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Journal Name RSCPublishing

ARTICLE

Ionic Group-mediated Crosslinked Polyimide Membranes for Enhanced CO_2 Separation

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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The dual cation-forming DABCO- or bisimidazolium-based ionic groups were introduced as crosslinkage sites and CO_2-solubilizing groups into 6FDA-durene polyimide (PI). The two resulting crosslinked PI membranes showed good chemical resistance to common polar organic solvents, along with excellent thermal and mechanical properties. Unlike other typical crosslinked polymers, the pendant ionic group-mediated crosslinked PI membranes, and in particular the DABCO-mediated crosslinked PI, displayed a very high CO_2 permeability of 469.4 Barrer, together with high CO_2/CH_4 (33.8) and CO_2/N_2 (23.1) permselectivities. In addition, these novel ionic group-mediated crosslinked PI membranes showed a high tolerance to plasticization by CO_2.

Introduction

Polymer membranes have been widely used in gas separation devices over the past several decades because polymer membrane gas separation methods have many advantages over traditional separation processes.[1-4] These separation methods are promoted as energy-efficient approaches to industrial scale separation, especially of CO_2/CH_4 and CO_2/N_2 mixtures.[4,5] Desirable polymeric membrane materials for gas separation should offer good separation, such as high gas permeability and permselectivities, and they must maintain their intrinsic gas separation properties under complex and harsh environmental conditions.

Membranes composed of polymeric ionic liquids (IL)s, also known as poly(IL)s, have recently emerged as promising CO_2 separation materials due to their high CO_2 solubility and their selectivity of CO_2 over light gases (N_2, O_2, and CH_4).[6-10] Strictly speaking, poly(IL)s are not ionic liquids, but are polymers containing several ionic salts. They nevertheless share many features with ILs, such as their high CO_2 solubility. Several promising approaches have been applied toward combining ILs with polymer membranes, including polymerized room temperature ILs,[7] IL composite membranes,[11] and ionene polymers (in which the ILs are present on the main chains).[12] Despite the high solubility of CO_2 in these membranes, poly(IL)s suffered from a low permeability.

Polyimides (PI)s have been widely used as gas separation membrane materials because they display moderate to high gas separation properties and excellent mechanical properties. Several studies have attempted to change the chemical structures of the PIs, with the goal of achieving both highly permeable and permselective membrane materials.[13,14] Most glassy polymer membranes, such as PIs, however, suffer from a marked increase in permeability and decrease in selectivity at feed pressures exceeding a critical level, the so-called "plasticization effect". Researchers have attempted to overcome the plasticization behavior of the polymeric membranes through blending,[15,16] thermal treatments,[17,18] and crosslinking.[19-21] Polymer crosslinking, particularly chemical crosslinking, provides an efficient approach to reducing plasticization behavior and increasing the thermal and chemical stability properties of the membranes.

The present work combines the benefits of the high CO_2 solubilizing effects of the IL groups with the benefits of crosslinking to prepare IL-mediated crosslinked PIs. Most crosslinked PIs convert the PI structure into a poly(amide-imide) structure.[19-20] Here, however, with the few exceptions of PI backbone retention,[21,22] our newly designed ionic liquid (or more correctly ionic group)-mediated crosslinked PIs retained their rigid PI backbone and provided a method for controlling the three-dimensional structure of the crosslinked polymer membranes. 1,4-Diazabicyclo[2.2.2]octane (DABCO) and 1,4-di(1H-imidazol-1-yl)butane (bisimidazole) crosslinkers were used here due to their ability to offer two reactive nitrogen atoms for crosslinking and their high rates of CO_2 absorption and desorption in their quaternary ammonium salt forms (Figure 1).[23]

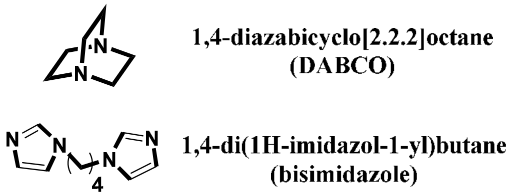


Fig. 1 Ionic group-mediated crosslinkers used in this study.

To the best of our knowledge, this is the first example of using the highly CO_2-solubilizing DABCO and imidazolium ionic groups to crosslink a PI backbone for selective CO_2 separation. The newly designed ionic group-mediated crosslinked membranes displayed excellent thermal, mechanical, and chemical stabilities, as well as good resistance to plasticization. Furthermore, excellent CO_2/CH_4 and CO_2/N_2 gas separation performances were achieved using the DABCO-mediated crosslinked PI.

Experimental

Materials

4,4'-(Hexafluoroisopropylidene) diphthalic anhydride (6FDA), 2,3,5,6-tetramethyl benzene-1,4-diamine (durene), and N-bromosuccinimide (NBS) were purchased from Tokyo Chemical Industry (TCI) Co., Ltd. (Tokyo, Japan) and used as obtained. 6FDA and durene were dried under vacuum at 60°C for 24 h prior to polymerization.

1,4-Diazabicyclo[2.2.2]octane (DABCO), imidazole, 1,4-dibromobutane, triethyl amine and acetic anhydride were obtained from Aldrich Chemical Co. All other chemicals, unless otherwise noted, were obtained from commercial sources and used as received.

Synthesis

Synthesis of 1,4-di(1H-imidazol-1-yl)butane(bisimidazole)

In a two-necked flask equipped with a condenser, a N_2 inlet, and a magnetic stirrer, imidazole (4 g, 58.75 mmol) was dissolved in THF (~50 cm^3). NaH (4.2 g 176.26 mmol) was added portion-wise to the solution at 0°C, and the reaction mixture was allowed to stir for 1 h at room temperature. 1,4-Dibromobutane (3.52 cm^3, 29.38 mmol) was added, and the reaction mixture was heated under reflux (70°C) overnight. The resultant mixture was then cooled to room temperature, and the solid NaBr salt was filtered off and washed with THF. The filtrate was evaporated to dryness and subsequently extracted with methanol and hexane. The methanol phase was washed three times with hexane, and white solid crystals of 1,4-di(1*H*-imidazol-1-yl)butane was obtained by rotary evaporation (9.6 g, 86%); ^{1}H NMR (d_6-DMSO) δ 7.58 (s, 2H, 2×N=C*H*–N), 7.11 (br signal, 2H, 2×N–C*H* =C), 6.85 (br signal, 2H, 2×C=C*H*–N), 3.93 (br signal, 4H, 2×N-CH_2–C), and 1.59 (br signal, 4H, 2× C–CH_2–C) (Figure S1 in ESI).

Synthesis of 6FDA-durene polyimide (1)

6FDA-durene polyimide was synthesized through a typical two-step sequence involving the formation of the polyamic acid, followed by imidization of the polymer backbone. In a 250 cm^3 two-necked flask equipped with a magnetic stirrer, nitrogen inlet, and a condenser, 6FDA (8.00 g, 18 mmol) and durene (2.96 g, 18 mmol) were dissolved in DMAc (60 cm^3). The reaction mixture was then allowed to stir for 12 h at –5°C (in an ice bath) to form the corresponding polyamic acid. Triethyl amine (5.3 cm^3, 37.8 mmol) and acetic anhydride (3.6 cm^3, 37.8 mmol) were added to the reaction mixture and heated to 110°C with vigorous stirring for 3 h to induce complete imidization of the polyamic acid to form polyimide. The resultant viscous mixture was cooled to r.t. and dissolved in DMAc (10 cm^3), followed by precipitating into methanol (400 cm^3). White polymer beads were collected by filtration, washed several times with deionized water, and dried for 48 h under vacuum at 80°C to give the 6FDA-durene polyimide (9.5 g, 92%); δ_H (400 MHz, CDCl$_3$) 8.10–8.08 (2 H, br signal, Ar*H*), 8.00–7.96 (4H, br signal, Ar*H*), and 2.14 (12H, s, CH_3); (ATR-FTIR)/cm^{-1} 2925, 1786, 1712, 1370, 1250, 1187, 1112, and 980; GPC (DMF, RI)/Da M_n 111.2 Kg/mol, M_w 159.8 Kg/mol and M_w/M_n 1.44.

Bromination of 6FDA-durene polyimide (1) to give the bromobenzylated PI (2)

In a 250 cm^3 two-necked flask equipped with a magnetic stirrer, nitrogen inlet, and a condenser, the 6FDA-durene polyimide (6 g, 10.5 mmol) and a catalytic amount of biphenyl peroxide (BPO) were dissolved in tetrachloroethane (30 cm^3). The reaction mixture was allowed to heat at 85 °C for a complete dissolution, followed by the addition of N-bromosuccinimide (2.24 g, 12.58 mmol), and allowed for further 12 h stirring at the same temperature. The resultant red colored polymer solution was cooled to r.t. and precipitated into methanol (400 cm^3). The yellow-colored polymer beads were collected by filtration and washed several times with deionized water, and dried for 48 h under vacuum at 80 °C to give the brominated polyimde (6.1 g, 90%); δ_H(400 MHz, CDCl$_3$) 8.27-7.90 (6 H, br signal, Ar*H*), 4.38 (2H, s, ArCH_2) and 2.27-2.14 (9H, br signal, CH_3); (ATR-FTIR)/cm^{-1} 2923, 1795, 1714, 1362, 1269, 1191, 1100, 986 and 748.0

Membrane preparations

Synthesis of pristine PI (6FDA-duerene) membrane

The pristine 6FDA-durene membrane was prepared as follows. The 6FDA-duerene polymer (1.0 g) was dissolved in 5.0 cm^3 of dry DMF and stirred at r.t. overnight. The resultant solutions were filtrated thoroughly through a plug of cotton and poured onto glass plates. The plates were then placed in an oven, covered with aluminum foils having small holes and allowed to slow solvent evaporation at 70 °C for 24 h and further dried at 90 °C for 16 h in a vacuum oven. After a complete drying process the resultant membranes were cooled to r.t. and peeled off from the glass plate, and then being dried at the ambient temperature.

Synthesis of ionic-group-mediated crosslinked PI membranes

The brominated polymer (1.0 g) was dissolved in 5.0 cm^3 of dry DMF and stirred at r.t. overnight. Then the corresponding crosslinker (DABCO (0.14 g, 1.2 mmol) or bisimidazole (0.23 g, 1.2 mmol)) was added into the solution and stirred for another 10-15 min. The resultant solutions were filtrated thoroughly through a plug of cotton and poured onto glass plates. The plates were then placed in an oven, covered with aluminum foils having small holes and allowed to slow solvent evaporation at 70 °C for 24 h and further dried at 90 °C for 16 h in a vacuum oven to evaporate the residual solvent, together with the unreacted crosslinkers.[24] After a complete drying process the resultant membranes were cooled to r.t. and peeled off from the glass plate, and then being dried at the ambient temperature. The thickness of each membrane was controlled to be 70 to 90 µm.

Characterization and measurements

^{1}H NMR spectra were obtained on an Agilent 400-MR (400 MHz) instrument using d_6-DMSO or CDCl$_3$ as a reference or internal deuterium lock. FT-IR spectra of the materials were recorded with membranes using Nicolet MAGNA 560-FTIR spectrometer in the range of 4000 - 400 cm^{-1}. Molar masses were determined by Gel Permeation Chromatography (GPC) using two PL Gel 30 cm × 5 µm mixed C columns at 30 °C running in DMF and calibrated against polystyrene (M_n = 600-10^6 g/mol) standards using a Knauer refractive index detector. The glass transition temperature (T_g) of each polymer was measured using a Perkin-Elmer Pyris-1 DSC from 20 °C to 400 °C with a scan rate of 10 °C min^{-1} under nitrogen. The X-ray diffraction patterns of the membranes were measured using a Rigaku DMAX-2200H diffractometer by employing a scanning rate of 4°/min in a 2θ range from 5° to 30° with a Cu Kα1 X-ray (λ =

0.1540598). The d-spacings were claculated using the Bragg's law (d = λ/2 sinθ).

The gel fraction of crosslinked membranes was measured by immersing the corresponding membranes in THF for 48 h. The extracted membranes were dried at 100 °C for 24 h, and the weights before and after extraction were measured to determine the gel fraction by the following equation:

$$\text{Gel fraction (\%)} = \frac{W_2}{W_1} \times 100$$

where, W_1 and W_2 are membrane weights before and after THF immersion, respectively.

The densities of the membranes ($g.cm^{-3}$) were determined experimentally using a top-loading electronic Mettler Toledo balance (XP205, Mettler-Toledo, Switzerland) coupled with a density kit based on Archimedes' principle. The samples were weighed in air and a known-density liquid, that is, high purity water. The measurement was performed at room temperature by the buoyancy method and the density was calculated as follows:

$$\rho_{\text{polymer}} = \frac{W_0}{W_0 - W_1} \times \rho_{\text{liquid}}$$

where, W_0 and W_1 are the membrane weights in air and water respectively. The water sorption of the membranes was not considered due to their extremely low water uptake property.

Gas permeation procedure

The pure gas permeation performance of newly designed ionic-group-mediated crosslinked PI and pristine PI membranes were measured using a high-vacuum time lag measurement unit based on constant-volume/variable-pressure method. All the gas separation experiments were conducted at a feed pressure of 2 atm and a feed temperature of 35 °C, and further permeability measurements of CO_2 and N_2 was carried out over the pressure range between 5 and 25 atm with 5 atm increments for the isotherm experiments at the same feed temperature. Before the gas permeation measurements, both the feed and the permeate sides were thoroughly evacuated to below 10^{-5} Torr until the readout showed zero values to remove any residual gases. The downstream volume was calibrated using a Kapton membrane and was found to be 50 cm^3. The upstream and downstream pressures were measured using a Baraton transducer (MKS; model no. 626B02TBE) with a full scale of 100,000 and 10 Torr, respectively. The pressure rise versus time transient of the permeate side, equipped with a pressure transducer, was recorded and passed to a desktop computer through a shield data cable. The permeability coefficient of each gas was determined from the linear slope of the downstream pressure rise versus time plot (dp/dt) according to the following equation:

$$P = \frac{273}{76} \times \frac{Vl}{ATp_0} \times \frac{dp}{dt} \qquad \textbf{(1)}$$

where P is the permeability coefficient expressed in Barrer (1 barrer = 10^{-10} $cm^3(STP)cmcm^{-2}\ s^{-1}\ cmHg^{-1}$); V (cm^3) is the downstream volume; l (cm) is the thickness of the membrane; A (cm^2) is the effective area of the membrane; T (K) is the temperature of measurement; p_0 (Torr) is the pressure of the feed gas in the upstream chamber and dp/dt is the rate of the pressure rise under the steady state. The gas permeation tests of each gas were repeated for more than three times, and the standard deviation from the mean values of permeabilities was within ca. ±3%. Sample to sample reproducibility was found be high and within ±3%. The effective membrane areas where gas permeates were 15.9 cm^2. The ideal permselectivity, $\alpha_{A/B}$, of the membrane for a pair of gases (A and B) was calculated from the ratios of the individual gas permeability coefficients, and can be described as shown in Eqn. (2):

$$\alpha_{A/B} = \frac{P_A}{P_A} \qquad \textbf{(2)}$$

The diffusivity and solubility coefficients were obtained from the time-lag (θ) value according to the following equations:

$$D = \frac{l^2}{6\theta} \qquad \textbf{(3)}$$

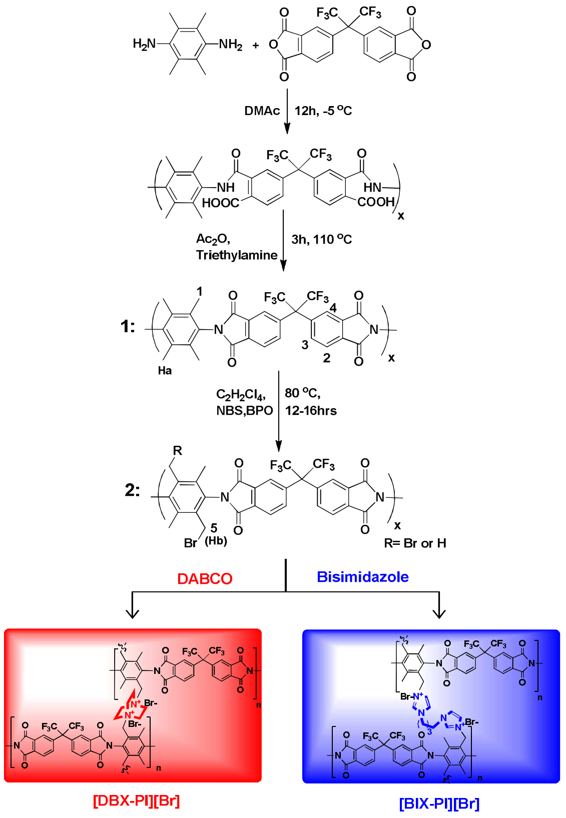
$$S = \frac{P}{D} \qquad \textbf{(4)}$$

where D ($cm^2\ S^{-1}$) is the diffusivity coefficient, l is the membrane thickness (cm) and θ is the time lag (s), obtained from the intercept of the linear steady state part of downstream pressure rise versus time plot. Solubility, S, was calculated from Eqn.(4) with permeability and diffusivity obtained from Eqn.(1) and (3).

Results and Discussion

Synthesis and characterization of the ionic group-mediated crosslinked PI membranes

The 6FDA-durene PI (**1**) was first synthesized through a polycondensation reaction between durene and 6FDA, followed by selective bromination at the benzylic groups to produce the brominated-PI (**2**) (Scheme 1). The 6FDA-durene PI had a high molecular weight (M_w = 159.8 kDa, as confirmed by GPC). The selective bromination at the $ArCH_3$ unit using 1.2 equiv NBS and catalytic amounts of BPO was conducted in a tetrachloroethane solution of pristine PI to produce the bromobenzylated PI. Comparative ^1H NMR spectroscopic analysis of the pristine PI (**1**) and the bromobenzylated PI (**2**) revealed that the intensity of the benzylic proton (H_a) decreased and a new bromobenzyl proton peak (H_b) appeared (Figure 2). Furthermore, no changes were observed in the other aromatic peaks, indicating the selective bromination of the benzyl group. The degree to which PI was brominated was estimated based on the ratio of the integrals of the bromobenzyl protons (H_b) in brominated PI to the benzylic protons (H_a) in pristine PI. This value was found to be 98%.



Scheme 1. Schematic representation of the preparation of DABCO and bisimidazolium-based ionic group-mediated crosslinked PI membranes.

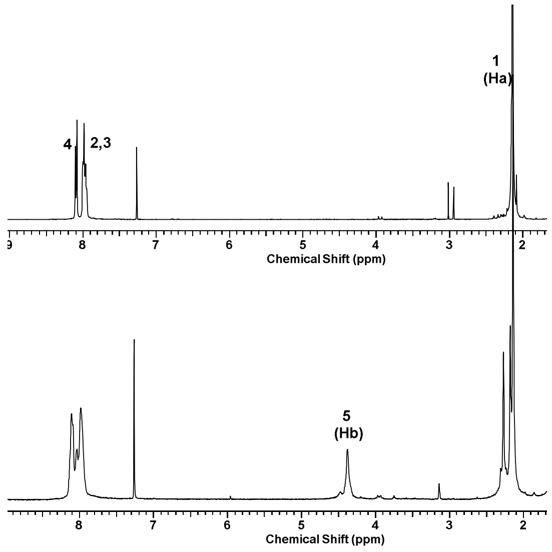


Figure 2. ^{1}H NMR spectra of the 6FDA-durene polyimide (**1**) and brominated polyimide **(2)** in $CDCl_3$.

The ionic group-mediated crosslinked PI membranes were simply and efficiently prepared by reacting the brominated PI with the corresponding crosslinkers, such as DABCO and bisimidazole (Scheme 1). The respective crosslinkers were dissolved in a DMF solution of brominated PI (**2**), followed by membrane casting and thermal drying. During the drying process, the reactive benzyl bromide group in **2** reacted with the amine unit of the crosslinkers upon thermal irradiation to produce the quaternary ammonium-functionalized crosslinked PI membranes in their bromide forms. The DABCO-based and bisimidazolium-based crosslinked PI membranes were termed [DBX-PI][Br] and [BIX-PI][Br], respectively.

The ionic group-mediated crosslinked PI structures were verified using FT-IR spectroscopy by observing the peaks corresponding to each crosslinker (Figure 3). The [DBX-PI][Br] ion-crosslinked membrane displayed the characteristic peak of the DABCO cation units at 1210 cm^{-1}, whereas the [BIX-PI][Br] membrane displayed the characteristic peaks of imidazolium cation units at 750 cm^{-1} and 1560 cm^{-1}, indicating the successful incorporation of each type of ionic group.[25-27]

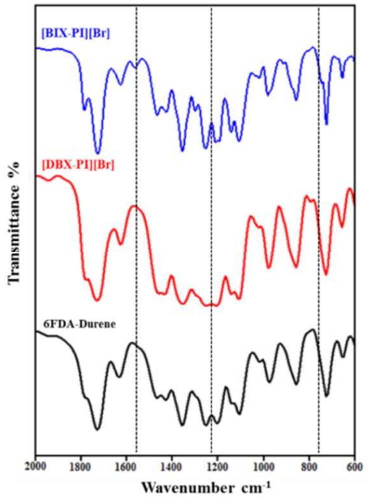


Figure 3. FT-IR spectra (600–2000 cm^{-1}) of the 6FDA-durene, [DBX-PI][Br] and [BIX-PI][Br] membranes.

Physical properties

Both of the ionic group-mediated crosslinked PIs, [DBX-PI][Br] and [BIX-PI][Br], formed transparent, tough, and dense membranes adequate for gas permeation testing (Figure 4). Solubility tests on the crosslinked PI membranes revealed that the crosslinked membranes were insoluble, whereas the pristine PI (6FDA-Durene) membrane was completely soluble in common organic polar solvents, including DMF, DMAc, and DMSO (Figure 4 and Table 1).

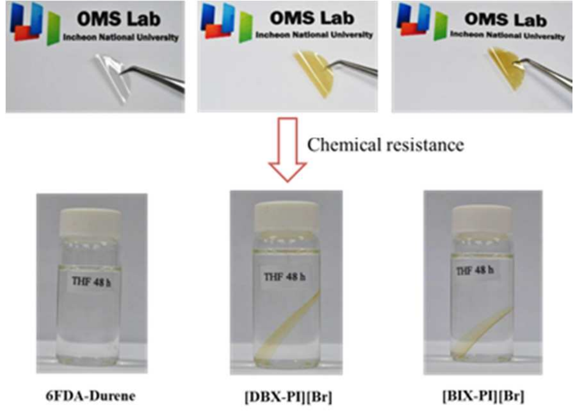


Figure 4. Photographs of the pristine PI (6FDA-durene), crosslinked [DBX-PI][Br], and [BIX-PI][Br] membranes, and their chemical resistance.

The gel fraction, which offers a quantitative measure of crosslinking density, was obtained by measuring the fraction of undissolved polymer remaining after extended soaking in THF. The calculated gel fraction was high for both crosslinked PIs, [DBX-PI][Br] and [BIX-PI][Br], indicating efficient crosslinking (Table 2). The gel fractions of the membranes changed only slightly after storage in THF over one month, indicating a high chemical stability among the crosslinked PIs.

Table 1. Solubility data for the 6FDA-durene and crosslinked PIs.

Solvent	Before Crosslinking (6FDA-Durene)	After Crosslinking ([DBX-PI][Br] and [BIX-PI][Br])
Chloroform	+	-
THF	+	-
DMF	+	-
NMP	+	-
DMSO	+	-

+: Soluble and −: insoluble.

Table 2. Physical parameters characterizing the crosslinked PIs and pristine PI membranes.

Membrane	Gel fraction (%)		T_g (°C)	d-spacing (Å)	Density
	2 days	30 days			
6FDA-Durene	-	-	424$^{(28)}$	6.7	1.33
[DBX-PI][Br]	96.2	92.2	330	6.0	1.40
[BIX-PI][Br]	95.9	91.8	320	5.8	1.42

As expected, the crosslinked membranes were found to have a high thermal stability, which is desirable for gas separation applications. Although crosslinking generally stiffens a polymer backbone and significantly enhances the T_g of the crosslinked polymers, the T_g obtained from the ionic group-mediated crosslinked PIs was lower than the value obtained from the pristine PI. This result was attributed to the presence of ionic groups in the crosslinkers, and poly(IL)s are well known to have a low T_g.[29] Nevertheless, the T_g values of the crosslinked membranes ([DBX-PI][Br] and [BIX-PI][Br]) exceeded 300 °C (Table 2 and Figure 5) and were much higher than the values obtained from poly(IL)s and other typical glassy polymers. The alkyl substituted bisimidazolium crosslinked PI, [BIX-PI][Br], had a low T_g value of 320 °C compared to [DBX-PI][Br], possibly due to the plasticizing effects of the flexible alkyl chains.

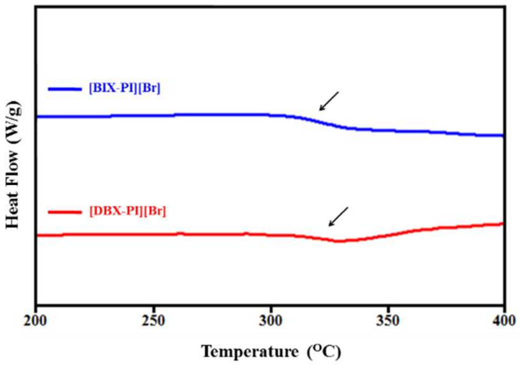


Figure 5. DSC graphs obtained from the crosslinked membranes.

Wide-angle X-ray scattering (WAXS) data revealed that the intersegmental (d-) spacings between the polymer chains decreased upon crosslinking, and the alkyl-substituted imidazolium crosslinked membrane, [BIX-PI][Br], displayed the smallest d-spacing measured among the three membranes (Table 2 and Figure 6), suggesting a reduced free volume and increased density in this membrane. In fact, the [BIX-PI][Br] membrane displayed the highest density among the three membranes measured (Table 2).

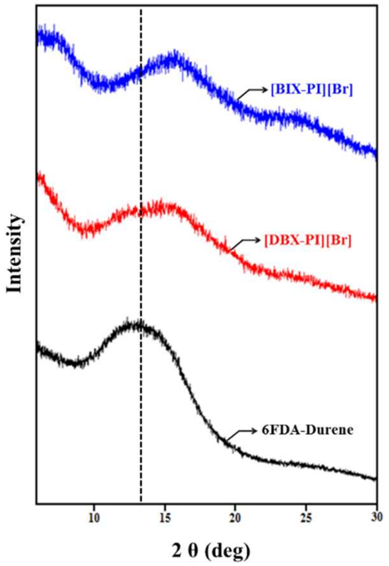


Figure 6. Wide-angle X-ray diffraction plots obtained from the 6FDA-durene, [DBX-PI][Br], and [BIX-PI][Br] membranes.

Gas separation properties

The ideal gas permeability and permselectivity values of the crosslinked PI membranes were measured at 2 atm and 35 °C, and the data were compared with data collected from the non-crosslinked pristine PI (6FDA-durene, Table 3). The DABCO-mediated crosslinked PI membrane, [DBX-PI][Br], exhibited a high CO_2 permeability coefficient (469.4 Barrer) that was slightly lower than the value obtained from the pristine 6FDA-durene (495 Barrer). Very high CO_2/N_2 and CO_2/CH_4 selectivities were obtained. Although enhanced selectivities, which originated from crosslinking, together with the CO_2 affinity derived from the ionic group were expected, the high CO_2 permeability (which approached that of the pristine 6FDA-durene) PI was surprising because crosslinking usually densifies polymer chains and reduces the permeability. The high permeability and the high CO_2 selectivity in [DBX-PI][Br] were ascribed to a combination of the enhanced CO_2 solubility and the relatively small loss of CO_2 diffusivity in this membrane (Table 4), which in turn resulted from the pendant DABCO ionic crosslinker and CO_2-philic unit.

By contrast, [BIX-PI][Br] displayed a much lower permeability to all gases due to a low diffusivity, possibly due to the presence of flexible alkyl chains between the imidazolium groups, which reduced the free volume in the polymers.

Table 3. Gas permeability (*P*) and permselectivity (*α*) of the pristine PI and crosslinked membranes at 2 atm and 35°C.

Membrane	P_{CO2}	P_{O2}	P_{N2}	P_{CH4}	$\alpha_{CO2/N2}$	$\alpha_{CO2/CH4}$
6FDA-Durene	495	132.5	41.1	37.3	12.1	13.3
[DBX-PI][Br]	469.4	65.1	20.3	13.9	23.1	33.8
[BIX-PI][Br]	200	30.9	11.2	6.03	17.7	33.2

P in barrers, where 1 barrer = 10^{-10} [cm^3 (STP) cm]/(cm^2 s cm Hg).

Table 4. Gas diffusivity coefficients[a] and solubility coefficients[b] at 2 atm and 35 °C

Membrane	D_{CO2}	D_{N2}	D_{CH4}	S_{CO2}	S_{N2}	S_{CH4}	$S_{CO2/N2}$	$S_{CO2/CH4}$
6FDA-Durene	29.1	18.1	6.57	0.17	0.023	0.057	7.39	2.9
[DBX-PI][Br]	15.58	13.53	3.33	0.30	0.015	0.041	20.07	7.2
[BIX-PI][Br]	8.55	7.88	1.46	0.23	0.014	0.041	16.79	5.7

[a] Diffusivity coefficient (10^{-8} cm^2/s).

[b] Solubility coefficient (cm^3 (STP)/cm^3 cmHg).

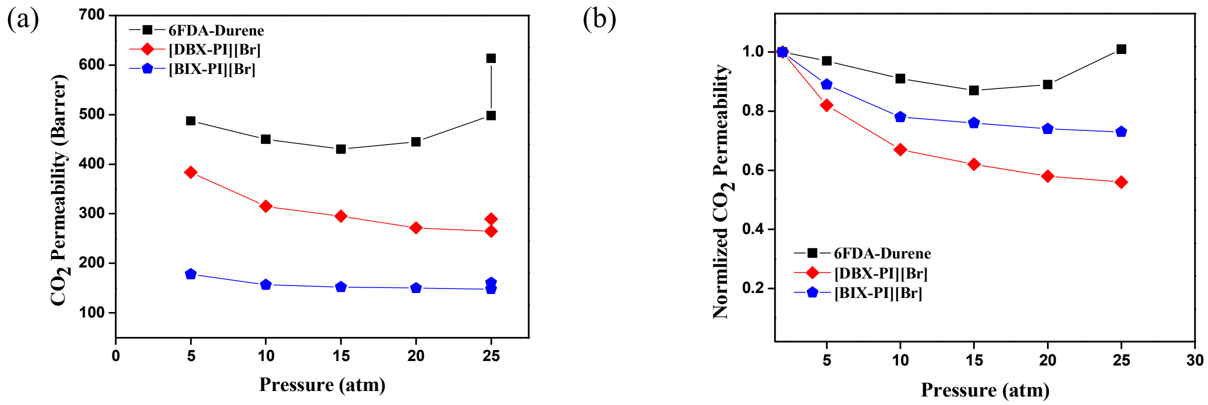


Figure 7. Pure gas CO_2 permeability (a) and normalized permeabilities (b) of the ionic group-mediated crosslinked PI and 6FDA-durene membranes as a function of the feed pressure.

Plasticization resistance of the crosslinked membranes

Plasticization is a common phenomenon in polymer membranes, in which penetrant gas species (particularly CO_2) increase the mobility of polymer chain segments, thereby losing the size and shape discrimination ability of the polymer matrix, and increasing the diffusivity coefficients of all penetrants in the membrane. Generally, an increase in CO_2 permeability with increasing feed pressure is indicative of plasticization, therefore, a pressure-dependent permeability showing the plasticization resistance of the crosslinked polymers was carried out by measuring CO_2 permeabilities up to 25 atm (Figure 7a). As expected, both the crosslinked membranes did not display an increase in CO_2 permeability with increasing pressure, in fact the crosslinked membranes showed a slight decrease in permeability with increasing feed pressure up to 25 atm, whereas, the non-crosslinked 6FDA-durene showed an upturn at 15 atm as reported in the literature.[28] Furthermore, there were no much increment in the CO_2 permeability of both crosslinked membranes after being exposed to the high CO_2 pressure of 25 atm for 20 h. While non-crosslinked 6FDA-durene showed about 20% of increase in the permeability of CO_2 under these conditions, the ionic group-mediated crosslinked membranes [DBX-PI][Br] and [BIX-PI][Br] showed an increase of only 8% and 9%, respectively. These results suggest that the newly developed ionic group-mediated crosslinked PI membranes have good plasticization resistance, and no significant signs of plasticization up to 25 atm. The plasticization behavior of all the crosslinked membranes was further confirmed by examining the normalized permeability (Figure 7b). The resistance of the crosslinked membranes to plasticization at feed pressures as high as 25 atm makes them strong candidate materials for practical applications for gas separation.

Permeability vs. selectivity for ionic group-mediated crosslinked membranes

The CO_2 separation performances of the newly designed ionic group-mediated crosslinked PI membranes were compared at the upper bound of the Robeson plot.[30,31] The CO_2 permeability versus the CO_2/CH_4 selectivity values, as well as the CO_2 permeability versus the CO_2/N_2 selectivity values of both crosslinked PI membranes were also compared with the value obtained from crosslinked PIs reported recently, such as diamino crosslinked 6FDA-durene,[20] DABA-based crosslinked PI (3:2),[21] XTR-BPOI,[32] and poly(IL)s[7,8,33] (Figure 8). Although the permeability-selectivity values of the [BIX-PI][Br] membrane fell below the upper bound lines for CO_2/CH_4, the [DBX-PI][Br] membrane did fall on the upper bound line for CO_2/CH_4 and performed comparably to the best crosslinked PI membranes reported in the literature (Figure 8(a)). By contrast, both ionic group-mediated crosslinked membranes fell below the upper bound for CO_2/N_2; however, these membranes outperformed previously described crosslinked and poly(IL)-based membranes (Figure 8(b)). These results indicated that the newly developed crosslinked ion-functionalized PIs offer remarkable performances in CO_2 gas separation applications.

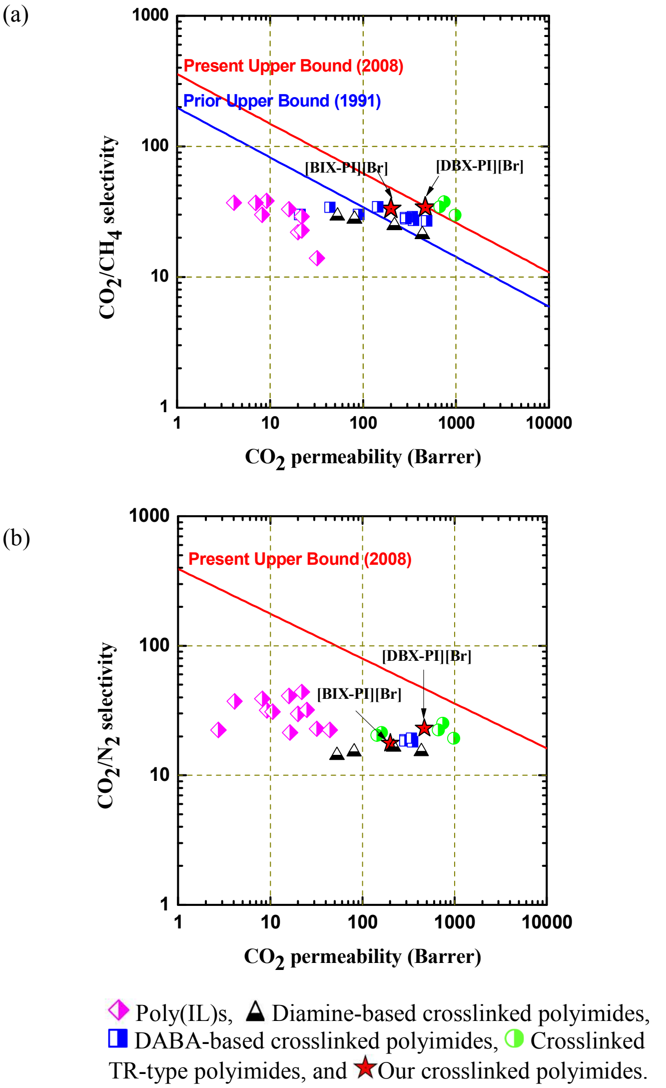


Figure 8. "Robeson upper bound" plot for comparing (a) the CO2/CH4 and (b) CO2/N2 separation performances of the ionic group-mediated crosslinked PIs with other previously reported crosslinked PIs and poly(IL)s; data taken from [7,8,20,21,30,31,32,33].

Mechanical Properties

The mechanical properties of the ion-mediated crosslinked membranes were measured at 50% RH, and the results are summarized in Table 5. Both crosslinked membranes displayed excellent tensile strengths up to 76.2 MPa with Young's moduli as high as 2.1 GPa (Figure S2 in ESI†). These outstanding mechanical properties indicated that the newly designed crosslinked PI membranes were suitable for gas separation applications.

Table 5 Tensile properties of the ionic group-mediated crosslinked membranes.

Membrane	Maximum tensile strength, MPa	Elongation at break, %	Young's modulus, GPa
6FDA-Durene	77.05	10.43	1.7
[DBX-PI][Br]	76.17	6.72	2.1
[BIX-PI][Br]	66.65	5.53	2.0

Conclusions

Novel ionic group-mediated crosslinked PIs prepared with DABCO and alkyl-bisimidazolium pendant cations as CO_2-solubilizing and crosslinking groups were successfully prepared, and the potential utility of the corresponding membranes for CO_2 gas separation was demonstrated. The ionic group-mediated crosslinked polyimide membranes provided high crosslinking densities and showed excellent thermal, mechanical, and chemical stabilities. Both DABCO- and bisimidazolium-based crosslinked PI membranes showed excellent CO_2/CH_4 and CO_2/N_2 permselectivities, together with a high resistance to CO_2 plasticization. This simple and efficient strategy may be readily applied to the development of superior polymer membranes for CO_2 separation applications.

Acknowledgements

This work was supported by the Korea Carbon Capture and Sequestration R&D Center under the Korea CCS2020 Program of the Ministry of Education and Science and Technology, Republic of Korea.

Notes and references

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†Electronic Supplementary Information (ESI) available: [details of ^1H NMR and stress-strain curve data]. See DOI: 10.1039/b000000x/

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