Abstract: The growing concern for climate change and global warming has given rise to investigations in various research fields, including one particular area dedicated to the creation of solid sorbents for efficient CO$_2$ capture. In this work, a new family of poly(ionic liquid)s (PILs) comprising cationic polyureas (PURs) with tetrafluoroborate (BF$_4$) anions has been synthesized. Condensation of various diisocyanates with novel ionic diamines and subsequent ion metathesis reaction resulted in high molar mass ionic PURs ($M_w = 12 \div 173 \times 10^3$ g/mol) with high thermal stability (up to 260 $^\circ$C), glass transition temperatures in the range of 153–286 $^\circ$C and remarkable CO$_2$ capture (10.5–24.8 mg/g at 0 $^\circ$C and 1 bar). The CO$_2$ sorption was found to be dependent on the nature of the cation and structure of the diisocyanate. The highest sorption was demonstrated by tetrafluoroborate PUR based on 4,4$'$-methylene-bis(cyclohexyl isocyanate) diisocyanate and aromatic diamine bearing quinuclidinium cation (24.8 mg/g at 0 $^\circ$C and 1 bar). It is hoped that the present study will inspire novel design strategies for improving the sorption properties of PILs and the creation of novel effective CO$_2$ sorbents.

Keywords: poly(ionic liquid)s; ionic polyureas; ionic polyurethanes; CO$_2$ capture; solid adsorbent

1. Introduction

The anthropogenic emission of CO$_2$, particularly from fossil fuel combustion, is one of the main sources of greenhouse gas emission and global warming [1,2]. The search for effective methods to address the effects of climate change due to increased CO$_2$ emissions relates to important challenges facing the global chemical community [2,3].

Purification of flue gas streams can add important value to the fight against CO$_2$ emissions. Recently, among other promising approaches, the application of polymeric ionic liquids or poly(ionic
Liquid(s) (PILs) as potential solid sorbent materials for CO₂ capture and separation gained significant attention [4]. Such attention was deserved due to the fact that PILs, being a subclass of polyelectrolytes, combine the advantages of polymers (processability, film-forming properties, solid state, light weight, etc.) and ionic liquids (high thermal and electrochemical stabilities, enhanced ionic conductivity, high gas absorption, affinity to CO₂, etc.) [4–11]. The broad variety of PILs that can be prepared using countless combinations of cations (ammonium, pyridinium, imidazolium, phosphonium, 1,2,3-and 1,2,4-triazolium . . .) and anions (halide, perfluorinated sulfonimide . . .) allows the ability to control their properties and CO₂ sorption in particular [4,10]. Among other tools for gaining the desirable control is the variation in the nature of polymer backbone and side groups as well as playing with macromolecular architecture by synthesis of linear, branched, star-shaped or cross-linked polymers. Moreover, it was recently shown that PILs possess several orders of magnitude higher CO₂ sorption capability than respective ionic-liquid-like monomers and higher CO₂ capture and desorption rates in comparison with ionic liquids (ILs) [12–15]. The light weight, the ease of handling, comparatively low cost and safety for humans and the environment were named among other advantages of PILs in the CO₂ sorption process [4,10,12,16].

Over the past 10 years, various sorbents derived from both linear [4,17–19] and cross-linked [20–22] PILs have been investigated (see the examples in Scheme 1 and in Table 2). To enhance PILs’ CO₂ sorption capacity, a number of approaches have been applied, such as PILs’ immobilization on carbon fibers [23,24], grafting of PILs on silica nanoparticles [25–27], incorporation of PILs into a metal–organic framework (MOF) [28–31] or preparation of ordered porous PIL-based crystallines [32]. It was found that the CO₂ adsorption behavior of PILs is dependent on many factors, such as their chemical composition (nature of the cation and anion, type of the polymer backbone), molar mass and pore structure (surface area, pore size, atomic packing, etc.) [4,10].

Despite the fact that cross-linked PILs generally demonstrate higher sorption properties than their linear analogues, the study of the later is crucial for a more detailed fundamental insight into how the polymer structure affects the complex CO₂ sorption mechanism [4,33]. Previously, the attention was mainly focused on understanding the influence of cations’ and anions’ structures on the CO₂ sorption properties of PILs [4,13]. Effect of the cation’s structure. Comparing the influence of the cation’s structure on PILs’ CO₂ capture, it was found that aliphatic cations (ammonium, quinuclidinium, etc.) commonly demonstrate higher CO₂ sorption capacity than polyelectrolytes with aromatic cations (pyridinium, imidazolium, etc.) [16,17,34]. Effect of the number of cations. The higher the number of cations in the monomer unit (repeat unit charge density), the better the CO₂ sorption ability of PILs [16]. Effect of the anion’s structure. The nature of the counter anion has a pronounced effect on the CO₂ sorption of PILs as well. This was widely studied using such anions as R₃COO (R₃=CF₃, C₃F₇, CH₃), R₂SO₃ (R₂=CF₃, CH₃, C₆H₄–), (CF₃SO₂)₂N, BF₄, PF₆, NO₃, N(CN)₂, B(CN)₃, FeCl₃Br, ZnCl₂Br, CuCl₂Br [14–16,18,19,27,35,36]. Among this vast variety of anions, the best CO₂ uptake was demonstrated by CH₃COO, B(CN)₃, BF₄ and PF₆ containing PILs [15,16]. These results were in part explained for cellulose-based PILs by semi-empirical molecular dynamics simulations suggesting that different CO₂ sorption capacities of PILs are driven by the cation–anion coordination
peculiarities [15]. Comparing (CF$_3$SO$_2$)$_2$N and PF$_6$ anions, it was revealed that bulkier and significantly polar bis(trifluoromethylsulfonyl)imide ion is located near the most CO$_2$-philic groups of imidazole cation and cellulose backbone, thus shielding them from interaction with CO$_2$. In contrast, the same effect is much less pronounced for PF$_6$ containing PILs, thus allowing for a higher number of centers for interaction with CO$_2$ molecules and for higher CO$_2$ sorption, respectively [15].

**Effect of the polymer backbone.** To date, the majority of PILs studied for CO$_2$ capture are based on carbochain polymers, namely those derived from radical polymerization of styrene derivatives and (metha)acrylates (see Scheme 1 and Table 2) [4,10,14,17,37]. However, more detailed consideration allows for the conclusion that the polymer backbone plays an important role [4,10]. Thus, the subsequent transfer from carbochain to heterochain polymers is often accompanied by a significant increase in CO$_2$ sorption [15,16,38,39]. This can be explained by the presence of polar groups in the polymer backbone capable of additional interaction with CO$_2$ molecules—for example, by hydrogen bonding [4,10,40].

In ionic polyesters and polyethers, CO$_2$ can additionally interact with the oxygen atom of the ester or ether linkages, as was shown by the dissolution study of various esters in supercritical scCO$_2$ by Raman vibrational spectroscopy [41]. The secondary amine groups provide an effective adsorbate–adsorbent interaction in the capture of CO$_2$ by polyamines [42]. In the same way, the amine group in ionic polyamides and polyurethanes [16,38,40] will offer an additional interaction with CO$_2$ molecules and, as a result, increased CO$_2$ capture capacity in comparison with carbochain PILs with similar cation/anion pairs. Therefore, the increase in the content of amine groups from two in ionic polyurethanes to four in ionic polyureas potentially should increase the points of interaction and subsequently the CO$_2$ sorption capacity of PILs. Moreover, the synthesis of ionic polyureas with structures identical to previously developed ionic polyurethanes [16] will serve as a convenient model system for the comparison and estimation of the influence of hydrogen bonding on PILs’ CO$_2$ capture.

Utilization of PILs in the commercial CO$_2$ capture process requires the elaboration of low-cost and simple ionic monomers. Thus, for the synthesis of ionic polyureas, two ionic diamines, namely 3,3-bis(4-aminophenyl)-1-ethylquinuclidin-1-ium iodide and 3-amino-1-(5-(3-aminoquinuclidin-1-ium-1-yl)penty1)-quinuclidin-1-ium bromide, were suggested (Scheme 2). The first one was previously developed by our group [43], while the second is newly designed, taking into account the aim of the work consisting of the comparison of ionic polyureas with ionic polyurethanes reported antecedently [16]. Both monomers differ from known ionic diamines [44–46] by the simplicity of their synthesis, which consists of only two reaction steps (see Materials and Methods for details).

![Scheme 2. Structures of ionic diamines (monomers) used in the present study.](image)

Relying on the assumption that the increase in the number of secondary amino groups in the polymer backbone can improve the CO$_2$ sorption properties of PILs, the aim of the present study was to synthesize a series of ionic polyureas and to investigate their ability for CO$_2$ capture (Scheme 3). Thus, in this work, we report synthesis and properties investigation of five novel tetrafluoroborate PILs based on ionic polyureas (PURs) varying in the structure of diisocyanate (PUR1:BF$_4$–PUR3:BF$_4$), the nature of the cations (PUR3:BF$_4$–PUR6:BF$_4$) and their quantity (PUR3:BF$_4$ and PUR6:BF$_4$).
2. Materials and Methods

2.1. Materials

N-Methyldiethanolamine (>99%, Aldrich, Darmstadt, Germany), quinuclidinol-3 (99%, Aldrich, Darmstadt, Germany), 3-aminoquinuclidine dihydrochloride (98%, TCI Europe, Zwijndrecht, Belgium), potassium tetrafluoroborate (99%, Acros, Geel, Belgium), potassium carbonate (K\textsubscript{2}CO\textsubscript{3}, > 98%, Aldrich, Darmstadt, Germany), tin(II) 2-ethylhexanoate (98%, Aldrich, Darmstadt, Germany), iodoethane (99%, Aldrich, Darmstadt, Germany), N,N-dimethylformamide (DMF, anhydrous, 99.8%, Acros, Geel, Belgium), dichloromethane (CH\textsubscript{2}Cl\textsubscript{2}, anhydrous, 99.8%, Aldrich, Darmstadt, Germany), diethyl ether (Et\textsubscript{2}O, > 99%, Aldrich, Darmstadt, Germany), acetonitrile (CH\textsubscript{3}CN, anhydrous, 99.8%, Acros, Geel, Belgium), ethyl acetate (AcOEt, anhydrous, 99.8%, Acros, Geel, Belgium), 1,1,1,3,3,3-hexafluoro-propan-2-ol (HFIP, 99%, Apollo Scientific, Stockport, UK), 4,4′-methylenediisocyanate (H\textsubscript{12}MDI, 2, 99%, Covestro AG, Leverkusen, Germany) and isophorone diisocyanate (IPDI, 3, 98%, Aldrich, Darmstadt, Germany) were used without purification.

Toluene-2,4-diisocyanate (TDI, 1, 95%, Aldrich, Darmstadt, Germany) was purified by vacuum distillation. Meanwhile, 1,5-Dibromopentane (97%, Aldrich, Darmstadt, Germany) and N,N-bis-(3-aminopropyl)methylamine (6, 96%, Aldrich, Darmstadt, Germany) were purified by vacuum distillation over CaH\textsubscript{2} and NaOH, respectively.

2.2. Synthesis of Ionic Diamine 3,3-Bis(4-Aminophenyl)-1-Ethylquinuclidin-1-Ium Iodide (4)

The 3,3-Bis(4-aminophenyl)-1-ethylquinuclidin-1-ium iodide monomer (4) was obtained according to the procedure reported by our group previously [43] (Scheme 4).
m.p. 293–294 °C; 1H NMR (400 MHz, DMSO-d6, δ ppm): 7.02–7.04 (d, 4H, J = 8.2 Hz, -C6H4-(10)), 6.46–6.48 (d, 4H, J = 8.2 Hz, -C6H4-(11)), 4.95 (s, 4H, -NH2), 4.07 (m, 2H, Q(2)), 3.10–3.36 (m, 7H, Q(4,6,7), N-CH2CH3), 1.77–1.88 (m, 3H, N-CH2CH3); 13C NMR (100 MHz, DMSO-d6, δ ppm): 145.5 (-C6H4-(12)), 137.4 (-C6H4-(9)), 126.9 (-C6H4-(10)), 113.9 (-C6H4-(11)), 59.4 (Q(2)), 49.2 (N(CH3)), 46.8 (Q(3,4)), 43.5 (Q(6,7)), 28.1 (Q(5)), 23.3 (q(8), N-CH2CH3). 

2.3. Synthesis of 3-Amino-1-(5-(3-Aminoquinuclidin-1-Ium-1-Yl)Pentyl)-Quinuclidin-1-Ium Bromide (5)

Synthesis of ionic monomer 5 was conducted via two reaction steps, as presented in Scheme 5.

Scheme 5. Synthesis of ionic monomer 5.

3-Aminoquinuclidine dihydrochloride (3.00 g, 0.015 mol) was dissolved in 30% NaOH aqueous solution at room temperature. The solution was further extracted with diethyl ether (5 × 25 mL) and the combined extracts were dried over K2CO3. Potash was filtered off and diethyl ether was evaporated under reduced pressure. Then, 3-Aminoquinuclidine (Scheme 6) was obtained as white crystalline solid and was dried for 8 h at 40 °C/12 mm Hg. Yield: 1.23 g (64%); m.p. = 219–222 °C (218–220 °C [47]); 1H NMR (400 MHz, DMSO-d6, δ ppm): 2.93 (m, 1H, Q (2a)), 2.79 (m, 1H, Q (3)), 2.72–2.30 (m, 6H, Q (6,7), NH2), 2.14 (m, 1H, Q (2b)) 1.84 (m, 1H, Q (5a)), 1.53 (m, 1H, Q (8b)), 1.48 (m, 1H, Q (4)), 1.39 (m, 1H, Q (8a)), 1.18 (m, 1H, Q (5b)). 13C NMR (100 MHz, DMSO-d6, δ ppm): 57.20 (Q(2)), 47.25 (Q(3)), 46.67 (Q(6)), 45.44 (Q(7)), 28.23 (Q(4)), 25.45 (Q(8)), 18.43 (Q(5)).

The solution of 1,5-dibromopentane (1.30 g, 5.67 mmol) in 20 mL of anhydrous CH3OH was added dropwise to the solution of 3-aminoquinuclidine (1.50 g4, 11.91 mmol) in 30 mL of CH3OH at room temperature under inert atmosphere. The reaction mixture was stirred for 24 h at ambient temperature,
whereupon product was isolated by precipitation into the excess of anhydrous Et₂O and subsequent filtration. Diamine 5 was obtained as white powder that was dried for 8 h at 60 °C/1 mm Hg. Yield: 2.50 g (93%); m.p. 89-90 °C; ¹H NMR (400 MHz, DMSO-d₆, δ ppm): 4.0–3.7 (br. m., 4H, NH₂) 3.66 (m, 2H, Q (2a)), 3.39 (br. m., 10H, Q (3,6,7)), 3.22 (br. t, 4H, N-CH₂-CH₂-CH₂-J = 7.3 Hz), 2.98 (m, 2H, Q (2b)), 1.98 (m, 2H, Q (4)), 1.89–1.60 (m, 12H, Q (5,8), N-CH₃); ¹³C NMR (100 MHz, DMSO-d₆, δ ppm): 67.30 (Q (2)), 63.88 (Q(3)), 62.94 (N-CH₂-CH₂-CH₂-J), 1.22–1.24 (m, 2H, N-CH₂-CH₂-CH₂-J); Calc. for C₁₉H₃₈N₄Br₂: C 47.31; H 7.94; N 11.62; found: C 47.06; H 7.99; N 11.45.

2.4. Polycondensation

Iodide PURs, namely PUR1.I–PUR3.I, were synthesized by polycondensation of respective diisocyanates with ionic diamine 4. Bromide PUR6.Br and neutral PUR4 were prepared by reaction of IPDI diisocyanate with ionic diamine 5 and noncharged diamine 6, respectively. All mentioned polyureas were synthesized following the general procedure reported for PUR1.I below, with the exception that PUR1.I–PUR3.I were precipitated from DMF solution into the excess of water, while PUR6.Br and PUR4 were precipitated into the acetone excess.

Ionic diamine 4 (1.0370 g, 2.3 mmol) and disiocyanate 1 (0.4019 g, 2.3 mmol) were dissolved in 7 mL of anhydrous DMF in a Schlenk flask inside an argon-filled glovebox (MBRAUN MB-Labstar, Garching, Germany, H₂O and O₂ content < 0.5 ppm). The flask was closed with a rubber septum, taken out of the glovebox and placed in a preheated to 60 °C oil bath.

Then, 2-(Ethyl)hexanoate tin (II) (0.0233 g, 0.06 mmol, 2.5% mol with respect to 4) was dissolved separately in 0.5 mL of anhydrous DMF inside the glovebox. The flask was then taken out of the glovebox and the catalyst solution was injected via syringe technique into the preheated solution of monomers. The reaction mixture was stirred at RT for 12 h. The desired polymer was isolated by precipitation into the excess of ethyl acetate, thoroughly washed with water and acetone, and thoroughly washed with water and acetone. PUR1.I was isolated as yellow powder and dried for 12 h at 100 °C/1 mm Hg. Yield: 1.24 g (87%).

2.5. Quaternization of PUR4

The solution of C₂H₅I (4.67 g, 29.93 mmol) in 20 mL of DMF was added dropwise to the solution of PUR4 (1.10 g, 2.99 mmol) in 50 mL of DMF preheated at 40 °C. Stirring was continued at 40 °C for 12 h, whereupon polymer was isolated by precipitation into the excess of ethyl acetate and thoroughly washed with ethyl acetate. PUR5.I in a form of white powder was dried for 12 h at 70 °C/1 mm Hg. Yield: 1.48 g (95%).

2.6. Ion Exchange

All ionic PURs with tetrafluoroborate anions, namely PUR1.BF₄–PUR6.BF₄, were synthesized via anion metathesis reaction with the excess of KBF₄. In the case of hydrophobic PUR1.I–PUR3.I, the ion exchange reaction was performed in DMF:CH₃CN mixture (4:1 by volume), while for hydrophilic PUR5.I and PUR6.Br, metathesis was carried out in water. General procedures are reported below for PUR1.BF₄ and PUR6.BF₄.

KBF₄ (0.48 g, 3.82 mmol) was added in one shot to the solution of PUR1.I (1.59 g, 2.55 mmol) in 50 mL of DMF:CH₃CN (4:1 by volume). The reaction suspension was stirred at RT for 12 h. The desired polymer was isolated by precipitation into the excess of water, thoroughly washed with water and dried for 4 h at ambient temperature. Further on, the polymer was redissolved in HFIP and precipitated into the excess of ethyl acetate. PUR1.BF₄ in the form of yellow-beige powder was dried for 12 h at 100 °C/1 mm Hg. Yield: 1.37 g (92%).

The solution of KBF₄ (1.12 g, 8.87 mmol) in 10 mL of water was added dropwise to the solution of PUR6.Br (2.50 g, 3.55 mmol) in 45 mL of water. The precipitation of the polymer was immediately observed, whereupon it was collected by centrifugation (15,000 rpm, 10 min, 5 °C), thoroughly washed
with water and dried for 4 h at ambient temperature. Afterwards, polymer was redissolved in HFIP and precipitated into the excess of ethyl acetate. **PUR6.BF₄** in the form of yellow powder was dried for 12 h at 160 °C/1 mm Hg. Yield: 1.71 g (67%).

**PUR1.BF₄**

$^{1}$H NMR (600 MHz, DMSO-d$_6$, δ ppm, Scheme 7): 9.04, 8.68, 8.57 (m, 4H, NH), 7.90 (m, 1H, T-2), 7.39 (m, 8H, B-2, B-3), 7.22 (m, 1H, T-6), 7.07 (m, 1H, T-5), 4.20 (m, 2H, Q-2), 3.43 (m, 2H, NCH$_2$CH$_3$), 3.33 & 3.14 (m, 4H, Q-6 & Q-7), 3.32 (m, 1H, Q-4), 2.18 (s, 3H, CH$_3$), 1.94 & 1.77 (m, 4H, Q-5 and Q-8), 1.33 (m, 3H, NCH$_2$CH$_3$); $^{13}$C NMR (151 MHz, DMSO-d$_6$, δ ppm): 152.43 (CONH), 138.84 (B-1,4), 137.47 (T-3), 126.94 (B-2,6), 120.59 (T-4), 118.69 (B-3,5), 113.15 (T-6), 111.33 (T-2), 62.50 (Q-2), 59.14 (NCH$_2$CH$_3$), 52.97 (Q-6, Q-7), 45.95 (Q-3), 27.04 (Q-4), 21.12 (Q-5, Q-8), 17.83 (CH$_3$), 7.98 (NCH$_2$CH$_3$); IR, (ATR mode, ν cm$^{-1}$): 3645 (w), 3625 (w), 3392 (w, νNH), 3250 (w, νNH), 1689 (s, νC=O), 1595 (s), 1512 (vs, νC=O), 1409 (s, νCN), 1409 (m), 1320 (m), 1293 (m), 1210 (vs), 1127 (w), 1049 (vs, νBF), 741 (m), 664 (w), 640 (w), 598 (w), 556 (vs), 530 (m); $M_w = 12,000$ g/mol; $M_w/M_n = 1.42$ (GPC); $T_{g} = 286$ °C (TMA).

![Scheme 7. Structure of PUR1.BF₄ and its NMR assignment.](image)

**PUR2.BF₄**

$^{1}$H NMR (600 MHz, DMSO-d$_6$, δ ppm, Scheme 8): 8.31 (m, 2H, NH), 7.28 (m, 8H, B-2, B-3), 6.26–5.49 (m, 2H, NH), 4.16 (m, 2H, Q-2), 3.40 (m, 2H, NCH$_2$CH$_3$), 3.31 & 3.13 (m, 4H, Q-6 & Q-7), 3.31 (m, 1H, Q-4), 1.95 & 1.75 (m, 4H, Q-5 & Q-8), 1.32 (m, 3H, NCH$_2$CH$_3$). 1.82–0.90 (br.m., 20H, CH-C$_{2}$-CH, D-2, D-3, D-4); $^{13}$C NMR (151 MHz, DMSO-d$_6$, δ ppm): 154.33 (CONH), 138.24 (B-1,4), 126.22 (B-2,6), 117.54 (B-3,5), 61.85 (Q-2), 52.97 (Q-6, Q-7), 45.44 (Q-3), 48.03 & 44.00 (D-1), 26.53 (Q-4), 20.58 (Q-5, Q-8), 7.98 (NCH$_2$CH$_3$). 32.91 & 32.21 (D-4), 32.66 (D), 31.50 (D), 29.46 (CH-C$_{2}$-CH), 27.29 (D); $^{19}$F NMR (565 MHz, DMSO-d$_6$, δ ppm): -148.2; IR, (ATR mode, ν cm$^{-1}$): 3645 (w), 3427 (w, νNH), 3332 (w, νNH), 2922 (m, νCH=O), 2852 (m, νCH=O), 1675 (s, νC=O), 1595 (m), 1513 (vs, νC=O), 1451 (m, νCN), 1407 (m), 1323 (s), 1197 (s), 1048 (vs, νBF), 740 (w), 713 (w), 664 (w), 643 (w), 598 (w), 556 (s), 509 (m); $M_w = 15,800$ g/mol; $M_w/M_n = 1.61$ (GPC); $T_{g} = 271$ °C (TMA).

![Scheme 8. Structure of PUR2.BF₄ and its NMR assignment.](image)

**PUR3.BF₄**

$^{1}$H NMR (600 MHz, DMSO-d$_6$, δ ppm, Scheme 9): 8.95 & 8.48–8.30 (br m, 2H, NH), 7.28 (m, 8H, CH(Ar)), 6.2–5.5 (br m, 2H, NH), 4.14 (m, 2H, Q-2), 3.76 (m, 1H, IP-1), 3.40 (m, 2H, NCH$_2$CH$_3$), 3.28 (m, 3H, Q-4, Q-6 & Q-7), 3.12 (m, 2H, Q-6 & Q-7), 2.88 & 2.79 (m, 2H, CH$_2$NHCO), 1.91 & 1.78 (m, 4H, Q-5 and Q-8), 1.57 (m, 1H, IP-6), 1.52 (m, 1H, IP-2), 1.31 (m, 3H, NCH$_2$CH$_3$), 1.13 & 1.02 (m, 2H, IP-4), 0.96 (s, 2.25H, CH$_3$ at trans-IP-3), 0.89 (s, 4H, IP-6 & CH$_3$ at IP-5), 0.85 (m, 1H, 1H, N).
1.00 (s, 3H, CH₃ at IP-5), 0.96 (s, 2.25H, CH₃ at trans-IP-3), 0.89 (s, 4H, IP-6 & CH₃ at IP-5), 0.85 (m, 1H, IP-2), 0.82 (s, 0.75H, cis-IP-3); ¹³C NMR (151 MHz, DMSO-d₆, δ ppm): 155.33 & 154.41 (CONH), 138.46–138.15 (B-1,4), 126.16 (B-2,6), 117.34 (B-3,5), 61.91 (Q-2), 58.34 (NCH₂CH₂), 52.54 (CH₃NΗCO), 52.23 (Q-6, Q-7), 46.65 (IP-4), 46.02 (IP-6), 45.44 (Q-3), 42.15 (IP-1), 41.96 (IP-2), 35.99 (IP-3), 34.74 (CH₃ at IP-5), 31.33 (IP-5), 29.63 (CH₃ at cis-IP-3), 27.28 (CH₃ at IP-5), 26.29 (Q-4), 23.01 (CH₃ at trans-IP-3), 20.40 (Q-5, Q-8), 7.16 (NCH₂CH₂); IR, (ATR mode, ν, cm⁻¹): 3648 (w), 3422 (w, vNH), 3339 (w, vNH), 2951 (w, vCH₂), 2904 (w, vCH₃), 1681 (s, νC=O), 1596 (s), 1513 (vs, νC=O), 1464 (m, vCN), 1408 (m), 1321 (s), 1226 (s), 1197 (s), 1050 (vs, νBF), 740 (w), 698 (w), 645 (w), 601 (w), 556 (vs), 506 (m); Mₘ = 101,500 g/mol; Mₘ/Mₙ = 4.12 (GPC); Tₛ = 276 °C (TMA).

**Scheme 9. Structure of PUR3.BF₄ and its NMR assignment.**

**PUR5.BF₄**

¹H NMR (600 MHz, DMSO-d₆, δ ppm, Scheme 10): 6.3–5.2 (br m, 4H, NH), 3.69 (m, 1H, IP-1), 3.40 (m, 2H, NCH₂CH₃), 3.18 (m, 4H, NCH₂CH₂CH₂), 3.05 (s, 3H, NCH₃), 3.00 (m, 4H, NCH₂CH₂CH₂), 2.77 & 2.71 (m, 2H, CH₂NΗCO), 1.51 (m, 1H, IP-6), 1.47 (m, 4H, NCH₂CH₂CH₂), 1.46 (m, 1H, IP-2), 1.20 (m, 3H, NCH₂CH₃), 1.09 (m, 1H, IP-4), 0.98 (s, 3H, CH₃ at IP-5), 0.95 (m, 1H, IP-4) 0.92 (s, 2.25H, CH₃ at trans-IP-3) 0.87 (s, 3H, CH₃ at IP-5), 0.82 (m, 1H, IP-6), 0.76 (s, 0.75H, cis-IP-3). 0.75 (m, 1H, IP-2); ¹³C NMR (151 MHz, DMSO-d₆, δ ppm): 158.40 & 157.40 (CONH), 58.26 (NCH₂CH₂CH₂), 56.24 (m, 2H, NCH₂CH₃), 52.97 (CH₂NΗCO), 47.14 (s, 3H, NCH₃), 46.75 (IP-4), 46.28 (IP-6), 42.94 (IP-1), 42.08 (IP-2), 36.04 (IP-3), 34.96 (NCH₂CH₂CH₂), 34.72 (CH₃ at IP-5), 31.40 (IP-5), 29.53 (CH₃ at cis-IP-3), 27.27 (CH₃ at IP-5), 23.20 (NCH₂CH₂CH₂), 22.90 (CH₃ at trans-IP-3), 7.39 (NCH₂CH₃); ¹⁹F NMR (565 MHz, DMSO-d₆, δ ppm): -148.1; IR, (ATR mode, ν, cm⁻¹): 3291 (w, vNH), 3139 (w, vCH₂), 1637 (s, νC=O), 1563 (vs, νC=O), 1478 (m, vCN), 1446 (m), 1399 (m), 1305 (w), 1258 (s), 1024 (vs, νBF), 772 (w), 661 (w), 630 (w), 590 (w), 521 (m); Mₘ = 173,500 g/mol; Mₘ/Mₙ = 2.32 (GPC); Tₛ = 153 °C (TMA).

**Scheme 10. Structure of PUR5.BF₄ and its NMR assignment.**

**PUR6.BF₄**

¹H NMR (600 MHz, DMSO-d₆, δ ppm, Scheme 11): 7.8–5.7 (br m, 4H, NH), 3.96 (m, 2H, Q-3), 3.72 (m, 3H, Q-2 and IP-1), 3.34 (m, 8H, Q-6 & Q-7), 3.15 (m, 4H, NCH₂CH₂CH₂), 3.01 (m, 2H, Q-2), 2.84 & 2.71 (m, 2H, CH₂NΗCO), 2.02 (m, 4H, Q-4 and Q-5), 1.92 (m, 4H, Q-8), 1.84 (m, 2H, Q-5), 1.67 (m, 4H, NCH₂CH₂CH₂), 1.53 (m, 1H, IP-6), 1.45 (m, 1H, IP-2), 1.24 (m, 2H, NCH₂CH₂CH₂), 1.12 (m, 1H, IP-4), 0.99 (s, 2.25H, CH₃ at trans-IP-5), 0.98 (m, 1H, IP-5), 0.96 (s, 0.75H, cis-IP-5), 0.93 (s, 3H, CH₃ at trans-IP-3 & cis-IP-5), 0.88 (s, 2.25H, CH₃ at trans-IP-5), 0.86 (m, 1H, IP-6), 0.79 (s, 0.75H, cis-IP-3), 0.79 (m, 1H, IP-2); ¹³C NMR (151 MHz, DMSO-d₆, δ ppm): 157.89 & 156.96 (CONH), 62.37 (NCH₂CH₂CH₂),
61.19 (Q-2), 53.08 (CH2NHCO), 52.75 (Q-6, Q-7), 46.53 (IP-4), 46.13 (IP-6), 44.58 (Q-3), 42.16 (IP-1),
41.96 (IP-2), 35.91 (IP-3), 34.77 (CH3 at trans-IP-5), 34.51 (CH3 at cis-IP-5), 31.32 (IP-5), 29.80 (CH3 
at cis-IP-3), 27.23 (CH3 at trans-IP-5), 26.63 (CH3 at cis-IP-5), 24.24 (Q-4), 22.07 (Q-8), 18.03 (Q-5),
20.54 (NCH2CH2CH2), 22.70 (NCH2CH2CH2), 22.98 (CH3 at trans-IP-3);19F NMR (565 MHz, DMSO-d6,
δ ppm): -148.2; IR, (ATR mode, ν, cm−1): 3604 (w), 3565 (w), 3409 (w, νNH), 3308 (w, νNH), 2952 (m,
νCH3), 1650 (s, νC=O), 1549 (vs, νC=O), 1492 (m), 1466 (m, νCN), 1387 (m), 1366 (m), 1307 (m),
1286 (m), 1246 (m), 1190 (m), 1052 (vs, νBF), 898 (m), 833 (m), 733 (m), 649 (s), 585 (s); Mw = 39,000
g/mol; Mw/Mn = 1.97 (GPC); Tg = 209 °C (TMA).

Scheme 11. Structure of PUR6.BF4 and its NMR assignment.

2.7. Methods

NMR spectra were recorded on AMX-400 and Avance III HD 600 MHz spectrometers (Bruker,
Billerica, MA, USA) at 25 °C in the indicated deuterated solvents and are listed in ppm. The signal
corresponding to the residual protons of the deuterated solvent was used as an internal standard for
1H and 13C NMR, while the C6F6 was utilized as an external standard for 19F. Signal assignment
was performed using 2D NMR techniques: heteronuclear single quantum coherence (HSQC),
hetoronuclear multiple bond correlation (HMBC), H-H correlation spectroscopy (H-H COSY).
The following abbreviations were used in the spectra description in order to refer to the fragments:
dicyclohexylmethane (D), benzene (B), toluene (T), isophorone (IP) and quinuclidine (Q). IR spectra
were acquired on a Nicolet Magna-750 Fourier IR-spectrometer using KBr pellets or on Brucker Tensor
27 Fourier IR-spectrometer (Bruker, Billerica, MA, USA) using ATR technology (128 scans, resolution
is 2 cm−1) and Spectragryph optical spectroscopy software [48].

A 1200 Infinity gel permeation chromatograph (GPC, Agilent Technologies, Santa Clara, CA,
USA) was used to determine Mn, Mw and Mw/Mn of the ionic polyureas. The chromatograph was
equipped with an integrated IR detector, a PL PolarGel-M column and a PL PolarGel-M guard column
(Agilent Technologies, Santa Clara, CA, USA). The 0.1 M solution of NH4BF4 in DMF was used as an
eluent, the flow rate was maintained at 1.0 mL/min and the measurements were performed at 50 °C.
Polystyrene standards (EasiVial PS-M, Agilent Technologies, Santa Clara, CA, USA, Mw = 162–500 ×
103) were used to perform calibration.

Thermal gravimetric analysis (TGA) was carried out in air and under inert atmosphere (N2) on a
TGA2 STaRe System (Mettler Toledo, Greifensee, Switzerland), applying a heating rate of 5 °C/min.
Thermal mechanical analysis (TMA) of PURs was performed under inert atmosphere (Ar) using a DIL
402C dilatometer (NETZSCH, Selb, Germany) at a heating rate of 5 °C/min and a constant load of
0.08 MPa. PUR samples were hermetically sealed in aluminum pans inside the argon-filled glovebox
(MBRAUN MB-Labstar, Garching, Germany, H2O and O2 content < 0.5 ppm).

The CO2 adsorption isotherms of the synthetized PILs were determined at 0 °C in a Nova 4200
volumetric apparatus (Quantachrome, now Anton Paar, Graz, Austria) in accordance with the standard
procedures established by Quantachrome for measuring CO2 adsorption capacities at 0 °C in porous
materials. Around 250 mg of PILs sample in powder form (all ionic PURs in this work were precipitated
from the diluted solutions as powders with low particle size (see vide supra)) were introduced in the
cell consisting of a glass tube with a bulb and were degassed at 80 °C for 18 h under vacuum prior to
measurement in order to eliminate the sample humidity and any other adsorbed gases. For the selected
PIL samples, CO2 adsorption and desorption cycles were carried out and five correlative isotherms
were done without degasification step between the measurements. The 25 adsorption points (and 22 desorption points when it was measured) were selected in the pressure range from 0.006 to 1 bar, corresponding to a relative pressure range from 0.0002 to 0.03 (note: $P_0$ for CO$_2$ at 0 °C is 34.85 bar). The equilibrium time (both for the adsorption and desorption) was 300 s. A non-ideality factor of $8.93 \times 10^{-6} \text{ mmHg}^{-1}$, obtained using the Helmholtz equation-of-state proposed by Span and Wagner [49] and recommended by the National Institute of Standards and Technologies of USA (NIST), was used for determining the real CO$_2$ density.

Cycling in thermobalance. Several cycles under an alternative CO$_2$ or N$_2$ flow at room temperature were evaluated in a thermogravimetric analyser (CI Electronics microbalance, now CI Precision, Salisbury, UK). All experiments were carried out at atmospheric pressure and using a gas flow rate (both for CO$_2$ and N$_2$) of 50 mL/min. PUR1.BF$_4$ or PUR1.BF$_4$ samples (about 70 mg) were placed in the quartz cap and the weight was recorded at regular intervals (6 s). The samples were heated at 80 °C for 4 h under a N$_2$ flow of 50 mL/min to remove any adsorbed gas (i.e., to degas the samples). The temperature was controlled at 25 °C using a thermostatic bath and then the gas was changed to CO$_2$ and kept under this CO$_2$ stream for 1 h (in this time, saturation and a constant weight were reached). The gas was switched back to N$_2$ and held for 2 or 3 h. In this time, the complete desorption of the CO$_2$ was not achieved since the initial weight was not recovered. At the end of the third cycle, the samples were kept under current of N$_2$ for 8 h to achieve the initial weight (i.e., complete desorption of CO$_2$ was reached) and the other two cycles were repeated.

3. Results

3.1. Synthesis of Ionic Diamines

Previous investigation performed by our group on CO$_2$ sorption of PILs demonstrated the advantage of quinuclidinium and diquinuclidinium cations over ammonium and imidazolium ones [16]. Keeping this in mind, the work started with the design of ionic diamines. Mono quinuclidinium diamine 4, namely 3,3-bis(4-aminophenyl)-1-ethylquinuclidin-1-ium iodide, was prepared in accordance with the procedure reported by our group previously [43]. As for the diquinuclidinium monomer 5, the reaction pathway consisting of two steps was developed (Scheme 4).

The first step consisted of treatment of 3-aminoquinuclidine dihydrochloride with 30% NaOH aqueous solution and subsequent extraction with diethyl ether to give 3-aminoquinuclidine. The double excess of the latter in a second step was quarternized by 1,5-dibromopentane, applying mild conditions (Scheme 4). It should be mentioned that the slight excess of 3-aminoquinuclidine is required to produce difunctional monomer. Afterwards, the precipitation from methanol solution into the excess of diethyl ether results in purification of monomer 5 and its isolation in 93% yield.

The structure and purity of ionic diamines 4 and 5 were proven by $^1$H and $^{13}$C NMR spectroscopy as well as by elemental analysis. Diamine 4 represented beige-yellow crystalline solid, while 5 was isolated as white crystalline powder. The melting points determined for 4 and 5 were equal to 293–294 and $>360$ °C, respectively.

3.2. Synthesis of Ionic Polyureas

A series of ionic polyureas were synthesized by combining ionic monomers 4 and 5 with three commercial diisocyanates, as shown in Scheme 12. The optimal conditions (4 mol/L solution in DMF, 2.5 mol of catalyst 2-(ethyl)hexanoate tin (II) with respect to diamine, 60 °C for 15 h) determined previously for polycondensation of diisocyanates with ionic diols [16] were applied for the synthesis of PUR1.J-PUR3.J, PUR4 and PUR6.Br (Scheme 12). The reaction was rather slow for aromatic ionic diamine 4, while for aliphatic 6, it proceeded faster and required no catalyst addition. The resultant polymers were isolated in 86–89% yield.
3.3. Properties of Ionic Polyureas

3.3.1. Solubility and Molecular Weights

**PUR1.BF₄–PUR6.BF₄** are amorphous polymers and were found to be soluble in polar aprotic solvents (i.e., DMF, DMSO, DMAc and NMP) and HFIP. Probably due to the hydrogen bonding, they were not soluble in acetone or acetonitrile, in contrast to structurally similar ionic PUs [16]. The same relates to methanol, ethyl acetate and diethyl ether, where the ionic PURs were not soluble either. Finally, tetrafluoroborate anion imparted hydrophobic properties to all obtained PURs.

The molar masses of ionic PURs were estimated by size exclusion chromatography (SEC). To suppress the insufficiently charged screening or the so-called “polyelectrolyte effect” during SEC studies, an electrolyte, namely NH₄BF₄, was added to the polymer solution in DMF. Polycondensation of ionic monomers 4 and 5 resulted in the formation of high molar mass polyureas with weight average molar masses ($M_w$) ranging from 12 to 174 kg/mol for **PUR1.BF₄–PUR6.BF₄** (Table 1).
Table 1. Selected properties of ionic PURs and PUs.

| No | Abbrev. | Poly(Ionic Liquid) | M_w, (g/mol) | M_w/M_n | T_g (°C) | T_onset (°C) | T_onset (°C) | CO_2 Uptake, (mg/g) |
|----|---------|--------------------|--------------|---------|----------|-------------|-------------|---------------------|
| 1  | PUR1.BF4 | ![Ionic Polyurea](image) | 12,000       | 1.42    | 286      | 240         | 250         | 18.3                |
| 2  | PUR2.BF4 | ![Ionic Polyurea](image) | 15,800       | 1.61    | 271      | 230         | 240         | 24.8                |
| 3  | PUR3.BF4 | ![Ionic Polyurea](image) | 101,500      | 4.12    | 276      | 240         | 255         | 19.8                |
| 4  | PUR5.BF4 | ![Ionic Polyurea](image) | 173,500      | 2.32    | 153      | 195         | 240         | 10.5                |
| 5  | PUR6.BF4 | ![Ionic Polyurea](image) | 39,000       | 1.97    | 209      | 260         | 265         | 18.1                |
| 6  | PU1.BF4  | ![Polyurethane](image)  | 8500         | 1.51    | 195      | 265         | 265         | 13.1                |

*a* By GPC in 0.1 M solution of NH_4 BF_4 in DMF; *b* By TMA; *c* By TGA in air; *d* By TGA in N_2 atmosphere; *e* 0 °C, 1 bar; *f* For comparison.
3.3.2. Thermal Properties

Thermal properties of ionic PUR1.BF4–PUR6.BF4 were assessed via mechanical (TMA) and thermogravimetric analyses (TGA). TMA of polyelectrolytes performed in inert atmosphere revealed the following evolution of glass transition temperatures:

\[ T_g \text{PUR1.BF4 (286 °C)} > T_g \text{PUR3.BF4 (276 °C)} \approx T_g \text{PUR2.BF4 (271 °C)} > T_g \text{PUR6.BF4 (209 °C)} > T_g \text{PUR5.BF4 (153 °C)} \]

It can be concluded that PUR1.BF4 based on aromatic polymers demonstrated the highest \( T_g \) among studied polyureas. The change in aromatic toluene-2,4-diisocyanate (1) to aliphatic isophorone diisocyanate (3) and 4′-methylene-bis(cyclohexyl isocyanate) (2) monomers resulted in the decrease in polymers \( T_g \) (Table 1, entries 2–3). Further transfer to completely aliphatic polymers PUR5.BF4–PUR6.BF4 allowed us to significantly decrease polyelectrolytes’ heat resistance (Table 1, entries 4–5). At this, PUR6.BF4 with cycloaliphatic quinuclidinium cation showed higher \( T_g \) values in comparison with PUR5.BF4 based on quaternary ammonium (Table 1, entries 4–5).

Thermal stability of PILs was performed under air and under inert atmosphere (Figure 1 and Table 1). PUR temperatures of onset weight loss (\( T_{\text{onset}} \)) on air ranged from 195 to 265 °C (Table 1). The weight loss profiles of PUR1.BF4–PUR6.BF4 on air revealed a two-step degradation mechanism (Figure 3). The first weight loss step took place between 240 and 360 °C and can be probably attributed to the degradation of aliphatic quinuclidinium cation. The second step occurred over 400 °C (Figure 1). In contrast, the TGA analysis performed under inert atmosphere showed a one-step degradation mechanism. However, the \( T_{\text{onset}} \) values practically coincided with those determined by TGA on air (Table 1).

![Figure 1. TGA traces of PUR1.BF4 under air (solid line) and inert atmosphere (dash line).](image)

3.3.3. CO\(_2\) Sorption

Experimental results of CO\(_2\) sorption for all synthesized PILs are shown in Figure 2 and Table 1. As CO\(_2\) adsorption is temperature dependent, the measurements were performed at 0 °C as it is a standard temperature for porosity studies of solids with CO\(_2\) as adsorbate as well as for characterization of materials with narrow microporosity [4,10,50–52]. The variation in the comonomers’ structure in five synthesized ionic polyureas allowed us to investigate the effect of the isocyanate’s nature (aromatic/cycloaliphatic) (Table 1, entries 1–3) and the effect of the cation’s structure (Table 1, entries 3–5)
on PILs’ CO2 sorption. At the same time, the anion nature was fixed to the tetrafluoroborate counter ion as it imparted the highest CO2 sorption capacity for ionic polyurethanes in our previous study [16].

![Figure 2. CO2 gas absorption isotherms of ionic PURs at 0 °C.](image)

Depending on the chemical nature of diisocyanate, the CO2 sorption values determined at 0 °C for synthesized PILs varied from 14.4 to 24.8 mg/g (Table 1, entries 1–3). The influence of the diisocyanate chemical structure on CO2 adsorption of ionic PURs can be ranked as follows:

\[
\text{PUR2.BF}_4 \text{ (dicycloaliphatic, 24.8 mg/g)} > \text{PUR3.BF}_4 \text{ (cycloaliphatic, 19.8 mg/g)} > \text{PUR1.BF}_4 \text{ (aromatic, 18.3 mg/g)}
\]

This order fully correlates with the previously reported influence of diisocyanate structure on the CO2 sorption of ionic PUs [16]. As in the case of ionic PUs, the utilization of cycloaliphatic isophorone diisocyanate 3 in PUR3.BF4 and dicycloaliphatic diisocyanate 2 in PUR2.BF4 provides a higher amount of the absorbed CO2 in comparison with PUR1.BF4 derived from aromatic diisocyanate 1.

In this endeavor, the effect of the cation’s nature on CO2 sorption of ionic PURs was investigated by varying the diamines’ structure in three different PILs and keeping diisocyanate 3 and the BF4 anion constant (Table 1, entries 3–5). The nature of the cation in ionic PURs was found to significantly impact the CO2 sorption capability, which can be summarized in the following decreasing order:

\[
\text{PUR3.BF}_4 \text{ (quinuclidinium, 19.8 mg/g)} > \text{PUR6.BF}_4 \text{ (diquinuclidinium, 18.3 mg/g)} > \text{PUR5.BF}_4 \text{ (ammonium, 10.5 mg/g)}
\]

The observed superiority of the quinuclidinium-based PUR3.BF4 and PUR6.BF4 over the ammonium PUR5.BF4 is in full agreement with the results obtained previously for the CO2 sorption of ionic PUs [16]. The cyclic quinuclidinium cation is much bulkier in comparison with ammonium that, in its turn, can prevent the compact packing of the polymer chains and favor the increase in free volume, thus leading to the increase in CO2 capture capabilities.

We have recently stated that, in the case of ionic PUs, the CO2 sorption does not occur by a simple physisorption mechanism, which is directly dependent on the porosity of the samples [16]. In contrast, the mechanism of CO2 sorption in ionic PUs was found to be complex and consists not only of the physisorption process but may also involve the specific interactions between CO2, ionic species and
–NH–CO–O– functional groups of PILs [16,53,54]. To fulfill the aim of the study, namely to understand the influence of the additional secondary amine group on CO$_2$ sorption of PILs, the ionic polyurethane PU1.BF$_4$ with a similar structure to PUR6.BF$_4$ has been additionally prepared (Table 1, entry 6). It can be seen that the transfer of –NH–CO–O– groups in PU1.BF$_4$ to –NH–CO–NH– fragments in PUR6.BF$_4$ leads to an increase in the adsorbed amount of CO$_2$ (Table 1, lines 5 and 6). This can be explained by the difference in hydrogen bonding in polyureas and polyurethanes. While, in polyurethanes, the single NH group forms hydrogen bonding mainly with the C=O group of the other polymer chain, in polyureas, the second NH group remains free for the generation of additional H bonding with the CO$_2$ molecule. This, in its turn, increases the capacity for CO$_2$ capture in ionic PURs in comparison with ionic PUs.

Table 2 presents a comparison for CO$_2$ sorption values for the best PURs and PUs selected from this study and PILs described in the literature. To the knowledge of the authors, to date, the highest CO$_2$ sorption among linear PILs was demonstrated by the following polyelectrolytes: (1) positively charged cellulose (38.0 mg/g at 0.1 MPa (1 bar), 25 °C [15]); (2) cationic polyurethanes (24.8 mg/g at 0.1 MPa, 0 °C [16]); (3) poly(p-vinylbenzyl)trimethylammonium tetrafluoroborate (17.1 mg/g at 0.078 MPa, 22 °C [37]) and (4) anionic polyurethanes (16.7 mg/g at 0.1 MPa, 30 °C [40]). The results obtained for linear PUR2.BF$_4$ (24.8 mg/g at 0.1 MPa, 0 °C) can be listed among top five highest CO$_2$ sorption capacities reported for PILs to date, making it a potential candidate for CO$_2$ capture processes.
Table 2. Comparison of the CO\textsubscript{2} absorption data for the best PILs reported in the literature and for those obtained in the present work.

| N | PIL | Structure | CO\textsubscript{2} Sorption (mg/g) | Conditions (P, T) | Reference |
|---|-----|-----------|-----------------------------------|-------------------|-----------|
| 1 | CL-TBA | ![CL-TBA Structure](image) | 44.0 | 0.1 MPa, 25 °C | [55] |
| 2 | [CelEt\textsubscript{3}N][PF\textsubscript{6}] | ![CelEt\textsubscript{3}N][PF\textsubscript{6} Structure](image) | 38.0 | 0.1 MPa, 25 °C | [15] |
| 3 | PIL-8.1.BF\textsubscript{4} | ![PIL-8.1.BF\textsubscript{4} Structure](image) | 24.8 | 0.1 MPa, 0 °C | [16] |
| 4 | PUR2.BF\textsubscript{4} | ![PUR2.BF\textsubscript{4} Structure](image) | 24.8 | 0.1 MPa, 0 °C | This work |
| 5 | Mesoporous PIL | ![Mesoporous PIL Structure](image) | 20.2 | 0.1 MPa, 0 °C | [20] |
| 6 | PUR3.BF\textsubscript{4} | ![PUR3.BF\textsubscript{4} Structure](image) | 19.8 | 0.1 MPa, 0 °C | This work |
| 7 | PIL-8.1.CH\textsubscript{3}COO | ![PIL-8.1.CH\textsubscript{3}COO Structure](image) | 18.3 | 0.1 MPa, 0 °C | [16] |
| 8 | PUR1.BF\textsubscript{4} | ![PUR1.BF\textsubscript{4} Structure](image) | 18.3 | 0.1 MPa, 0 °C | This work |
Table 2. Cont.

| N   | PIL                        | Structure | CO₂ Sorption (mg/g) | Conditions (P, T) | Reference |
|-----|----------------------------|-----------|---------------------|------------------|-----------|
| 9   | PUR6.BF₄                   | ![Structure](image1) | 18.1                | 0.1 MPa, 0 °C    | This work |
| 10  | Meso-SiO₂- P[VBTMA][BF₄]    | ![Structure](image2) | 17.7                | 0.1 MPa, 30 °C   | [25]      |
| 11  | P[VBTMA][BF₄]              | ![Structure](image3) | 17.1                | 0.0078 MPa, 22 °C| [37]      |
| 12  | Meso-SiO₂- P[VBTMA][PF₆]    | ![Structure](image4) | 16.7                | 0.1 MPa, 30 °C   | [25]      |
| 13  | PU-TABPU-TAB               | ![Structure](image5) | 16.1                | 0.0082 MPa, 30 °C| [40]      |
| 14  | P[VBTMA][PF₆]              | ![Structure](image6) | 14.6                | 0.0078 MPa, 22 °C| [37]      |
| 15  | P[MATMA][BF₄]              | ![Structure](image7) | 14.4                | 0.0078 MPa, 22 °C| [37]      |
| 16  | P[(AMIM) BF₄-AN]           | ![Structure](image8) | 14.3                | 0.1 MPa, 0 °C    | [56]      |

Sorption (mg) Conditions (P, T) Reference
Table 2. Cont.

| N  | PIL      | Structure            | CO₂ Sorption (mg/g) | Conditions (P, T)          | Reference   |
|----|----------|----------------------|---------------------|---------------------------|-------------|
| 17 | PU1.BF₄  | ![PU1.BF₄ Structure](image) | 13.1                | 0.1 MPa, 0 °C              | This work   |
| 18 | PIL-8.1.NO₃ | ![PIL-8.1.NO₃ Structure](image) | 13.1                | 0.1 MPa, 0 °C              | [16]        |
| 19 | P[BEMA][CH₃COO] | ![P[BEMA][CH₃COO] Structure](image) | 12.5                | 0.1 MPa, 25 °C             | [19]        |
| 20 | P[VBEA][PF₆] | ![P[VBEA][PF₆] Structure](image) | 10.4                | 0.1 MPa, 25 °C             | [21]        |
| 21 | P[VBEA][BF₄] | ![P[VBEA][BF₄] Structure](image) | 6.9                 | 0.0078 MPa, 22 °C          | [37]        |
| 22 | P[VBM][BF₄] | ![P[VBM][BF₄] Structure](image) | 4.6                 | 0.0078 MPa, 22 °C          | [14]        |
3.3.4. Recycling Experiments

Both ionic polyurea PUR2.BF4 and ionic polyurethane PU1.BF4 showed very good cyclability, with practically total reversibility in CO2 adsorption at 0 °C (Figure 3). After five adsorption–desorption cycles without degassing between each isotherm, the decrease in the adsorption capacity reached only 7.3% for PUR2.BF4 and 5.5% for PU1.BF4. In the case of polyurea PUR2.BF4, more pronounced loss of CO2 adsorption capacity was observed between the first and the second cycles due to the fact that part of the CO2 is not desorbed in the short time (about 15 min) that the device evacuates the sample cell between consecutive measurements. This can be caused by the presence of -NH-CO-NH- functional groups with high affinity for CO2 (i.e., high adsorption energy) that prevent its desorption in the mild vacuum conditions between isotherms. However, between the second and fifth cycles, no decrease in the amount of adsorbed CO2 was observed, which could indicate that all these functional groups have been saturated. In any case, the initial adsorption capacity was recovered, for both PUR2.BF4 and PU1.BF4, simply by degassing the samples at 80 °C for 4 h (results are not shown in Figure 3).

This good cyclability was also observed at atmospheric pressure and room temperature under alternating streams of N2 and CO2 in a thermobalance (Figure S3). Under the conditions indicated in the Materials and Methods, both samples PUR2.BF4 and PU1.BF4 reached saturation in less than 1 h and adsorbed 13.8 and 7.7 mg/g of CO2, respectively. Desorption under N2 flow was slower than adsorption and, after 2 or 3 h, complete desorption was not achieved. However, saturation was reached at the same value of 7.7 mg/g for PU1.BF4 and at a slightly higher value (14.2 mg/g) for PUR2.BF4 when the CO2 stream was again passed. Total desorption of CO2 can be achieved by increasing the purge time up to 8 h for PU1.BF4, but, in the case of PUR2.BF4, longer times are needed because incomplete desorption occurred in this time (see Figure S3). This is in agreement with what was discussed above (Figure 3) on the loss of adsorption capacity between the first and second adsorption–desorption cycles due to the presence of some functional groups (i.e., -NH-CO-NH- groups) with high affinity for

Figure 3. Five correlative CO2 adsorption/desorption isotherms (from 0.006 to 1 bar) at 0 °C for PUR2.BF4 (blue squares) and PU1.BF4 (green circles) carried out without degasification step between cycles.
Therefore, in the case of PUR2.BF4, stronger conditions are needed to desorb all the CO2 (e.g., longer time or higher temperature). It should be noted that both samples showed very good CO2/N2 selectivity, as demonstrated by the good cyclability in the thermobalance experiment.

3.4. Future Outlook

For the combustion of fossil fuels, the content of CO2 in flue gas varies from 10 to 15%. The other components are N2 (73–77%), O2 (4–5%), H2O (6–9%), CO (ppm quantity) and NOx (ppm quantity). In the case of natural gas, the main components are CH4, CO2, N2 and a small amount of hydrocarbons [42]. Hence, the application of PILs as well as any other material as CO2 sorbents will face mainly the problem of CO2 separation from N2 and from CH4 because these are the gases that are in greater proportion in these gaseous streams. Another problem that can arise from a practical point of view is the presence of water vapor. This is especially important in the case of adsorbents having a significant number of polar groups that will have a high affinity for water.

As demonstrated in Figure S3, PILs synthesized in the present work show very good CO2/N2 selectivity in the thermobalance experiment. It was noticed that PUR1.BF4–PUR6.BF4 can also absorb some H2O upon long storage at room temperature. However, as in the case of ILs bearing NH2 groups in the side chain [57,58], the presence of traces of water in PURs will only increase the CO2 sorption capacity. Although the results presented here can serve as a proof-of-concept and are quite promising for sustainable CO2 capture, PILs, to be applied in an industrial process, should be further tested under more representative postcombustion conditions and natural gas purification; this will be the subject of our future investigations.

4. Conclusions

The aim of this study was to synthesize a new class of PILs, namely ionic polyureas, and to evaluate their potential for CO2 capture. To expand the chemistry of PILs, a synthetic route for the preparation of two ionic diamines bearing quinuclidinium cations and distinguished by simplicity and high yields was suggested. Their condensation with commercial diisocyanates and subsequent ion exchange reaction with KBF4 afforded series of high molecular weight (Mw = 12.0–173.5 × 103 g/mol) and thermally stable (Tonset = 195–265 °C) ionic polyureas.

All synthesized PILs represent novel materials and differ by the structure of diisocyanate, the nature and the quantity of cations. All these factors were found to affect the heat resistance and the CO2 sorption properties of the polymers. PUR1.BF4 based solely on aromatic monomers demonstrated the highest glass transition temperature (Tg = 286 °C), while aliphatic PUR5.BF4 and PUR6.BF4 showed the lowest ones (Tg = 153 and 209 °C, respectively). From comparative evaluation, it becomes evident that aliphatic 4,4′-methylene-bis(cyclohexyl isocyanate) imparts the highest CO2 capture capacity to respective ionic polyureas. The observed superiority of the quinuclidinium-based PUR3.BF4 and PUR6.BF4 over the ammonium PUR5.BF4 was in full agreement with the results obtained previously for the CO2 sorption of ionic polyurethanes. The addition of the second quinuclidinium cation did not significantly affect the CO2 sorption of PILs. The comparison of structurally similar ionic polyurea PUR6.BF4 and polyurethane PU1.BF4 revealed that the transfer from –NH–CO–O– groups to –NH–CO–NH– fragments leads to an increase in the adsorbed amount of CO2, which was explained by the presence of the additional amine group and the possibility of hydrogen bonding CO2 molecules. Finally, these materials presented very good cyclability both in consecutive cycles of adsorption and desorption between vacuum and atmospheric pressure at 0°C and in alternating streams of N2 and CO2 at room temperature. This last result also proves good CO2/N2 selectivity.

To conclude, the demonstrated results present a new sustainable CO2 capture option and add important value to novel design strategies for improving the sorption properties of PILs and the creation of novel effective CO2 sorbents.
Supplementary Materials: The following are available online at http://www.mdpi.com/2077-0375/10/9/240/s1, Explanations of the choice of non-ideality factor for CO2 sorption calculations; Figure S1: (a) 1H, (b) HMBC and (c) 19F NMR spectra of polyurea PUR6.BF4 (25 °C, DMSO-d6); Figure S2: FT-IR spectrum of polyurea PUR6.BF4; Figure S3: CO2 sorption/desorption tests for PUR2.BF4 and PUR1.BF4 at atmospheric pressure and room temperature under alternating streams of N2 and CO2 in a thermostable.

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