

Synthesis, characterization, and gas transport properties of novel iptycene-based poly[bis(benzimidazobenzisoquinolinones)]



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ARTICLE INFO

Article history:

Received 5 September 2013

Received in revised form

19 November 2013

Accepted 23 November 2013

Available online 3 December 2013

Keywords:

Poly[bis(benzimidazobenzisoquinolinones)]

Iptycene

Gas separation

ABSTRACT

Two novel iptycene-based tetramine monomers were successfully synthesized by nucleophilic aromatic substitution of triptycene-1,4-diol and pentyptycene-6,13-diol with 5-chloro-2-nitro-aniline, followed by reduction, respectively. These monomers were polymerized with 4,4'-binaphthyl-1,1',8,8'-tetracarboxylic dianhydride to obtain two novel iptycene-based poly[bis(benzimidazobenzisoquinolinones)]s (PBIBI-TPD and PBIBI-PPD) by a one-step, high-temperature solution polycondensation. Incorporation of iptycene groups especially the pentyptycene group in the polymer backbones improved their solubility and thermal stability. The resulting membranes exhibited good gas permeability owing to the high internal free volume elements introduced by the iptycene groups as well as high gas selectivity due to the restricted local segmental mobility arising from the interlocking of these groups in the polymer backbone. The membrane of PBIBI-PPD showed high CO₂ permeability (112 barrer) and moderately good CO₂/N₂ and CO₂/CH₄ selectivity (22 and 31) for mixed gas separation.

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1. Introduction

The research activity of polymeric gas separation membranes is growing significantly because of their good gas separation properties, ease of processing and mechanical stability properties [1,2]. Currently, membrane gas separation is utilized worldwide on large scale for hydrogen recovery, natural gas “sweetening”, air separation and treatment of flue gas [3–5]. Ideal membranes should be both highly permeable and selective. However, the well-known permeability and selectivity “trade-off” constrain the further development of polymeric membranes [6,7]. This problem has stimulated many efforts in the development of new materials and procedures for membrane fabrication.

Polypyrrolones (PPys) [8], which are obtained from dianhydride and teraamine, are synthesized by further thermal cyclization of polyimide backbone with amine groups in the α -position to the imide groups [–N(C=O)₂]. They possess better thermal stability and chemical resistance in comparison to polyimide because of their more rigid and multiaromatic structures in the polymer backbone [9–11]. Therefore, they have found wide applications as conducting materials or fluid separation materials [12,13]. In the

field of polymeric membrane for gas separation, PPys have been extensively studied because it can behave in a manner analogous to organic molecular sieves [14–16]. Zimmerman and Koros et al. have published a series of papers investing the gas separation properties of polypyrrolones and some of them have been shown to possess results above the upper bound for both O₂/N₂ and CO₂/CH₄ separations [15,17]. According to these studies, better performing polymers equipped with both high selectivity and permeability could be obtained by the combination of high-chain rigidity and bulky groups in the polymer [18,19]. The highly rigid backbone associated with reduced rotational mobility is able to more accurately discriminate between penetrant shape and size than flexible polymers [15]. On the other hand, high gas permeability could be maintained by ensuring high free volume through the incorporation of bulky groups [19].

Compared to PPys, poly[bis(benzimidazobenzisoquinolinones)] (PBIBI), which are synthesized when bis(naphthalic anhydrides) are employed as monomers, display superior chemical, thermal stabilities [20–22]. Especially, this ladder and semiladder polymer is extremely rigid, which could lead to their high permselectivity for gas separation. As a consequence, in view of design of materials possessing excellent gas separation properties, PBIBIs seem to be more perspective than PPys. However, most of these polymers are only soluble in strong acids, which severely restrict these attractive polymer materials for the fabrication of gas separation membrane.

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In our previous papers [23], we reported the processable PBIBIs based on new aromatic tetraamine possessing flexible ether linkages and 4,4'-binaphthyl-1,1,8,8-tetracarboxylic dianhydride which contained twist non-coplanar naphthalene rings. As a result, these novel PBIBIs were completely soluble not only in strong acids but also in organic solvents. Moreover, they could be cast into tough films and showed good gas separation properties. Nevertheless, according to the relationship between internal structures of polymer and anticipated gas separation properties revealed by the intensive study of PPys, the gas separation performance of PBIBI could be further improved by the introduction of bulky groups, which can increase the fractional free volume and thus improve their performance. One particular structure that has been gaining interest is iptycene, which differs from typical bulky groups for its containing a structural characteristic defined as the internal molecular-free volume [24]. It was reported that the separation properties of these internal free volume were suitable for gas separation [25].

Iptycenes are a class of compounds that consist of a number of phenyl groups attached to the [2.2.2] bicyclooctatriene bridgehead system [26]. Triptycene and pentiptycene are known as the most common members of this family, with three and five phenyl rings, respectively [27]. The high energy barrier to twisting or deformation of the [2.2.2] bridgehead system keeps the angle between aromatic rings at 120°, providing rigidity, symmetric geometries, and creating void spaces in the clefts (termed internal molecular free volume) between the rings [28,29]. Because of these features, iptycene has been found to have attractive applications in molecular rotors [30], host-guest chemistry [31] or as ligands [32]. Additionally, iptycene units have also been attractive building blocks employed to design a variety of high performance polymer [33]. The first iptycene-containing polymers were reported in the late 1960s, when rigid triptycenes were incorporated into a wide range of polymer systems, including polyesters, polyamides, polyurethanes, and a polyoxadiazole [34,35]. Recently, the polyimide containing triptycene and other iptycene units have been synthesized and their properties were intensively investigated. Zhang et al. synthesized triptycene polyimides with triptycene included in the dianhydride through the 1,4-positions and revealed to improve polyimide solubility while preserving moderately high T_g and good thermal stability [36]. Leu et al. also reported their research on polyimides based on two novel diamine monomers containing triptycene groups and exhibited similar results [37]. More recently, Park et al. reported a new platform of high performance polyimide based on 2,6-diaminotriptycene, which had internal free volume elements and thus lead to the formation of high fractional free volume with proper cavity size to separate small gas molecules with high selectivities as high permeabilities [25]. As a result, it seems advantageous to incorporate the iptycene groups containing the internal free volume elements into the backbone of the PBIBI that is more rigid than polyimide.

In this study, we designed and synthesized two novel tetraamine monomers containing triptycene and pentiptycene respectively, from which two types of processable PBIBI (PBIBI-TPD, PBIBI-PPD) with high free volume were prepared via a conventional one-step method. Physical, thermal, and gas separation properties of them were studied. In order to establish the effect of the iptycene groups on these properties, the results were compared with the properties of their non-iptycene counterparts, i.e. the PBIBIs based on 4,4'-bis(3,4-aminophenoxy)biphenyl (PBIBI-DOD) and 2,2'-bis[4-(3,4-diaminophenoxy)phenyl]-propane (PBIBI-BPA), respectively [23]. It was expected that the introduction of iptycene groups into the polymer could improve the solubility and the gas separation properties of the highly rigid PBIBI.

2. Experimental

2.1. Materials

Triptycene-1,4-diol (TPD) and pentiptycene-6,13-diol (PPD) were synthesized according to the literature [38,39]. Anthracene, quinone, hydrobromic acid (40%) were purchased from China National Pharmaceutical Group Corporation and used as received. 5-Chloro-2-nitro-aniline and 1,8-naphthalic anhydride (NA) were purchased from Aldrich. *m*-Cresol was distilled under reduced pressure prior to use. *N,N*-Dimethylacetamide (DMAc) was distilled over CaH₂ under reduced pressure. 4,4'-Binaphthyl-1,1,8,8-tetracarboxylic dianhydride (BTDA) was prepared according to a previously reported method [40]. All other reagents were obtained from commercial sources and used as-received. The PBIBI-DOD and PBIBI-BPA were prepared as previously described [23].

2.2. Measurement

¹H NMR spectra were measured at 300 MHz on an AV300 spectrometer. FT-IR spectra were obtained with a Bio-Rad Digilab Division FTS-80 FT-IR spectrometer. Elemental analysis were performed on an Elemental Analysis MOD-1106. The reduced viscosities were determined with an Ubbelohde capillary viscometer at 30 ± 0.1 °C on 0.5 g dL⁻¹ concentrations of polymer in *m*-cresol. Thermogravimetric analysis (TGA) was performed in nitrogen or air atmosphere with a Perkin-Elmer TGA-2 thermogravimetric analyzer at a heating rate of 10 °C min⁻¹. Differential scanning calorimetry (DSC) was performed on Perkin-Elmer DSC-7 system at a heating rate of 20 °C min⁻¹ under air atmosphere. Tensile measurements were carried out with an Instron-1211 mechanical testing instrument at a speed of 1 mm min⁻¹.

2.3. Monomer synthesis

2.3.1. Synthesis of 1,4-bis[4-(3-amino-4-nitrophenoxy)]-triptycene (1)

A mixture of triptycene-1,4-diol (14.3 g, 0.05 mol), 5-chloro-2-nitro-aniline (18.1 g, 0.105 mol), anhydrous K₂CO₃ (15.2 g, 0.11 mol) and 100 ml DMAc in 250 ml flask was stirred at 120 °C for 12 h and then at 140 °C for another 12 h. No toluene and Dean Stark trap was used for this run. After cooling, the resulting solution was slowly added into 500 ml ethanol/water (volume ratio: 1:4). The precipitated yellow solid was collected by filtration, and then was washed with ethanol and water several times respectively, and dried in vacuum. The product was obtained in a yield of 78.1% (21.8 g). ¹H (DMSO-*d*₆): 8.01–8.03 (d, 2H), 7.38 (s, 4H), 7.27–7.25 (m, 4H), 9.98–6.96 (m, 4H), 6.92 (s, 2H), 6.24–6.28 (dd, 2H), 6.16 (s, 2H), 5.60 (s, 2H).

2.3.2. Synthesis of 1,4-bis(3,4-aminophenoxy)-triptycene (2)

To a 100-ml three-necked flask equipped with a magnetic stirring device and nitrogen inlet were charged with the dinitro compound (5.6 g, 10 mmol), 10% Pd/C (0.2 g), 1,4-dioxane (20 ml) and ethanol (20 ml). Subsequently, under a nitrogen atmosphere, hydrazine monohydrate (10 ml) was slowly added at the reflux temperature and the mixture was stirred at this temperature for about 12 h. The reaction solution was filtered when cooled to remove Pd/C, and the filtrate was dried by rotary evaporation. The product was dried in vacuum and obtained in a yield of 91.0% (4.48 g). ¹H (DMSO-*d*₆): 7.36–7.33 (m, 4H), 6.96–6.99 (m, 4H), 6.42 (s, 2H), 6.38–6.39 (d, 2H), 6.14–6.15 (d, 2H), 6.90–6.94 (dd, 4H), 5.80 (s, 2H), 4.58 (s, 4H), 4.24 (s, 4H).

2.3.3. Synthesis of 6,13-bis[4-(3-amino-4-nitrophenoxy)]-pentiptycene (3)

This compound was prepared from pentiptycene-6,13-diol (23.12 g, 0.05 mol) and 5-chloro-2-nitro-aniline (18.1 g, 0.105 mol) with the same procedure described previously. The product was obtained in a yield of 75.2% (27.6 g). ^1H (DMSO- d_6): 8.04–8.06 (d, 2H), 7.37 (s, 4H), 7.14–7.17 (m, 8H), 6.87–6.90 (m, 8H), 6.17–6.21 (dd, 2H), 5.96 (s, 2H), 5.45 (s, 4H).

2.3.4. Synthesis of 6,13-bis(3,4-aminophenoxy)-pentiptycene (4)

This compound was prepared according to the procedures described earlier for 2a. The product was obtained in a yield of 87.2% (5.88 g). ^1H (DMSO- d_6): 7.10–7.13 (m, 8H), 6.86–6.89 (m, 8H), 6.37–6.38 (d, 2H), 6.29 (s, 2H), 5.56–5.57 (d, 2H), 5.52 (s, 2H), 4.63 (s, 4H).

2.4. Polymer synthesis

A typical polymerization procedure is as follows: a 100 ml completely dried, three-necked flask was charged with equimolar amounts of each monomer (1.00 mmol of the dianhydride and 1.00 mmol of the tetraamine) and 10 ml of *m*-cresol which was equipped with a mechanical stirrer, nitrogen inlet and outlet. After obtaining a homogeneous solution, 2 mmol of benzoic acid was added. The mixture was stirred at room temperature for 2 h and then heated to 80 °C. It was maintained at this temperature for 4 h, heated to 180 °C and kept there for 20 h. After cooling to 80 °C, an additional 5 ml of *m*-cresol was added so as to dilute the highly viscous solution, after which the solution was poured into 200 ml ethanol. The fiber-like precipitate was filtered off, extracted overnight with ethanol and dried in a vacuum oven for 24 h at 150 °C thus giving a product with a yield of 97%.

2.5. Membrane preparation

The polymers were dissolved in *m*-cresol (7–8% w/v, g/ml) and then filtered. Film cast onto the glass plate from the clear solution and dried at 80 °C for 12 h, after which the membrane was dried in a vacuum oven (60 °C for 2 h, 120 °C for 8 h and 220 °C for 10 h). Tough, ductile membranes were prepared with a controlled thickness of 40–60 μm . Fractional free volume (FFV) is calculated using the following equations:

$$\text{FFV} = \frac{V_{sp} - 1.3V_w}{V_{sp}}$$

where V_{sp} is the specific volume of the polymer determined by density measurement and V_w is the van der Waals volume of the polymers was calculated from Bondi's contribution method [41].

2.6. Gas permeability measurement

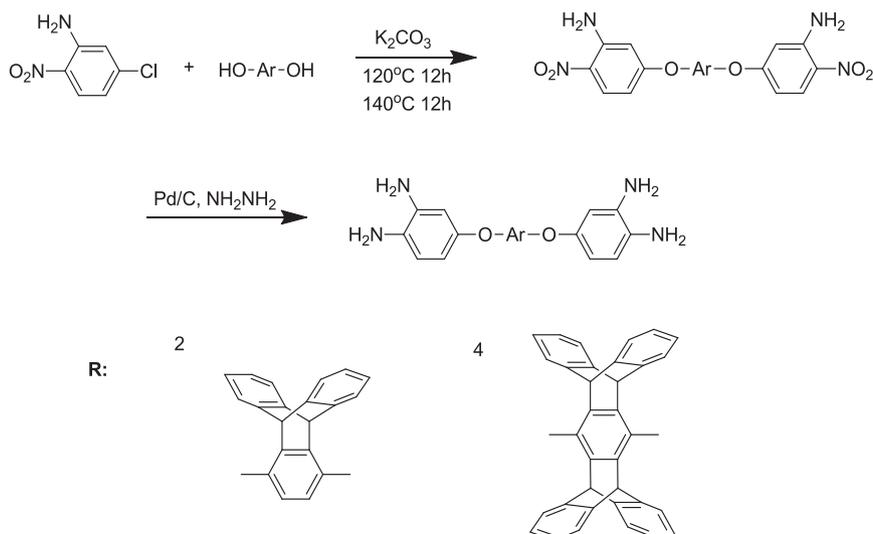
Gas permeation measurements were performed using a constant-volume/variable-pressure method at a feed pressure of 1 atm and a feed temperature of 25 °C. The permeability was determined in the sequence of O_2 , N_2 , CH_4 , and CO_2 . The design of the permeation apparatus and the experimental procedure are described in detail elsewhere. The permeability coefficient of all gases was calculated by:

$$P = DS = 10^{10} \frac{V_d l}{ART p_{up}} \left(\frac{dp}{dt} \right)$$

where P is the permeability coefficient of a membrane to gas in barrers (1 barrer = $10^{-10} \text{ cm}^3 [\text{STP}] \text{ cm cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$), p_{up} is the upstream pressure (cmHg), dp/dt is the steady-state permeate-side pressure increase (cmHg/s), V_d is the calibrated permeate volume (cm^3), l is the membrane thickness (cm), A is the effective area of the film (cm^2), R is the universal gas constant ($0.278 \text{ cm}^3 \text{ cmHg}/(\text{cm}^3(\text{STP})\text{K})$), T is the absolute temperature (K). The apparent diffusion coefficient D (cm^2/s) of the polymer membrane was calculated by $D = l^2/6\theta$, where θ is the time lag of the permeability measurement. The solubility coefficient S ($\text{cm}^3 (\text{STP})/(\text{cm}^3 \text{ cmHg})$) was obtained from the relationship $S = P/D$.

Mixed gas permeability coefficients were measured using a constant pressure/variable volume system equipped with a gas chromatograph. The measuring temperature was 25 °C. The concentrations of each gas were detected using a gas chromatograph equipped with a thermal conductivity detector. The mixed-gas selectivity was calculated by the ratio of downstream (y) and upstream (x) mole fraction of the two gases by the following equation:

$$\alpha_{ij} = \frac{y_i/y_j}{x_i/x_j}$$



Scheme 1. The synthetic route for tetraamine monomers 2 and 4.

where y_i and y_j are the mole fractions of components i and j respectively in the downstream, x_i and x_j are the mole fractions of components i and j respectively in the upstream.

3. Results and discussion

3.1. Synthesis and characterization of monomer and polymer

The synthetic route for new triptycene and pentaptycene tetraamine monomers (2, 4) was shown in Scheme 1. The dinitrosubstituted compounds were prepared in high yields by treatment of 5-chloro-2-nitro-aniline with triptycene-1,4-diol and pentaptycene-6,13-diol in DMAc containing K_2CO_3 . The tetraamines were obtained by reduction of the corresponding dinitro compounds with hydrazine hydrate and Pd/C catalyst in the mixture of ethanol and 1,4-dioxane. The proposed structure of target monomer 2 and 4 was confirmed by 1H NMR spectra as shown in Fig. 1. The 1H NMR spectra were consistent with the assigned structure of the monomer.

Two kinds of novel poly[bis(benzimidazobenzisoquinolinones)] containing triptycene and pentaptycene groups in the main chain were, respectively, prepared from tetraamines 2 and 4 with 4,4-Binaphthyl-1,1,8,8-tetracarboxylic dianhydride by a one-step, high-temperature solution polycondensation, according to Scheme 2. The polymerizations were carried out in *m*-cresol using benzoic acid as a catalyst. The polymerizations were initially run at the ambient temperature for 2 h and at 80 °C for 4 h. Then, the mixture was heated to 180 °C and kept for 20 h. Two PBIBIs were obtained in high yields and the inherent viscosities were 1.09 and 1.12 g dL⁻¹, respectively (Table 1).

The chemical structures of two PBIBIs were characterized by element analysis and FT-IR (Fig. 2). Both IR spectra showed absorption bands at 1700 cm⁻¹ attributed to the stretching vibrations of the >C=O and weak absorption bands at 1620 cm⁻¹ and

1550 cm⁻¹, typical of the of =C=N group vibrations. The absorption bands at 1706 and 1658 cm⁻¹ which correspond to the C=O stretching vibration in a six-membered imide ring, could not be found. This result also confirmed that the polymer was completely cyclized into pyridinone rings by the one-stage polycondensation method.

3.2. Polymer properties

Properties of the newly synthesized polymers are listed in Table 2. The solubility of PBIBI–TPD and PBIBI–PPD similar to PBIBI–TPD and PBIBI–PPD, was found to be soluble in strong acids (concentrated H_2SO_4 , methanesulfonic acid, polyphosphoric acid) and phenolic solvents (*m*-cresol and *p*-chlorophenol). The high solubility of all PBIBIs compared to PPys might be associate with the flexible ether moieties introduced. In addition, PBIBI–PPD exhibited improved solubility, which was dissolved in TCE and NMP. The better solubility of the PBIBI–PPD could be attributed to the rigid bulky pentaptycene groups, which disrupted the intermolecular attraction forces in the polymer. These results also indicated that iptycenes smaller than pentaptycene might be not fully effective at preventing strong interchain interactions in the polymer.

The thermal properties of the PBIBIs were investigated by means of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) (Table 3). The rigid and multiaromatic conjugated structures of the polymer led to all the PBIBIs exhibiting a high T_g 's. The PBIBI–TPD and PBIBI–PPD containing triptycene and pentaptycene groups showed glass transition temperatures 451 °C and 457 °C respectively, which were higher than PBIBI–DOD and PBIBI–BPA. The higher T_g 's of PBIBI–TPD and PBIBI–PPD could be explained by the fact that the phenyl rings of triptycene and pentaptycene perpendicular to polymer chain might interlock to some extent and thus prevent the segmental thermal motions even at high temperatures [25].

Typical TGA curves for PBIBI–TPD and PBIBI–PPD were illustrated in Fig. 3. When defining the degradation temperature as the temperature where 10% loss was achieved, PBIBI–TPD and PBIBI–PPD exhibited degradation temperatures of 561.8 °C and 567.8 °C in the nitrogen respectively, which were higher than PBIBI–DOD (552.2 °C) and PBIBI–BPA (537.9 °C). The char yields of the two PBIBIs were 73.9% and 75.8% in nitrogen at 800 °C, respectively.

Crystallinity of the two PBIBIs was evaluated by wide-angle X-ray diffraction experiments (WAXRD). Fig. 4 shows the XRD patterns of the PBIBI–TPD and PBIBI–PPD, which indicated that the polymers were amorphous. From Fig. 4, it can be seen that in general, two peaks were observed, as noted previously for similar types of materials [15,42]. The smaller spacing of the PBIBI–TPD and PBIBI–PPD was 3.8 and 4.1 Å respectively; however, the larger one remained very similar. The observation of two d spacings also indicated the likelihood of a bimodal distribution of free volume.

Table 4 summarized the densities and fractional free volumes (FFVs) of PBIBI membranes. It was well known that the fractional free volume had a direct relationship with permeability. The FFVs of PBIBI–TPD and PBIBI–PPD were higher than those of PBIBI–DOD and PBIBI–BPA which confirmed the positive effect of iptycene groups contained the internal free volume elements. In addition, it was also noteworthy the PBIBI–PPD showed higher FFV than PBIBI–TPD. This indicated that the amount of FFV in the PBIBI was related to the size of the iptycene groups in the polymer.

Both PBIBIs could be processed into highly cohesive and good quality films. The tensile properties of the two PBIBI films were summarized in Table 5. The films had tensile strengths of 95 and 118 MPa, an elongation at break of 5.5–11.1%, and a tensile modulus of 1.03–1.15 GPa, respectively.

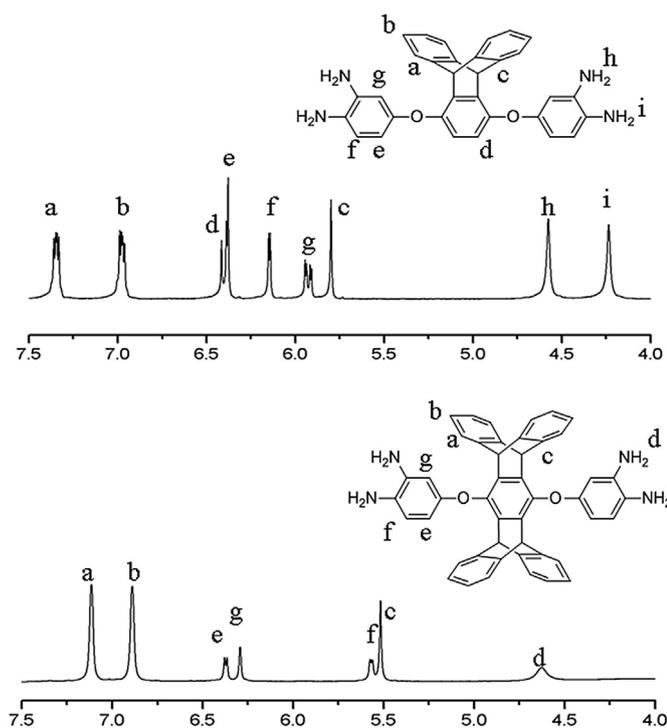
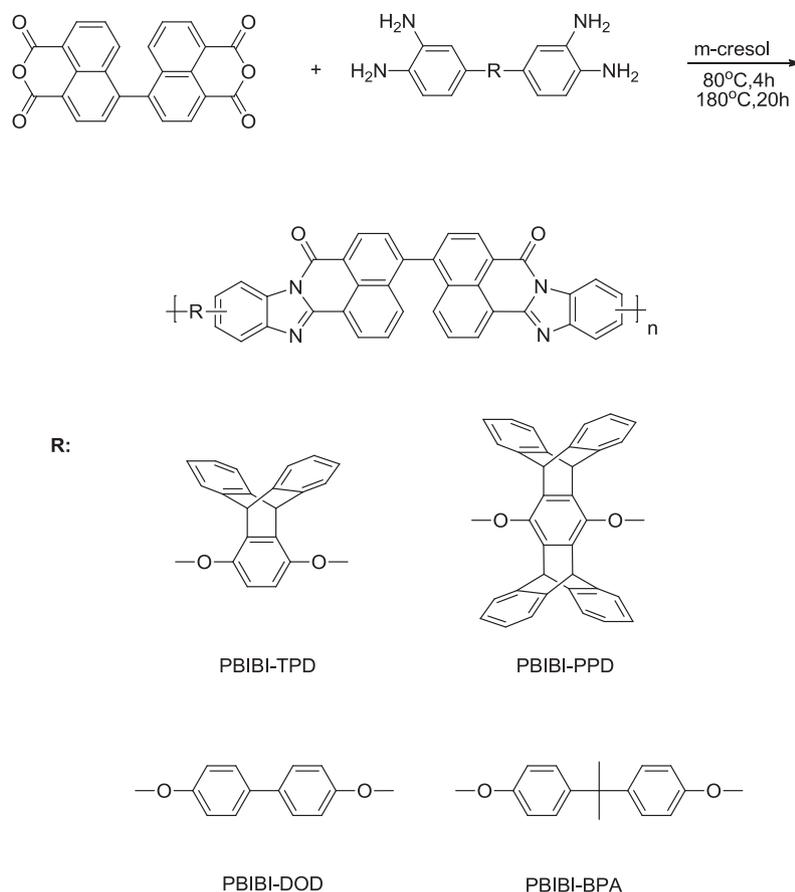


Fig. 1. 1H NMR spectra of the tetraamine monomer 2 and 4 in $DMSO-d_6$.



Scheme 2. Synthesis of the poly[bis(benzimidazobenzisoquinolinones)] (PBIBIs).

3.3. Gas separation properties

Gas permeation properties of the PBIBI membranes were measured at 25 °C and 1 atm. The pure gas permeability and gas pair ideal selectivity results were summarized in Table 6. To establish the effect of the iptycene groups, the results were compared with the gas separation properties of PBIBI–DOD and PBIBI–BPA. To compare the results properly, we had measured the gas separations properties from new membranes of the two PBIBIs that was measured under identical conditions that PBIBIs containing iptycene groups.

The order of gas permeability tested in the study was $\text{CO}_2 > \text{O}_2 > \text{N}_2 > \text{CH}_4$, which was typically in the reversed order of their respective kinetic diameter. Owing to the high internal free volume imparted by the iptycene groups in the polymer, PBIBI–TPD and PBIBI–PPD showed higher permeability coefficients than PBIBI–DOD and PBIBI–BPA. The PBIBI–PPD containing the larger

iptycene groups was much more permeable than PBIBI–TPD for all gases tested, while PBIBI–TPD was slightly more permeable than PBIBI–DOD and PBIBI–BPA. For example, the CO_2 permeability coefficients of PBIBI–TPD and PBIBI–PPD were 92 and 137 barrers, respectively, which were an increment of 29% and 69% as compared to PBIBI–DOD. The results were consistent with the results of the

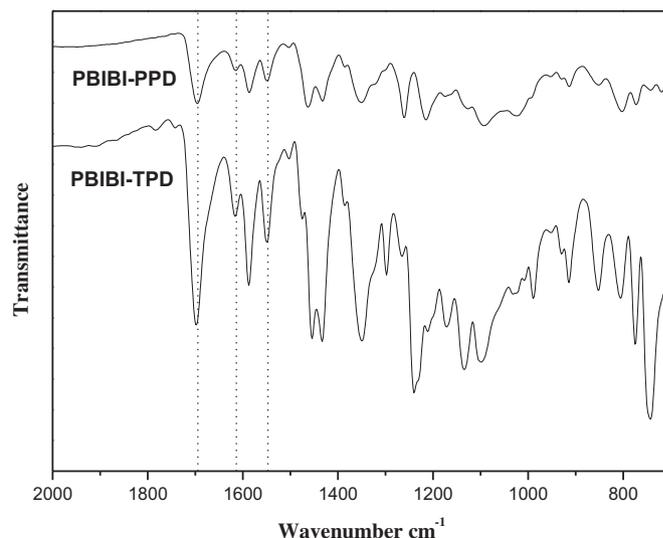


Fig. 2. Infrared absorption spectra of the PBIBI–TPD and PBIBI–PPD.

Table 1
Inherent viscosity and elemental analysis of the PBIBIs.

Polymer	η^a (dL/g)	Empirical formula	Elemental analysis (%)			
			C	H	N	
PBIBI–TPD	1.09	$(\text{C}_{56}\text{H}_{28}\text{N}_4\text{O}_4)_n$	Calcd.	81.74	3.67	6.81
			Found	81.86	3.61	6.93
PBIBI–PPD	1.12	$(\text{C}_{70}\text{H}_{36}\text{N}_4\text{O}_4)_n$	Calcd.	84.15	3.83	5.61
			Found	84.01	3.74	5.55

^a Inherent viscosity measured was at a concentration of 0.5 g dL⁻¹ in m-cresol at 30 °C.

Table 2
Solubility^a of the PBIBIs.

Polymers	H ₂ SO ₄	CF ₃ SO ₃ H	m-Cresol	TCE	NMP
PBIBI-TPD	++	++	++	--	--
PBIBI-PPD	++	++	++	++	++
PBIBI-DOD	++	++	++	--	--
PBIBI-BPA	++	++	++	--	--

^a ‘++’ easily soluble, ‘--’ insoluble.

Table 3
Thermal properties of the PBIBIs.

Polymer	T _g ^a (°C)	T ₅ ^b (°C)	T ₁₀ ^c (°C)	Char yields ^d (%)
PBIBI-TPD	451.2	533.1	561.8	73.9
PBIBI-PPD	457.1	547.0	567.8	75.8
PBIBI-DOD ^e	430.5	537.5	552.2	74.4
PBIBI-BPA ^e	429.3	510.9	537.9	76.9

^a From the second trace of DSC measurements conducted at a heating rate of 20 °C min⁻¹.

^b 5% weight loss temperature in TGA at 10 °C min⁻¹ heating rate.

^c 10% weight loss temperature in TGA at 10 °C min⁻¹ heating rate.

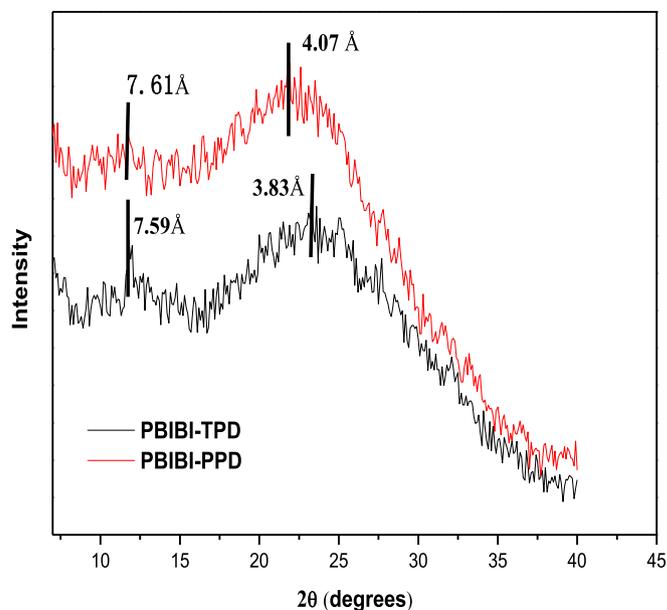
^d Weight retain at 800 °C.

^e Data from Ref. [23].

FFV. Since the PBIBI-PPD exhibited the highest FFV and reasonably, it showed the highest permeability coefficients. The observation also confirmed that the increment of gas permeability in the PBIBI membranes was greatly affected by the size of the iptycene groups in the polymer which related to the amount of the internal free volume elements imparted by them.

The CO₂/CH₄ selectivity of PBIBI-TPD and PBIBI-PPD films was 5.7% and 11% lower than that of PBIBI-DOD, which followed the trade-off relationship between selectivity and permeability that generally the selectivity of the membrane decreased as permeability increased for a pair of gas. For O₂/N₂, the PBIBI-PPD also showed decreased selectivity than PBIBI-DOD and PBIBI-BPA according to its much higher permeability coefficient of O₂ than them. However, the O₂/N₂ selectivity of PBIBI-TPD was not affected and it was even slightly higher than that of PBIBI-BPA and PBIBI-DOD.

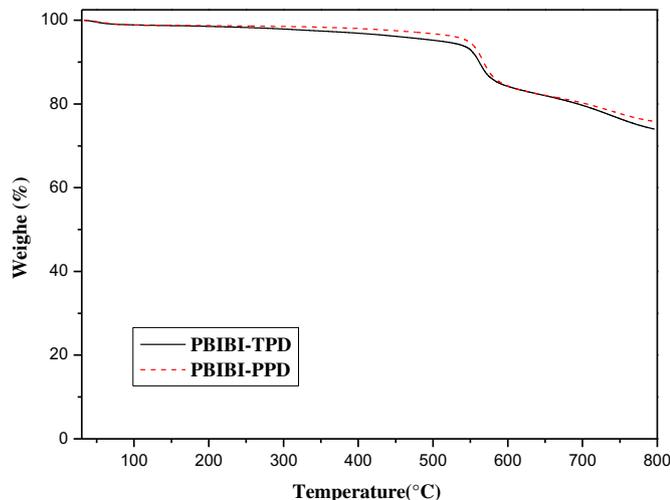
The gas permeability P could be split into a kinetic parameter, the diffusion coefficient (D), and a thermodynamic parameter, the solubility coefficient (S). Thus the selectivity (α) also could be split into the diffusion selectivity (D_x/D_y), which reflected the different molecular sizes of gases, and solubility selectivity (S_x/S_y), which

**Fig. 4.** Wide-angle X-ray diffractograms of the PBIBIs.

reflected the relative condensabilities of gas molecules interacting with a polymeric matrix.

Diffusion coefficients, solubility coefficients and selectivities of the PBIBIs were shown in Tables 7 and 8, respectively. For a given gas O₂, the diffusion coefficient values in the PBIBI membranes followed the order PBIBI-PPD > PBIBI-TPD > PBIBI-BPA > PBIBI-DOD. The increments of D were probably due to the gain of fractional free volume brought about by the iptycene groups in the two PBIBI membranes. Despite higher diffusion coefficients of PBIBI-PPD, it showed comparable or even higher diffusion selectivity in comparison with PBIBI-DOD and PBIBI-BPA. On the other hand, the sorption selectivity of these PBIBI membranes for O₂/N₂ was quite similar. Judging from these results, diffusion selectivity could be a dominant factor for enhancing permselectivity rather than sorption selectivity. Considering that D was highly related to the structure of the polymer, the increased selectivity of PBIBI-TPD could be probably due to greater molecular sieving associated with the restricted segmental thermal motions introduced by the interlocking of the phenyl rings in the triptycene group. As for CO₂/CH₄, a detailed analysis of the data from Table 7 revealed that the decrease in the PBIBI-TPD and PBIBI-PPD was mainly due to the solubility selectivities as differences of the diffusion selectivities were relatively small.

Figs. 5 and 6 described gas permeability and selectivity of the four PBIBIs membranes for CO₂/CH₄ and O₂/N₂, compared to present upper bounds established by Robeson in 2008. Data from the PBIBIs based on 1,4,5,8-naphthalenetetra-carboxylic dianhydride (PBIBI-NTDA) and PPys are also included for comparison. Although all the PBIBIs fell slightly below the present upper bound limit for CO₂/CH₄ gas pair, PBIBI-TPD and PBIBI-PPD showed better

**Fig. 3.** The TGA curves of the PBIBI-TPD and PBIBI-PPD.**Table 4**
Physical properties of PBIBI films.

Polymer	Density (g/cm ³)	V _{sp} (cm ³ /mol)	V _w (cm ³ /mol)	FFV ^a
PBIBI-TPD	1.256	654	423	0.159
PBIBI-PPD	1.227	817	521	0.171
PBIBI-DOD	1.283	562	369	0.148
PBIBI-BPA	1.245	612	400	0.151

^a Fractional free volume of polymer membranes by Bondi method.

Table 5
Mechanical properties of the PBIBI membranes.

Polymer	Film properties	Tensile strength (MPa)	Tensile Modulus (GPa)	Elongation at break (%)
PBIBI-TPD	Tough flexible	95	1.03	5.5
PBIBI-PPD	Tough flexible	118	11.5	11.1

Table 6
Pure gas permeabilities^a and selectivities (α) of the PBIBI membranes at 25 °C and 1 atm.

Polymer	Permeabilities (barrer)				Selectivities (α)	
	$P(O_2)$	$P(N_2)$	$P(CO_2)$	$P(CH_4)$	$\alpha(O_2/N_2)$	$\alpha(CO_2/CH_4)$
PBIBI-TPD	19.55	3.13	92.1	2.43	6.22	38.32
PBIBI-PPD	26.22	4.94	137.2	3.78	5.37	36.22
PBIBI-DOD	15.16	2.61	70.81	1.74	5.78	40.52
PBIBI-BPA	16.14	2.89	83.26	2.16	5.59	38.66

^a P is permeability coefficient; units: 1 Barrer = 10^{-10} cm³ [STP] cm cm⁻² s⁻¹ cmHg⁻¹.

combination of permeability and selectivity because they were placed closer to the upper bound line. In the case of O₂/N₂, especially, the PBIBI-TPD membrane exhibited outstanding permeation and air separation performance, lying on the Robeson upper line. The PBIBI-TPD and PBIBI-PPD showed much higher permeability than PBIBI-NTDA, which further confirmed that the bulky groups just like iptycene were needed for the favorable gas transport properties. In spite of their relatively low selectivities compared to PPys due to the ether linkages in the polymer, they exhibited similar gas separation performance as those of PPys that had been termed “pseudo molecular sieves.

Table 9 showed the separation performance of mixed gas tests conducted using binary feed mixture of CO₂/CH₄ and CO₂/N₂ for the two PBIBI membranes. To our knowledge, the mixed gas separation properties of PBIBI have been much less studied than other materials, though it would give results more applicable to industrial applications. Generally, the transport of one gas is to some extent affected by the presence of the other, which results in a lowered permeability of the preferentially permeating gas and thus reduces the mixed gas selectivity [43,44]. The performance of the two

Table 7
Gas diffusion coefficient $D \times 10^8$ (cm²/s) and solubility coefficient in 10^{-2} cm³ (STP)/cm³ cmHg of the PBIBIs at 25 °C and 1 atm.

Polymer	CO ₂		CH ₄		O ₂		N ₂	
	D	S	D	S	D	S	D	S
PBIBI-TPD	5.31	17.3	1.76	1.36	15.5	1.26	3.77	0.83
PBIBI-PPD	6.63	20.7	1.86	2.03	18.3	1.43	4.62	1.07
PBIBI-DOD	4.21	16.8	1.48	1.18	11.2	1.35	3.22	0.81
PBIBI-BPA	4.85	17.1	1.64	1.32	11.7	1.38	3.44	0.84

Table 8
Diffusivity selectivity (α_D) and selectivity (α_S) values for different gas pairs of the PBIBIs at 25 °C and 1 atm.

Polymer	α_D		α_S	
	(CO ₂ /CH ₄)	(O ₂ /N ₂)	(CO ₂ /CH ₄)	(O ₂ /N ₂)
PBIBI-TPD	3.01	4.11	12.7	1.52
PBIBI-PPD	3.56	3.96	10.2	1.34
PBIBI-DOD	2.88	3.49	14.1	1.66
PBIBI-BPA	2.95	3.41	13.1	1.64

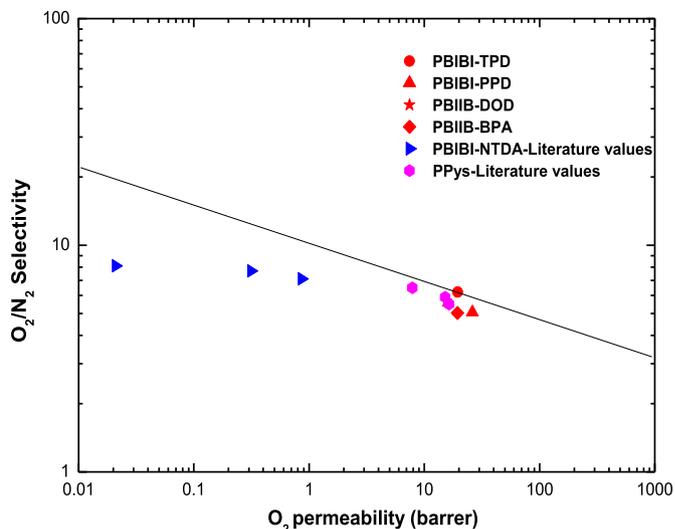


Fig. 5. Robeson plot [7] for a comparison of O₂/N₂ selectivity vs. O₂ permeability coefficients of the PBIBIs with some other polymers reported earlier, values taken from Refs. [17,42,45].

PBIBIs generally followed this trend. Both the permeability and selectivity of them slightly decreased as compared to those pure gas tests. However, PBIBI-TPD still exhibited high CO₂ permeability (>100 barrer) [14] and moderately good CO₂/N₂ and CO₂/CH₄ selectivity (22.6 and 31.6) for mixed gas separation.

4. Conclusion

Two iptycene group containing PBIBI polymers were successfully obtained by a one-step, high-temperature solution polycondensation. The incorporation of the iptycene groups especially the pentiptycene group further improved the solubility of the resulting polymers. The two PBIBIs also exhibited high glass transition temperatures that were below their corresponding decomposition temperatures while exhibiting high thermal stability.

High fractional free volume was introduced by the iptycene groups in the two PBIBI polymer and thus led to relatively high gas

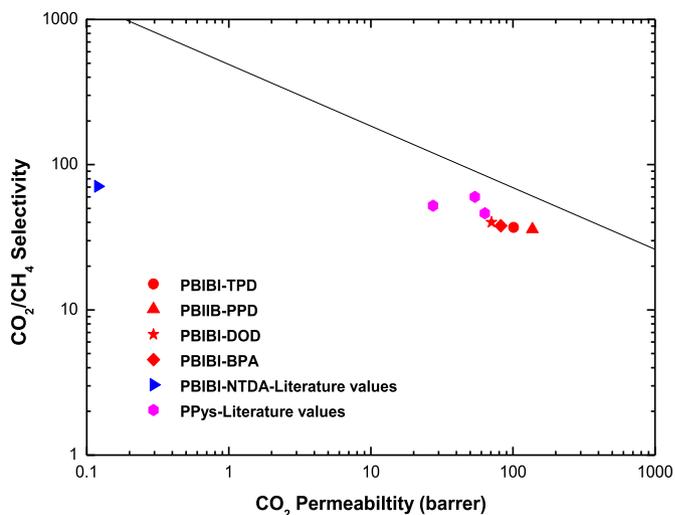


Fig. 6. Robeson plot [7] for a comparison of CO₂/CH₄ selectivity vs. CO₂ permeability coefficients of the PBIBIs with some other polymers reported earlier, values taken from Refs. [17,42,45].

Table 9
CO₂/CH₄ and CO₂/N₂ mixed-gas selectivity and permeability measured for PBIBI membranes.

Polymer	Permeabilities (barrer)		Selectivity CO ₂ /CH ₄	Permeabilities (barrer)		Selectivity CO ₂ /N ₂
	CO ₂	CH ₄		CO ₂	N ₂	
PBIBI–TPD	77.5 (92.1)	2.35 (2.43)	33.1 (38.3)	74.7 (92.1)	2.89 (3.13)	26.0 (29.1)
PBIBI–PPD	112.4 (137.2)	3.61 (3.78)	31.6 (36.2)	111.6 (137.2)	4.94 (4.72)	22.6 (27.7)

() Pure gas permeability value.

permeability. On the other hand, the reduced segmental thermal motions associated with the interlocking of the phenyl rings of ipitycene groups contributed to the improved permselectivity. As a result, the PBIBI–TPD and PBIBI–PPD showed better gas separation performance than PBIBI–DOD and PBIBI–BPA, lying slightly below the upper bound limit. In particular, the highest permeability (137 barrer) of the PBIBI–PPD for CO₂ was achieved and the PBIBI–TPD lied on the boundary limit for O₂/N₂ gas pair. The result of mixed gas separation tests further confirmed that they were materials with promising performance for the CO₂ separation applications. In addition, the common structural features of PBIBI and PPys may allow for further performance enhancement by reducing or even eliminating mobile linkages in the backbone that proved successful for PPys. Further studies are aimed at optimizing polymer design by preparing novel tetramine monomers containing more rigid and noncoplanar structures (i.e. kink, spiro, and cardo structures) which could improve both the processability and gas separation properties of PBIBI.

Acknowledgments

This research was financially supported by the National Basic Research Program of China (no. 2012CB932802), the National Science Foundation of China (no. 51133008, 51021003, 21074133), the National High Technology Research and Development Program of China (no. 2012AA03A601), and the Development of Scientific and Technological Project of the Jilin Province (no. 20100322).

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