



Polybenzimidazole based polymeric ionic liquids possessing partial ionic character: Effects of anion exchange on their gas permeation properties



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ABSTRACT

Polymeric ionic liquids (PILs) are emerging as promising membrane materials for CO₂ separation. Present work is in continuation with our earlier efforts on evaluating gas permeation properties (especially, CO₂) of film forming PILs based on polybenzimidazoles and efforts towards improving their permeability by structural tuning. This work specifically aims at evaluating effect of anion variation in chosen PILs possessing partial *N*-quaternization of imidazole moiety of PBI-Bul. Three anions (viz., Tf₂N⁻, BF₄⁻ and Ac⁻) were chosen for the bromide exchange of two PILs, viz., [TBzPBI-Bul][Br]₁₀ and [TBzPBI-Bul][Br]₁₈, possessing degree of PBI *N*-quaternization (DQ) as 10 and 18%, respectively. Concurrent effects of variation in anion and DQ were analyzed in terms of physical and gas permeation properties of the resulting PILs. All of them possessed amorphous nature, adequate thermal stability (≥ 250 °C) and solvent solubility, which are primary requisites towards their applicability as a membrane material. PILs possessing BF₄⁻ anion exhibited improved CO₂ permeability coefficient as well as its permselectivity over CH₄ and N₂, in comparison to their counterparts with other anions.

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1. Introduction

Increased concentration of CO₂ in the atmosphere arising from fossil fuel combustion is becoming one of the most important environmental issues, globally [1,2]. The CO₂ capture followed by its sequestration is being looked as one of the possible remedies to address this issue. The first step can be achieved by several techniques such as absorption, adsorption, membranes and cryogenics [3]. Membrane separation processes provide inherent advantages over other conventional separation techniques. The process equipments are simple, have no moving parts, they are compact thus easy to scale-up, relatively easy to operate and control. Since membrane based separation does not require any phase transformation, it could be a viable alternate for CO₂ separation [2]. Nonetheless, for membranes to be economically competitive, materials with high permeability, selectivity and ability to withstand operational conditions is highly desirable. Intrinsic gas permeability and selectivity of a membrane material are usually inversely related (those with high permeability have lower selectivity and vice-versa, a trade-off relationship demonstrated by 'Robeson Plot', [4,5]).

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Towards improving CO₂ permeation properties of membrane materials, a new approach utilizing excellent CO₂ absorption in ionic liquids (ILs) is being explored in a new family of materials, termed as polymeric ionic liquids (PILs) [6–12]. PILs combining crucial characteristics of ILs and macromolecular architecture possess high CO₂ sorption, faster CO₂ adsorption/desorption rates and good thermal stability [7,8]. These properties can further be tuned by the choice of cations and anions [9,12,13]. The key problem with most of the demonstrated PILs is that they are mechanically weak and thus could not be used as membranes at higher pressure [6,14,15]. To conquer this issue, various methodologies, such as crosslinking [15–20], copolymerization [14,21,22], polymerization of IL-monomers on porous polymer support [15,17,20,23,24] and recently, PILs based on *N*-quaternization of fully aromatic polybenzimidazole (PBI) backbone [25–27] are being explored.

PILs obtained by *N*-quaternization of PBI-Bul exhibited high CO₂ sorption and sorption selectivity over N₂ and CH₄ [27]. In order to improve their permeability coefficient, we recently have demonstrated PILs possessing partial ionic character [28]. This family exhibited interesting variations in their permeation properties, due to concurrent effects of increasing bulk and ionic character. Gas permeability coefficient showed maxima at just 13% degree of quaternization (DQ) of PBI, but the selectivity of various gas pairs were lowest within the series (as could be anticipated

based on trade-off relationship). The two immediate neighboring PILs possessing 10 and 18% DQ, (viz., [TBzPBI-Bul][Br]₁₀ and [TBzPBI-Bul][Br]₁₈, respectively) exhibited good combination of permeability coefficient and permselectivity. These PILs possessed bromide as an anion. It is well known that by variation of anion, CO₂ permeation (especially sorption) properties can be improved in PILs [7,8,27,29]. It is thus worth to examine effects of variation in anion in these PILs on their selectivity performance (especially CO₂ based), and became the objective of this study. Three anions (Tf₂N⁻, BF₄⁻ and Ac⁻) that are known to improve CO₂ sorption characteristics in PILs [27,29,30] were chosen for the bromide exchange of [TBzPBI-Bul][Br]₁₀ and [TBzPBI-Bul][Br]₁₈. Investigations towards physical, CO₂ sorption and permeation properties of resulting PILs are reported.

2. Experimental

2.1. Materials

3,3'-Diaminobenzidine (DAB), 5-*tert*-butylisophthalic acid (Bul), sodium hydride (60% dispersion in mineral oil), *N,N*-dimethylacetamide (DMAc), dimethyl sulphoxide (DMSO, 0.01% H₂O), 4-*tert*-butylbenzyl bromide (BzBr), silver nitrate (AgNO₃), sodium tetrafluoroborate (NaBF₄) and lithium bis(trifluoromethane)sulfonimide (LiTf₂N) were procured from Aldrich Chemicals. Polyphosphoric acid (PPA, Ca 84% as phosphorus pentoxide) was procured from Alfa Aesar, while sodium acetate (CH₃COONa) was procured from Merck. Potassium thiocyanate (KSCN), sodium chloride (NaCl) and common solvents used (chloroform (CHCl₃), methanol (CH₃OH), acetone and acetonitrile) were procured from S.D. Fine Chemicals. Dialysis bag (molecular weight cut off, MWCO of 10,000) was procured from Aldrich Chemicals. Pure gases viz., He, H₂ and N₂ were procured from Vadilal Chemicals Ltd.; while CH₄ and CO₂ (purity of 99.995%) were procured from Air Liquide.

2.2. Anion exchange

Two PILs, viz., [TBzPBI-Bul][Br]₁₀ and [TBzPBI-Bul][Br]₁₈ as reported recently [28] were chosen for the anion exchange. The bromide anion of PILs was exchanged using LiTf₂N, NaBF₄ and CH₃COONa in DMAc (Scheme 1). A 3 g (0.0043 mol) of [TBzPBI-Bul][Br]₁₀ was dissolved in 100 ml of DMAc while stirring. A 2.35 g (5 eq) of NaBF₄ was added and stirred at RT for 48 h in order to

ensure maximum possible exchange. The same procedure was followed for the exchange of Br⁻ with other anions [Tf₂N⁻ and Ac⁻] as well as for exchanging Br⁻ of [TBzPBI-Bul][Br]₁₈.

The formed byproduct, LiBr/NaBr was separated from the polymer solution by precipitating the reaction mixture in water; while in case of Ac⁻ as an anion, dialysis bags were used to separate the product PILs and byproduct NaBr. This was needed since PIL with acetate anion exhibited partial solubility in water. The detailed procedure of separation using dialysis bag is given in ESI. Obtained PILs were dried at 80 °C for 24 h, followed by vacuum drying at 80 °C for 1 week.

2.3. Characterizations

The extent of Br⁻ exchanged by Tf₂N⁻, BF₄⁻ and Ac⁻ in a PIL was estimated by titrating formed LiBr/NaBr with 0.01 M AgNO₃ by Volhard's method [31]. For this, 0.1 g of PIL powder was stirred in 10 ml of 0.01 M AgNO₃ solution for 24 h. Excess of unreacted AgNO₃ was titrated against 0.01 M KSCN. This led to amount of AgNO₃ consumed with remainder bromide anion of a PIL, and thus extent of anion exchange could be estimated.

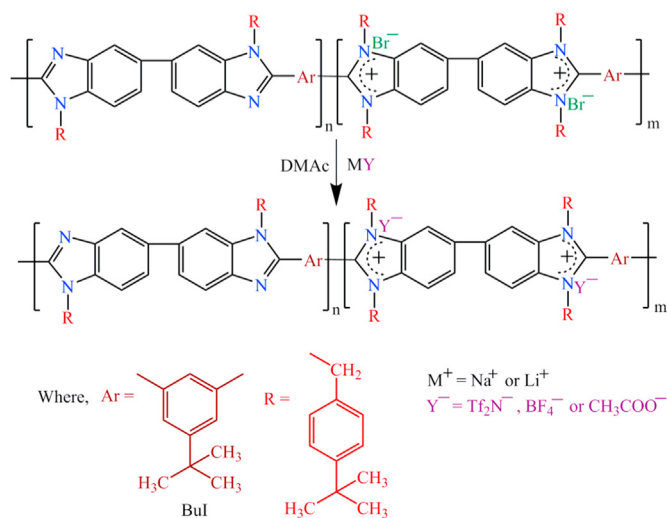
Inherent viscosity (η_{inh}) of PIL solution (0.2 g dL⁻¹) was determined at 35 °C using DMSO as the solvent. FT-IR spectra of polymers in thin film (~10 μm) form were recorded initially at the ambient and then at 180 °C on Perkin Elmer Spectrum GX spectrophotometer provided with high temperature assembly of Mettler Toledo make with FP90 central processor. Wide angle X-ray diffraction (WAXD) pattern of polymers in the film form was recorded using Phillips PAnalytical diffractometer in reflection mode using CuKα radiation ($\lambda = 1.5418 \text{ \AA}$). The 2θ range from 4° to 40° was scanned with a scan rate of 2.5° min⁻¹. The average intersegmental d-spacing (d_{sp}) for the amorphous peak maxima was calculated using Bragg's equation ($n\lambda = 2d\sin\theta$). The density (ρ) measurement was carried out at 35 °C with ~100 μm thick film of a PIL using specific gravity bottle and decalin as the solvent. This solvent was chosen based on its negligible sorption (< 1.4 wt%) in present PILs. Thermogravimetric analysis (TGA) was performed using Perkin Elmer TGA-7 in a N₂ atmosphere with a heating rate of 10 °C min⁻¹. A dynamic mechanical thermal analyzer (DMA, Rheometric Scientific) was employed for determining the glass transition temperature (T_g) of these PILs. The experiment was performed under tensile mode at a frequency of 1 Hz and the heating rate was 10 °C min⁻¹. The scan was recorded up to ~20 °C below the IDT of respective PIL. The solvent solubility of PILs in common organic solvents was determined by adding 0.1 g of polymer in 10 ml of a solvent while stirring at ambient for 24 h. In case of insolubility, further heating at 80 °C (or near boiling point, in case of the low boiling solvents) was performed for 8 h.

2.4. Membrane preparation

The solution casting method was used to prepare dense membranes of PIL. The 3% w/v solution was prepared in DMAc and centrifuged at 12,000 rpm (in order to remove undissolved particles, if any). It was poured on to the flat glass surface and heated at 90 °C for 18 h under the inert atmosphere. Formed membrane was peeled off and dried in a vacuum oven at 80 °C for a week in order to remove the residual solvent and then used for subsequent gas sorption and permeation analysis (average thickness: 35 μm, max deviation in thickness: ± 3 μm). The complete removal of solvent from these membranes was confirmed by TGA.

2.5. Gas permeation and sorption

The pure gas permeability coefficient measurement using He, H₂, N₂, CH₄ and CO₂ was carried out by standard variable volume



Scheme 1. PIL synthesis by anion exchange of partially quaternized PBIs.

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