



Incorporation of rigid polyaromatic groups in polybenzimidazole-based polymeric ionic liquids: Assertive effects on gas permeation properties



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ABSTRACT

Polymeric ionic liquids (PILs) have emerged as promising membrane materials for CO₂ separation. The present work is aimed at investigating the effects of incorporation of rigid polyaromatic hydrocarbons, viz., pyrene and anthracene, in polybenzimidazole-based PILs. The effects of substituent and anion variation on the gas permeation properties of PILs using pure gases were examined at 20 atm upstream pressure. The results were correlated with physical properties of PILs. The pyrene substituted PIL exhibited ~10 fold increase in CO₂ permeability as compared to its precursor polymer PBI-Bul. The combination of a CO₂ specific anion and bulky group substitution offered higher CO₂ permeability as well as appreciable permselectivity than their structural analogue that was devoid of IL functionality. The permeation properties of present PILs were superior to those of conventional glassy polymers such as polysulfone, matrimid and polycarbonate which are widely studied for their gas permeation properties.

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1. Introduction

Anthropogenic CO₂ emission has increased dramatically since the beginning of the industrial age, due largely to the burning of fossil fuels such as coal and natural gas for the production of electricity, utilization of petroleum and diesel for transportation. This has led to severe environmental issues [1,2]. The increasing amount of CO₂ in the earth's atmosphere is believed to be the key factor to cause the global warming [3]. There is a pressing need to sequester CO₂ from the flue gas before it is released to the atmosphere. Towards CO₂ capture, the use of membranes seems to be a preferred option over other separation technologies such as absorption, adsorption and cryogenic distillation [3,4]. This is ascribed to their low capital cost, scalable design, high energy efficiency, and ease of operation. Amongst the new generation separation materials, imidazolium ionic liquids (ILs) exhibit remarkable CO₂ solubility that is dependent on structure of the cation and anion they hold [5–7]. Moving forward from ILs in order to mitigate their known inherent limitations for membrane formation [3], polymeric ionic liquids (PILs) that combine unique properties of ionic liquids and solid polymer are being investigated [8,9]. It has been reported

that PILs synthesized using IL-monomers exhibit higher CO₂ absorption capacity as well as faster and reversible adsorption/desorption rate than the low molecular weight ILs [8–10]. Although significant benefits are anticipated from PILs, those possessing aliphatic backbones are mechanically weak [8,11] and are not suitable to be transformed into a membrane for practical separation purposes. The efforts are currently focused on transforming PILs into membranes that can withstand high pressures by employing methodologies such as cross-linking or copolymerization for flat film form [11].

We have recently demonstrated a unique methodology for obtaining film-forming PILs possessing rigid aromatic backbone [12,13]. The *N*-quaternization of polybenzimidazoles (PBIs) by different substituent followed by metathesis using a range of anions led to the PILs with improved CO₂ sorption and permeation characteristics [13]. The substituent as well as anion present in the PIL were found to have profound roles in governing CO₂ sorption and permeation properties. These attempts covered incorporation of bulky substituents in the PBI main chain, controlled degree of quaternization, and use of the CO₂ specific anions [14,15]. In our recent work on PILs possessing 'substitution asymmetry', gas diffusivity and solubility analyses conveyed a need to further enhance the diffusivity of CO₂ by structural tuning of the PILs [15].

There are some reports describing the effects of incorporation of

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polycyclic aromatic hydrocarbons (PAHs) onto polymer backbone on their gas permeation properties [16–20]. The naphthalene ring containing polyimides and polyarylates showed enhancement in selectivity for various gas pairs, which was associated with some drop in permeability [16,20]. Incorporation of pyrene in benzimidazole-linked nanofibers exhibited high CO₂/N₂ sorption selectivity value of ~128 [17]. Similarly, pyrene-based benzimidazole-linked polymers showed higher CO₂ binding affinity and its uptake over CH₄ and N₂ under pressure and vacuum swing adsorption conditions [18]. The intermolecular interactions between the ‘polymer of intrinsic microporosity’, PIM-1 and PAH, pyrene were investigated recently by Tom et al. [19]. The blending of PIM-1 with pyrene and 1-aminopyrene (11 wt% of pyrene incorporation) gave materials that displayed improved gas sorption selectivities for CO₂ over N₂ as compared to the unmodified PIM-1.

In the present work, we have chosen pyrenyl (Py) and anthryl(An) groups for the *N*-substitution of thermally and mechanically stable PBI. Further, *N*-quaternization was performed using 4-*tert* butylbenzyl (Bz) group in order to obtain PILs. The halide anion of these PILs was subsequently exchanged with two chosen anions, viz., Tf₂N and BF₄. The choice was dictated by their attractive sorption-permeation properties [13]. The obtained PILs were characterized by requisite physical property, pure gas sorption and permeation testing.

2. Experimental

2.1. Materials

Lithium bis(trifluoromethane)sulfonimide (Li-Tf₂N), *N,N*-dimethylacetamide (DMAc), *N*-methyl-pyrrolidinone (NMP) and dimethyl sulfoxide (DMSO, 0.01% H₂O) were procured from Aldrich Chemicals. Polyphosphoric acid (PPA, 85% P₂O₅) was procured from Alfa Aesar, while conc. H₂SO₄ and *N,N*-dimethylformamide (DMF) were procured from Merck. Other common solvents (chloroform, methanol, toluene, acetone and acetonitrile) were obtained from S.D. Fine Chemicals. Pure gases, viz., He, H₂ and N₂ (minimum purity 99.9%) were procured from Vadilal Chemicals Ltd., while CH₄ and CO₂ (99.995%) were procured from Air Liquide.

2.2. PIL synthesis, characterization and membrane preparation

The chemical structures of PILs investigated in the present work

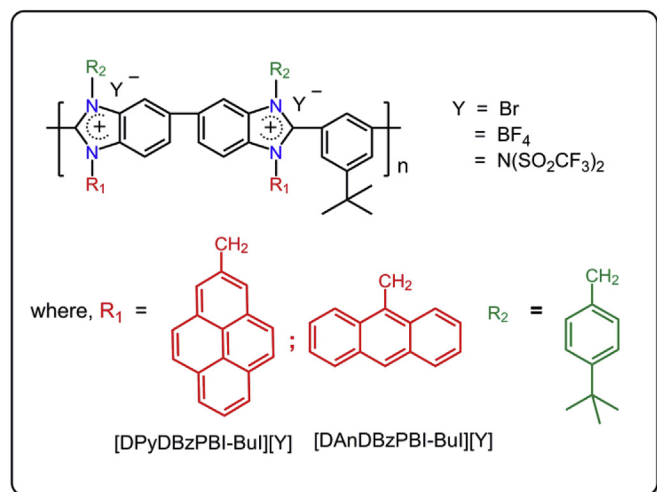


Fig. 1. Chemical structures of PILs investigated.

are given in Fig. 1. Their synthesis scheme is given in ESI (Scheme S1). The procedure for synthesis of PILs based on PBI and their further anion exchange has been described in our recent paper [24].

The solubility of PILs in organic solvents was determined by addition of 0.1 g PIL in 10 mL of solvent while stirring at the ambient for 24 h. In case of insolubility in low boiling solvents, heating near boiling point was employed. Inherent viscosity (η_{inh}) of PBI-Bul was determined using Ubbelohde viscometer with 0.2 g dL⁻¹ polymer concentration in 98% H₂SO₄ at 35 °C. Wide angle X-ray diffraction (WAXD) analysis of membranes was carried on a Phillips Analytical diffractometer in reflection mode using CuK α radiation ($\lambda = 1.54 \text{ \AA}$). The 2 θ range from 5° to 40° was scanned with a scan rate of 2.5° min⁻¹. The average intersegmental d_{sp} was calculated from the amorphous peak position (reproducibility: $\pm 0.05 \text{ \AA}$). The thermogravimetric analysis (TGA) was performed on samples which were vacuum dried at 100 °C for a week. The TGA was carried out in the temperature range of 50–900 °C using TGA-7 at a heating rate of 10 °C min⁻¹ under N₂ atmosphere. The dynamic mechanical analysis (DMA, Rheometric Scientific, USA) of present PILs (films of 0.045 × 8 × 10 mm³ size) was employed to determine the glass transition temperature (T_g) of PILs. The scans were recorded in the dynamic temperature ramp test mode at a frequency of 1 Hz. The testing temperature ranged from 50 to 280 °C and the heating rate was 10° min⁻¹. The density (ρ) of membranes was measured at 35 °C using specific gravity bottle and decalin as the solvent that exhibited < 1.2% sorption in PILs. The density measurements were repeated with three samples and the deviation from the average value was < 0.01 g cm⁻³. The dense films of PILs were prepared by the solution casting method using 3% (w/v) DMAc solution at 80 °C for 18 h under dry conditions. After evaporation of the solvent, the formed film ($-40 \pm 4 \text{ \mu m}$ thick) was peeled off from the glass plate and kept in a vacuum oven at 80 °C for 7 days in order to ensure complete removal of the solvent.

2.3. Gas sorption and permeation

The pure gas sorption isotherms for H₂, N₂, CH₄ and CO₂ were obtained at 35 °C using equipment that consisted of the dual-volume, single-transducer set up based on the pressure decay method [21–23]. The estimated experimental error was up to $\pm 1.7\%$, as calculated based on the uncertainty principle. The gas sorption in glassy polymers is described by Eq. (1) and the dual mode sorption parameters (k_D , b and C_H) were determined by non-linear regression analysis of the experimentally determined data at varying pressures [23,24].

$$S_A = \frac{C}{p} = K_D + \frac{C_H b}{(1 + bp)} \quad (1)$$

where, ‘C’ is the gas concentration in the polymer, ‘p’ is the applied gas pressure, ‘ k_D ’ is the Henry’s solubility coefficient, ‘ C_H ’ is the Langmuir saturation constant and ‘ b ’ is the Langmuir affinity constant. Membrane samples (5 cm in diameter) after removing from the vacuum oven were immediately mounted in the permeation cell for gas permeability measurements. The permeation analysis for pure gases viz., He, H₂, N₂, CH₄ and CO₂ was carried out by the standard variable volume method at upstream gas pressure of 20 atm and at 35 °C, while maintaining the permeate side at the atmospheric pressure [23,25]. The gas permeability was calculated using following equation:

$$P = \frac{N \cdot l}{(P_1 - P_2)} \quad (2)$$

where, ‘P’, the permeability coefficient expressed in Barrer, ‘N’ is the

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