7$H$_7$/PEGDA$_{(20\%)}$/IL$_{(0.5eq.)}$** | -22.5 | 6.05 |
| **MIL-C$_7$H$_7$/PEGDA$_{(20\%)}$/IL$_{(1eq.)}$** | -35.2 | 6.63 |

## Gas permeation measurements and CO$_2$ separation performance of anionic poly(IL)-IL composite membranes.

The gas separation performances of all the newly developed anionic poly(IL)-IL composite membranes were measured using a lab-made high-vacuum time-lag unit according to the constant volume/variable-pressure method. The pure gas permeabilities of $CO_2$, $H_2$, $N_2$, and $CH_4$ and permselectivities of $CO_2/H_2$, $CO_2/N_2$, and $CO_2/CH_4$ are summarized in Table 2, while the solubility and diffusivity coefficients are depicted in Table 3. Generally, the $CO_2$-preferential separation membranes are either rubbery polymers or contain polar functional groups to interact with the quadrupolar $CO_2$ molecules, the $CO_2$ solubility in such polymers are one to two orders of magnitude higher than that of the other typical gases.[48, 49] On the other hand, Bernardo et al. reported that the incorporation of a strongly sorbing component apparently reduces the size-sieving ability and enhances the permeability due to a drastic increase in diffusivity.[50] Therefore, in the present work, the incorporation of free IL into anionic poly(IL) matrix anticipated to have a double effect of high $CO_2$ solubility and an increase in the diffusivity, which even could be more favorable for $CO_2/H_2$ reverse-selectivity behavior. The obtained results revealed that the permeability of each single gas for the composite membranes are in the order of $CO_2$ (3.3 Å) > $H_2$ (2.89 Å) > $N_2$ (3.6 Å) > $CH_4$ (3.8 Å) (see Table 2). Most notably, $CO_2$ displayed the highest gas permeability among the four gases, even much higher than that of $H_2$ with a smaller diameter, due to the high $CO_2$-philic behavior of the newly developed anionic poly(IL)-IL composite membranes.

| **Membrane** | $P_{CO2}$ | $P_{H2}$ | $P_{N2}$ | $P_{CH4}$ | $\alpha_{CO2/H2}$ | $\alpha_{CO2/N2}$ | $\alpha_{CO2/C}$ |
|---|---|---|---|---|---|---|---|

**Table 2**. Pure gas permeabilities (P)[a] and permselectivities (α) of anionic poly(IL)-IL composite membranes at 3 atm and 20 °C

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **MIL-CF$_3$/PEGDA$_{(20\%)}$/IL$_{(0.5eq.)}$** | 7.69 | 2.83 | 0.165 | 0.136 | 2.71 | 46.6 | 56.54 |
| **MIL-CF$_3$/PEGDA$_{(20\%)}$/IL$_{(1eq.)}$** | 5.94 | 1.87 | 0.115 | 0.096 | 3.18 | 51.65 | 61.88 |
| **MIL-C$_7$H$_7$/PEGDA$_{(20\%)}$/IL$_{(0.5eq.)}$** | 4.67 | 1.65 | 0.071 | 0.066 | 2.83 | 65.77 | 70.75 |
| **MIL-C$_7$H$_7$/PEGDA$_{(20\%)}$/IL$_{(1eq.)}$** | 20.4 | 4.97 | 0.235 | 0.172 | 4.1 | 86.81 | 118.6 |

[a] *P* in barrers, where 1 barrer = $10^{-10}$ [cm$^3$ (STP) cm]/(cm$^2$ s cm Hg)

**Table 3**. Pure gas diffusivity coefficients[a] and solubility coefficients[b] of anionic poly(IL)-IL composite membranes at 3 atm and 20 °C

| Membrane | $D_{CO2}$ | $D_{N2}$ | $D_{CH4}$ | $S_{CO2}$ | $S_{N2}$ | $S_{CH4}$ |
|---|---|---|---|---|---|---|
| **MIL-CF$_3$/PEGDA$_{(20\%)}$/IL$_{(0.5eq.)}$** | 2.81 | 0.989 | 0.48 | 2.74 | 0.167 | 0.283 |
| **MIL-CF$_3$/PEGDA$_{(20\%)}$/IL$_{(1eq.)}$** | 2.49 | 0.875 | 0.45 | 2.39 | 0.131 | 0.213 |
| **MIL-C$_7$H$_7$/PEGDA$_{(20\%)}$/IL$_{(0.5eq.)}$** | 2.14 | 0.689 | 0.39 | 2.18 | 0.103 | 0.169 |
| **MIL-C$_7$H$_7$/PEGDA$_{(20\%)}$/IL$_{(1eq.)}$** | 8.31 | 1.39 | 1.12 | 2.46 | 0.169 | 0.154 |

[a] Diffusivity coefficient ($10^{-8}$ cm$^2$/s). [b] Solubility coefficient ($10^{-2}$ cm$^3$ (STP) cm$^{-3}$ cm$^{-1}$ Hg$^{-1}$)

As shown in Table 2, the gas permeabilities of –SO$_2$–N$^{(-)}$–SO$_2$–C$_7$H$_7$ segments containing composite membranes displayed a dramatic increase in permeabilities with respect to their free IL contents; for example, the CO$_2$ permeabilities of MIL-C$_7$H$_7$/PEGDA$_{(20\%)}$/IL$_{(0.5eq.)}$ and MIL-C$_7$H$_7$/PEGDA$_{(20\%)}$/IL$_{(1eq.)}$ were 4.67 and 20.4 barrer, respectively. This drastic increase in permeability is due to the enhanced diffusivity as a result of effectively improved flexibility in the polymer chain, which agrees with the d-spacing data and the thermal transition properties (a much lower $T_g$ and higher d-spacing value was obtained for MIL-C$_7$H$_7$/PEGDA$_{(20\%)}$/IL$_{(1eq.)}$). In contrast, an odd behavior was also observed in the present work with the –SO$_2$–N$^{(-)}$–SO$_2$–CF$_3$ segments containing composite membranes. There was no increment in permeability observed with increasing amount of free IL content in –SO$_2$–N$^{(-)}$–SO$_2$–CF$_3$ segments containing composite membranes, even slight reduction in permeability was obtained; for example, the CO$_2$ permeabilities of MIL-CF$_3$/PEGDA$_{(20\%)}$/IL$_{(0.5eq.)}$ and MIL-CF$_3$/PEGDA$_{(20\%)}$/IL$_{(1eq.)}$ were 7.69 and

5.94 barrer, respectively (Table 2). This was an unexpected result from a poly(IL)-IL system attributed due to the decrease of gas diffusivity (see Table 3) in MIL-$CF_3$/PEGDA$_{(20\%)}$/IL$_{(1eq.)}$ membrane, plausible because of dense amorphous chain packing regardless to the free IL contents, which is in a good agreement with the XRD and DSC data of newly developed anionic poly(IL)-IL composites.

At the same time, all the newly developed anionic poly(IL)-IL composite membranes exhibited much higher $CO_2$ solubility than the $N_2$, or $CH_4$ solubilities, due to a stronger affinity of ionic liquid groups toward quadrupolar $CO_2$ molecules. Consequently, all the anionic poly(IL)-IL composite membranes presented excellent $CO_2/CH_4$, $CO_2/N_2$, and $CO_2/H_2$ permselectivities, in particular, the MIL-$C_7H_7$/PEGDA$_{(20\%)}$/IL$_{(1eq.)}$ showed an extraordinary high $CO_2$ selectivity for three gas pairs of $\alpha CO_2/CH_4$=118.6, $\alpha CO_2/N_2$ = 86.8, and $\alpha CO_2/H_2$ = 4.1. The $CO_2$ permeability versus $CO_2/CH_4$, $CO_2/N_2$, and $CO_2/H_2$ selectivity values of anionic poly(IL)-IL composite membranes (Fig. 7(a), 7(b), and 7(c), respectively) were then compared to the upper bound of the Robeson plot and the upper bound proposed by Freeman, et al.[51-53] The permeability–selectivity tradeoff data reported in literature for other cationic poly(IL)-IL composites are also illustrated in the upper bound plot for comparison.[35-37, 44, 54-57]

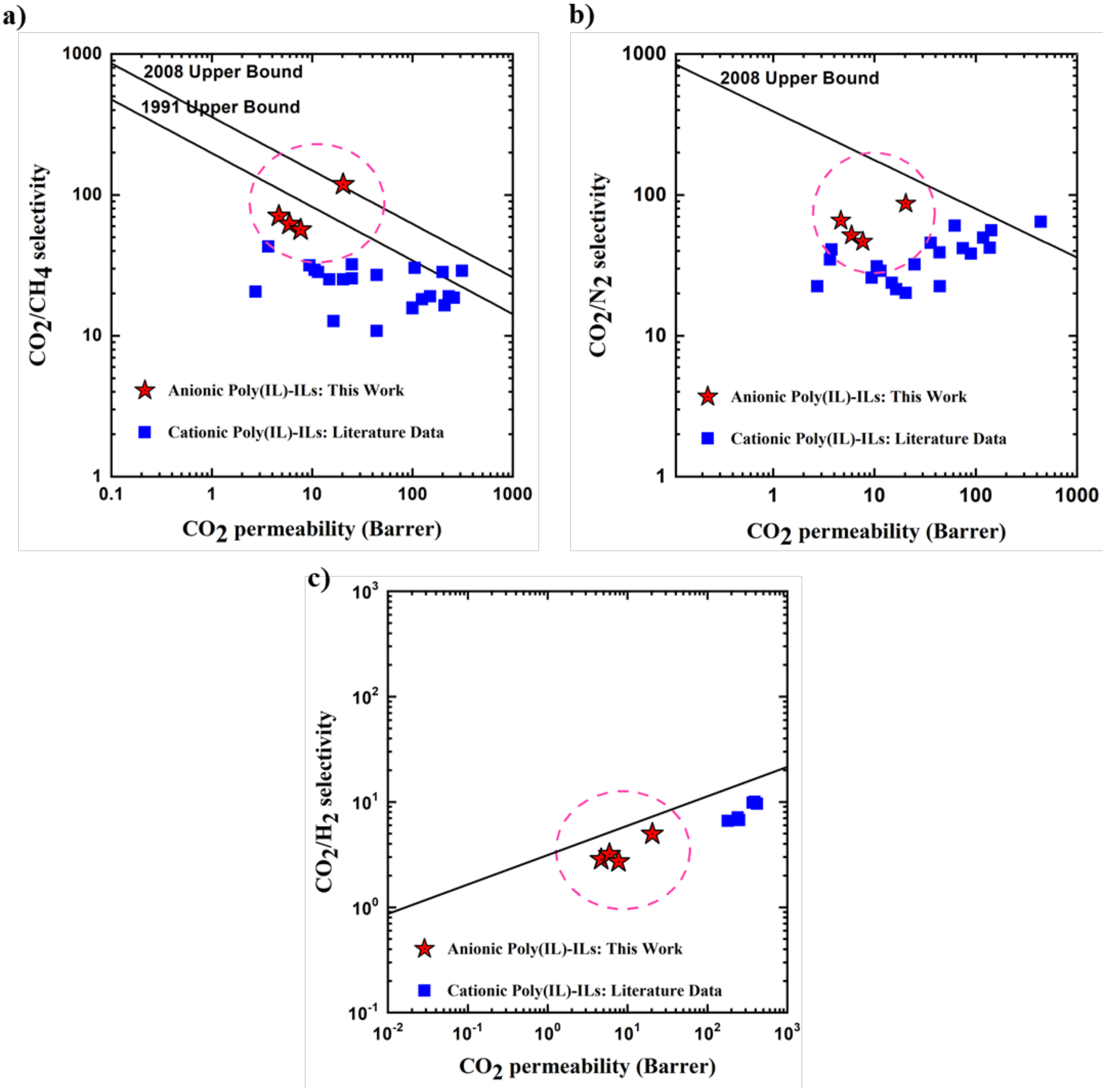


**Figure 7.** "Upper bound" plot for comparing the $CO_2/CH_4$ (a), $CO_2/N_2$ (b), and $CO_2/H_2$ separation performances of anionic poly(IL)-IL composites with other previously reported poly(IL)-ILs composite membranes.

All anionic poly(IL)-IL composite membranes exhibited outstanding $CO_2/CH_4$ performances with curves positioned above the Robeson upper bound of 1991. Moreover, the MIL-$C_7H_7$/PEG DA$_{(20\%)}$/IL$_{(1eq.)}$ membrane curves appeared above even the 2008 upper bound with extraordinary separation factor of 118.6. To the best of our knowledge, this is the highest selectivity value yet reported for $CO_2/CH_4$ separation in poly(IL)-IL systems. Although all anionic poly(IL)-IL composite membranes fell below the upper bound line for $CO_2/N_2$, they were comparable and within the general range of other poly(IL)-IL systems. Furthermore, as can be seen from Fig. 7(c), the separation performance level of all the anionic poly(IL)-IL membranes reached the reverse $CO_2/H_2$ upper bound limit. These results clearly indicated that all the anionic poly(IL)-IL composite membranes have remarkable capacities for enhanced selective separation of $CO_2$.

It is also important to note here that a direct comparison of newly developed anionic poly(IL)-IL composites with their crosslinked PEO units have not been focused due to the amounts of PEGDA monomer that can be incorporated in the anionic poly(IL) matrix, thanks to the modest amount of 20 wt% PEGDA monomer to form thin flexible anionic poly(IL)-IL composite membranes. The feature to tailor the structure-property relationships and the $CO_2$ separation capacity of anionic poly(IL)-IL with various amount of PEO units will be the subject of our further research. We also foresee an extension study to develop many anionic poly(IL)s with potentially fine-tuned substructures by introducing more flexible spacers (e.g., extended alkyl chains or ethylene oxide chains) and high polar delocalized anions (e.g., cyanamide anions) in our forthcoming works.

## CONCLUSION

This study provides a facile method to develop novel anionic poly(IL)-IL composite membranes for high-performance $CO_2$ separation. Two types of photopolymerizable methacryloxy-based ionic liquid monomers (MILs) with highly delocalized anions ($–SO_2–N^{(-)}–SO_2–CF_3$ and $–SO_2–N^{(-)}–SO_2–C_7H_7$) and mobile $[C_2mim]^+$ counter cations were successfully synthesized. Further, the photopolymerization of these two anionic MILs with the two distinct amounts of free IL containing the same structural cation ([$C_2$mim][$Tf_2$N]) and 20 wt% PEGDA crosslinker, to serve as a composite matrix, were led to form four novel anionic poly(IL)-IL composite membranes. All the newly developed flexible, transparent, and free-standing anionic poly(IL)-IL composite membranes exhibited excellent compatibility, high thermal stability, and enhanced $CO_2$ separation properties. The anionic poly(IL)-IL membranes showed superior $CO_2/CH_4$ and $CO_2/N_2$ selectivities with moderate $CO_2/H_2$ selectivity, whilst obtaining reasonable gas permeabilities. Moreover, the MIL-$C_7H_7$/PEGDA$_{(20\%)}$/IL$_{(1eq.)}$ membrane was able to surpass the $CO_2/CH_4$ upper bound limit, due to the simultaneous improvement in permeability and selectivity. The results showed that the newly developed anionic poly(IL)-IL composite membranes have remarkable potential to separate $CO_2$ from flue gas, natural gas, and syngas streams, making them strong candidate materials for practical applications.

## ASSOCIATED CONTENT

### Supporting Information

The supporting information is available free of charge via the Internet at http://pubs.acs.org.

NMR spectra of monomers of [$C_2$mim][Br] and [$C_2$mim][$Tf_2$N].

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Notes

The authors declare no competing financial interest.

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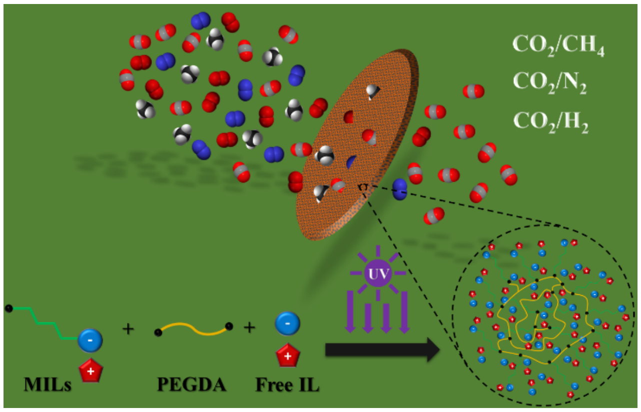
# Figure for Table of Contents



Introducing the first example of anionic poly(IL)-IL composite membranes for effective CO$_2$ separation with many more aspects that convey green chemistry and polymer membrane-based separation engineering.