



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



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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).

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