

Polymer Chemistry

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Turning Into Polymeric Ionic Liquids as a Tool for Polyimide Modification: Synthesis, Characterization and CO₂ Separation Properties

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In an attempt to improve the mechanical and thermal properties of poly(ionic liquid)s (PILs), a new synthetic method for the modification of polyimides is here reported for the first time. The proposed methodology consists in the transformation of polyimides into their ionic form via subsequent N-alkylation and quaternization of benzimidazole or quinuclidine moieties. Finally, an ion exchange reaction was also carried out in order to prepare polymers bearing the bis(trifluoromethylsulfonyl)imide anion. The elaboration of optimal conditions for the reactions afforded the preparation of high molecular weight ($M_n = 2.2 \div 9.7 \times 10^4$) cationic polyelectrolytes with a degree of quaternization as high as 96%. Among the unique features of these new PILs are the preservation of excellent mechanical and thermal properties inherent for polyimides, the adjustable surface wettability with variable water contact angle from 70.5 to 94.3°, the enhanced hydrolytic stability (up to 9 h in boiling water) and improved gas transport properties (CO₂ permeability up to 28.9 Barrer for neat film and 85.0 Barrer for filled membrane at 20 °C and 100 KPa).

Introduction

Poly(ionic liquids) or polymeric ionic liquids (PILs) are a new class of polymer electrolytes which combines the unique properties of ionic liquids (ILs) and polymer architecture, and has attracted considerable attention in recent years.^{1–6} Compared to ILs, PILs have film forming ability and improved processability, delivering performance that could not readily be afforded by liquid organic salts. Simultaneously, the IL species in each repeating unit impart to PILs some of the unique properties such as ionic conductivity, high thermal and electrochemical stability, improved solubility, etc. Rapid advances in the chemistry, physics, and macromolecular architecture of PILs prompted the development of new polyelectrolytes that have found applications across diverse fields, namely energy (batteries, supercapacitors, fuel cells, solar cells),^{2,3} environment (water treatment, ion exchange resins),⁴ gas separation,^{7–14} catalysis,^{15,16} microelectronics (electrochromic devices, transistors, OLEDs),¹ and bio-related applications.^{17,18}

Although different polymerization techniques have earned tremendous success in the synthesis of various PILs, the use of condensation reactions has not received comparable attention.^{2,3,19,20} Up to date, the following classes of condensation

PILs are known: ionic polyimides,^{21–26} polyesters,²⁷ polybenzimidazoles,^{28–30} polyurethanes,³¹ polyepoxides,^{32–34} polyethersulfones^{35,36} and ionenes.^{37,38} The synthesis of these PILs is usually conducted either by condensation of the respective ionic monomers^{21,26,27,31,34} or via polymer modification.^{29,30} The main advantages of the first route is the well-defined structure of the obtained condensation PILs, as well as the possibility to vary the macromolecular architecture by copolymerization of ionic monomers with the neutral ones. However, the introduction of ionic species into the monomers, such as diamines and diols, is typically achieved by a minimum of three reactions that involve complex preparation and/or purification steps and may result in quite low molecular weight of PILs.^{26,27,31} Conversely, the second route allows to work with commercially available polymers having defined high molecular weight, though it faces the difficulty to achieve high conversions due to the steric hindrance of the polymer chains.^{29,30}

Unlike the majority of PILs tested for the preparation of CO₂ separation membranes^{7,10,13,39,40} that are unable to be processed into mechanically stable membranes due to the brittle nature of their films or due to very low T_g , polyimides (PIs) are generally characterized by excellent mechanical strength, as well superior heat resistance, chemical and thermal stability. Owing to these advantageous properties, PIs seem to be highly desirable precursors for gas separation membranes, in particular for separation of CO₂ from other light gases.^{41,42} However, one of the identified critical challenges in developing of polymeric membranes for gas separation is to cope with the trade-off behaviour between gas permeability and selectivity, where a high permeable membrane is generally obtained at the cost of poor selectivity and *vice-versa*. Nowadays the development of gas separation membranes with

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superior permeability and selectivity overcoming this trade-off is the focus of much research on polymeric membranes.

All the above mentioned aspects suggest that the modification of PIs into respective PILs can promote the development of new membranes for more efficient gas separation processes. Thus, in the present work, we report an efficient method for transformation of polyimides bearing benzimidazole or quinuclidine moieties into novel polyimide-based PILs with fully aromatic rigid backbones that are able to be processed into mechanically strong films by a straightforward solvent casting procedure. Furthermore, the most distinctive feature of the method proposed herein is the nearly quantitative degree of polymer modification, yielding novel polyelectrolytes with enhanced hydrophobicity, increased hydrolytic stability, higher CO₂ permeability along with excellent film forming ability.

Experimental section

Materials

Lithium bis(trifluoromethylsulfonyl)imide (LiTFSI, 99%, Solvionic), 1-methyl-3-ethyl imidazolium bis(trifluoromethylsulfonyl)imide ([1-Me-3-Et im]TFSI, 99%, Solvionic), 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP, 99%, Aldrich), N,N-dimethylformamide (DMF, anhydrous, 99.8%, Acros), iodoethane (99%, Aldrich), benzoic acid (>99.5%, Aldrich), acetone (99.8%, Aldrich) and lithium hydride (97%, Acros) were used without purification. Potassium carbonate (>99%, Donetskyi plant of chemical reagents) was dried at 140 °C for 12 h immediately prior to each use. Sodium hydride (60 % dispersion in mineral oil, Aldrich) was washed two times with anhydrous hexane in a Schlaker reaction tube under inert atmosphere and dried at 25 °C/15 mm Hg for 30 min.

Bromoethane (98%, Aldrich) and diethyl ether (98%, Acros) were distilled over CaH₂ and P₂O₅, respectively. m-Cresol (>98%) was purified by vacuum distillation and kept in the freezer.

3,3-bis(4-aminophenyl)quinuclidine (AQ) was synthesized according to a previously reported procedure²¹, and was purified by vacuum sublimation at 200 °C/10⁻² Torr. The 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (HFDA, 99%, Fluorochem) was purified by vacuum sublimation at 220 °C/10⁻² Torr., while the 5(6)-amino-2-(4'-aminophenyl) benzimidazole (ABIZ) was dried at 120 °C/1 mm Hg for 5 h.

Polymer synthesis

Polyimide PI-1

0.7090 g (3.0 mmol) of ABIZ, 1.4050 g (3.0 mmol) of HFDA and 12 mL of m-cresol were stirred at room temperature (RT) for 10 min. The temperature was gradually increased up to 180 °C under an inert gas atmosphere and stirring was continued for 6 h. Polyimide was isolated by precipitation into an excess of methanol, and then was thoroughly washed with acetone (Soxhlet apparatus) and dried at 80 °C/1 mm Hg for 48 h. The polymer yield was almost quantitative. $\eta_{inh} = 1.68 \text{ dL g}^{-1}$ (DMF); ¹H NMR (400 MHz, DMSO-*d*₆, δ): 13.3 (br. s, 1H, NH), 8.37 (m, 2H, Ar-imide H), 8.23 (m, 2H, Ar-imide H), 8.02 (m, 2H, Ar-imide H), 7.83 (m, 1H, Ar-benzimidazole H), 7.77 (m, 2H, Ar H), 7.69 (m, 2H, Ar H), 7.32 (m, 1H, Ar-benzimidazole H); ¹³C NMR (100 MHz, DMSO-*d*₆, δ): 166.5, 166.4, 165.9, 165.8 (C=O), 151.9 (benzimidazole-2), 137.4, 137.3

(phthalimide-5), 135.8 (CH), 133.1, 133.0, 132.7, 132.5 (phthalimide), 129.5 (benzimidazole), 127.6 (CH in Ph), 127.1 (CH in Ph), 126.0, 126.2 (q ¹J_{CH} = 285) 124.8 (part of CF₃), 124.4, 124.3 (CH), 123.6 (CH), 122.0, 119.1, 64.6 (septet, ²J_{CF} = 26 Hz, $\underline{\text{C}}\text{CF}_3$); IR (KBr): $\nu = 3120$ (br m, $\nu(\text{NH})$), 2926 (m, $\nu(\text{CH})$), 2853 (w, $\nu(\text{CH})$), 1787 (s, $\nu_s(\text{C=O})$), 1722 (vs, $\nu_{as}(\text{C=O})$), 1622 (s, $\nu(\text{C=C})$), 1493 (s, $\nu(\text{C=C})$), 1434 (s), 1365 (vs, $\nu(\text{CN})$), 1325 (m, $\nu(\text{CF})$), 1257 (vs, $\nu(\text{CN})$), 1209 (s), 1190 (s, $\nu(\text{CF})$), 1144 (vs, $\nu(\text{CF})$), 1105 (vs, $\nu(\text{CF})$), 982 (m), 962 (m), 839 (m), 801 (m), 718 (s, $\nu(\text{C=O})$), 682 (w), 613 (w), 523 (m) cm⁻¹; Anal. calcd. for C₃₂H₁₄N₄O₄F₆ (632.5): C 60.76, H 2.22, found: C 60.24, H 2.57.

Polyimide PI-1.2

1.60 g (0.003 mol) of PI-1 were dissolved in 20 mL of anhydrous DMF by stirring at RT under inert atmosphere. Further on the 0.83 g (0.006 mol) of K₂CO₃, dried immediately before use, was added to the solution in one portion. The obtained suspension was stirred for 20 min. Then the 2.18 g (0.020 mol) of bromoethane were injected into suspension and the reaction mixture was heated to 80 °C for 25 h. The resulting suspension was cooled down to RT and filtered to remove KBr, as well the excess of K₂CO₃. The obtained polymer was isolated by precipitation into an excess of acetone, repeatedly washed with acetone and dried at 80 °C/1 mm Hg for 48 h. Yield: 1.59 g (95%); $\eta_{inh} = 1.58 \text{ dL g}^{-1}$ (DMF); ¹H NMR (400 MHz, acetone-*d*₆, δ): 8.45-7.50 (m, 13H, Ar), 4.50 (m, 2H, Et-1), 1.47 (m, 3H, Et-2); IR (KBr): $\nu = 2978$ (m, $\nu(\text{CH})$), 2924 (m, $\nu(\text{CH})$), 2853 (m, $\nu(\text{CH})$), 1787 (s, $\nu_s(\text{C=O})$), 1725 (vs, $\nu_{as}(\text{C=O})$), 1624 (s, $\nu(\text{C=C})$), 1490 (s, $\nu(\text{C=C})$), 1466 (m), 1439 (m), 1367 (vs, $\nu(\text{CN})$), 1330 (m, $\nu(\text{CN})$), 1129 (m), 1255 (vs, $\nu(\text{CN})$), 1187 (s, $\nu(\text{CF})$), 1138 (vs, $\nu(\text{CF})$), 1082 (vs, $\nu(\text{CF})$), 960 (m), 842 (m), 743 (m), 717 (s, $\nu(\text{C=O})$), 665 (m), 617 (w), 590 (w), 517 (w), 524 (w) cm⁻¹.

Polyimide PI-1.3

In a glass vial the 1.43 g (2.0 mmol) of PI-1.2 were dissolved in 20 mL of anhydrous DMF by stirring at RT under inert atmosphere. Then, 2.39 g (1.3 mmol) of iodoethane were injected into the reaction solution and the vial was tightly closed. The temperature was raised to 80 °C and the solution was stirred for 30 h. After cooling down to RT, the resulting polymer was precipitated into an excess of diethyl ether, thoroughly washed with acetone, and dried at 80 °C/1 mm Hg for 48 h. Yield: 1.41 g (80%); $\eta_{inh} = 0.57 \text{ dL g}^{-1}$ (0.5M LiBr in DMF); ¹H NMR (400 MHz, DMSO-*d*₆, δ): 8.37 (m, 2H, Ar-imide H), 8.23 (m, 2H, Ar-imide H), 8.02 (m, 2H, Ar-imide H), 7.83 (m, 2H, Ar-benzimidazole H), 7.77 (m, 2H, Ar H), 7.69 (m, 2H, Ar H), 7.32 (m, 1H, Ar-benzimidazole H), 4.36 (m, 4H, Et-1), 1.43 (m, 6H, Et-2); IR (KBr): $\nu = 2969$ (m, $\nu(\text{CH})$), 2925 (m, $\nu(\text{CH})$), 2854 (m, $\nu(\text{CH})$), 2752 (m), 1781 (s, $\nu_s(\text{C=O})$), 1718 (vs, $\nu_{as}(\text{C=O})$), 1608 (s, $\nu(\text{C=C})$), 1487 (s, $\nu(\text{C=C})$), 1461 (s), 1371 (vs, $\nu(\text{CN})$), 1296 (m, $\nu(\text{CN})$), 1247 (vs, $\nu(\text{CN})$), 1187 (s, $\nu(\text{CF})$), 1144 vs, $\nu(\text{CF})$), 1091 (vs, $\nu(\text{CF})$), 1022 (m), 960 (m), 885 (w), 830 (w), 743 (w), 714 (s, $\nu(\text{C=O})$), 523 (w) cm⁻¹; Anal. calcd. for C₃₆H₂₄N₄O₄F₆I (817.5): F+I 29.46, found: F+I 29.50, Br<0.001.

Polyimide PI-1.TFSI

A solution of 0.92 g (3.2 mmol) of LiTFSI in 3 mL of DMF was added dropwise to the solution of 1.30 g (1.6 mmol) of PI-1.3 in 20 mL of DMF at RT. The stirring was continued at RT for 24 h. The resulting

solution was precipitated into an excess of diethyl ether, repeatedly washed with acetone, and then dried at 80 °C/1 mm Hg for 48 h. Yield: 1.42 g (92%); $\eta_{inh} = 0.73$ dL g⁻¹ (0.5M LiTFSI in DMF); ¹H NMR (400 MHz, DMSO-d₆, δ): 7.77-8.23 (m, 13H, Ar H), 4.21 (m, 4H, CH₂-N⁺R₃), 1.35 (t, 6H, CH₃); ¹H NMR (400 MHz, DMSO-d₆, δ): 8.31 (m, 2H, Ar-imide H), 8.22 (m, 2H, Ar-imide H), 8.05 (m, 2H, Ar-imide H), 7.99 (m, 2H, Ar-benzimidazole H), 7.84 (m, 2H, Ar H), 7.76 (m, 2H, Ar H), 7.63 (m, 1H, Ar-benzimidazole H), 4.21 (m, 4H, Et-1), 1.35 (m, 6H, Et-2); ¹³C NMR (100 MHz, DMSO-d₆, δ): 166.0, 165.8, 165.6, 165.5 (C=O), 150.4 (benzimidazole-2), 137.4, 136.0, 135.7 (CH), 132.9, 132.5, 131.0 (2 CH in Ph), 130.9, 130.5, 130.0, 129.7, 127.9 (2 CH in Ph), 127.0, 126.3, 124.6 (2 CH), 123.7 (2 CH), 122.3 (q, ¹J_{CF} = 285 Hz), 120.4, 119.6 (q, ¹J_{CF} = 322 Hz, TFSI), 114.3 (CH), 113.3 (CH), 64.6, 41.7 (Et-1), 14.3, 14.1 (Et-2); ¹⁹F NMR (376 MHz, DMSO-d₆, δ): -62.83 (s, CF₃ Ar), -78.74 (s, CF₃ anion); IR (KBr): $\nu = 2984$ (m, v(CH)), 2323 (m, v(CH)), 1786 (w, ν_s (C=O)), 1724 (vs, ν_{as} (C=O)), 1608 (m, v(C=C)), 1528 (w), 1488 (s, v(C=C)), 1464 (m), 1438 (w), 1365 (s, v(CN)), 1347 (vs, ν_{as} (S=O)), 1325 (m, v(CF)), 1298 (s), 1254 (s, v(CN)), 1240 (m), 1180 (vs, v(CF)), 1133 (vs, ν_s (S=O)), 1045 (m), 1054 (s, v(CF)), 962 (m), 890 (w), 845 (m), 812 (w), 787 (w), 740 (w), 718 (s, v(C=O)), 652 (m), 614 (m), 598 (m), 508 (w) cm⁻¹; Anal. calcd. for C₃₈H₂₃N₅O₈F₁₂S₂ (969.7): C 47.07; H 2.39; N 7.22; found: C 45.54; H 2.41; N 7.12;

Polyimide PI-2

1.1736 g (4.0 mmol) of AQ, 1.7769 g (4.0 mmol) of HFDA, 0.3175 g (3.0 mmol) of benzoic acid and 10 mL of m-cresol were mixed by stirring at RT for 10 min. The temperature was gradually increased to 180 °C, and the solution was stirred for 10 h under inert atmosphere. Polymer was isolated by precipitation into an excess of methanol, thoroughly washed with acetone (Soxhlet apparatus), and then dried at 80 °C/1 mm Hg for 48 h. Yield: 2.66 g (95%), $\eta_{inh} = 0.55$ dL g⁻¹ (DMF); ¹H NMR (400 MHz, DMSO-d₆, δ): 8.15 (m, 2H, phthalimide-7), 7.93 (m, 2H, phthalimide-6), 7.75 (m, 4H, -C₆H₄-), 7.62 (2H, phthalimide-4), 7.37 (4H, -C₆H₄-), 3.25-3.05 (br. m, 2H, quinuclidine-2), 2.90-2.60 (br. m, 4H, quinuclidine-6,7), 1.85-1.25 (br. m, 5H, quinuclidine-4,5,8); ¹³C NMR (100 MHz, DMSO-d₆, δ): 166.0, 165.9 (C=O), 148.1 (phthalimide-5), 137.3, 135.9, 134.1, 132.9, 132.4, 131.2, 129.1, 128.9, 127.9, 127.0, 124.3, 123.4, 122.1, 119.8, 64.5 (septet, ²J_{CF} = 26 Hz, CCF₃), 58.2 (quinuclidine-2), 48.5, 45.9, 45.5 (quinuclidine-6,7), 27.5, (quinuclidine-4), 22.4 (quinuclidine-5,8); IR (KBr): $\nu = 2952$ (m, v(CH)), 2873 (w, v(CH)), 1787 (w, ν_s (C=O)), 1727 (vs, ν_{as} (C=O)), 1603 (m, v(C=C)), 1514 (s, v(C=C)), 1438 (w), 1372 (s, v(CN)), 1297 (m), 1256 (vs, v(CN)), 1210 (vs, v(CN)), 1192 (s, v(CF)), 1142 (s, v(CF)), 1102 (m, v(CF)), 1074 (m), 965 (m), 827 (m), 721 (s, v(C=O)), 671 (w), 591 (w), 543 (w) cm⁻¹.

Polyimide PI-2.2

The solution of 3.09 g (1.7 mmol) of iodoethane in 15 mL of anhydrous DMF and a solution of 1.50 g (2.0 mmol) of PI-2 in 30 mL of DMF were mixed in a glass vial by stirring at RT under inert atmosphere. The vial was tightly closed and the reaction solution was further heated to 80 °C for 30 h. After cooling down to RT, polyimide was precipitated into an excess of diethyl ether and then repeatedly washed with acetone. The polymer was collected by filtration and dried at 80 °C/1 mm Hg for 48 h. Yield: 1.63 g (89%); $\eta_{inh} = 0.28$ dL g⁻¹ (0.5M LiBr in DMF); ¹H NMR (400 MHz,

DMSO-d₆, δ): 8.19 (m, 2H, phthalimide-7), 7.96 (m, 2H, phthalimide-6), 7.75 (m, 4H, -C₆H₄-), 7.67 (m, 2H, phthalimide-4), 7.45 (m, 4H, -C₆H₄-), 4.44, 4.28 (br. m, 2H, quinuclidine-2), 3.76 (br. m, 2H, Et-1), 3.52, 3.22 (br. m, 4H, quinuclidine-6,7), 3.22 (m, 1H, quinuclidine-4), 2.09, 1.83 (m, 4H, quinuclidine-5,8), 1.38 (m, 3H, Et-2); IR (KBr): $\nu = 2952$ (m, v(CH)), 2915 (m, v(CH)), 2844 (m, v(CH)), 2743 (w), 1785 (m, ν_s (C=O)), 1721 (vs, ν_{as} (C=O)), 1700 (s), 1603 (m, v(C=C)), 1514 (s, v(C=C)), 1463 (w), 1437 (w), 1372 (s, v(CN)), 1327 (w, v(CF)), 1299 (m), 1255 (s, v(CN)), 1208 (s), 1141 (s, v(CF)), 1096 (m, v(CF)), 1073 (m), 1010 (w), 960 (m), 885 (w), 829 (m), 745 (w), 717 (m, v(C=O)), 574 (w), 525 (w) cm⁻¹.

Polyimide PI-2.TFSI

Polymer PI-2.TFSI was obtained following the same procedure used for the preparation of PI-1.TFSI. Yield: 73%; $\eta_{inh} = 0.24$ dL g⁻¹ (0.5M LiTFSI in DMF); ¹H NMR (400 MHz, DMSO-d₆, δ): 8.16 (m, 2H, phthalimide-7), 7.94 (m, 2H, phthalimide-6), 7.76 (m, 4H, -C₆H₄-), 7.67 (m, 2H, phthalimide-4), 7.47 (m, 4H, -C₆H₄-), 4.45, 4.28 (br. m, 2H, quinuclidine-2), 3.46 (br. m, 2H, Et-1), 3.41, 3.18 (br. m, 4H, quinuclidine-6,7), 3.19 (m, 1H, quinuclidine-4), 2.08, 1.86 (m, 4H, quinuclidine-5,8), 1.38 (m, 3H, Et-2); ¹³C NMR (100 MHz, DMSO-d₆, δ): 165.9, 165.8 (C=O), 145.8, 145.1, 140.9, 140.2, 139.7, 139.1, 137.4, 135.9, 135.2, 133.4, 132.9, 132.8, 132.5, 132.4, 129.9, 129.7, 129.4, 129.1, 127.4, 126.7, 126.6, 124.3, 123.5, 123.4 (q, ¹J_{CF} = 286 Hz), 119.9, 119.5 (q, ¹J_{CF} = 322 Hz, TFSI), 61.7 (2q), 58.8 (Et-1), 55.2, 52.7 (6q, 7q), 51.2, 47.2, 46.8, 46.4, 26.5, 25.4, 20.7 (5q, 8q), 7.4 (Et-2); ¹⁹F NMR (376 MHz, DMSO-d₆, δ): -62.83 (s, CF₃ Ar), -78.74 (s, CF₃ anion); IR (KBr): $\nu = 2962$ (w, v(CH)), 2903 (w, v(CH)), 1785 (w, ν_s (C=O)), 1719 (vs, ν_{as} (C=O)), 1604 (m, v(C=C)), 1513 (s, v(C=C)), 1491 (w), 1467 (w), 1437 (w), 1375 (s, v(CN)), 1349 (s, ν_{as} (S=O)), 1325 (m, v(CF)), 1299 (w), 1255 (s, v(CN)), 1183 (vs, v(CF)), 1134 (vs, ν_s (S=O)), 1103 (m), 1056 (vs, v(CF)), 983 (m), 963 (m), 884 (w), 829 (m), 796 (m), 722 (s, v(C=O)), 655 (m), 616 (m), 600 (s), 570 (s), 544 (w), 511 (m), 415 (m), 388 (w) cm⁻¹; Anal. calcd. for C₄₂H₃₁N₄O₈F₁₂S₂ (1011.8): C 49.86, H 3.09; found: C 51.17, H 2.93.

Membranes preparation

Dense flat form polyimide membranes were prepared by a solvent casting method from 6 (w/v)% solutions in appropriate solvents (DMF, HFIP or Acetone). The respective solution was cast on the glass support (Petri dish) and the solvent was left to evaporate at 65 °C (DMF) or at RT (HFIP and acetone) for 2 days. The solvent was slowly evaporated in a saturated solvent environment in order to obtain dense homogeneous membranes. Finally, the membranes were dried at 80 °C/0.13 kPa until a constant weight was attained.

Membranes containing 50 wt% of 1-ethyl-3-methylimidazolium (trifluoromethylsulfonyl) imide ([C₂mim][TFSI]) were prepared by a similar procedure.

Membrane thicknesses (35 – 60 μ m) were measured using a digital micrometer (Mitutoyo, model MDE-25PJ, Japan). Average thickness was calculated from six measurements taken at different locations of each membrane sample.

Polymer characterization

NMR spectra were recorded on a Bruker AMX-400 spectrometer at 25 °C in the indicated deuterated solvent and are listed in ppm

relative to tetramethylsilane. The signal corresponding to the residual protons of the deuterated solvent was used as an internal standard for ^1H and ^{13}C NMR, while for ^{19}F NMR the CHCl_2F was utilized as an internal standard. IR spectra were acquired on a Nicolet Magna-750 Fourier IR-spectrometer using KBr pellets or thin polymer films on KBr. All spectra were collected after 128 scans with a resolution of 2 cm^{-1} .

Inherent viscosities (η_{inh}) of polyimides were measured in an Ostwald type capillary viscometer at $25\text{ }^\circ\text{C}$ for 0.05 g of polymer in 10.0 mL of the respective solvent (DMF for non-ionic polymers, 0.5M LiBr in DMF for iodide polymers and 0.5M $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ in DMF for TFSI containing polyelectrolytes). The molecular weights (M_n , M_w) and polydispersity index (M_w/M_n) of the prepared polymers were estimated at $50\text{ }^\circ\text{C}$ using an Agilent PL-GPC 50 chromatograph (GPC, Agilent Technologies, USA) equipped with a column (Shodex KD806-M) and a refractive index detector. 0.01 M LiBr in DMF solution was used as an eluent, with a flow rate of 1.0 mL min^{-1} . The calibration was performed using polystyrene standards (Waters Corporation).

The glass transition temperatures (T_g) of polymers were determined by thermomechanical analysis (TMA) using a Q400 analyzer (TA Instruments, USA) at a heating rate of $5\text{ }^\circ\text{C min}^{-1}$ and a constant load of 80 kPa. Thermogravimetric analysis (TGA) was performed in air on a Q50 model (TA Instruments, USA) applying a heating rate of $5\text{ }^\circ\text{C min}^{-1}$.

Mechanical properties (d_t - tensile strength (MPa), E_t - tensile modulus (MPa) and e_t - elongation at break (%)) of polyimide films, were determined at RT using a dynamometer "Polyani" (Polyani, Hungary).

Wettability

Water contact angle (CA) measurements were performed using the sessile drop method on a Krüss Drop Shape Analysis System DSA100-Mk2 (Krüss GmbH, Germany), at RT and atmospheric pressure. A $10\text{ }\mu\text{L}$ drop of deionized water (MilliQ purity) was released through a motor-driven syringe onto the surface of the tested polyimide film. The video signal of the drop image was acquired by a numerical camera and transmitted to a computer workstation in order to calculate the contact angle. Each reported value is the average of at least six independent measurements. The standard deviation due to experimental error was estimated to be approximately 5%.

Hydrolytic stability

The hydrolytic stability of polymers was studied by placing the respective polyimide into a Soxhlet extractor with refluxing water. Polymer samples were taken out at a regular time intervals, drying firstly at RT and then at $80\text{ }^\circ\text{C}/1\text{ mm Hg}$ for 12 h, whereupon their inherent viscosities were measured.

Polyimide alkylation kinetics

2.50 g (4.0 mmol) of **PI-1** were dissolved in anhydrous DMF by stirring at RT and under inert atmosphere. The 1.36 g (1.0 mmol) of dried K_2CO_3 , dried immediately prior to use, were further added into the solution in one portion and the mixture was stirred for 20 min at RT. Then, 3.50 g (0.032 mol) of bromoethane were injected into suspension and the reaction mixture was heated up to $80\text{ }^\circ\text{C}$.

Polymer samples were collected within specified time intervals and the alkylation degree was calculated from ^1H NMR data.

Gas permeation experiments

Single gas permeabilities through the prepared membranes were measured using a time-lag apparatus, whose construction and operation details were entirely described elsewhere.⁸ In order to remove entrained gases and traces of water all membranes were degassed under vacuum inside the permeation cell during 12 h before testing. The single CO_2 , CH_4 , and N_2 permeation experiments were conducted at $20\text{ }^\circ\text{C}$ and $35\text{ }^\circ\text{C}$ with an upstream pressure of 100 kPa (feed) and initial vacuum ($< 0.1\text{ kPa}$) as the initial downstream pressure (permeate). At least three separate experiments of each gas on a single membrane sample were carried out. Between the experiments membrane sample was degassed under dynamic vacuum until the downstream pressure was below 0.1 kPa. No residual ionic liquid was found inside the permeation cell at the end of the experiments and, likewise, the membranes mass remained constant throughout the experiments. The resulting membranes look like transparent yellow films.

The single CO_2 , CH_4 , and N_2 permeation experiments were performed using a time-lag apparatus. The permeability coefficient or permeability (P), which is a measure of the membrane's ability to permeate gas, was calculated from the membrane thickness (ℓ), the transmembrane pressure drop (Δp) and the steady state volume flux through the membrane (J) as follows:⁴³

$$P = J \frac{\ell}{\Delta p} \quad (1)$$

The flux J was determined experimentally using Eq. (2), where V^p is the permeate volume, Δp_d is the variation of downstream pressure, A is the effective membrane surface area, t is the experimental time, R is the Ideal Gas Law constant and T is the absolute temperature.

$$J = \frac{V^p \Delta p_d}{AtRT} \quad (2)$$

RESULTS AND DISCUSSION

Synthesis of precursor neutral polyimides

Taking into account that PILs, according to their definition, contain ionic species with chemical structures similar to the commonly used ILs,^{1,2,4,5,19} the primary task of this study was the synthesis of reactive polyimides bearing various N-heterocycles (Scheme 1). For this purpose, we first focused our efforts on the preparation of high molecular weight PIs bearing benzimidazole (Scheme 1, **PI-1**) and quinuclidine (Scheme 1, **PI-2**) fragments. It is worth noting that while the first heterocycle is fairly common in the synthesis of ILs, the second one represents a rather rare case. Both N-heterocycles were incorporated into the polymer chain through the respective diamines (Scheme 1). The HFDA was chosen as the pairing monomer for condensation due to the presence of hexafluoropropylidene group, that usually improves the solubility and processability of the resulting polymers. The one-step solution polycyclization was selected for the synthesis of **PI-1** and **PI-2** as an

efficient method for the preparation of soluble and/or meltable PIs.⁴⁴ The polycondensation reaction was performed in *m*-cresol at 180 °C, affording PIs with high molecular weight (Table 1, entries 1 and 7). The inherent viscosities (η_{inh}) of **PI-1** and **PI-2** were found to be 1.68 and 0.53 dL g⁻¹, respectively. The polymer molar masses (M_n) estimated by GPC for **PI-1** and **PI-2** were 11.1×10⁴ and 4.6×10⁴ g mol⁻¹, correspondingly.

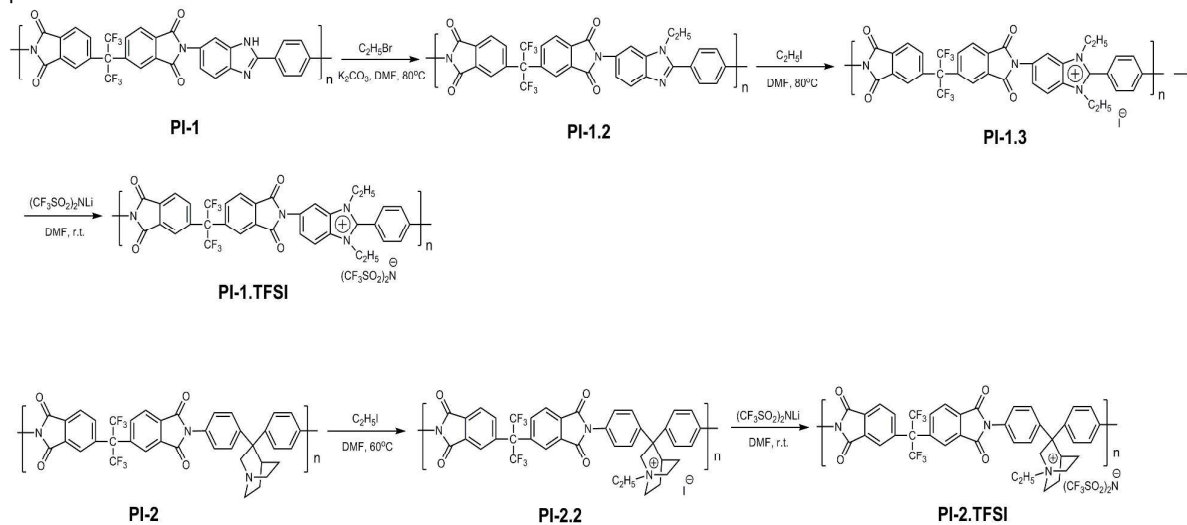
The chemical structures of the synthesized **PI-1** and **PI-2** were confirmed by IR, ¹H and ¹³C NMR spectroscopy. The success of the polycondensation reaction can be clearly seen from the ¹H NMR spectra (Fig. 1). In spite of a good agreement of proton spectra with the polymer structures, their downfield area contains only general group attribution of the signals. Both HMBC and HSQC techniques were not able to resolve a more detailed assignment in the aromatic area due to the unexpected cross-peaks. The structures were further supported by IR spectra, where the characteristic absorption bands for **PI-1** and **PI-2** appear around 717, 1105, 1144, 1160, 1190, 1255, 1325, 1365, 1494, 1601, 1703 and 1770 cm⁻¹ are assigned, respectively, to the C=O bending (717-718 cm⁻¹), C-F stretching (several peaks i.e. 1105, 1144, 1190 and 1325 cm⁻¹), C-C bending (1160 cm⁻¹), C-N stretching (two peaks i.e. 1255 and 1365 cm⁻¹), aromatic C=C ring stretch (two peaks i.e. 1494 and 1601 cm⁻¹), C=O symmetrical stretching (1787 cm⁻¹) and C=O asymmetrical stretching (1722 cm⁻¹). Apart of that, the IR spectrum of **PI-1** presents a broad band at 3120 cm⁻¹ which is attributed to the NH

stretching of the benzimidazole ring, while the IR spectrum of **PI-2** shows a strong band at 1210 cm⁻¹ that is assigned to tertiary amine in quinuclidine cycle, as well a set of bands between 2952 and 2873 cm⁻¹, resulting from C-H stretching.

The solubility of **PI-1** and **PI-2** in different organic solvents was found to be similar (Table S1 in the ESI). For instance, **PI-1** and **PI-2** are both soluble in aprotic solvents such as DMF, DMSO, and γ -butyrolactone, as well as in HFIP and *m*-cresol.

The thermal properties of the prepared PIs were studied by TMA and TGA. From Table 1, it can be observed that **PI-1** has higher glass transition temperature (T_g) than that of **PI-2**, probably due to the presence of additional H-bonding through the benzimidazole ring. Although the onset mass loss temperatures (T_{onset}) of both PIs are above 300 °C, the thermal stability of **PI-2** is significantly lower, which can be essentially attributed to the alicyclic nature of the quinuclidine fragment.

The mechanical properties of **PI-1** and **PI-2** based films are presented in Table 1. The **PI-1** film displayed quite high tensile strength (120 MPa), tensile modulus (2.5×10³ MPa) and elongation at break (40 %) when compared to **PI-2** film (Table 1, entry 7). This difference can be associated with the introduction of the quinuclidine moiety in **PI-2** that certainly hinders the polyimide chains interactions and packing, reducing the stiffness of the resulting membrane.



Scheme 1 Synthetic route for the synthesis of ionic polyimides.

Table 1 Selected properties of the prepared polyimides.

no	Polymer	η_{inh} (dL g ⁻¹) ^a	M_n ^b	M_w/M_n ^b	T_g (°C) ^c	T_{onset} (°C) ^d	Water CA (°)	σ_t (MPa) ^e	$E_t \times 10^3$ (MPa) ^e	ϵ_t (%) ^e
1	PI-1	1.68	111000	1.70	395	460	84.3	120	2,5	40
2								110 ^f	2,2 ^f	7 ^f
3	PI-1.2	1.58	124500	1.71	355	170	78.7	70	1,7	7

ARTICLE										
4	PI-1.3	0.57	81000	1.55	230	170	70.5	80	2,0	5
5	PI-1.TFSI	0.73	97000	1.46	305	380	94.3	110	2,7	5
6								110 ^f	2,3 ^f	6 ^f
7	PI-2	0.53	46000	1.32	330	330	74.2	90	1.4	6
8	PI-2.TFSI	0.24	22000	1.51	325	380	88.5	80	1.4	5

^a For solution of 0.05g of polymer in 10.0 mL of DMF (0.5M LiBr in DMF for **PI-1.3** and 0.5M Li(CF₃SO₂)₂N in DMF for **PI-1.TFSI** and **PI-2.TFSI**) at 25.0 °C. ^b Determined by GPC in 0.01 M LiBr in DMF with polystyrene standards. ^c Measured by TMA. ^d Onset loss temperature determined by TGA. ^e Mechanical properties of the films: tensile strength, tensile modulus and elongation at break, respectively. ^f Measured after immersing the films in water for 48 h at RT.

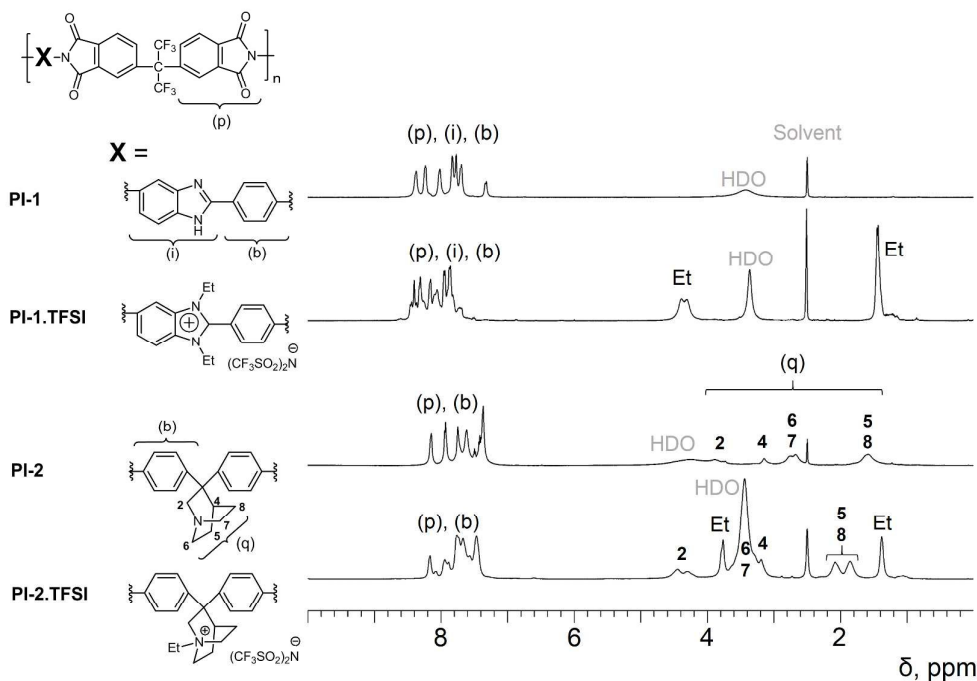


Fig. 1 ¹H NMR spectra (25 °C, DMSO-*d*₆) of polyimides: **PI-1**, **PI-1.TFSI**, **PI-2**, and **PI-2.TFSI**. Shortcuts for the polymer fragments: (p) - phthalimide, (i) - benzimidazole, (b) - benzene, (q) - quinuclidine.

Thus, it can be assumed that **PI-1** and **PI-2** are attributed as typical representatives of such class of polymers as polyimides.

Polyimides modification

The synthetic route used to modify PIs was selected in accordance with the type of amine (secondary or tertiary) in the incorporated heterocycle (Scheme 1). For **PI-1**, the benzimidazole moiety was firstly deprotonated and N-alkylated with bromoethane (Scheme 1, **PI-1.2**), then quaternized with iodoethane (Scheme 1, **PI-1.3**), and finally the resulting **PI-1.3** was subjected to metathesis ion exchange reaction with LiTFSI (Scheme 1, **PI-1.TFSI**). Regarding the case of **PI-2** bearing the quinuclidine fragment, its tertiary amine was straightly exposed to quaternization with iodoethane. The formed **PI-2.2** containing the iodide anion underwent metathesis ion exchange reaction with LiTFSI (Scheme 1, **PI-2.TFSI**).

In order to achieve high degrees of polymer modification a survey on the reaction conditions was required. Initially, the N-alkylation of benzimidazole moiety in **PI-1** was carried out with

bromoethane varying the nature of the deprotonating agent used in the reaction. For that purpose, lithium hydride (LiH), sodium hydride (NaH) and potassium carbonate (K₂CO₃) were tested. The degree of substitution (DS) was calculated from the ratio of aromatic protons to the protons of the side ethyl group obtained from the analysis of H¹ NMR spectrum. In such a way, the use of LiH or NaH during 5 h leads to a maximum DS of 0.3 and 0.5, respectively. On the other hand, the use of K₂CO₃ enables an increment on the DS up to 0.7. Therefore, the N-alkylation of **PI-1** with K₂CO₃ was studied as a function of time. From Fig. S1 in the ESI, it can be seen that after 25 h the alkylation of **PI-1** was almost entirely completed, whereupon the quaternization started to take place. However, from this point the reaction slows down and after 55 h less than 20 % of disubstituted benzimidazole moieties can be obtained.

To increase the rate of the quaternization reaction, a more reactive halogenoalkane, namely iodoethane, was tested for the preparation of **PI-1.3** (Scheme 1). After 30 h of reaction, the DS was

found to be almost quantitative. It is worthy to note that, according to NMR the isolated **PI-1.3** contained no monosubstituted benzimidazolium rings and only 4 mol % of unsubstituted NH groups, meaning that the degree of polymer modification was equal to ~96 %.

Likewise **PI-1.2**, the iodoethane was selected to perform the quaternization of **PI-2** (Scheme 1). The use of similar reaction conditions allowed for the synthesis of **PI-2.2** with a DS equal to 0.89.

Due to the insolubility of **PI-1.3** and **PI-2.2** in water, the metathesis ion exchange was performed in DMF (Scheme 1). Contrary to the synthesis of TFSI-based ILs,⁴⁵ and considering that the metathesis reactions occurred in DMF homogeneously, a larger excess of LiTFSI was necessary to achieve complete anion exchange.

The structure of the final polyimide-based PILs, **PI-1.TFSI** and **PI-2.TFSI**, was confirmed by IR, ¹H, ¹³C and ¹⁹F NMR spectroscopy. The IR spectra reveals the increased intensity of the C-H stretching (2950 - 2850 cm⁻¹) and the presence of the bands related to the (CF₃SO₂)₂N anion (1347, 1325, 1180, 1133, 1054 cm⁻¹). The presence of ethyl groups is clearly visible in the ¹H NMR spectra (Fig. 1) and their chemical shifts are typical of those in quaternary ammonium compounds (4.30-4.40 & 1.43 and 3.76 & 1.38 ppm for **PI-1.TFSI** and **PI-2.TFSI**, respectively). The ¹³C NMR spectra shows the signals of ethyl groups at 41.8 & 14.3 and 52.8 & 7.4 ppm for **PI-1.TFSI** and **PI-2.TFSI**, respectively, as well as a quadruplet around 119 ppm that is originated from the CF₃ groups of the TFSI anion. The attribution of the polymer backbone signals was assessed by DEPT, HSQC and H-H COSY techniques and is entirely described in the Experimental section.

Thus, the suggested modification pathways allow the conversion of neutral **PI-1** and **PI-2** into their ionic forms with a DS up to 0.96.

Ionic polyimides properties

Some of the physico-chemical properties of prepared polyimide-based PILs are summarized in Table 1. The polymers molecular weight was firstly estimated by viscosity measurements. The quaternization reaction in both polymers was accompanied by the decrease of h_{inh} (Table 1, entries 1 & 4 and 7 & 8), whereas the metathesis ion exchange reactions prompted a slight increase of PILs h_{inh} (Table 1, entries 5 and 8). The same conclusions can also be withdrawn from the GPC results. Actually, the **PI-1.TFSI** and **PI-2.TFSI** have lower M_n when compared to that of the starting **PI-1** and **PI-2** (Table 1). This behavior can probably be attributed to the loss of some polymer rigidity resulting from the incorporation of the side alkyl moieties.

The starting PIs synthesized in this work were found to be soluble in *m*-cresol, γ -butyrolactone, HFIP, and amide type solvents such as DMF, DMSO, N-methylpyrrolidone. From Table S1, it can be observed that the newly prepared polyimide-based PILs, ionic **PI-1.TFSI** and **PI-2.TFSI**, differ from their respective parent polymers **PI-1** and **PI-2** by improved solubility in acetone and methanol.

TMA analysis revealed relatively high T_g values (> 300 °C) for all polyimides, with the only exception being the **PI-1.3** (Table 1). The loss of intermolecular H-bonding in **PI-1.2**, after the alkylation of **PI-1**, led to a decrease of the T_g in 40 °C (Table 1, entries 1 and 3). Subsequently, the incorporation of an additional alkyl side chain in

PI-1.3 probably further disrupted the packing of the polymer chains, reducing the T_g to 230 °C (Table 1, entry 4). In sum, it can be concluded that the transformation of PIs into their ionic forms (**PI-1.TFSI** and **PI-2.TFSI**) is accompanied by a decrease of the T_g in comparison to that of the unmodified polymers (**PI-1.1** and **PI-1.2**).

Thermal behavior of modified PIs was evaluated by TGA (Table 1 and Fig. 2). From Fig. 2 it can be seen that the TGA profiles of the monoalkylated **PI-1.2** and quaternized **PI-1.3** (curves 2 and 3, respectively) exhibit two weight loss steps. The first weight loss step between 170 - 400 °C is attributed to the degradation of the aliphatic substituents and coincides with the thermal stability of the majority of imidazolium-based ILs having bromide or iodide anions.^{46,47} The second step (over 410 °C) is related to the degradation of the respective polyimide chain. In contrast to **PI-1.2** and **PI-1.3**, the final **PI-1.TFSI** and **PI-2.TFSI** showed higher thermal stability, with the onset weight loss above 380 °C (Table 1 and Fig. 2, curve 4), coinciding with the thermal stability of other cationic PILs containing the TFSI anion.⁴⁸

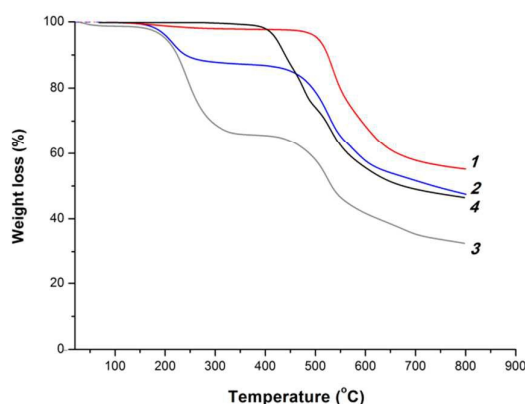


Fig. 2 TGA curves of **PI-1** (1), **PI-1.2** (2), **PI-1.3** (3) and **PI-1.TFSI** (4) in air (5 °C min⁻¹).

On the contrary to the majority of PILs derived from polymerization,^{1,49,50} the ionic polyimides synthesized in this work, particularly the **PI-1.TFSI** and **PI-2.TFSI**, were able to be processed into transparent, free standing and tough membranes (Fig. 3).

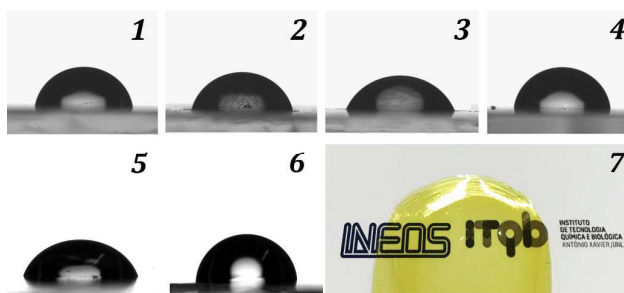


Fig. 3 Changes in water wettability: (1) **PI-1**, (2) **PI-1.2**, (3) **PI-1.3**, (4) **PI-1.TFSI**, (5) **PI-2** and (6) **PI-2.TFSI** and an appearance of the **PI-1.TFSI** membrane (7).

Even though the appending of an aliphatic substituent to the aromatic backbone of **PI-1** resulted in a decrease of the elongation at break, it only influences slightly both the tensile strength and the tensile modulus of the prepared polyimide-based PIL membranes

(Table 1, entries 1 and 3-5). Also worth mentioning is the fact that the modification of **PI-2** practically did not affect the mechanical properties of **PI-2.TFSI** based membrane (Table 1, entries 7 and 8).

The hydrophobicity of polymers was assessed by measuring the water contact angle (CA) using the sessile drop method (Fig. 3). The transformation of neutral **PI-1** into polyelectrolyte **PI-1.3** containing a hydrophilic iodide anion decreased the CA from 84.3 to 70.5° (Fig. 3, image 1 and 3). Conversely, the exchange of the iodide to the TFSI anion increased the CA up to 94.3°, making the resulting **PI-1.TFSI** unwettable (Fig. 3, image 4). Similarly, and when compared to the unmodified **PI-2**, the presence of the TFSI anion in the **PI-2.TFSI** increased the CA to 88.5° (Fig. 3, images 5 and 6). This means that the surface properties of the prepared ionic PIs are very sensitive to the nature of their counter-anion, and the water CA can vary significantly with the anion exchange reactions.

The hydrolytic stability of the neutral and ionic polyimide was investigated by immersing the prepared membranes into deionized water for 48 h. The mechanical properties of the treated membranes were also measured in order to be compared with those of the untreated ones. The results obtained before and after the water immersion are listed in Table 1 (entries 1-2 and 5-6). The immersion of **PI-1** membrane in water resulted in the decrease of its tensile strength, tensile modulus and elongation at break. Remarkably, a similar treatment did not affect the mechanical properties of the modified hydrophobic **PI-1.TFSI**.

Further studies on the hydrolytic stability of **PI-1** and **PI-1.TFSI** were performed by immersing the corresponding membrane into a refluxing water system and the change of the η_{inh} with time was monitored (Fig. 4). When the **PI-1** was immersed in boiling H₂O, a reduction in its viscosity to less than one third was observed after 1.5 h. Contrasting to **PI-1**, the degradation of the modified **PI-1.TFSI** occurred much slowly, allowing the membrane to keep its shape up to 6 h in boiling H₂O (Fig. 4, curve 2).

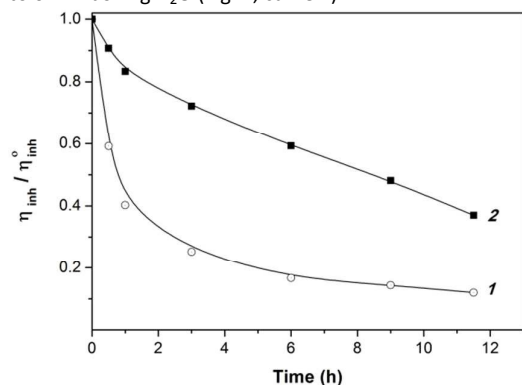


Fig. 4 Comparison of hydrolytical stability for **PI-1** (1) and **PI-1.TFSI** (2) by refluxing in H₂O.

To sum up, the prepared ionic polymers in comparison to neutral precursor polyimides show improved solubility, enhanced hydrolytic stability and tunable hydrophobicity.

Gas permeability

Neat polyimide membranes

In view of the fact that the prepared polyimide-based PIL membranes exhibited superior mechanical properties and higher

glass transition temperatures compared to those of other common PILs, as for instance the pyrrolidinium-based PILs,⁷ we also evaluated the potential of the novel PIs as candidates for membranes designed for natural gas purification (CO₂/CH₄) and flue gas separation (CO₂/N₂). Neat and composite membranes of the synthesized **PI-1** and **PI-1.TFSI** were successfully prepared by a solvent cast procedure using DMF and acetone, respectively. For comparison, the **PI-2.TFSI** was also selected to be tested. Although the neat **PI-2.TFSI** membrane was quite brittle and broke during the gas permeation experiments, the incorporation of 50 wt% of [1-Me-3-Et im]TFSI IL into the **PI-2.TFSI** enabled the preparation of a dense flat form membrane (**PI-2.TFSI-50**) with sufficient mechanical resistance to be handled and gas permeabilities to be measured. [1-Me-3-Et im]TFSI was chosen as IL for filling not only due to its structural similarity to the **PI-1** monomeric unit, but also due to its good CO₂/CH₄ (18.1) and CO₂/N₂ (35.5) permselectivities and high CO₂ permeability (589 Barrer).⁵¹ All prepared composite membranes were found to be homogeneous and exhibited no evidence of phase separation.

The measured gas permeability values in polyimide-based membranes are presented in Fig. 5. The same trend of gas permeability values ($P_{CO_2} \gg P_{CH_4} > P_{N_2}$) was obtained for all tested membranes at both studied temperatures, 20 and 35°C, thus indicating their aptitude to separate CO₂ from CH₄ and N₂. In fact, the CO₂ permeability is one or two orders of magnitude higher than that of CH₄ and N₂. While CO₂ permeability values vary from 19.1 to 103 Barrer, the CH₄ and N₂ change from 1.34 to 8.66 Barrer. According to Fig. 6, the CO₂, CH₄, and N₂ permeabilities of all membranes increase with the rise of temperature, from 20 to 35 °C.

The results presented in Fig. 5 show that the neat **PI-1.TFSI** membrane possesses CO₂, CH₄, and N₂ permeabilities considerably higher than those of neat **PI-1** membrane. It seems that both the presence of the aliphatic substituents in the benzimidazole ring, which reduce the intermolecular H-bonding, and the inclusion of the fluorinated TFSI anion promote a less effective polymer chain packaging, thus allowing for higher gas permeabilities through **PI-1.TFSI** membrane.

Thus it can be concluded, that transformation from neutral PI to its ionic form leads to the increase in membranes CO₂, CH₄ and N₂ permeabilities. *At this it was found that the CO₂ permeability of the **PI-1.TFSI** film obtained herein at 20 °C and 100 KPa (28.9 Barrer) is the best known result among PILs.*⁴⁰

Composite polyimide-IL membranes

As it has been observed by different authors, the presence of free IL generally enables a drastic increase in the gas permeabilities of polymer-based membranes.⁵²⁻⁵⁵ The incorporation of IL into both conventional polymers and PILs, not only decreases the glass transition temperature, but also increases the free volume of the composite membrane, resulting in higher polymer chain mobility and consequently enhanced gas permeabilities. Therefore, two composite membranes based on **PI-1** or **PI-1.TFSI** and 50wt% of [1-Me-3-Et im]TFSI were prepared and studied (hereinafter referred as **PI-1-50** and **PI-1.TFSI-50**, respectively). Upon the incorporation of 50 wt% of IL inside the polymer membrane the CO₂ permeabilities were significantly increased (Fig. 5). Remarkably, the CO₂

permeability increment was more pronounced for **PI-1.TFSI-50 IL** membrane than in the case of **PI-1-50 IL**. For instance, at 30 °C, the CO₂ permeability increased by 164% between **PI-1.TFSI** and **PI-1.TFSI-50 IL**, which is a larger enhancement than that observed amongst **PI-1** and **PI-1-50 IL**, where a CO₂ permeability increment was only equal to 63%. Albeit the composite membranes are dense blends that combine the permeation properties of its constituents, the polymer and the IL, it is important to point out that ILs within PILs are different from ILs in non-ionic polymers. While ILs have the ability to strongly interact with the charged backbone of PILs through the electrostatic interactions creating more free volume and enhancing the CO₂ permeability, in non-ionic polymers the IL is only entrapped in the tight spaces between the polymers chains.

In contrast to the effect on CO₂ permeability the transfer from neat **PI-1.TFSI** membrane to the filled **PI-1.TFSI-50 IL** led to unexpected decrease of CH₄ and N₂ permeabilities (Fig. 5b and 5c).

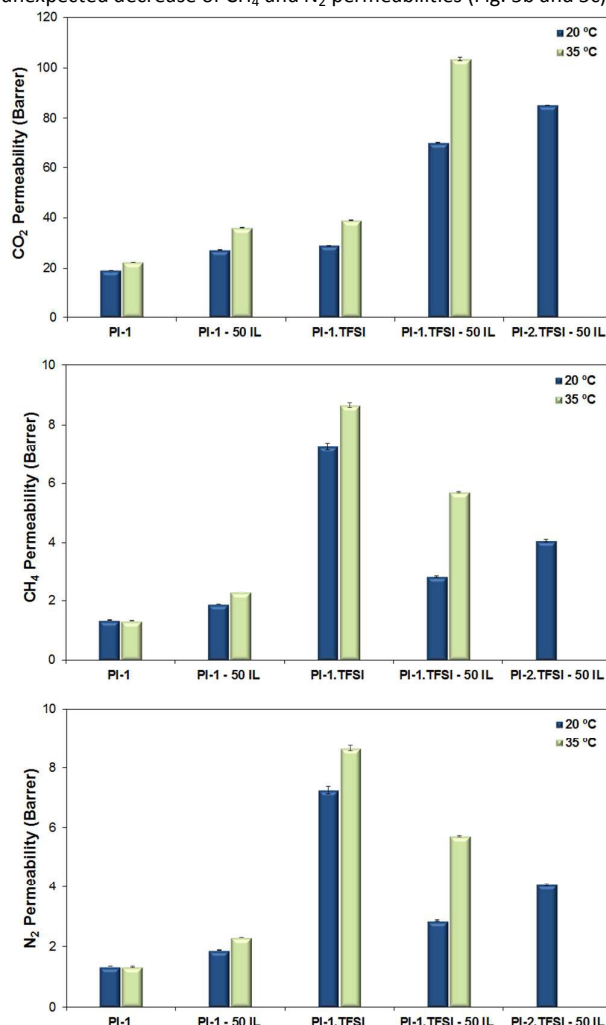


Fig. 5 Permeabilities (1 Barrer = 10⁻¹⁰ cm³(STP)cm cm⁻² s⁻¹ cm Hg⁻¹) of the prepared membranes towards (a) carbon dioxide, (b) methane, and (c) nitrogen, determined at 20 and 30°C under a transmembrane pressure differential of 100 kPa. Error bars represent standard deviations based on three experimental replicas.

Regarding the effect of the cation structure of the polyimide-based PIL on the membrane gas permeability, it can be observed from Fig. 5 that at 20 °C the presence of the quinuclidine moiety in the **PI-2.TFSI-50 IL** composite membrane increases the CO₂, CH₄, and N₂ permeabilities by 21, 42 and 57%, respectively, compared to those of the benzimidazole based **PI-1.TFSI-50 IL**. A probable explanation is the fact that the quinuclidine is a bulkier moiety than the benzimidazole, and thus contributes to a less packed membrane, with lower resistance to gas diffusion and higher gas permeabilities.

In conclusion, the incorporation of 50 wt% of IL inside the polymer membrane greatly increases the CO₂ permeability. At this, the CO₂ permeability improvement is more pronounced for ionic PIs.

Gas permselectivity

Neat polyimide membranes

Besides gas permeability, another important parameter of a membrane is its ability to separate two gases. The ideal permeability selectivity (or permselectivity), $\alpha_{i/j}$, which is a measure of how well a membrane discern one gas from another, was obtained by dividing the permeability of the more permeable specie *i* to the permeability of the less permeable specie *j*:

$$\alpha_{i/j} = \frac{P_i}{P_j} \quad (3)$$

The obtained ideal CO₂/CH₄ and CO₂/N₂ permselectivities of the studied membranes are shown in Fig. 6. As it can be seen, the transformation from neutral **PI-1** to ionic **PI-1.TFSI** has a negative effect on both the CO₂/CH₄ and CO₂/N₂ permselectivities, which roughly decreased 3 or 4 times.

Composite polyimide-IL membranes

The incorporation of 50 wt% of IL promotes the increase in CO₂/CH₄ and CO₂/N₂ permselectivities in both **PI-1-50 IL** and **PI-1.TFSI-50 IL** composite membranes (Fig. 6). Thus, the presence of IL in the **PI-1.TFSI-50 IL** composite membrane not only significantly increase the CO₂ permeability (Fig. 5), but also greatly enhanced the CO₂/CH₄ and CO₂/N₂ permselectivities that are about 6 times higher than those of the neat **PI-1.TFSI** membrane (Fig. 8). Indeed, a remarkable synergistic effect can be observed in this case probably due to the better compatibility between both phases, the PIL (**PI-1.TFSI**) and the imidazolium IL.

Therefore, the incorporation of IL into PI membranes enhances their CO₂/CH₄ and CO₂/N₂ permselectivities. At this, the enhancement effect is more pronounced in the case of ionic PIs. Within the same polymer/IL composition the ionic PIs possess higher CO₂/CH₄ and CO₂/N₂ permselectivities than their respective neutral analogues.

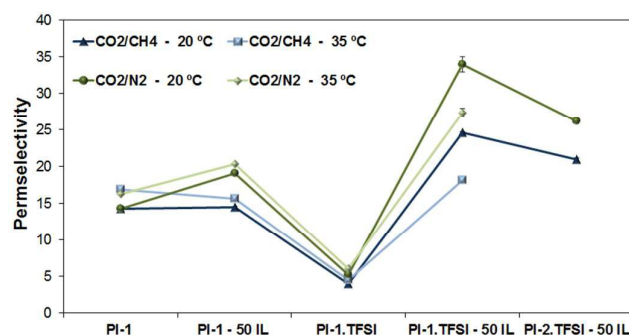


Fig. 6 Ideal CO₂/CH₄ and CO₂/N₂ permselectivities obtained in the prepared membranes at 20 and 30 °C under a transmembrane pressure differential of 100 kPa. The error is either within the size of the markers or shown by error bars which were determined by propagation of uncertainty based on three experimental replicas.

Comparison of gas separation properties with known analogues

The comparison of CO₂/CH₄ and CO₂/N₂ separation performances between the results obtained in this work and the recently published data for PIL–IL composite membranes comprising the TFSI anion and for other neat polyimide membranes is illustrated in Robeson plots (Fig. 7a and 7b).⁵⁶ This type of plot, also referred as “upper bound”, is widely used to evaluate the gas separation performance of membrane materials and displays the trade off line between the permeability and selectivity in the following form:

$$P_i = k\alpha_{ij}^n \quad (4)$$

where P_i is the permeability of the more permeable specie, α_{ij}^n is the permselectivity, n is the slope, and k is the front factor.

It is known that membranes based on neutral polyimides usually demonstrate intrinsic CO₂/CH₄ separation properties.^{57,58} In contrast to this, PIL–IL composite membranes often show better CO₂/N₂ separation.^{7,8,59,60} The Robeson plots (Fig. 7) indicate that for neutral PI-1 membrane both the CO₂/CH₄ (Fig. 7a) and CO₂/N₂ (Fig. 7b) separations are better than for ionic PI-1.TFSI film and can be considered as average compared to other PIs. Unfortunately, the results for neat PI-1.TFSI membrane lay far below than that of other known PIs and TFSI based PILs.

However, the situation significantly changes when the comparison is made for the filled membranes. In this way the composite PI-1.TFSI–50 IL film shows much better CO₂ separation than PI-1–50 IL (Fig. 7). The CO₂/N₂ and CO₂/CH₄ separation performance of PI-1.TFSI–50 IL and PI-2.TFSI–50 IL becomes equal to the best results published for other PIL–IL composite membranes with TFSI anions, although is still below the respective upper bound limits.

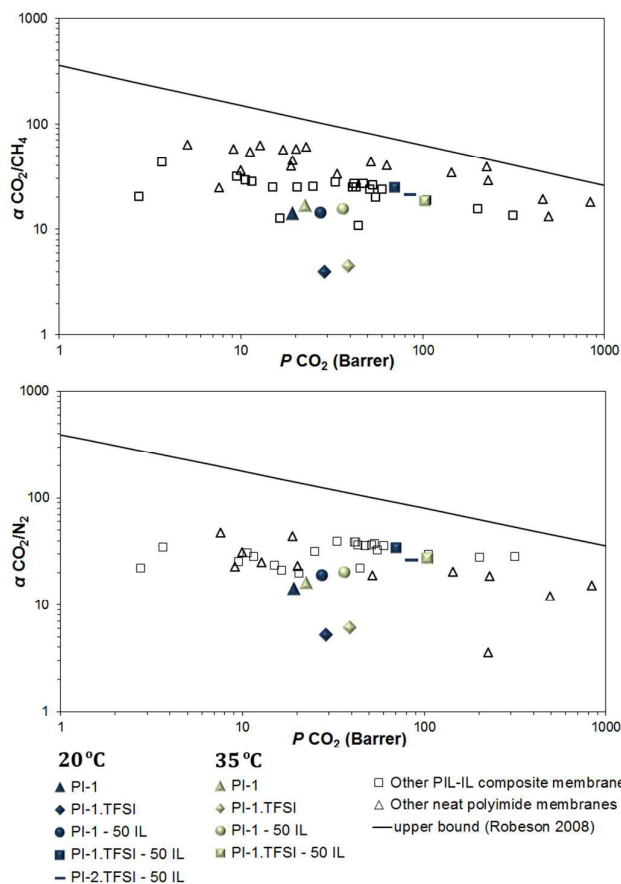


Fig. 7 CO₂ separation performances of the synthesized membranes plotted on (a) CO₂/CH₄ and (b) CO₂/N₂ Robeson plots. The experimental error is within the data points. Data are plotted on a log-log scale and the upper bound is adapted from Robeson.⁵⁶ The literature data reported for other (□) PIL–IL composite membranes,^{59,60} and (Δ) neat polyimide membranes^{41,61,62} are plotted for comparison.

Conclusions

In this work, poly(ionic liquid)s were prepared from polyimides using new efficient synthetic routes. The proposed methods afford high molecular weight ($M_n = 2.2 - 9.7 \times 10^4 \text{ g mol}^{-1}$) thermally stable (T_{onset} up to 380 °C) ionic polyimides with a degree of substitution up to 0.96. In comparison to neutral precursor polyimides, the prepared ionic polymers show improved solubility, enhanced hydrolytic stability, higher gas permeability and tuneable hydrophobicity, which was found dependent on the selected counter anion. It was revealed that the CO₂ permeability of the newly prepared PIL (28.9 Barrer) at 20 °C and 100 KPa is the best known result for PILs and is even higher than that of all other previously reported composite membranes based on various cationic PILs and 10 wt% of ionic liquid (3.66 ÷ 20.4 Barrer). Further incorporation of IL in polyimide-based PILs additionally enhances the gas transport properties of composite membranes: $P(\text{CO}_2)$ up to 85 Barrer, $\alpha(\text{CO}_2/\text{N}_2)$ up to 33.9 and $\alpha(\text{CO}_2/\text{CH}_4)$ up to 24.6 at 20 °C.

Demonstrating similar CO₂/N₂ and CO₂/CH₄ separation, the suggested polyimide-based PILs differ from other PILs synthesized via free radical polymerization by better mechanical properties of the films.

Finally, the results obtained in this work show that turning polyimides into PILs is a promising strategy to prepare polymer matrices with improved properties.

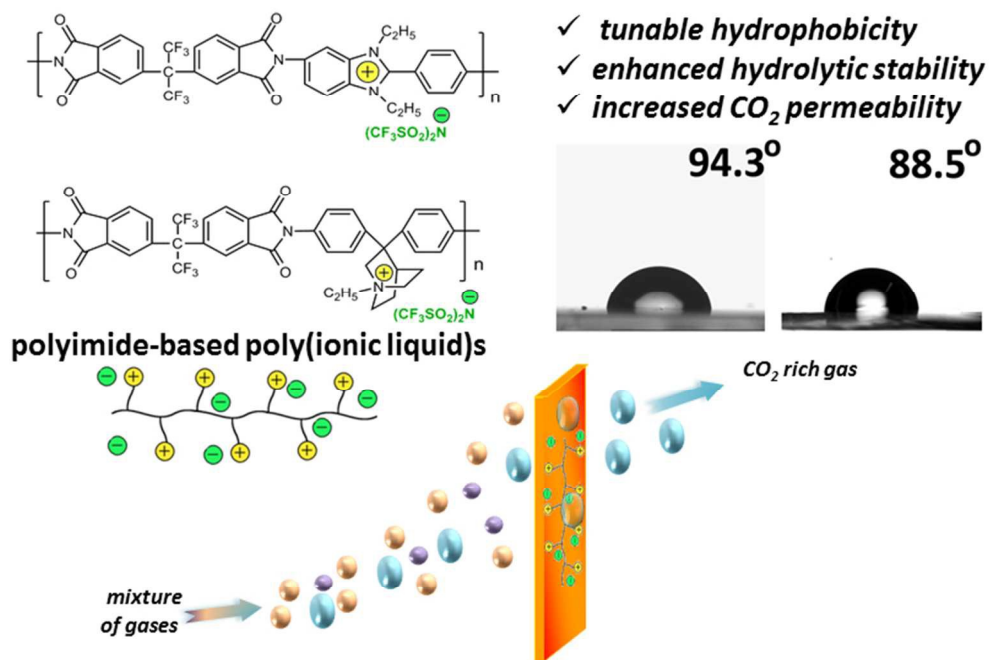
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