Supporting Information

Film Forming Polymeric Ionic Liquids (PILs) Based on Polybenzimidazoles for CO_2 Separation

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Synthesis of PBI-BuI

PBI-BuI was synthesized by polycondensation reaction of DAB (*3,3′*-diaminobenzidine) and *5-tert*-butyl isophthalic acid as reported earlier.[1] A three-necked round bottom flask equipped with a mechanical stirrer, N_2 inlet and $CaCl_2$ drying tube was charged with 1200 g of PPA (polyphosphoric acid), 40 g (0.18668 mol) of DAB and temperature was elevated to 140 ºC. After dissolution of DAB, 0.18668 mol of *5-tert*-butyl isophthalic acid (41.48784g) was added; temperature was raised to 170 ºC and maintained for 5 h under constant flow of N_2. The temperature was further raised to 200 ºC and maintained for 12 h. The polymer was obtained by precipitation in water. It was crushed, washed thoroughly with water, kept in 10% $NaHCO_3$ for 16 h; followed by water wash. It was soaked in acetone for 16 h and dried in vacuum oven at 100 ºC for 3 days. Further purification by dissolving in DMAc (3% w/v) and reprecipitation in water yielded yellow colored fibrous polymer (yield of purified polymer = 98%). Its inherent viscosity (η_{inh}) was determined at the polymer concentration of 0.2 g/dL in DMSO at 35 °C. It was found to be 1.0 dL/g.

Synthesis of Polymeric ionic liquids

N-Quaternization of PBI-BuI (15 g) was performed in a single step by in-situ formation of the Na-salt using 2.1 molar equivalents of NaH at ambient, followed by addition of a small excess of methyl iodide (4.2 molar equivalents). A precipitate formation was indicative of fast nature of reaction. It was dissolved after the temperature was raised to 80 ºC; which was further maintained for 24 h to ensure completion of the reaction. This solution remained clear and homogeneous even after the temperature was lowered to the ambient. It was then precipitated in a mixture of toluene and acetone (1:1) in order to recover the polymer. Obtained polymer after vacuum drying was purified by dissolving in DMF and reprecipitation in the mixture of toluene and acetone (1:1). The yield of this reaction was 94%.

The ^{1}H-NMR spectra of *N*-quaternized PBI is given in Fig. S1. In the spectra of PBI-BuI, broad peak appeared in the range of δ 13-14 correspond to N-H. After the substiution, this peak was disappeared. This elimination of N-H proton indicates almost complete quaternization. The quantitative estimation of *N*-quaternization was evaluated by comparing integrations of methyl group protons (δ 4.2 - 4.5 ppm) with that of aromatic protons (δ 7.5 - 9.5 ppm).

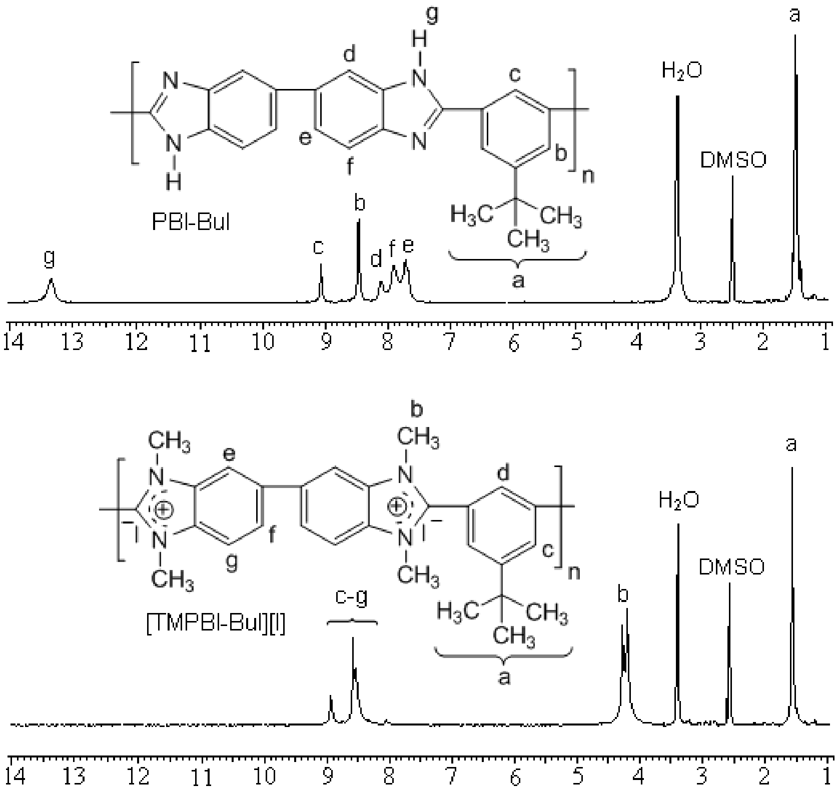

Fig. S1 ^{1}H-NMR spectra of PBI-BuI and PIL

Anion exchange

A 5 g of [TMPBI-BuI][I] was dissolved in DMF, added 2 molar equivalents of silver salt of an anion ($AgBF_4$ or CH_3COOAg) while stirring. Immediate formation of AgI precipitate after the addition of silver salt provided an indication of quick exchange of anion. In view of polymeric nature of the cationic species, the reaction mixture was further stirred for 24 h in order to ensure maximum possible anion exchange and then centrifuged at 12000 rpm for 90 min in order to separate the fine precipitate of AgI. The solvent from supernatant polymer solution was evaporated to recover formed PIL.

In case of exchange by Tf_2N^{-}, a 5 g of [TMPBI-BuI][I] was dissolved in DMF and 2 molar equivalents of $LiTf_2N$ was added at ambient and stirred for 24 h. PIL was obtained by precipitating the reaction mixture in water (in which the byproduct, LiI is soluble), followed by water wash.

Estimation of anion exchange by Volhard’s method

Iodide present in formed PILs was determined by Volhard’s method,[2] in which 0.1 g of polymer in powder form was stirred in 25 ml of 0.01M $AgNO_3$ solution for 24 h. Excess of unreacted $AgNO_3$ was titrated with 0.01 M KSCN to deduce the amount of $AgNO_3$ consumed with iodide present in the polymer.

Membrane preparation

Dense membranes of PILs were prepared by solution casting using 3% (w/v) DMAc solution at 80 °C for 18 h under dry conditions on a flat glass surface. After initial evaporation of the solvent, formed membrane (thickness of 40 μm) was peeled off and dried in a vacuum oven at 100 °C for a week in order to remove the residual solvent.

Spectral analysis of PILs

FT-IR spectra of polymers in thin film (~10 μm) form were recorded at ambient as well as at 150 °C (in order to remove absorbed water) using Perkin Elmer Spectrum GX spectrophotometer provided with high temperature assembly of Mettler Toledo make with FP90 central processor.

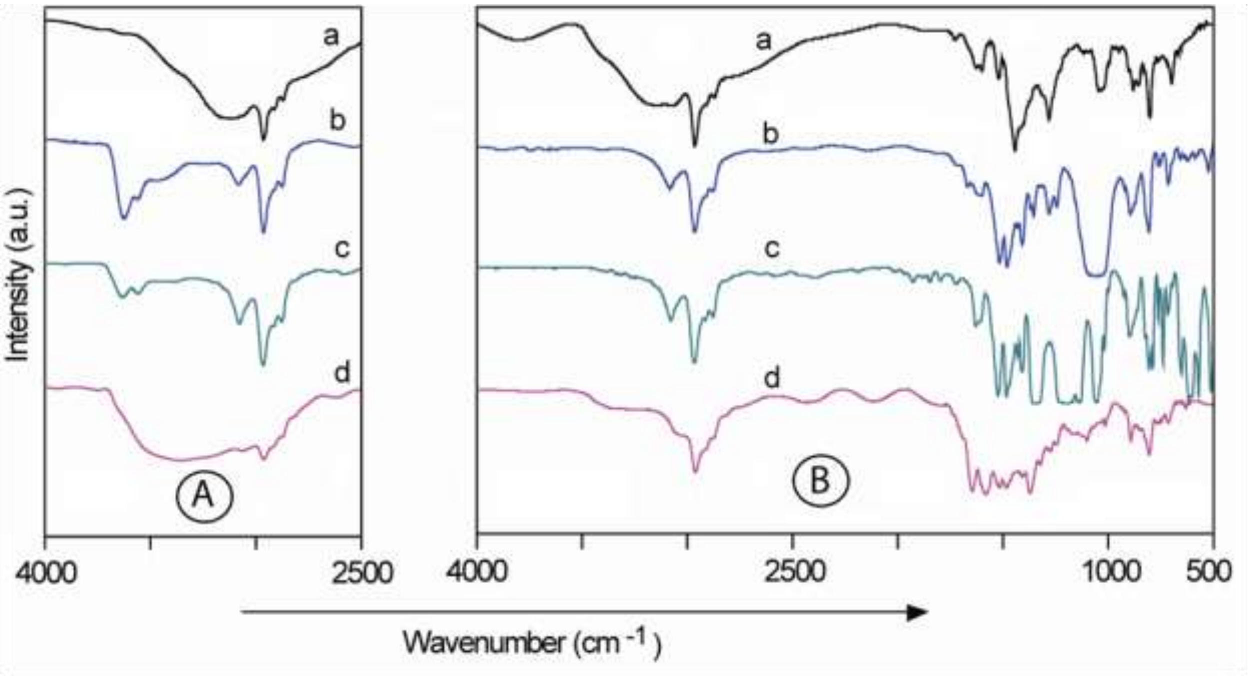

Fig. S2 FT-IR spectra recorded at (A) ambient and (B) 150 °C (where, a: PBI-BuI, b: [TMPBI-BuI][BF_4], c: [TMPBI-BuI][Tf_2N], d: [TMPBI-BuI][Ac]

FTIR spectra of PILs scanned at ambient showed a broad band at ~3610 cm^{-1} attributable to the moisture absorbed. It was disappeared when scans were recorded at 150 ºC. For unsubstituted PBI, band at ~ 2400-3500 cm^{-1} originating from N-H stretching is observed.[1,3,4] After PIL formation, this band was disappeared confirming *N*-substitution. For PILs with BF_4 as the counterion, a band at ~1050 cm^{-1} was attributable to the B-F stretching vibrations.[5,6] In case of PILs with Tf_2N as the counterion, bands at ~1330 cm^{-1} and 612 cm^{-1} could be attributed to the asymmetric stretching and bending vibrations of sulfone group, respectively.[7] In these spectra, a band at 1130-1240 cm^{-1} is attributable to the symmetric stretching vibrations of C-F bond.[7] In a spectrum of [TMPBI-BuI][Ac] showed a typical C=O stretching (belonging to the ester group) at 1651 cm^{-1}. The characteristic bands for benzimidazole in the range of 1500-1650 cm^{-1} attributable to C=C/C=N stretching vibrations[1,3] were observed in all the PILs.

Wide angle X-ray diffraction (WAXD) spectra of polymers were recorded using Rigaku X-ray diffractometer (D-max 2500) with Cu-K_α radiation.

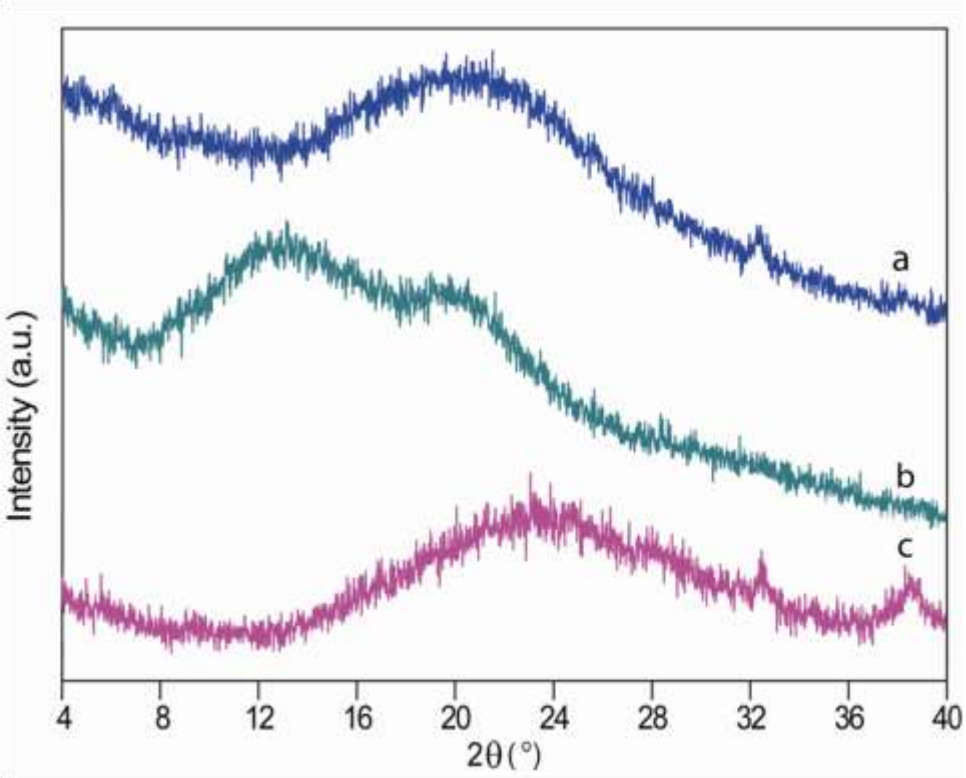

Fig. S3 Wide angle X-ray diffraction spectra (where, a: [TMPBI-BuI][BF_4], b: [TMPBI-BuI][Tf_2N], c: [TMPBI-BuI][Ac].

Thermal analysis

Thermogravimetric analysis (TGA) was performed using Perkin Elmer TGA-7 in a N_2 atmosphere with a heating rate of 10 °C/minute.

Gas sorption and permeation analysis

Pure gas sorption isotherms for PILs using N_2, CH_4 and CO_2 were obtained by incremental pressure rise up to 20 atm and at 35 °C using equipment that consisted of dual-volume single-transducer set up based on pressure decay method.[8,9]

The pure gas permeability measurement using N_2, CH_4 and CO_2 was carried out by standard variable volume method as used earlier[9] at upstream gas pressure of 20 atm at 35 °C, while maintaining the permeate side at atmospheric pressure.

References

1 S. C. Kumbharkar, Md. N. Islam, R. A. Potrekar and U. K. Kharul, *Polymer*, 2009, **50,** 1403.

2 G. H. Jeffery, J. Bassett, J. Mendham, C. Denneyv, Vogel's Textbook of Quantitative Chemical Analysis, *British Library Cataloguing in Publication Data*, Fifth edn., 1989, pp. 355-356.

3 P. Musta, F. E. Karasz and W. J. Macknight, *Polymer,* 1993, **34,** 2934.

4 N. W. Brooks, R. A.Duckett, J. Rose and I. M. Ward, *Polymer*, 1993, **34,** 4038.

5 P. A. Z. Suarez, J. E. L. Dullius, S. Einloft, R. F. Desouza and J. Dupont, *Polyhedron*, 1996, **15,** 1217.

6 B. Yu, F. Zhoua, G. Liu, Y. Liang, W. T. S. Huck and W. Liu, Supplementary Material for *Chem. Comm.*, 2006, **22**, 2356.

7 P. Y. Pennarun and P. Jannasch, *Solid State Ionics*, 2005, **176,** 1849.

8 W. J. Koros and D. R. Paul, *J. Polym. Sci. Part B: Polym. Phys.,*1976, **14,** 1903.

9 S. C. Kumbharkar, P. B. Karadkar and U. K. Kharul, *J. Membr. Sci.*, 2006, **286,** 161.