RSC Advances

Syntheses and characterization of new poly(ionic liquid)s designed for CO$_2$ capture

T. O. Magalhães,[a] A. S. Aquino,[a] F. Dalla Vecchia,[c] F. L. Bernard,[ab] M. Seferin,[ab] S. C. Menezes,[d] R. Ligabue[ab] and S. Einloft*[ab]

A series of new poly(ionic liquid)s-p(IL)s based on polyurethane structures were synthesized and characterized and their behavior evaluated in CO$_2$ sorption tests under different pressures. The synthesized materials were characterized according to structure, composition, and thermal stability, by techniques such as FTIR, ^{1}H-NMR, TGA and DSC. The CO$_2$ sorption measurements were carried out in a Magnetic Suspension Balance-PTGA and proved that the change of the components of the polymer chain directly indicates the sorption behavior. The best performance for CO$_2$ sorption (75.7 mol% at 20 bar) was achieved with the p(IL) PUA-02a obtained from HDI and PTMG-2000 with [bmim]$^+$ as a counter-ion. The synthesized p(IL)s presenting nitrogenated and polyether structures into the backbone allied to imidazolium counter-cations proved to be worthy of note in the CO$_2$ sorption besides being based on poly(urethane) a versatile and low-cost material. The results also highlighted the good performance of PUA-02 when compared with traditional solvents used in pre-combustion process, as well as the p(IL)s described in the literature.

Introduction

Technologies for the capture, storage and utilization of CO$_2$, the primary greenhouse gas contributing to recent climate change, have been exhaustively designed. The investigation of efficient methods for CO$_2$ capture is imperative for any economically viable process, both for CO$_2$ transformation and sequestration in geological sites. In 1999, Blanchard and co-workers described the solubility of CO$_2$ in ionic liquids (ILs), highlighting the possibility of the use of these compounds as promising solvents for CO$_2$ capture.[1] More interesting than its dissolution ability, various ionic liquids show high selectivities for CO$_2$ absorption when compared with other flue gases. The search for the most promising ILs for CO$_2$ capture and its efficient separation from industrial gas streams is ongoing, but solubility studies continue to highlight the importance of such materials for this purpose.[2–9] On the other hand, Tang and co-workers reported that when ionic liquids are turned into polymeric forms, the CO$_2$ sorption capacity increases significantly,[10] and polymers obtained from tetraalkylammonium ionic liquids have increased sorption capacity 6.0 to 7.6 times, when compared with the ionic liquid 1-butyl-3-methylimidazolium

tetrafluoroborate [BMIM][BF$_4$].[11] Blasig and colleagues described the synthesis of p(LI)s: p[VBTMA][BF$_4$] and p[MATMA][BF$_4$], where the monomers [VBTMA][BF$_4$] and [MATMA][BF$_4$] were synthesized from *p*-vinyl benzyl trimethyl-ammonium chloride and 2-(methacrylate) ethyl trimethyl-ammonium, respectively, with NaBF$_4$ by free radical polymerization.[6] Recently, p(IL)s were synthesized to perform a facilitating role in some fields of polymer chemistry and materials science because these compounds combine the unique properties of ionic liquids with the flexibility and properties of macromolecular structures. The p(IL)s can be tailored to have properties that confer great potential for this material in a wide variety of applications, including its use as solid absorbents, ionic conductors, dispersant and stabilizer precursors, carbon materials, and porous polymers.[12,13] The sorption/desorption rates of solid polymers are very fast, and the desorption step is completely reversible. These polymers are highly promising alternatives for use as sorbent materials and membranes for CO$_2$ separation.[10,11,14–16] Recently, Luo and co-authors (2014) reported a pioneering work for chemical absorption of CO$_2$ that employs an anion-functionalized IL exploring gas chemisorp-tion with improved capacity.[17] Various combinations of ILs monomers, including esters and polyols, could be used to form new ionic polymeric structures for further examination in CO$_2$ capture. In this context, the goal of this work is to present new polymeric structures by using ionic liquids, both as a monomer in the main chain and as a counter ion, as well as the charac-terization of new structures and their behaviour in CO$_2$ sorption.

[a]PUCRS-Pontifical Catholic University of Rio Grande do Sul, Post-Graduation Program in Materials Engineering and Technology, Av. Ipiranga, 6681, Porto Alegre, Brazil. E-mail: einloft@pucrs.br; Tel: +55-51-3320-3500

[b]PUCRS-School of Chemistry, Porto Alegre, Brazil

[c]PUCRS-School of Engineering, Porto Alegre, Brazil

[d]CENPES-Centro de Pesquisas e Desenvolvimento Leopoldo Américo Miguez de Mello, Petrobras, Cidade Universitária, Av. Horácio Macedo, 950, Rio de Janeiro, Brazil

Paper

Experimental section

Polymer syntheses

Two different strategies for p(IL)s syntheses were performed, using experimental procedures described in literature: one protocol with two steps for anionic polyurethanes syntheses and a one-step method for a cationic polymer synthesis. The first method starts with an ionic polyurethane synthesis, followed by an ion exchange step. The polymers were obtained by the reaction between diols and/or polyols and diisocyanate in a solvent medium,[18] and further ion exchange was performed by the usual procedures for ILs anion exchange.[19–21] Neutralization procedures were performed according to common polyurethane syntheses.[22–24] Table 1 presents the p(IL)s annotation and raw materials used in all syntheses. For the cationic polymer synthesis, only one step is needed, which is reacting diisocyanate and polyol with a bishydroxy imidazolium functionalized ionic liquid replacing the diol. The representation of the anionic polymers is PUA-xx and for the cationic polymer, PUC-02c.

The PUA is formed in the first stage by using DBTDL (dibutyl tin dilaurate(IV)); (0.1% w/w) as a catalyst, the TMXDI (*m*-tetramethylxylene diisocyanate) or HDI (hexamethylene diisocyanate) as diisocyanate, DMBA (dimethylol butanoic acid) as a diol, and PTMG (polytetramethylene glycol, MM = 2000 or 1000g mol^{-1}) as polyol. The ion exchange step was performed by using imidazolium ionic salts (butyl methylimidazolium chloride) [bmim][Cl] or (dimethylbutyl methylimidazolium chloride) [dmbmim][Cl], which act as counter-cations for anionic polyurethanes. The byproduct HCl was removed from the reaction medium by reducing the system pressure. For polycation synthesis, the [dhim][Tf$_2$N] (bis (trifluoromethylsulfonyl)imide-dihidroxiimidazol-1,3) was used as a diol. The NCO/OH molar ratio of 1.01 was used in all reactions, as well as the temperature of 60 °C. In a typical reaction, a mixture of polyols (PTMG 0.01 mol/0.14 mol diol) were placed in a glass reactor under N$_2$ atmosphere, equipped with a mechanical stirrer, thermocouple, reflux condenser and addition funnel, followed by the addition of the catalyst and acetone (solvent), as shown in Fig. 1.

A solution of diisocyanate (0.15 mol in acetone) was then added *via* addition funnel. After the end of the reaction, the solid content as well as the acidity of the polymer (by titration with KOH) was quantified. The neutralization step occurred at a molar ratio COOH/IL = 1 : 1. Scheme 1 shows the chemical equations corresponding to the steps of the reaction synthesis of anionic and cationic polyurethane.

The reactions for polyurethane syntheses were followed by Fourier Transform Infrared Spectroscopy (FTIR), by the consumption of diisocyanates (TMXDI and HDI) over time, checked by the decreasing of the characteristic band of free NCO (2300–2200 cm^{-1}), being considered the end of the reaction, or the time when the characteristic NCO band was not detected by FTIR. After that, the neutralization step of the DMBA (anion exchange) was performed with [bmim][Cl].

Polymer characterization

The p(LI)s synthesized were characterized in solid form by Fourier Transform Infrared Spectroscopy (FTIR) using a Perkin-Elmer Model 100 FTIR Spectrum, in the range 4000–650 cm^{-1} and in hexadeuterated dimethylsulphoxide (DMSO-d6) solution (6% wt) by Proton Nuclear Magnetic Resonance (^{1}H-NMR) in a Varian Spectrometer 300 MHz (7.05 T of magnetic field) and a Bruker Spectrometer 400 MHz (9.4 T of magnetic field). The spectra were acquired at ambient temperature by using 5 mm NMR tubes. Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA) were performed in TA Instruments, models DSC Q20 and Q600 SDT, respectively. The DSC analyses were performed between −90 °C to 110 °C, with heating rate of 10 °C min^{-1} in a nitrogen atmosphere, and TGA ranging from room temperature to 1000 °C for 30 min, and a heating rate of 10 °C min^{-1} in a nitrogen atmosphere.

Sorption measurements

The sorption of CO$_2$ into the samples were gravimetrically assessed in a Magnetic Suspension Balance (MSB), (Rubotherm

Table 1 Representation of cationic and anionic polyurethanes

2-step reactions: polyanions (PUA)

Step 1:

PUs	Polyol	Diol	Diisocyanate
PUA-01	PTMG-1000	DMBA	HDI
PUA-02	PTMG-2000	DMBA	HDI
PUA-03	PTMG-1000	DMBA	TMXDI
PUA-04	PTMG-2000	DMBA	TMXDI

Step 2:

P(LI)s	PU	Counter-cation
PUA-01a	PUA-01	[bmim]$^+$
PUA-02a	PUA-02	[bmim]$^+$
PUA-02b	PUA-02	[dmbmim]$^+$
PUA-03a	PUA-03	[bmim]$^+$
PUA-04a	PUA-04	[bmim]$^+$

One-step reactions: polycations (PUC)

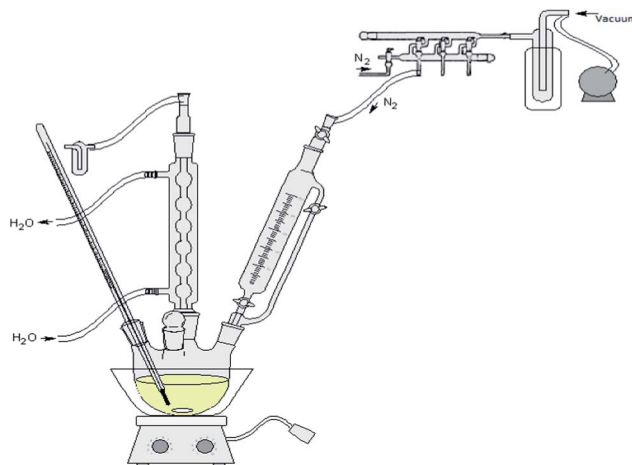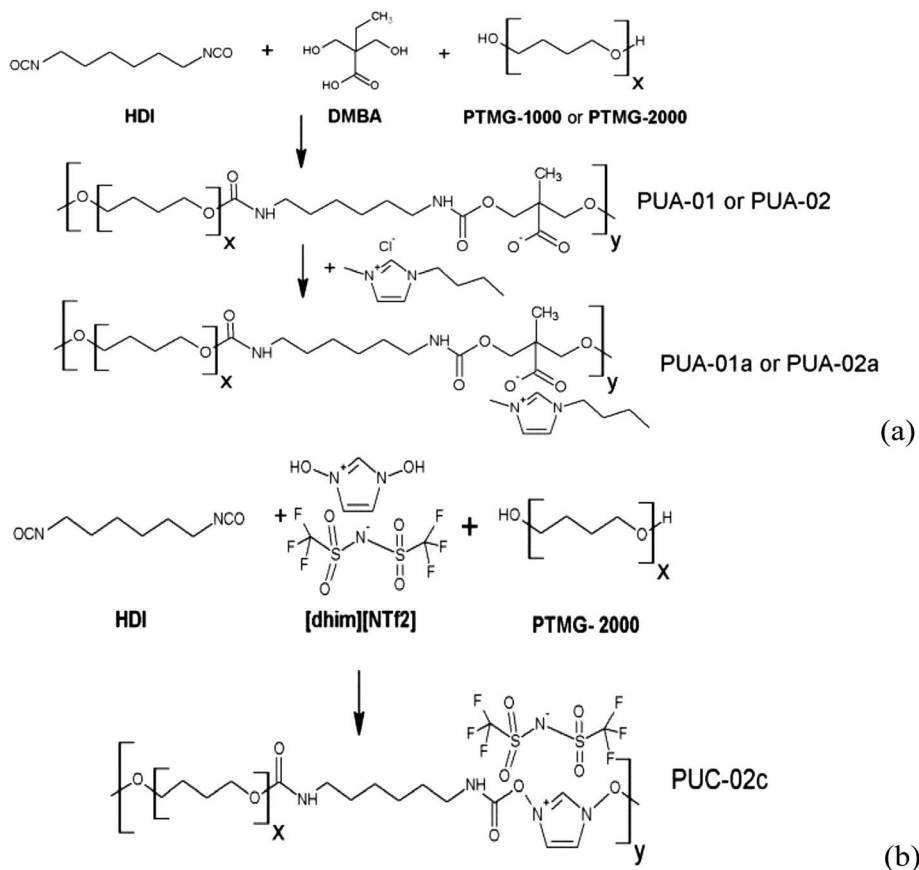| P(LI)s	Polyol	Diol	Diisocyanate	Counter-anion
PUC-02c	PTMG-2000	[dhim]$^+$	HDI	[NTf$_2$]$^-$

Fig. 1 Reaction apparatus.

Scheme 1 General reactions for polymer formation; polyanion synthesis (a) and polycation synthesis (b).

Prazisionsmesstechnik GmbH, 350 bar and 400 °C) equipped with a single sinker device for absorbate density determination and thermostatized with an oil bath (Julabo F25/±0.01 °C). The apparatus details are well described elsewhere.[6,25] When compared with other gravimetrical sorption methods, the MSB device has the advantage of allowing high-pressure sorption measurements because the sample can be potted into a closed chamber coupled with an external precise balance (accuracy of ±10 μg). The samples (0.06 to 0.09 g) were weighted and transferred to MSB sample containers, and the system was subjected to a 10^{-3} mbar vacuum at the temperature of the sorption measurement, 25 °C, for 24 h for polymer and IL and 5 min for MDEA. For all tests, constant weight was achieved during this time. The CO_2 (Air liquide/99.998%) was admitted into the MSB pressure chamber until the desired pressure was achieved, 1–20 bar in this study, pressure gauges with an accuracy of 0.01 bar. The solubility of CO_2 in the samples for each isotherm and pressure considered was measured 3–4 h after no additional weight increase for CO_2 sorption was observed. At this step of solubility of CO_2 in the polymer, the weight reading from the microbalance at pressure P and temperature T is recorded as $W_t(P,T)$. After each sorption test, CO_2 desorption was performed and with the exception of MDEA, all samples returned to their original weight at the end. The mass of dissolved CO_2 in the polymer, (W_g), was calculated using the eqn (1)

$$W_g = [W_t(P,T) - W_{sc}(P,T) + \rho(P,T) \times (V_{sc}(T) + V_s(T) + V_{sw}(P,T))] - W_s(vac,T) \quad (1)$$

where $W_{sc}(P,T)$ is the weight of sample container, and $\rho(P,T)$ stands for CO_2 density, directly measured with the MSB coupled single-sinker device, dismissing the application of any equation of state to calculate the sorption of CO_2. $V_{sc}(T)$ is the volume of the sample container, determined from a buoyancy experiment when no sample is charged into the sample container; $V_s(T)$ is the original volume of the sample; $V_{sw}(P,T)$ is the increase of the original polymer volume due to swelling; and $W_s(vac,T)$ is the weight of the sample at vacuum. The term $\rho(P,T) \times (V_{sc}(T) + V_s(T) + V_{sw}(P,T))$ represents the buoyancy force. In this work, the polymer volume change due to swelling was set to zero. For this reason, the solubility of CO_2 in the polymer is treated as the apparent solubility, as described by Blasig et al. (2007).[26] For the non-polymeric samples, the swelling was also disregarded. The results of CO_2 sorption were expressed in mol% (in terms of mer units).

Results and discussions

With respect to the characterization, the typical assignments of FTIR for PUA before ion exchange are the bands at 3333 cm^{-1} (N–H urethane), 2934 cm^{-1} (C–H of CH$_2$), 2859 cm^{-1} (C–H of CH$_3$), 1704 cm^{-1} (C=O urethane), 1531 cm^{-1} (H–N), 1463 cm^{-1}

(C–H of CH₃), 1416 cm⁻¹ (COO⁻), 1228 cm⁻¹ (C–N and C–O of urethane), and 1095 cm⁻¹ (C–O–C). The band at 1242 cm⁻¹ (C–H of Ar) is attributed to TMXDI (PUA-03 and PUA-04). The presence of the imidazolium group after ion exchange are confirmed by the bands at 1565 cm⁻¹ and 1438 cm⁻¹ (C=C and C=N) and 1170 cm⁻¹ (C–N) in the samples of PUA-(01-a,02-a,02-b,03-a,04-a; see Table 1). The polycation (PUC-02c) synthetized with [dhim][Tf₂N] as diol presents specific band assignments for anion at 1060 cm⁻¹ (S=O), 846 cm⁻¹ (N–S), 789 cm⁻¹ (C–S), 751 cm⁻¹ and 652 cm⁻¹ (C–F).

A typical ¹H-NMR spectrum of the sample PUA-02a is presented, as an example, in Fig. 2, where the signals corresponding to the polymer are detailed at the polymer structure represented in the same figure.

The peaks of the NMR spectrum showing the presence of the imidazolium cation are proven at 9.31 ppm, 7.86 ppm and 7.80 ppm, referring to protons H₂, H₄ and H₅ of the imidazolium ring, respectively. The alkyl chain of IL is presented in the NMR spectrum by three triplets (1.83 ppm, 1.32 ppm and 4.24 ppm, referring to CH₂) and two singlets (0.97 ppm and 3.98 ppm. referring to CH₃). The other signals are assigned to the polyurethane chain. The scheme of polymeric structure of the anionic and cationic poly(ionic liquid)s is shown in Fig. 3. For PUA-01a and PUA-02a HDI as the diisocyanate, DMBA as a diol and PTMG as a polyol were used as reactants and [bmim]⁺ as the counter-ion. The only difference among them is the molar mass of the polyol PTMG 1000 employed for PUA-01a synthesis and PTGM 2000 for PUA-02a. For the p(IL) PUA-02b, the same reactants as for PUA-02a were used except for the counter-anion, [dmbmim]⁺. For PUA-03a and PUA-04a TMXDI was used as the diisocyanate, DMBA as a diol, and PTMG as a polyol PTMG 1000 for PUA-03a and PTGM 2000 for PUA-04a and [bmim]⁺ as a

counter-anion in both cases. In addition, the poly(ionic liquid) PUC-02c was used as a reactant HDI in the diisocyanate, with [dhim][Tf₂N] (bis(trifluoromethylsulfonyl)imide-dihidroxi-imidazol-1,3) as a diol and PTMG 2000 as a polyol. In this case, the imidazolium is introduced in the main polymeric chain, and [Tf₂N]⁻ is the counter-anion.

The synthesized polymers presented thermal decomposition temperatures (onset temperature) varying from 205 °C to 249 °C because the structure containing the imidazolium cation into the polymeric chain is the most stable. The DSC results showed that the samples presented glass transition temperatures (Tg) (PUA-02, −18.7 °C; PUA-04, −13.8 °C; PUA-01a, −47.5 °C; PUA-02b, −24.4 °C; PUC-02c, −18.7 °C; and PUA-04a, −46.3 °C) except PUA-01, PUA-02a, PUA-03 and PUA-03a, which could not have Tg determined by the same technique. For the polymers where polyol with a molar mass of 2000 was employed, a small endothermic peak is observed, which could be assigned to the melting (Tm 22.7 °C, approximately) of a crystalline micro-phase.²⁷ The samples PUC-02c and PUA-04a presented Tc (−8.15 °C). The choice for the production of p(IL)s based on poly(urethane) structures had been taken based both in the versatility and low costs of these materials. They present basic nitrogenated and polyether groups in its backbone and can also allow the insertion of aromatic groups into its structures. All these chemical groups can improve the CO₂ sorption,²⁸⁻³⁰ the studies of which began with the assessment of the performance of polymer PUA-02, at which time there was no introduction of imidazolium cation as a counter-ion. It is apparent in Fig. 4 the sorption capacity of this polymer was lower than the value achieved for the materials that had the same polymeric structures and imidazolium as a counter-cation (PUA-02a).
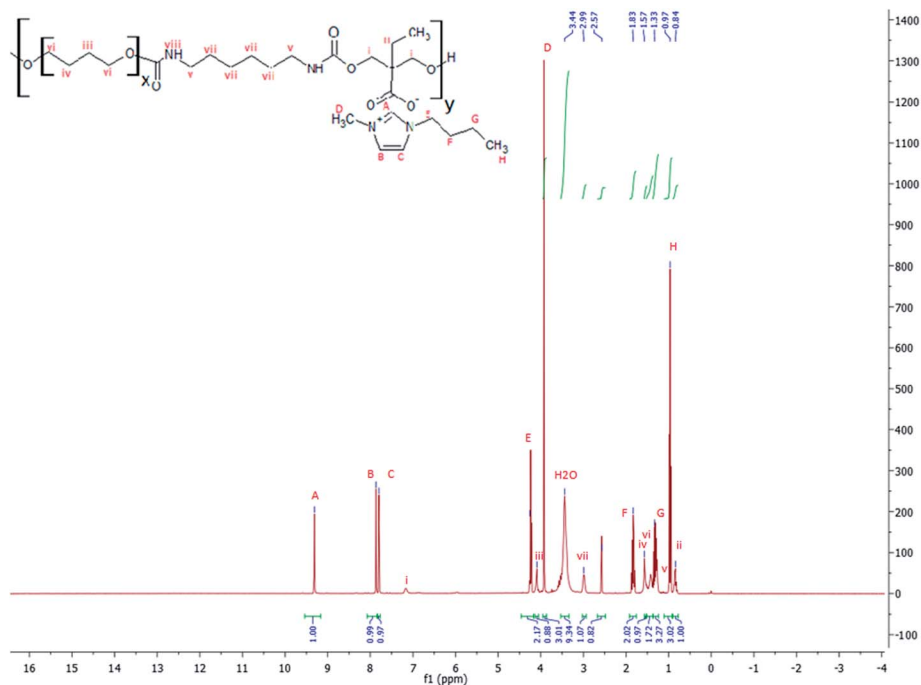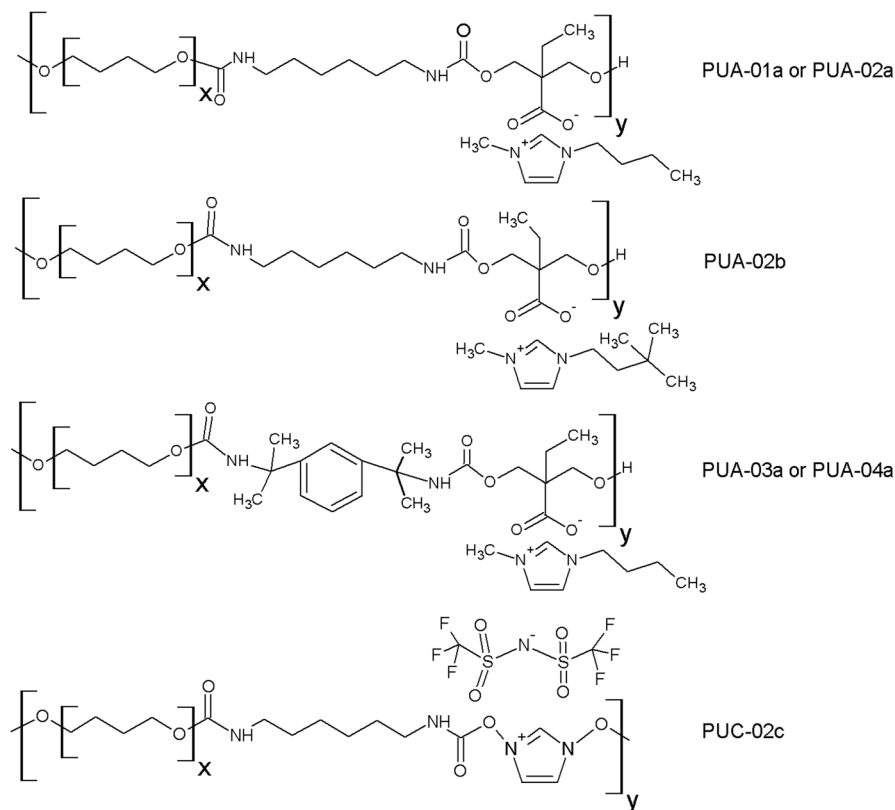

Fig. 2 ¹H-NMR spectra for the polyanion PUA-02a.

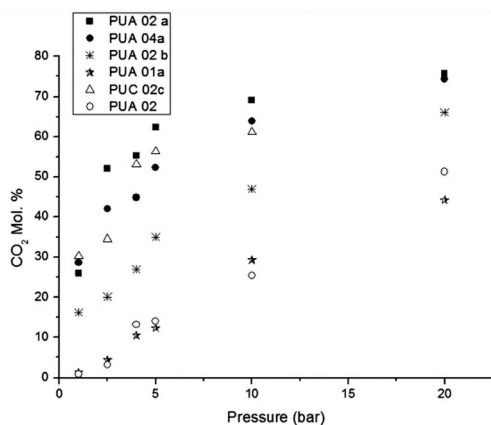Fig. 3 Scheme of the polymeric structures.

Fig. 4 CO_2 sorption at 25 °C for synthesized polymers.

For a pressure of 20 bar, PUA-02a presented a CO_2 sorption of 75.7 mol%, and PUA-02 presented a value of 51.2 mol%, showing that the absorption capacity of a material can be influenced by the presence of an imidazolium cation. To study the influence of the polyether groups in the polymers' CO_2 sorption capacities, two polymeric structures were synthesized by using the same reactants but the molar mass of the PTMG (1000 and 2000) was varied. It is apparent in Fig. 4 that when the polymer contains polyether with a higher molar mass in its structure, CO_2 sorption was improved. PUA-01a and PUA-02a presented respective CO_2 sorption values at 20 bar of 44.2 mol% and 75.7 mol%. This

result is in agreement with the conception of an "ideal" physical solvent for CO_2 capture, partially based on Pearson's "hard and soft acid–base" principles in which a Pearson "hard base" (polyether groups) allows a strong affinity to CO_2. A second point of emphasis is the influence of PTMG molar mass in the distance between the ionic sites. It was previously mentioned in the literature that when the ionic sites are distant from one another, the steric hindrance is smaller, thereby promoting CO_2 interaction with the polymer and, consequently, CO_2 sorption.[12]

The insertion of an aromatic structure into the polymeric chain did not significantly improve CO_2 sorption. Comparing the sorption results for PUA-02a that used HDI as a diisocyanate with that of PUA-04a that used TMXDI as a diisocyanate, it can be seen that PUA-02a presented a CO_2 sorption of 62.3 mol% at 5 bar and PUA-04a presented a sorption value of 52.2 mol% at the same pressure. At higher pressures, the behavior is different, and the polymer that contains the aromatic structure showed high absorption capacity (74.3 mol% *versus* 75.7 mol% for the linear structure). Although the aromatic structures are known to enhance absorption of CO_2,[27,29] the steric hindrance of the aromatic structure can be taken in account, making CO_2 interaction difficult with the polymeric structures at lower pressures.[28] These results showed that CO_2 interacts preferentially with polar/ionic groups of the polymer chain at low pressures and begins to interact with the aromatic groups (electronic interaction) surpassing the steric hindrance at high pressures. When the imidazolium cation was introduced in the polymeric chain (PUC-02c), the sorption results were lower
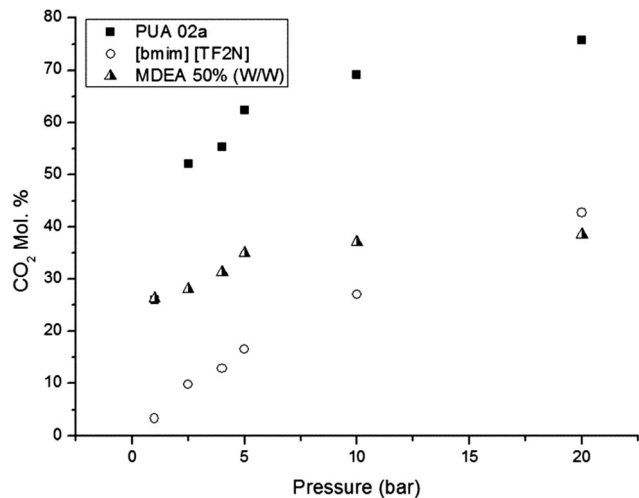
Fig. 5   Comparison of p(IL) with amine solution and IL.

when compared with the imidazolium structure as a counter-cation (PUA-02a). The sorption values at 5 bar were 56.3 mol% and 62.3 mol%, respectively. It is known that imidazolium-based ionic liquids with branched alkyl chains have improved CO_2 sorption capacity than those with linear alkyl chains,[31] but this tendency was not observed in this study. When comparing PUA-02a and PUA-02b with counter-cation $[bmim]^+$ and $[dmbmim]^+$, respectively, it is apparent that with $[bmim]^+$, the sorption values are considerably elevated (at 20 bar, PUA-02a presented a CO_2 sorption of 75.7 mol%, and PUA-02b presented a CO_2 sorption of 66.1 mol%). This behavior can likely be attributed to steric hindrance of the branched structure when compared with that of the linear. The CO_2 sorption values for PUA-02a (69.0 mol% of CO_2, at 10 bar and 25 °C) and for p(IL) P [VBTMA][BF$_4$] (approximately 39 mol% at 10 atm (10, 13 bar) and 22 °C) synthesized by Tang and co-workers (2005)[10] proved the higher capacity for CO_2 sorption presented for PUA-02. The comparison among the CO_2 sorption performance of PUA-02a, an ionic liquid ($[bmim][Tf_2N]$) and a commercial solvent (MDEA) at different total pressures was also assessed, and the results are presented in Fig. 5. The tests were performed with an aqueous MDEA 50% (w/w) because this solvent is commonly employed for CO_2 capture in the pre-combustion process. For MDEA, CO_2 solubility has increased until 5 bar, remaining almost constant for higher pressures, whereas for PUA-02a the CO_2 sorption continued to increase significantly with pressure augmentation, which was the same trend showed by the IL. The PUA-02a showed higher CO_2 sorption capacity than MDEA for the entire pressure range evaluated. When compared with MDEA, the IL has poorer CO_2 dissolution capacity for low pressures. However, at high pressures (20 bar), this behaviour is reversed, and the respective sorption capacities for IL and MDEA are 42.7 mol% and 38.6 mol%.

Conclusions

Novel poly(ionic liquid)s based on polyurethane, a versatile and low-cost material, were synthesized and characterized. The structure of these p(IL)s was designed to improve CO_2 sorption by the modification of poly(urethane) structures. The presence of nitrogenated and polyether structures in their backbones allied to the imidazolium ring has proved to be interesting for CO_2 capture. The best performance for CO_2 sorption (75.7 mol% at 20 bar) was achieved with the p(IL) PUA-02a obtained from HDI and PTMG-2000 with $[bmim]^+$ as a counter ion. The results also highlighted the good performance of PUA-02 when compared with traditional solvents used in the pre-combustion process, as well as the p(IL)s described in the literature.

Notes and references

1 L. A. Blanchard, D. Hancu, J. Eric and J. F. Brennecke, *Nature*, 1999, **399**, 28.
2 J. L. Anthony, E. J. Maginn and J. F. Brennecke, *J. Phys. Chem. B*, 2002, **106**, 7315.
3 C. Cadena, J. L. Anthony, J. K. Shah, T. I. Morrow, J. F. Brennecke and E. J. Maginn, *J. Am. Chem. Soc.*, 2004, **126**, 5300.
4 J. Jacquemin, P. Husson, V. Majer and I. Cibulka, *J. Chem. Eng. Data*, 2007, **52**, 2204.
5 Y. S. Kim, W. Y. Choi, J. H. Janf, K. P. Yoo and C. S. Lee, *Science*, 2005, 439.
6 A. B. Blasig, J. Tang, X. Hu, Y. Shen and M. Radosz, *Fluid Phase Equilib.*, 2007, **256**, 75.
7 E. K. Shin, B. C. Lee and J. S. Lim, *J. Supercrit. Fluids*, 2008, **45**, 282.
8 S. Raeissi and C. J. Peters, *J. Chem. Eng. Data*, 2009, **54**, 382.
9 Y. S. Sistla, L. Jain and A. Khanna, *Sep. Purif. Technol.*, 2012, **97**, 51.
10 J. Tang, H. Tang, W. Sun, H. Plancher, M. Radosz and Y. Shen, *Chem. Commun.*, 2005, 3325.
11 J. Tang, W. Sun, H. Tang, M. Radosz and Y. Shen, *Macromolecules*, 2005, **38**, 2037.
12 J. Yuan and M. Antonietti, *Polymer*, 2011, **52**, 1469.
13 J. Yuan, D. Mecerreyes and M. Antonietti, *Prog. Polym. Sci.*, 2013, **38**, 1009.
14 J. Tang, Y. Shen, M. Radosz and W. Sun, *Ind. Eng. Chem. Res.*, 2009, **48**, 9113.
15 J. Tang, H. Tang, W. Sun, M. Radosz and Y. Shen, *Polymer*, 2005, **46**, 12460.
16 J. Tang, H. Tang, W. Sun, M. Radosz and Y. Shen, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**, 5477.
17 X. Y. Luo, F. Ding, W. J. Lin, Y. Q. Qi, H. R. Li and C. M. Wang, *J. Phys. Chem. Lett.*, 2014, **5**, 381.
18 V. Lima, N. Pelissoli, J. Dullius, R. Ligabue and S. Einloft, *J. Appl. Polym. Sci.*, 2010, **115**, 1797.

19 J. S. Wilkes, J. A. Levisky, R. A. Wilson and C. L. Hussey, *Inorg. Chem.*, 1982, **21**, 1263.

20 R. F. Souza, J. Dupont and J. E. d. L. Dullius, *J. Braz. Chem. Soc.*, 2006, **17**, 48.

21 C. C. Cassol, G. Ebeling, B. Ferrera and J. Dupont, *Adv. Synth. Catal.*, 2006, **348**, 243.

22 M. A. Perez-Liminana, F. Aran-Aís, A. M. Torro-Palau, A. C. Orgilés-Barcelo and J. M. Martín-Martínez, *J. Adhes. Adhes.*, 2005, **25**, 507.

23 Z. Yang, D. Wicks, C. Hoyle, H. Pu, J. Yuan, D. Wan and Y. Liu, *Polymer*, 2009, **50**, 1717.

24 V. García-Pacios, V. Costa, M. Colera and J. M. Martín-Martínez, *Prog. Org. Coat.*, 2011, **71**, 136.

25 F. Dreisbach and H. W. Losch, *J. Therm. Anal. Calorim.*, 2000, **62**, 515.

26 A. Blasig, J. Tang, X. Hu, S. P. Tan, Y. Shen and M. Radosz, *Ind. Eng. Chem. Res.*, 2007, **46**, 5542.

27 P. Król, *Prog. Mater. Sci.*, 2007, **52**, 915.

28 S. Mallakpour and M. Dinari, *e-Polym.*, 2007, **35**, 1.

29 H. W. Pennline, D. R. Luebke, K. L. Jones, C. R. Myers, B. I. Morsi, Y. J. Heintz and J. B. Ilconich, *Fuel Process. Technol.*, 2008, **89**, 897.

30 J. Lu, F. Yan and J. Texter, *Prog. Polym. Sci.*, 2009, **34**, 431.

31 M. J. Muldoon, S. N. V. K. Aki, J. L. Anderson, J. K. Dixon and J. F. Brennecke, *J. Phys. Chem. B*, 2007, **111**, 9001.

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