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Polyurethane-based poly (ionic liquid)s for CO₂ removal from natural gas

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ABSTRACT: Carbon dioxide separation from CH_4 is important to the environment and natural gas processing. Poly (ionic liquid)s (PILs) based on polyurethane structures are considered as potential materials for CO_2 capture. Thus, a series of anionic PILs based on polyurethane were synthesized. The effects of polyol chemical structure and counter-cations (imidazolium, phosphonium, ammonium, and pyridinium) in CO_2 sorption capacity and CO_2/CH_4 separation performance were evaluated. The synthesized PILs were characterized by NMR, DSC, TGA, dinamical mechanical thermo analysis (DMTA), SEM, and AFM. CO_2 sorption, reusability, and CO_2/CH_4 selectivity were assessed by the pressure-decay technique. The counter-cation and polyol chemical structure play an important role in CO_2 sorption and CO_2/CH_4 selectivity. PILs exhibited competitive thermal mechanical properties. Results showed that PILPC-TBP was the best poly (ionic liquid) for CO_2/CH_4 separation. Moreover, poly (liquid ionic) base polyol (polycarbonate) with phosphonium (PILPC-TBP) demonstrated higher CO_2 sorption capacity (21.4 mgCO₂/g at 303.15 K and 0.08 MPa) as compared to other reported poly (ionic liquids). © 2019 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2019**, *136*, 47536.

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INTRODUCTION

Carbon dioxide (CO₂) is a greenhouse gas found in many natural gas wells. Removal of CO₂ from natural gas is industrially important to obtain fuel with enhanced energy content and prevent corrosion problems in gas transportation via pipeline systems.¹ Moreover, as regards to the environment, carbon capture and storage is one of the most important technologies to reduce CO₂ emissions and mitigate global warming.^{2,3} Development of low-cost materials for CO₂ separation is an urgent priority in this field.

There are numerous publications on CO_2 capture using based room-temperature ionic liquids (RTILs), a special class of green solvents.^{4–6} RTILs based on alkyl-imidazolium cations are the most investigated for CO_2 capture application.^{7–12} However, different cations including pyrrolidinium, pyridinium, and phosphonium have also been explored in an effort to enhance CO_2 solubility.^{6,13}

Anthony *et al.*¹⁴ investigated the solubility of nine different gases $(CO_2, CH_4, C_2H_4, Ar, C_2H_6, and O_2)$ in 1-n-butyl-3-methylimidazolium hexafluorophosphate ([bmim]-[PF₆]) at 25 °C by means of a gravimetric microbalance. It was found that CO_2 has the largest solubility and strongest interactions with ionic liquids (ILs) compared to other gases solubility. It suggests that ILs show good potential for use as a gas separation solvent. However, the RTILs high viscosity can represent a barrier to implementation in the oil and gas industry.⁵ One solution for overcoming this disadvantage is the use of poly (ionic liquid)s (PILs) or polymerized ionic liquids.^{15–21}

PILs appear as promising materials for CO₂ separation.^{15–21} These polymers represent a new platform for developing versatile sorbents for CO₂ capture.^{17,18,21–27} PILs refer to a special type of polyelectrolytes which feature an IL species in each monomer repeating unit, connecting through a polymeric backbone forming a macromolecular structure.^{18,19} The major advantages of PILs are enhanced stability, improved processability, flexibility, reversible, and fast sorption–desorption process than with conventional ILs.^{18,22,23,26,28–31}

PILs syntheses are normally performed following two different approaches: direct ILs monomer polymerization and chemical modification of polymeric precursors.^{18,19,21,22,30,32} Each route have advantages and disadvantages.^{19,30} Yet, chemical modification of polymeric precursors is more attractive because it uses commercial

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polymers to produce customized PILs of high molecular weight.^{30,33} We reported the first anionic PIL based on polyurethane (PU) structures for CO₂ capture synthesized by polymer modification methods.^{20,34} Recently, we developed new anionic PUs introducing three different types of cations (imidazolium, phosphonium, and ammonium)^{20,34} and evaluated their CO₂ sorption capacity. It has been reported that introduction of polar groups such as the hydroxy (-OH), carbonyl (-C=O), and hydroxyimino (-C=N-OH) into the polymer structure may be an effective way to facilitate interaction between CO2 and the polymer chains.^{35–37} In the present work, we investigated the effects of polyol chemical structure (polyol (polycarbonate [PCD] or polycaprolactone [PCL]) and counter-cations (imidazolium, phosphonium, ammonium, and pyridinium)) on CO2/CH4 selectivity of anionic PILs based on PU. The influence of pressure and temperature in CO₂ affinity was also evaluated.

EXPERIMENTAL

Materials

PCL (M_n = 2000 g/mol, Sigma-Aldrich, Japan), PCD (M_n = 2000 g/mol, Bayer, Germany), hexamethylene diisocyanate (HDI, 99%, Merck, France), dimethylol propionic acid (DMPA, 98%, Sigma-Aldrich, USA), dibutyl tin dilaurate (DBTDL, Miracemanuodex, Brasil), N-methyl-2-pyrrolidone (99.92%, Neon, Brasil), methylethylketone (MEK, 99%, Mallinckrodt), and potassium hydroxide (KOH, ≥85%, Sigma-Aldrich, USA) were used as received without further purification. Tetrabutylammonium bromide (99%, Acros Organics, USA), tetrabutylphosphonium bromide (98%, Sigma-Aldrich, USA), 1-butyl-1-methylpyrrolidinium chloride (BMPYRR, 99%, Sigma-Aldrich, USA), and 1-butyl-3-methylimidazolium chloride (bmimCl) were synthesized as described elsewhere.^{38,39} The synthesized bmimCl was characterized by proton nuclear magnetic resonance (¹H-NMR), in Varian spectrophotometer, VNMRS 300 MHz, using DMSO-d6 as solvent and glass tubes of diameter 5 mm. ¹H-NMR (300 MHz, DMSOd6, 25°C), δ (ppm): 1.01 (m, CH₃), 1.29 (m, CH₂CH₃), 1.83 (m, CH₂), 3.97 (s, CH₃), 4.25 (t, CH₂N), 7.79 (s, H₅), 7.91 (s, H₄), 9.48 (s, H₂). All ILs were dried under vacuum during 12 h at 60 °C prior to use.

Anionic PILs Synthesis

PILs synthesis was performed in two steps (Figure 1), as described elsewhere.^{20,34} First, PU was synthesized in a five-necked flask at 60 °C during 2 h using diisocyanate (HDI), PCL or PCD polyol, DMPA diol, and DBTDL (0.1 wt %) as catalyst in MEK (50 mL). The NCO/OH ratio of 1.05 (0.157 mol HDI/0.15 mol OH) was used. Ultimately, the solid content and the polymer acidity were identified by titration with KOH 0.5 M. The acid number reached a value of 135 mgKOH/g (2.43 mmol of IL/g polymer) using PCD and 148 mgKOH/g (2.66 mmol of IL/g polymer) using PCL. Second, the mixture was cooled down to 40 °C because IL was added (molar ratio COOH/IL of 1:1). The system was maintained at 40 °C during 4 h under stirring to obtain PILs. Afterward, films around 0.15 mm thick were produced by casting and dried at room temperature for 72 h. The synthesized PILs were labeled as PILW-X, where W is polyol (PL = PCL; PC = PCD) and X is counter cation (BMIM; TBP, TBA or BMPYRR). For example, PILPL-BMIM means PCL polyol and BMIM counter cation.



Figure 1. Structural variables of anionic poly (ionic liquid)s.

Characterization of the Anionic Poly (Ionic Liquid)s

Structures of samples were identified by ¹H-NMR spectroscopies. The ¹H-NMR spectra were obtained using Bruker Avance DRX-400 spectrometer at 400 MHz in THF-d₆. Molecular weights were obtained from a gel permeation chromatograph, measurements were conducted on a Waters 1515 pump equipped with a Waters 2412 refractive index detector, using THF as eluent at a flow rate of 1 mL/min; samples to be analyzed were dissolved in DMSO and then diluted with THF. The samples morphology was determined with a field emission scanning electron microscope using Inspect F50 equipment (FEI Instruments) in secondary electrons mode. AFM analysis was performed in the peak force tapping mode by Bruker Dimension Icon PT equipped with TAP150A probe (Bruker, resonance frequency of 150 kHz and 5 N m⁻¹ spring constant). The scanned area of the images was $1 \times 1 \ \mu m^2$ with resolution 512 frames per area. Thermal properties of the PUs and PILs were measured via differential scanning calorimetry (DSC Q20, TA) and thermogravimetric analysis (TGA Q600, TA). DSC measurements were performed at a rate of 10 °C/min across a temperature range of -90-170 °C. The TGA tests were initiated at room temperature and heated to 600 °C at a heating rate of 10 °C/min. Tensile tests (stress × strain curves) were acquired at 25 °C with rectangular-shaped films $(12 \times 7 \times 0.15 \text{ mm})$ in Dynamical Mechanical Thermo Analysis (DMTA) equipment (model Q800, TA Instruments), 1 N/min. The Young modulus was determined according to ASTM D638. All analyses were conducted in triplicate.

Sorption Measurements

CO₂ Sorption Capacity. The pressure-decay technique was used to determine CO₂ sorption capacity. The dual-chamber gas sorption cell was similar to Koros and Paul.⁴⁰ A detailed description of the sorption apparatus and the measuring procedure can be found in our previous works.^{41–43} Samples (1.0–1.5 g) were loaded in the sorption chamber and degassed under vacuum (10^{-3} mbar) at 298.15 K during 1 h. CO₂ sorption experiments were carried out at two different temperatures (303.15 and 313.15 K) with pressure ranging from 0.08 to 3 MPa.



Sorption/Desorption Experiments. Sorption/desorption experiments used CO₂. Six CO₂ sorption/desorption cycles were performed on the PIL. CO₂ sorption was evaluated at 303.15 K and 1.0 MPa and desorption under vacuum (10^{-3} mbar) at 298.15 K during 1 h.

CO₂/CH₄ Separation Selectivity. Experiments were also performed in a dual-chamber gas sorption cell similar to Koros and Paul.⁴⁰ In the test, samples (1.0–1.5 g) were also previously degassed under vacuum (10⁻³ mbar) at 298.15 K during 1 h. The CO₂/CH₄ selectivity tests were conducted using a binary mixture (35 mol % of CO₂ and CH₄ balance) at 303.15 K and 2 MPa. The apparatus and complete experimental procedure were described elsewhere.^{43,44}

RESULTS AND DISCUSSION

PILs molecular weight was similar to nonionic polyurethanes (PUPL, $M_n = 156.800$ and polydispersity (DPI) = 2.0; PUPC, M_n = 149.000 and DPI = 1.6). The insertion of IL cation reaction shows no interference in the polymer chain size, therefore not improving molecular weight.²⁰ Structures of all synthesized polymers were confirmed by ¹H NMR. The resonance peaks and their corresponding assignments were compared with the starting materials spectra from the Spectral Database for Organic Compounds and literature.^{20,45,46} The peaks of all NMR spectra showed the signals of PU chain. Samples synthesized using PCL exhibited peaks at $\delta_{\rm H}$ (ppm): 4.12 (4H, m, $-O-(CH_2)_5-COO (CH_2)_2$ -O-CH₂-CH₂-OCO-CH₂-OCONH- of PCL), 2.27 (4H, m, -O-(CH₂)₅-COO-(CH₂)₂-O-CH₂-CH₂-OCO-CH₂-C OCONH- of PCL), 2.72 (2H, m, -O-(CH₂)₅-COO-(CH₂)₂-O-CH₂-CH₂-OCO-CH₂-C OCONH- of PCL), 1.37 (2H, m -O-(CH₂)₅-COO- $(CH_2)_2$ -O-CH₂-CH₂-OCO-CH₂-OCONH- of PCL), 1.37 (2H, m -O-(CH2)5-COO-(CH₂)₂-O-CH₂-CH₂-OCO-CH₂-C OCONH of PCL), 1.15 (4H, m –O–(CH₂)₅–COO– (CH₂)₂-O-CH₂-CH₂-OCO-CH₂-C OCONH- of PCL), 3.95 (2H, m -O-(CH₂)₅-COO- $(CH_2)_2$ -O-CH₂-CH₂-OCO-CH₂-OCONH- of PCL), 1.37 (2H, m,N-CH2-CH2-(CH2)2- of HDI), 1.61 (2H, m, N-CH2-CH2- of HDI), 1.72 (2H m, N-CH2-CH2-, m, of HDI), 0.95 (3H, s,CH3 of DMPA), 4.02 (2 H,s, R-NH-CO-O-CH2-C of DMPA), and 6.38 (1H,s, NH urethane). While samples produced using PCD provided peaks at δ_H (ppm): 4.06 (m,OCO-CH₂CH₂CH₂CH₂CH₂CH₂CH₂OCONH of PCD), 1.64 (m,OCO-CH2CH2CH2CH2CH2CH2CH2OCONH of PCD), 1.39 (m,OCO-CH2CH2CH2CH2CH2CH2CH2OCONH of PCD), 4.06 (m,OCO-CH2CH2CH2CH2CH2CH2CH2OCONH of PCD), 1.39 (2H, m,N-CH₂-CH₂-(CH₂)₂- of HDI), 1.62 (2H, m, N-CH₂-CH₂of HDI), 1.72 (2H m,N-CH2-CH2-, m, of HDI), 1.08 (3H, s,CH3 of DMPA), 4.06 (2 H,s, R-NH-CO-O-CH2-C of DMPA), and 6.38 (1H,s, NH urethane). The presence of TBA cation was assigned by the following peaks at $\delta_{\rm H}$ (ppm): 3.27 (2H t, CH₃CH₂CH₂CH₂N of TBA), 1.64 (2H, m, CH₃CH₂CH₂CH₂N of TBA), 1.38 (2H, m, CH₃CH₂CH₂CH₂N of TBA), and 1.00 (3H, t, CH₃CH₂CH₂CH₂N of TBA). The signals of TBP cation were detected at $\delta_{\rm H}$ (ppm): 2.64 (2H, m, CH₃CH₂CH₂CH₂P of TBP), 1.52 (2H, m, CH₃ (<u>CH₂</u>)₂CH₂P of TBP), and 0.98 (3H, t, <u>CH₃</u>CH₂CH₂CH₂P of TBP). BMPYRR cation was detected by the following peaks at $\delta_{\rm H}$ (ppm): 3.39 (4H, m, CH₃N<u>CH₂</u>(CH₂)₂CH₂N of BMPYRR), 3.28 (2H, t, N<u>CH₂</u>(CH₂)₂CH₃ of BMPYRR), 3.06 (3H, s, N<u>CH₃</u> of BMPYRR), 2.51 (4H, s, CH₃NCH₂<u>CH₂</u>CH₂CH₂CH₂N of BMPYRR), 1.61 (2H, m, NCH₂<u>CH₂</u>CH₂CH₃ of BMPYRR), 1.35 (2H, m, N(CH₂)₂<u>CH₂</u>CH₃ of BMPYRR), and 0.95 (3H, t, N(CH₂)₃<u>CH₃</u> of BMPYRR). The presence of bmim cation is manifested by the following peaks at $\delta_{\rm H}$ (ppm): 9.73 (1H, s, N<u>CH</u>N of bmim), 8.01 (1H, t, CH₃NCH₂<u>CH₂N of bmim), 7.90 (1H, t, CH₃N<u>CH₂CH₂N of bmim), 4.25</u> (2H, t, N<u>CH₂(CH2)₂CH₃ of bmim), 3.91 (3H, s, N<u>CH₃ of bmim), 1.72 (2H, m, NCH₂<u>CH₂CH₂CH₂CH₃ of bmim), 1.39 (2H, m, N(CH₂)₂<u>CH₂CH₃ of bmim), and 0.90 (3H, t, N(CH₂)₃<u>CH₃ of bmim).</u></u></u></u></u></u>

SEM images (Figure 2) showed a porous morphology for samples poly (liquid ionic) base polycaprolactone with pyridinium (PILPL-BMPYRR) [pore diameter = 0.910 \pm 0.390 μ m; Figure 2(e)], PU-PC [pore diameter = 0.853 \pm 0.514 μ m; Figure 2(f)], poly (liquid ionic) base polyol (polycarbonate) (PILPC-BMIM) [pore diameter 1.363 \pm 0.902 μ m; Figure 2(g)], and PILPC-BMPYRR [pore diameter = 1.842 \pm 1.176 μ m; Figure 2(j)]. The other samples presented a nonporous morphology as depicted in Figure 2. Porosity may affect mechanical properties and increase CO₂ sorption capacity.

PUs and PILs AFM images are shown in Figure 3. AFM visualization results demonstrate that nonionic PUs and PILs contain hard domains (lighter regions) and soft domains (dark regions) randomly mixed. However, ILs cation insertion into polymeric structure leads to an increase in hard and soft segments segregation, suggesting microphase separation.

The samples thermal stability was analyzed by TGA (Table I). All synthesized polymers presented two typical thermal events. The first thermal event ($T_{1 \text{ onset}}$) is attributed mainly to decomposition of hard segments commonly related to urethane break bonds.^{47–49} The second event ($T_{2 \text{ onset}}$) is associated to decomposition of soft segments (PCL or PCD polyol).⁵⁰ IL thermal decompositions have been reported within 200 and 350 °C,⁵¹ suggesting that decomposition of IL cation can occur in both stages of PILs. Thus, PILs showed lower thermal stability than neutral PUs as can be seen in Table I. This behavior was reported in other urethane-based PILs.^{20,42} Carboxylate anion may be responsible for reducing PILs thermal stability, probably due to decarboxylation during thermogravimetric scanning.⁵²

PUs and PILs DSC thermograms are shown in Figure 4. DSC revealed a melting peak for PU-PL at 40.2 °C, PILPL-BMIM at 37.2 °C, PILPL-TBP at 42.5 °C, PILPL-TBA at 41.0 °C, and PILPL-BMPYRR at 38.0 °C corresponding to PCL crystalline phase melting (T_m) .^{53,54} PCL-based PILs melting enthalpy decreased compared to nonionic PU (Table I). The smaller degree of microcrystallinity in PCL-based PILs is reflected in the lower enthalpy values.

DSC curves also exhibited an endothermic peak and denote crystalline microphase melting $(T_{\rm ms})^{55}$ for PUPC at 43.0 °C, PILPC-BMIM at 41.0 °C, PILPC-TBP at 43.0 °C, PILPC-TBA at 38.6 °C, and PILPC-BMPYRR at 39.7 °C. $T_{\rm ms}$ appears only when soft segments are PCD with molecular weight of 2000 g/mol. In this case,



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Figure 2. SEM micrographs: (a) PU-PL, (b) PILPL-BMIM, (c) PILPL-TBP, (d) PILPL-TBA; (e) PILPL-BMPYRR, (f) PU-PC, (g) PILPC-BMIM, (h) PILPC-TBP, (i) PILPC-TBA; and (j) PILPC-BMPYRR.

the semicrystalline character of soft segment presents both higher purity and segregation degree, in other words lower amount of dissolved hard segments.⁵⁵ The enthalpy values related to PU-PC and polycarbonate-based PILs were low (Table I).

It is also interesting that the glass transition temperature (T_g) decreased for all PILs (Figure 4 and Table I), indicating better microphase separation.^{56,57} This observation was consistent with AFM results (Figure 3). The T_g to precursors PU-PL and PU-PC



Figure 3. DMT modulus maps obtained by AFM images: (a) PU-PC, (b) PILPC-BMIM, (c) PILPC-TBP, (d) PILPC-TBA; (e) PILPC-BMPYRR; (f) PU-PL, (g) PILPL-TBP, (i) PILPL-TBA; and (j) PILPL-BMPYRR. [Color figure can be viewed at wileyonlinelibrary.com]





Figure 4. DSC thermograms for PUs and PILs films.

were found to be -41.0 and -52.7 °C, respectively, while T_g for PILPL-BMIM, PILPL-TBP, PILPL-TBA, PILPL-BMPYRR, PILPC-BMIM, PILPC-TBP, PILPC-TBA, and PILPC-BMPYRR were T_g : -56.5, -47.6, -47.0, -45.3, -56.3, -55.0, -56.4, and -59.3 °C, respectively. Introduced counter-cation into polymeric structure acts as a driving force in microphase separation, improving polymer chain flexibility, facilitating motion and, consequently, reducing polymer $T_g^{56,58}$

PUs and PILs Young's moduli and tensile properties obtained by DMTA are shown in Figures 5 and 6. Changes evidenced by AFM and DSC when the ionic compound is formed probably influence mechanical behavior of the PILs. The effect of counter-cation in decreasing Young's modulus is evident when comparing the results of PILs with PUs without counter-cation as seen in Figure 6. However, PILs exhibited better elongation at break than their nonionic

Table I. TGA and DSC Data for PUs and PILs Films

	TGA		DSC		
Amostra	7 _{1 onset} (°C)	T _{2 onset} (°C)	<i>T_g</i> (°C)	<i>T_m</i> (°C)	ΔH_m (J/g)
PU-PL	216.0	350.8	-41.0	40.2	27.0
PILPL-BMIM	187.3	299.7	-56.5	37.2	16.9
PILPL-TBP	192.7	337.4	-47.6	42.5	16.0
PILPL-TBA	179.2	272.8	-47.0	41.0	17.0
PILPL-BMPYRR	187.3	290.6	-45.3	38.0	17.3
PU-PC	208.8	342.8	-52.7	43.0	0.80
PILPC-BMIM	201.3	366.4	-56.3	41.0	8.9
PILPC-TBP	176.0	269.6	-55.0	43.0	7.6
PILPC-TBA	172.2	369.7	-56.4	38.6	6.6
PILPC-BMPYRR	200.2	351.4	-59.3	39.7	5.1

precursors. The elongation at break for PU-PL, PU-PC, PILPL-BMIM, PILPL-TBP, PILPL-TBA, PILPL-BMPYRR, PILPC-BMIM, PILPC-TBP, PILPC-TBA, and PILPC-BMPYRR, occurred at 309.6 \pm 11.4%, 269.8 \pm 12.0%, 386 \pm 6.3%, 345 \pm 3.5%, 359.5 \pm 7.1%, 378.8 \pm 9.8%, 377.5 \pm 4.9%, 419.3 \pm 8.0%, 370.8 \pm 2.8%, and 308.1 \pm 2.1%, respectively. ILs cation insertion into polymeric structure might act as a plasticizer to improve flexibility of polymer chains and consequently reduce the Young's modulus of the polymer.^{56,57}

PILs and PU CO_2 sorption capacity at 1 MPa and 303.15 $^\circ \text{C}$ is shown in Figure 7. Generally, CO₂ affinity in a polymer is associated with the interaction between CO₂ and the polar groups.^{35,36} This behavior was observed in pure PU; CO₂ solubility increased with the increasing content of polar groups in the polymer (PU- $PL = 43.4 \text{ mgCO}_2/\text{g}$; $PU-PC = 40.1 \text{ mgCO}_2/\text{g}$). However, in the PILs CO₂ solubility is mostly influenced by ionization. PU-PC and PU-PL CO₂ solubility tended to increase with ionization into the polymer structure as seen in Figure 7. These CO₂ sorption values were higher than results found in our previous works.^{20,34,59} Electronic-structure simulations demonstrated that the TBA and TBP cations exhibiting weaker coordination of the carboxyl group promoting electrostatic binding of the CO₂ molecule and the carboxyl group.^{20,37} In PCL-based PILs (PU-PL) the highest results were obtained for TBP and BMPYRR cations, 53.0 and 51.5 mgCO₂/g, respectively. In polycarbonate-based PILs (PU-PC) the best result was found for BMPYRR cation (48.4 mgCO₂/g) followed by TBP and BMIM cation, which presented similar CO₂ sorption (PILPC-TBA = $45.3 \text{ mgCO}_2/\text{g}$; PILPC-BMIM = 46.1mgCO₂/g). The high performance of BMPYRR and BMIM cation is probably associated with porous morphology evidenced by SEM (Figure 2) while TBA and TBP cation high CO₂ sorption capacity is related to weak cation-anion coordination.

The effect of the polyol chemical structure and counter-cations on sorption selectivity at 2 MPa and 303.15 K is shown in



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Figure 5. Stress/strain curves for developed PUs and PILs films.

Figure 8. Interestingly, PUPC exhibited a high selective response than PU-PL. The increase in the number of polar groups may cause the mutual attraction between the polymer chains. Thus, these intermolecular forces may hinder specific interactions of CO_2 with polar groups. The selective capacity of PUs for CO_2 over CH₄ can be improved by counter-cations into the backbone to selectively interact with CO_2 . PILs showed high selective response than neutral PUs. The best performance was obtained for PILPC-TBP. The TBP belong to non-coordinating cations, in other words, promoting interactions between CO_2 and carboxyl groups of PU anion.²⁰ Selective capacity of 2.22 for PILPC-TBP is higher than in composite PU foam/ILs (PUF BF4 40: CO_2/CH_4 selectivity of 1.42 at 3 MPa).⁴³ These results indicated the importance of carboxyl groups on selective CO_2 sorption.

PILPC-TBP was selected for a CO_2 sorption study and recyclability behavior. Isotherm of pure CO_2 sorption with pressure from 0.08 to 3.0 MPa at two temperatures was tested (Figure 9) for PILPC-TBP due to higher CO_2/CH_4 selectivity compared to





Figure 7. Pure PU and poly (ionic liquid)s CO_2 sorption values at 1 MPa and 303.15 K.

all other samples. PILPC-TBP portray a typical behavior of a physical sorbent, in other words, gas solubility increases significantly as the temperature decreases and CO₂ partial pressure increases (Figure 9). It was also found that CO₂ sorption in PILPC-TBP (21.4 mg/g at 303.15 K and 0.08 MPa) is higher than in PIL PU-TBP synthesized with poly(tetramethylene ether) glycol polyol (15.7 mgCO₂/g at 0.08 MPa 303.15 K)²⁰ and other previously reported PILs.^{31,60,61} The obtained result for PILPC-TBP was similar to the high CO₂ sorption capacity reported for PIL-8.1.BF₄ (24.76 mg/g at 273 K and 1 bar) by Morozova *et al.*⁶⁰

Development of new sorbents to overcome the challenges, such as nonrecyclability, associated with conventional chemical sorbents is of utmost importance. CO_2 sorption in PILPC-TBP was



Figure 8. Pure PU and poly (ionic liquid)s CO_2/CH_4 selectivity values at 2 MPa and 303.15 K.





Figure 9. PILPC-TBP CO₂ sorption at different temperatures.



reversible for the six consecutive cycles (Figure 10). These results indicated high stability and reuse capacity in CO_2 capture processes of PILPC-TBP.

CONCLUSIONS

We reported the synthesis of PU based PILs using two polyols (PCD or PCL) and different ILs cations including imidazolium, phosphonium, ammonium, and pyridinium. All PILs exhibited high thermal stability and competitive mechanical properties. The counter-cation and polyol chemical structure play an important role in CO₂ sorption and CO₂/CH₄ selectivity. Although the increase in the number of polar groups may lead to increased CO₂ absorption it can reduce selectivity. It is possibly due to the mutual attraction between the polymer chains that may hinder the specific interactions of CO₂. The insertion of IL cation in the

polymeric structure leads to increase in CO_2 sorption and CO_2/CH_4 selectivity. The PIL from PCD and phosphonium cation (PILPC-TBP) showed the highest selective capacity for CO_2 over CH_4 . This result suggests that weak coordinating counter-cations for PU based PILs stabilize the system maintaining the CO_2 binding sites of the anion partially or fully nonoccupied, improving the selective capacity of PILs for CO_2 over CH_4 . The CO_2 sorption/desorption cycles showed that PILPC-TBP has both high stability and reuse capacity.

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CONFLICT OF INTEREST

All authors declare that there are no conflicts of interest regarding the publication of this article.

REFERENCES

- Kazemi, A.; Joujili, A. K.; Mehrabani-zeinabad, A.; Hajian, Z.; Salehi, R. *Energy Fuel.* 2016, 30, 4263.
- Manassaldi, J. I.; Mores, P. L.; Scenna, N. J.; Mussati, S. F. Ind. Eng. Chem. Res. 2014, 53, 17026.
- Flude, S.; Johnson, G.; Gilfillan, S. M. V.; Haszeldine, R. S. Environ. Sci. Technol. 2016, 50, 7939.
- Zeng, S.; Zhang, X.; Bai, L.; Zhang, X.; Wang, H.; Wang, J.; Bao, D.; Li, M.; Liu, X.; Zhang, S. *Chem. Rev.* 2017, 117, 9625.
- Hasib-ur-Rahman, M.; Siaj, M.; Larachi, F. Chem. Eng. Process. Process Intensif. 2010, 49, 313.
- Sarmad, S.; Mikkola, J.-P.; Ji, X. ChemSusChem. 2017, 10, 324.
- Blanchard, L. A.; Gu, Z.; Brennecke, J. F. J. Phys. Chem. B. 2001, 105, 2437.
- Anthony, J. L.; Anderson, J. L.; Maginn, E. J.; Brennecke, J. F. J. Phys. Chem. B. 2005, 109, 6366.
- Cadena, C.; Anthony, J. L.; Shah, J. K.; Morrow, T. I.; Brennecke, J. F.; Maginn, E. J. *J. Am. Chem. Soc.* 2004, *126*, 5300.
- Privalova, E. I.; Mäki-Arvela, P.; Murzin, D. Y.; Mikkhola, J. P. Russ. Chem. Rev. 2012, 81, 435.
- 11. Mao, J. X.; Steckel, J. A.; Yan, F.; Dhumal, N.; Kim, H.; Damodaran, K. Phys. Chem. Chem. Phys. 2016, 18, 1911.
- 12. Brennecke, J. F.; Gurkan, B. E. J. Phys. Chem. Lett. 2010, 1, 3459.
- Mahurin, S. M.; Hillesheim, P. C.; Yeary, J. S.; Jiang, D.; Dai, S. RSC Adv. 2012, 2, 11813.
- 14. Anthony, J. L.; Maginn, E. J.; Brennecke, J. F. J. Phys. Chem. B. **2002**, *106*, 7315.
- 15. Sadeghpour, M.; Yusoff, R.; Aroua, M. Rev. Chem. Eng. 2017, 33, 183.
- Zulfiqar, S.; Sarwar, M. I.; Mecerreyes, D. Polym. Chem. 2015, 6, 6435.



- 17. Tang, J.; Sun, W.; Tang, H.; Radosz, M.; Shen, Y. *Macro-molecules*. **2005**, *38*, 2037.
- 18. Yuan, J.; Antonietti, M. Polymer. 2011, 52, 1469.
- Yuan, J.; Mecerreyes, D.; Antonietti, M. Prog. Polym. Sci. 2013, 38, 1009.
- Bernard, F. L.; Polesso, B. B.; Cobalchini, F. W.; Donato, A. J.; Seferin, M.; Ligabue, R.; Chaban, V. V.; do Nascimento, J. F.; Dalla Vecchia, F.; Einloft, S. *Polymer*. 2016, 102, 199.
- Einloft, S.; Bernard, F. L.; Dalla Vecchia, F. CHAPTER 17. Capturing CO2 with poly(ionic liquid)s. In Polymerized Ionic Liquids; Eftekhari, A., Ed., Royal Society of Chemistry: London, 2017. pp 512–514.
- 22. Tome, L. C.; Marrucho, I. M. Chem. Soc. Rev. 2016, 45, 2785.
- 23. Tomé, L. C.; Mecerreyes, D.; Freire, C. S. R.; Rebelo, L. P. N.; Marrucho, I. M. J. Memb. Sci. 2013, 428, 260.
- 24. Zhu, J. M.; He, K. G.; Zhang, H.; Xin, F. Adsorpt. Sci. Technol. 2012, 30, 35.
- 25. Sedghamiz, M. A.; Rasoolzadeh, A.; Rahimpour, M. R. *J. CO2 Util.* **2015**, *9*, 39.
- 26. Qian, W.; Texter, J.; Yan, F. Chem. Soc. Rev. 2017, 46, 1124.
- 27. Yu, G.; Li, Q.; Li, N.; Man, Z.; Pu, C.; Asumana, C.; Chen, X. Polym. Eng. Sci. 2014, 54, 59.
- Tang, J.; Tang, H.; Sun, W.; Radosz, M.; Shen, Y. *Polymer*. 2005, 46, 12460.
- 29. Blasig, A.; Tang, J.; Hu, X.; Shen, Y.; Radosz, M. Fluid Phase Equilib. 2007, 256, 75.
- Shaplov, A. S.; Morozova, S. M.; Lozinskaya, E. I.; Vlasov, P. S.; Gouveia, A. S. L.; Tomé, L. C.; Marrucho, I. M.; Vygodskii, Y. S. *Polym. Chem.* **2016**, *7*, 580.
- 31. Privalova, E. I.; Karjalainen, E.; Nurmi, M.; Mäki-arvela, P.; Eränen, K. *ChemSusChem.* **2013**, *6*, 1500.
- 32. Sahiner, N.; Demirci, S. J. Appl. Polym. Sci. 2016, 133, 43478.
- 33. Bhavsar, R. S.; Kumbharkar, S.; Rewar, A. S.; Kharul, U. K. *Polym. Chem.* **2014**, *5*, 4083.
- Magalhaes, T. O.; Aquino, A. S.; Dalla Vecchia, F.; Bernard, F. L.; Seferin, M.; Menezes, S. C.; Ligabue, R.; Einloft, S. RSC Adv. 2014, 4, 18164.
- Gabrienko, A. A.; Ewing, A. V.; Chibiryaev, A. M.; Agafontsev, A. M.; Dubkov, K. A.; Kazarian, S. G. Phys. Chem. Chem. Phys. 2016, 18, 6465.
- Tomasko, D. L.; Li, H. B.; Liu, D. H.; Han, X. M.; Wingert, M. J.; Lee, L. J.; Koelling, K. W. Ind. Eng. Chem. Res. 2003, 42, 6431.
- Bernard, F. L.; Rodrigues, D. M.; Polesso, B. B.; Donato, A. J.; Seferin, M.; Chaban, V. V.; Vecchia, F. D.; Einloft, S. *Fuel Process. Technol.* 2016, 149, 131.
- 38. Welton, T. Chem. Rev. 1999, 99, 2071.
- 39. Jain, N.; Kumar, A.; Chauhan, S.; Chauhan, S. M. S. Tetrahedron. 2005, 61, 1015.

- 40. Koros, W. J.; Paul, D. R. J. Polym. Sci. Polym. Phys. Ed. 1976, 14, 675.
- Bernard, F. L.; Duczinski, R. B.; Rojas, M. F.; Fialho, M. C. C.; Carreño, L. Á.; Chaban, V. V.; Vecchia, F. D.; Einloft, S. *Fuel.* 2018, *211*, 76.
- Bernard, F. L.; Polesso, B. B.; Cobalchini, F. W.; Chaban, V. V.; do Nascimento, J. F.; Dalla Vecchia, F.; Einloft, S. *Energy Fuel.* 2017, 31, 9840.
- Fernández Rojas, M.; Pacheco Miranda, L.; Martinez Ramirez, A.; Pradilla Quintero, K.; Bernard, F.; Einloft, S.; Carreño Díaz, L. A. *Fluid Phase Equilib.* 2017, 452, 103.
- 44. Azimi, A.; Mirzaei, M. Chem. Eng. Res. Des. 2016, 111, 262.
- 45. Saito, T.; Aizawa, Y.; Tajima, K.; Isono, T.; Satoh, T. Polym. Chem. 2015, 6, 4374.
- 46. Oh, S.-Y.; Kang, M.-S.; Knowles, J. C.; Gong, M.-S. *J. Biomater. Appl.* **2015**, *30*, 327.
- Cervantes-Uc, J. M.; Espinosa, J. I. M.; Cauich-Rodríguez, J. V.; Ávila-Ortega, A.; Vázquez-Torres, H.; Marcos-Fernández, A.; San Román, J. *Polym. Degrad. Stab.* 2009, 94, 1666.
- 48. Petrović, Z. S.; Zavargo, Z.; Flyn, J. H.; Macknight, W. J. *J. Appl. Polym. Sci.* **1994**, *51*, 1087.
- 49. Barikani, M.; Fazeli, N.; Barikani, M. J. Polym. Eng. 2013, 33, 87.
- 50. Pashaei, S.; Siddaramaiah; Syed, A. A. J. Macromol. Sci., Part A. 2010, 47, 777.
- 51. Cao, Y.; Mu, T. Ind. Eng. Chem. Res. 2014, 53, 8651.
- 52. Mineo, P. G.; Livoti, L.; Giannetto, M.; Gulino, A.; Lo Schiavo, S.; Cardiano, P. J. Mater. Chem. 2009, 19, 8861.
- 53. Mi, H.-Y.; Jing, X.; Napiwocki, B. N.; Hagerty, B. S.; Chen, G.; Turng, L.-S. J. Mater. Chem. B. 2017, 5, 4137.
- 54. Lakatos, C.; Czifrak, K.; Papp, R.; Karger-Kocsis, J.; Zsuga, M.; Keki, S. *Express Polym. Lett.* **2016**, *10*, 324.
- Eceiza, A.; Martin, M. D.; de la Caba, K.; Kortaberria, G.; Gabilondo, N.; Corcuera, M. A.; Mondragon, I. *Polym. Eng. Sci.* 2008, 48, 297.
- 56. Gao, R.; Zhang, M.; Wang, S.-W.; Moore, R. B.; Colby, R. H.; Long, T. E. *Macromol. Chem. Phys.* **2013**, *214*, 1027.
- 57. Zhang, M.; Hemp, S. T.; Zhang, M.; Allen, M. H.; Carmean, R. N.; Moore, R. B.; Long, T. E. *Polym. Chem.* 2014, 5, 3795.
- Behera, P. K.; Usha, K. M.; Guchhait, P. K.; Jehnichen, D.; Das, A.; Voit, B.; Singha, N. K. *RSC Adv.* 2016, *6*, 99404.
- 59. Fernández, M.; Carreño, L. Á.; Bernard, F.; Ligabue, R.; Einloft, S. *Macromol. Symp.* 2016, *368*, 98.
- Morozova, S. M.; Shaplov, A. S.; Lozinskaya, E. I.; Mecerreyes, D.; Sardon, H.; Zulfiqar, S.; Suaez-García, F.; Vygodskii, Y. S. *Macromolecules.* 2017, 50, 2814.
- 61. Cheng, H.; Wang, P.; Luo, J.; Fransaer, J.; De Vos, D. E.; Luo, Z. H. Ind. Eng. Chem. Res. **2015**, 54, 3107.

