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Synthesis and properties of soluble poly[bis(benzimidazobenzisoquinolinones)] based on novel aromatic tetraamine monomers

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Four aromatic tetraamine monomers possessing flexible ether linkages were successfully synthesized by nucleophilic aromatic substitution of hydroquinone, 4,4′-dihydroxybiphenyl, 2,2′-bis(4-hydroxyphenyl)propane, and 2,7-dihydroxynaphthalene with 5-chloro-2-nitroaniline, followed by reduction, respectively. With these monomers, a new class of soluble poly[bis(benzimidazobenzisoquinolinones)] was prepared by a one-step, high-temperature solution polycondensation. The resulting polymers were completely soluble in phenolic solvents and had high inherent viscosities ranging from 1.2 to 1.5 g dL^{-1}. These polymers had glass transition temperatures in the range of 427–449 °C. Thermogravimetric analysis showed that all polymers were thermally stable, with 5% weight loss recorded above 510 °C in nitrogen. The tough polymer films, obtained by casting from solution, had tensile strength, elongation at break, and tensile modulus values in the range of 79.5–114.5 MPa, 10.3–23.0%, and 1.1–1.7 GPa, respectively. It is demonstrated that these semiladder polymer membranes displayed high CO_2 permeability coefficients ($P_{CO_2} = 31.6 - 96.5$barrer) and permeability selectivity of CO_2 to CH_4 ($P_{CO_2}/P_{CH_4} = 30.6 - 43.4$).

1. Introduction

Considerable research has been carried out to develop new condensation polymers containing heterocyclic units. Because of their outstanding strength and moduli, these polymers are generally used as high-temperature-resistant materials and fibers. Polycondensations of aromatic dianhydrides and tetraamines have given rise to a series of thermally stable ladder-like polyheterocycles, i.e. polypyrrolones (PPys) [1] and poly[bis(benzimidazobenzisoquinolinones)] (PBIBI) [2]. Polypyrrolones, which synthesized by further thermal cyclization of polyimide backbone with amine groups in the α-position to the imide groups [–N(C═O)$_2$], possessed better thermal stability than polyimides because of their more rigid and multiaromatic structures in the polymer backbone [3–5]. It was reported that the PPy films also exhibited excellent alkaline hydrolysis stability, which retained their original shapes and toughness after boiling 7 days in 10% sodium hydroxide solution [6]. Therefore, they have found wide applications as gas permeable or fluid separation membranes [7,8], and conducting materials [9]. Preliminary investigations have shown that poly[bis(benzimidazobenzisoquinolinones)], which are formed when bis(naphthalic anhydrides) are employed as monomers, display superior chemical, thermal and fire resistance compared with the PPys derived from bis(phthalic anhydrides) [2,10,11]. As a consequence, in view of design of materials possessing improved properties, PBIBIs seem to be more perspective than PPys. The first PBIBIs were obtained by Van Deusen from the polycondensation of 1,4,5,8-naphthalenetetracarboxylic dianhydride with aromatic tetraamines [2]. These polymers showed high softening temperature and were soluble only in strong acids (polyphosphoric acid, concentrated H_2SO_4 and methanesulfonic acid), which severely restricted their applications. Thus, considerable efforts have been made to modify their molecular structure, aiming at giving satisfactory processability of products. Few promising results have been reported until now. For instance, Jedliński et al. reported on the processable PBIBIs with flexible ether linkages in the main chain, derived from commercial available tetraamines and new dianhydrides [12]. As a result, these polymers were soluble not only in strong acids but also in organic solvents and exhibited glass transition temperatures that were below their corresponding decomposition temperature values while preserving a relatively high thermal and oxidative stability. However, the low molecular weights of many polymers were not competent for film formation.

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Moreover, the limitation of the commercially available tetraamine monomers, the component in PPys and PBIBIs syntheses, greatly restricts the development of these high performance polymers.

In the present paper, we describe the successful synthesis of novel processable PBIBIs. The new aromatic tetraamine monomers possessing flexible ether linkages were successfully synthesized by nucleophilic aromatic substitution of hydroquinone, 4,4′-dihydroxybiphenyl, 2,2′-bis(4-hydroxyphenyl)propane, and 2,7-dihydroxynaphthalene with 5-chloro-2-nitroaniline, followed by reduction, respectively. The dianhydride monomer selected for their preparation was 4,4′-binaphthyl-1,1′,8,8′-tetracarboxylic dianhydride (BTDA) which prepared by Wang et al. and used as a monomer for the synthesis of organosoluble polyimides [13]. It was expected that the introduction of flexible ether linkages and twist non-coplanar naphthalene rings could improve the solubility and processability of the PBIBIs. Physical, thermal, and gas separation properties of these polymers were also investigated.

2. Experimental section

2.1. Materials

Hydroquinone, 4,4′-dihydroxybiphenyl, 2,2′-bis(4-hydroxyphenyl) propane, 2,7-dihydroxynaphthalene, 5-chloro-2-nitroaniline and 1,8-naphthalic anhydride (NA) were purchased from Aldrich. *m*-Cresol was distilled under reduced pressure prior to use. 4,4′-Binaphthyl-1,1′,8,8′-tetracarboxylic dianhydride (BTDA) was prepared according to a previously reported method [14]. All other reagents were obtained from commercial sources and used as-received.

2.2. Measurement

^{1}H and ^{13}C 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. All melting points were determined on a Mel-Temp melting point apparatus and were uncorrected. Elemental analyses were performed on an Elemental Analyses MOD-1106. The reduced viscosities were determined with an Ubbelohde capillary viscometer at $30 \pm 0.1\,^\circ$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 a 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}. The dynamic mechanical property of the polymer films was measured on a dynamic mechanical thermal analyzer (DMTA-Δ).

The permeability was determined in the sequence of O_2, N_2, CH_4, and CO_2. They were tested at 25 °C at 10 atm. The design of the permeation apparatus and the experimental procedure are described in detail elsewhere [15]. In short, the gas permeability was determined from the rate of the pressure increase in the permeation (downstream) side in the steady state with the following equation:

$$P = \frac{VL}{ART\Delta p}\left(\frac{\Delta p}{\Delta t}\right)$$

where P is the permeability coefficient of a membrane to gas in barrers (1 barrer = 10^{-10} cm^3 [STP] cm cm^{-2} s^{-1} cm Hg^{-1}), V is the downstream volume, L is the membrane thickness, A is the effective area of the film, R is the universal gas constant, T is the absolute temperature, Δp is the transmembrane pressure ($\Delta p = p_2 - p_1$, where p_2 and p_1 are the upstream and downstream pressures, respectively), and $\Delta p \Delta t$ is the steady rate at which the pressure increases on the downstream side. The temperature was controlled within ±1 °C with a thermal regulator connected to a heater in the permeation cell wall.

2.3. Monomer synthesis

2.3.1. Synthesis of 1,4-bis(3-amino-4-nitrophenoxy)phenyl (**1a**)

To a 250 mL round-bottomed flask were charged 11.0 g (0.10 mol) of hydroquinone, 36.2 g (0.21 mol) of 5-chloro-2-nitroaniline, 30.4 g (0.22 mol) of anhydrous K_2CO_3, and 100 mL of dry DMAc. The solution was stirred at 120 °C for 12 h and at 140 °C for another 12 h. No toluene and Dean Stark trap was used to remove water for this run. After cooling to room temperature, the reaction mixture was poured into 500 mL ethanol/water (volume ratio: 1:4), and the precipitated yellow solid was collected by filtration, washed with ethanol and water several times respectively, and dried in vacuum. The product was obtained in a yield of 82.5% (31.5 g). ^{1}H NMR (DMSO-d_6): 7.97–8.01 (2H, d), 7.49 (4H, –NH_2), 7.28 (4H, s), 6.41–6.42 (2H, d), 6.26–6.30 (2H, dd). Anal. Calcd. for $C_{18}H_{14}N_4O_6$ (382.33): C, 56.55%; H, 3.69%; N, 14.65%. Found: C, 56.78%; H, 3.62%; N, 14.71%.

2.3.2. Synthesis of 1,4-bis(3,4-aminophenoxy)phenyl (**2a**)

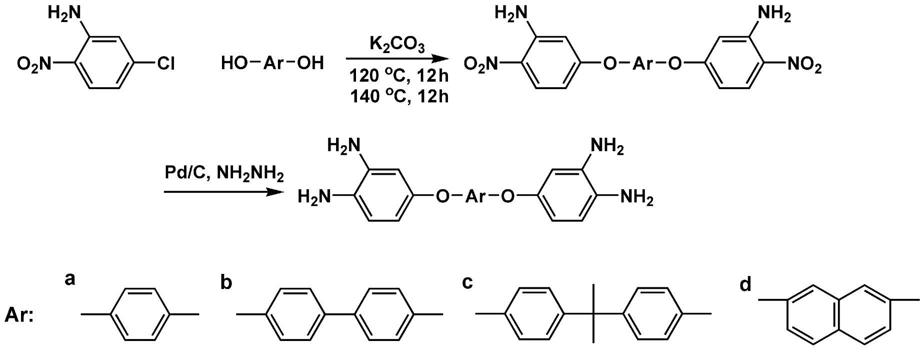
To a 100 mL three-necked flask equipped with a magnetic stirring device and nitrogen inlet were charged the dinitro compound **1a** (3.8 g, 10 mmol), 10% Pd/C (0.20 g) and ethanol (30 mL). Subsequently, under a nitrogen atmosphere, hydrazine monohydrate (10 mL) was slowly added at the reflux temperature 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 crude product was recrystallized from ethanol to afford 2.8 g (yield: 87.0%) of a gray powder. Mp: 226.5 °C. ^{1}H NMR (DMSO-d_6): 6.81 (4H, s), 6.45–6.49 (2H, d), 6.22–6.23 (2H, d), 6.12–6.17 (2H, dd), 4.60 (4H, –NH_2) and 4.24 (4H, –NH_2). ^{13}C NMR (DMSO-d_6): 153.2, 148.3, 136.5, 130.9, 118.2, 114.8, 107.3, 105.6. Anal. Calcd. for $C_{18}H_{18}N_4O_2$ (322.36): C, 67.07%; H, 5.63%; N, 17.38%. Found: C, 66.89%; H, 5.61%; N, 17.45%.

2.3.3. Synthesis of 4,4′-bis(3-amino-4-nitrophenoxy)biphenyl (**1b**)

This compound was prepared from 4,4′-dihydroxybiphenyl (18.6 g, 0.10 mol) and 5-chloro-2-nitroaniline (36.2 g, 0.21 mol) with the same procedure described previously. The product was obtained in a yield of 70.1% (32.1 g). ^{1}H NMR (DMSO-d_6): 8.01–8.05 (2H, d), 7.77–7.80 (4H, d), 7.49 (4H, –NH_2), 7.25–7.28 (4H, d), 6.44–6.45 (2H, d), 6.30–6.35 (2H, dd). Anal. Calcd. for $C_{24}H_{18}N_4O_6$ (458.42): C, 62.88%; H, 3.96%; N, 12.22%. Found: C, 62.78%; H, 4.01%; N, 12.14%.

2.3.4. Synthesis of 4,4′-bis(3,4-aminophenoxy)biphenyl (**2b**)

To a 100 mL three-necked flask equipped with a magnetic stirring device and nitrogen inlet were charged the dinitro compound **1b** (4.6 g, 0.01 mol), 10% Pd/C (0.20 g) and ethanol (50 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 36 h. After adding 30 mL DMF to dissolve the precipitate, the reaction solution was filtered after cooling and the product was recrystallized from DMF/H_2O (volume ratio: 5:1) to afford 3.5 g (yield: 88.5%) of white powders. Mp: 204.0 °C. ^{1}H NMR (DMSO-d_6): 7.50–7.54 (4H, d), 6.90–6.93 (4H, d), 6.50–6.53 (2H, d), 6.28–6.29 (2H, d), 6.10–6.14 (2H, dd), 4.50 (8H, –NH_2). ^{13}C NMR (DMSO-d_6): 158.1, 147.2, 136.6,



Scheme 1. The synthetic route for tetraamine monomers **2a**–**d**.

133.3, 131.3, 127.4, 114.0, 114.8, 108.0, 106.2. Anal. Calcd. for $C_{24}H_{22}N_4O_2$ (398.46): C, 72.34%; H, 5.57%; N, 14.06%. Found: C, 71.96%; H, 5.65%; N, 14.18%.

2.3.5. Synthesis of 2,2′-bis[4-(3-amino-4-nitrophenoxy)-phenyl]propane (*1c*)

This compound was prepared from 2,2′-bis(4-hydroxyphenyl)propane (22.8 g, 0.10 mol) and 5-chloro-2-nitroaniline (36.2 g, 0.21 mol) with the same procedure described previously. The product was obtained in a yield of 81.6% (40.8 g). ^{1}H NMR (DMSO-d_6): 7.99–8.03 (2H, d), 7.49 (4H, –NH_2), 7.33–7.36 (4H, d), 7.08–7.11 (4H, d), 6.40–6.41 (2H, d), 6.26–6.30 (2H, dd), 1.70 (6H, s). Anal. Calcd. for $C_{27}H_{24}N_4O_6$ (500.5): C, 64.79%; H, 4.83%; N, 11.19%. Found: C, 64.88%; H, 4.78%; N, 11.14%.

2.3.6. Synthesis of 2,2′-bis[4-(3,4-diaminophenoxy)phenyl]-propane (*2c*)

This compound was prepared according to the procedures described earlier for monomer **2a**. The product was obtained in a yield of 86.5% (3.81 g). Mp: 144.5 °C. ^{1}H NMR (DMSO-d_6): 7.09–7.13 (4H, d), 6.74–6.77 (4H, d), 6.46–6.50 (2H, d), 6.23–6.24 (2H, d), 6.05–6.10 (2H, dd), 4.51 (8H, –NH_2), 1.57 (6H, s). ^{13}C NMR (DMSO-d_6): 156.6, 147.3, 143.5, 136.5, 131.2, 127.4, 116.0, 114.8, 107.9, 106.1, 41.2, 30.68. Anal. Calcd. for $C_{27}H_{28}N_4O_2$ (440.54): C, 73.61%; H, 6.41%; N, 12.72%. Found: C, 73.48%; H, 6.31%; N, 12.89%.

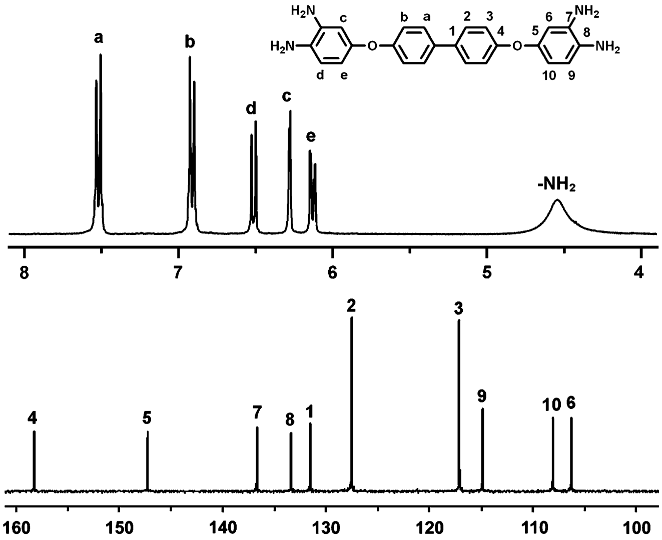


Fig. 1. ^{1}H NMR and ^{13}C NMR spectra of the tetraamine monomer **2b** in DMSO-d_6.

2.3.7. Synthesis of 2,7-bis(3-amino-4-nitrophenoxy)-naphthalene (*1d*)

This compound was prepared from 2,7-dihydroxynaphthalene (16.0 g, 0.10 mol) and 5-chloro-2-nitroaniline (36.2 g, 0.21 mol) with the same procedure described previously. The product was obtained in a yield of 77.5% (33.5 g). ^{1}H NMR (DMSO-d_6): 8.09–8.12 (2H, d), 8.02–8.05 (2H, d), 7.69–7.70 (2H, d), 7.48 (4H, –NH_2), 7.34–7.38 (2H, dd), 6.44–6.45 (2H, d) and 6.34–6.38 (2H, dd). Anal. Calcd. for $C_{22}H_{16}N_4O_6$ (432.39): C, 61.11%; H, 3.73%; N, 12.96%. Found: C, 60.89%; H, 3.62%; N, 12.89%.

2.3.8. Synthesis of 2,7-bis(3,4-aminophenoxy)naphthalene (*2d*)

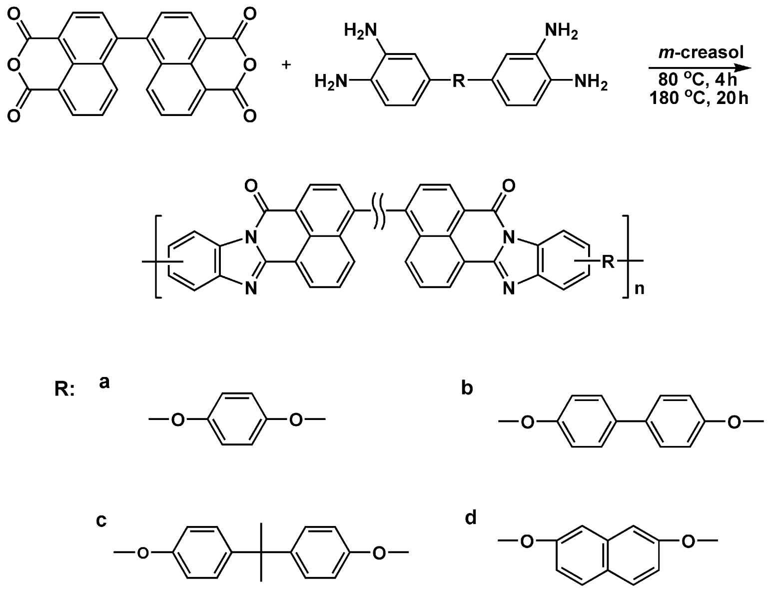
This compound was prepared according to the procedures described earlier for monomer **2b**. The product was obtained in a yield of 83.7% (3.12 g). Mp: 135.5 °C. ^{1}H NMR (DMSO-d_6): 7.78–7.81 (2H, d), 7.01–7.05 (2H, dd), 6.97–6.98 (2H, d), 6.50–6.53 (2H, d), 6.27–6.28 (2H, d), 6.12–6.16 (2H, dd), 4.66 (8H, –NH_2). ^{13}C NMR (DMSO-d_6): 157.4, 147.1, 136.6, 135.1, 131.5, 129.3, 124.9, 116.8, 114.9, 110.2, 108.1, 106.3. Anal. Calcd. for $C_{22}H_{20}N_4O_2$ (372.42): C, 70.95%; H, 5.41%; N, 15.04%. Found: C, 70.54%; H, 5.34%; N, 14.92%.

2.4. Model compound synthesis

Benzimidazobenzisoquinolinones (*3*) (Scheme 3). 0.1982 g (1 mmol) of 1,8-naphthalic anhydride (NA), 0.3985 g (0.5 mmol) of 4,4′-bis(3,4-aminophenoxy)biphenyl (**2b**), 0.122 g (2 mmol) of benzoic acid, 5 mL of *m*-cresol were successively placed into a 50 mL three-necked round-bottomed flask equipped with a reflux condenser, a nitrogen inlet/outlet, and a Teflon-coated stirring bar. The mixture was stirred at room temperature for a few minutes and then heated at 80 °C for 4 h. The vigorously stirred mixture was heated gradually to 180 °C for 2 h and then maintained at that temperature for 12 h. After being cooled to room temperature, the solution was poured into 100 mL of methanol. The precipitate was collected by filtration and washed with methanol thoroughly and afforded 0.346 g (yield: 96.0%) of fine yellow crystals. IR (KBr): 1697 cm^{-1} ($\upsilon_{\mathrm{symC=O}}$), 1619 and 1550 cm^{-1} ($\upsilon_{\mathrm{symC=N=C}}$) and 1369 cm^{-1} ($\upsilon_{\mathrm{C-N}}$). Anal. Calcd. for $C_{48}H_{26}N_4O_4$ (722.74): C, 79.77%; H, 3.63%; N, 7.75%. Found: C, 79.68%; H, 3.69%; N, 7.70%.

2.5. Polymer synthesis

The general procedure for the polycondensation reaction was 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 under a flow of nitrogen. After obtaining a homogeneous solution, 2 mmol of benzoic acid was added. The mixture was



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

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 36 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 99%.

2.6. Preparation of dense film

Tough, ductile dense membranes with a controlled thickness of 20–30 μm were prepared. A 5–8 wt% solution of polymer in *m*-cresol was stirred overnight and filtered. Film cast onto the glass plate from the clear solution and dried at 120 °C for 10 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).

3. Results and discussion

3.1. Monomer synthesis

These new tetraamine monomers containing flexible ether linkages (**2a**–**d**) were synthesized according to Scheme 1. 2,2′-Bis[4-(3,4-diaminophenoxy)phenyl]propane (**2c**) was prepared according to the literature [16]. The dinitrosubstituted compounds (**1**) were prepared in 70–87% yields by treatment of 5-chloro-2-nitroaniline with bisphenols in DMAc containing K_2CO_3. In this step, running the reaction for several hours at 80 °C followed by 12 h at 120 °C generally resulted in moderate yields of approximately 50%, whereas letting the reaction run for a longer period at high temperature (140 °C) produced dinitro compounds (**1**) with a slightly higher yield of 70%. The tetraamines (**2**) were obtained in high yield by reduction of the corresponding dinitro compounds (**1**) with hydrazine hydrate and Pd/C catalyst in refluxing ethanol. Due to the low solubility of **2b** and **2d** in ethanol, the reactions required long times and the products needed to be purified by recrystallization from DMF and water (5:1, v/v). Elemental analysis, IR, ^{1}H and ^{13}C NMR spectroscopies confirmed the structures of all the monomers. The ^{1}H and ^{13}C NMR of the monomer **2b** are shown in Fig. 1. ^{1}H NMR spectrum of tetraamines (**2b**) confirms that the nitro groups have been converted into amino groups by the high field shift of the aromatic protons and by the signal at ⊿ 4.50 ppm corresponding to the amino protons.

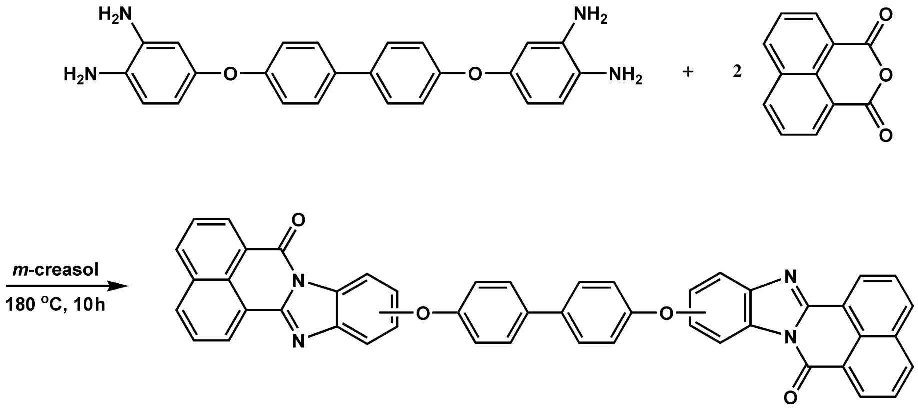
3.2. Polymer syntheses

A series of poly[bis(benzimidazobenzisoquinolinones)](PBIBIs) from these novel tetraamines and 4,4′-binaphthyl-1,1′,8,8′-tetracarboxylic dianhydride has been prepared by a one-step, high-temperature solution polycondensation, according to Scheme 2. The syntheses were carried out in *m*-cresol in the presence of

Table 1
Inherent viscosity, solubility and elemental analysis of the PBIBIs.

Polymer	η^a (dL/g)	Solubility[b]					Empirical formula	Elemental analysis (%)			
		H_2SO_4	CH_3SO_3H	*m*-Cresol	DMSO	$C_2H_2Cl_4$			C	H	N
PBIBI-a	1.26	++	++	++	−−	−−	$(C_{42}H_{20}N_4O_4)_n$	Calcd.	78.25	3.13	8.69
								Found	78.68	3.10	8.82
PBIBI-b	1.52	++	++	++	−−	−−	$(C_{48}H_{24}N_4O_4)_n$	Calcd.	79.99	3.36	7.77
								Found	79.76	3.28	7.70
PBIBI-c	1.44	++	++	++	−−	−−	$(C_{51}H_{30}N_4O_4)_n$	Calcd.	80.30	3.96	7.34
								Found	80.42	3.88	7.55
PBIBI-d	1.30	++	++	++	−−	−−	$(C_{46}H_{22}N_4O_4)_n$	Calcd.	79.53	3.19	8.06
								Found	79.60	3.26	8.14

[a] Inherent viscosity measured was at a concentration of 0.5 g dL^{-1} in *m*-cresol at 30 °C.
[b] '++' easily soluble, '−−' insoluble.



3

Scheme 3. Synthesis of the model compound **3**.

benzoic acid that acted as a catalyst. The polymerizations were initially run at an ambient temperature for 2 h and at 80 °C for 4 h. Subsequently, the temperature was raised slowly to 180 °C, and maintained at the temperature for 36 h. In all of the reactions, a homogeneous, intensely red clear viscous solution was formed. The PBIBIs were obtained in almost quantitative yields and displayed reduced viscosity values ranging from 1.2 to 1.5 g dL^{-1} (Table 1).

The IR spectra of the polymers were compared with those of the model compound **3**. The model compound was synthesized by the following reactions shown in Scheme 3.

The IR spectra of the polymers resembled those of the model compound **3**, especially in the wave number region of from 1300 to 1750 cm^{-1} (Fig. 2). Both in the IR spectra of the polymers studied and in the model compound **3** absorption bands at 1700 cm^{-1} were observed along with weak IR absorption bands at 1620 and 1550 cm^{-1}, typical of the =C=N group vibrations [11]. The former are known to result from the characteristic stretching vibrations of the >C=O group in the pyridinone ring. 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 title polymers were completely cyclized into pyridinone rings by the one-stage polycondensation method.

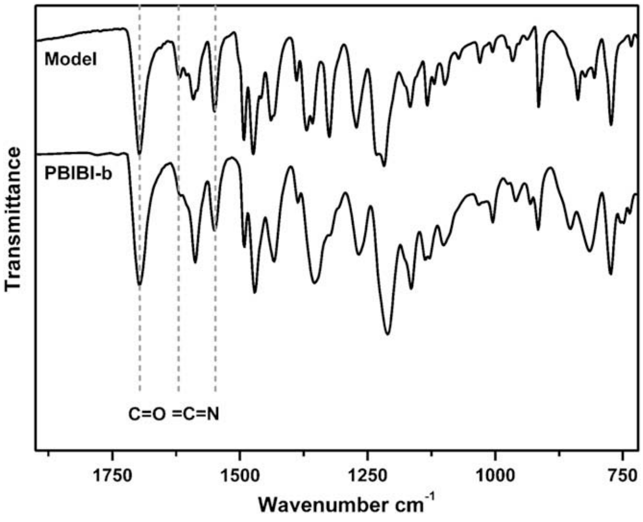


Fig. 2. Infrared absorption spectra of the model compounds **3** and the **PBIBI-b**.

3.3. Polymer properties

Properties of the newly synthesized polymers are listed in Table 1. The obtained polymers were found to be soluble in not only strong acids (concentrated H_2SO_4, methanesulfonic acid, polyphosphoric acid) but also phenolic solvents (*m*-cresol and *p*-chlorophenol). The high solubility of all PBIBIs may be attributed to the flexible ether moieties introduced. Molecular weight determinations on PBIBIs have not been attempted in this laboratory due to the lack of a suitable solvent in which to make conventional measurements. Nevertheless, some qualitative evidence that high molecular weight polymers have been obtained is rather convincing and further work to determine physical and mechanical properties more extensively is anticipated. For example, the PBIBIs have inherent viscosities ranging from 1.26 to 1.52 g dL^{-1} in *m*-cresol and exhibit good film-forming properties.

Influence of the presence of various linkages making the poly[bis(benzimidazobenzisoquinolinones)] chain more flexible on the thermal stability of the polymers was also investigated. The thermal properties of the PBIBIs were examined by means of thermogravimetric analysis (TGA) and dynamic mechanical thermal analyzer (DMTA) measurements (Table 2). In the TGA, all the PBIBIs exhibited an outstanding thermal stability in an inert atmosphere and in air. The temperature at 5% weight loss ($T_{d5\%}$) of PBIBI series stayed within 483–540 °C in air and within 510–541 °C in nitrogen, while weight loss at 800 °C amounted, on average, to some 24–32%. Typical TGA thermograms of **PBIBI-a** and **PBIBI-b** are shown in Fig. 3. The excellent thermal stabilities of the polymers could be interpreted by the stable multiaromatic conjugated structures in the polymer backbones. Thermal stability of these polymers was found to depend on the amount of flexible or kinked linkages per repeating unit of the chain. **PBIBI-b** and **PBIBI-d** having 4,4′-biphenyldioxy or 2,7-naphthalenedioxy linkages in

Table 2
Thermal properties of the PBIBIs.

Polymer	T_g[a] (°C)	T_5[b] (°C)		T_{10}[c] (°C)		Char yields[d] (%)
		Air	N_2	Air	N_2	
PBIBI-a	427.4	483.7	517.3	515.0	526.2	68.2
PBIBI-b	430.5	530.0	537.5	550.5	552.2	74.4
PBIBI-c	429.3	496.0	510.9	530.1	537.9	72.8
PBIBI-d	448.9	539.6	540.6	554.6	554.0	76.9

[a] Measured by DMTA. at 1 Hz and at a rate of 4 °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.

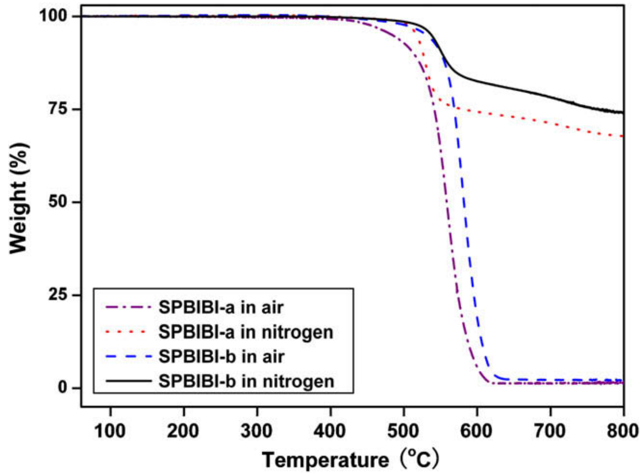


Fig. 3. The TGA curves of the **PBIBI-a** and **PBIBI-b**.

the repeating chain unit, exhibited the highest thermal stability. On the other hand, the introduction of further flexible linkages (**PBIBI-c**) and l,4-phenylenedioxy (**PBIBI-a**) was found to result in the reduction of the $T_{d5\%}$ by some 20–50 °C. The T_gs of PBIBIs were in the range of 427–449 °C on the basis of DMTA measurement. All these new polymers had glass transition temperatures T_g below their decomposition temperatures, a distinct relationship being found to exist between the molecular structure of the polymers studied and their T_g values. In general, the results of TGA and DMTA analyses showed the polymer thermal stabilities depending on the aromatic tetraamines used in the following order: 2,7-bis(3,4-aminophenoxy)naphthalene (**2d**) > 4,4′-bis(3,4-aminophenoxy)-biphenyl (**2b**) > 2,2′-bis[4-(3,4-diaminophenoxy)phenyl]propane (**2c**) > 1,4-bis(3,4-aminophenoxy)phenyl (**2a**). Consequently, an increase in the amount of linkages making the polymer chain more flexible was accompanied by a decrease of the polymer thermal stabilities.

The wide-angle X-ray diffraction patterns of PBIBI films indicated that the polymers were amorphous, which can be attributed to the reduction of crystallinity of the polymer chains caused by the presence of the flexible ether groups. In addition, twist non-coplanar binaphthyl moieties in PBIBIs is certainly responsible for lowering the interchain interactions associated with dissolution or reducing the stiffness of the polymer backbone. The amorphous nature of the PBIBI films could also be identified by the DSC measurements discussed below: no obvious crystalline melting transitions were observed during the measurement.

All the PBIBIs could be processed into highly cohesive and good quality films. These flexible films were subjected to tensile test, and the results are summarized in Table 3. The samples had tensile stress at maximum load of 79.5–114.5 MPa, Young's modulus of 1.1–1.7 GPa, and elongation at break of 10.3–23.0%. These PBIBI membranes showed high maximum stress, Young's modulus because of their rigid molecular structure.

Table 3
Mechanical properties of the PBIBI films.

Polymer	Film properties	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
PBIBI-a	Tough flexible	91.6	1.2	12.9
PBIBI-b	Tough flexible	93.0	1.1	23.0
PBIBI-c	Tough flexible	79.5	1.4	10.3
PBIBI-d	Tough flexible	114.5	1.7	15.5

Table 4
Gas permeability of the PBIBIs films.

Polymer	Permeabilities[a] (barrer)				Permselectivities (α)	
	$P(O_2)$	$P(N_2)$	$P(CO_2)$	$P(CH_4)$	$\alpha(O_2/N_2)$	$\alpha(CO_2/CH_4)$
PBIBI-a	9.04	1.61	61.82	1.84	5.61	33.60
PBIBI-b	15.52	2.74	79.81	1.98	5.66	40.31
PBIBI-c	19.43	3.87	96.51	3.15	5.02	30.59
PBIBI-d	7.36	1.21	31.68	0.73	6.08	43.40
6FDA-TABP	16.41	2.98	63.60	0.99	5.51	64.24

[a] P is permeability coefficient; units: 1 Barrer = 10^{-10} cm^3 [STP] cm cm^{-2} s^{-1} cm Hg^{-1}.

As discussed previously, the PBIBIs in this study displayed excellent solubility, thermal stability, and mechanical properties because of the introduction of the flexible ether linkages. These merits of such PBIBIs are just what are required for gas-separation membranes. The gas permeability and permeation selectivity of the dense PBIBI membranes for O_2, N_2, CH_4 and CO_2 were studied (Table 4). Their O_2 and CO_2 permeability coefficients were in the range 7.36–19.43 and 31.68–96.51 barrers, respectively, while O_2/N_2 and CO_2/CH_4 selectivity coefficients were in the range 5.02–6.08 and 30.59–43.40, respectively. For all the polymers, the selectivity decreased as the permeability increased and vice versa. This result

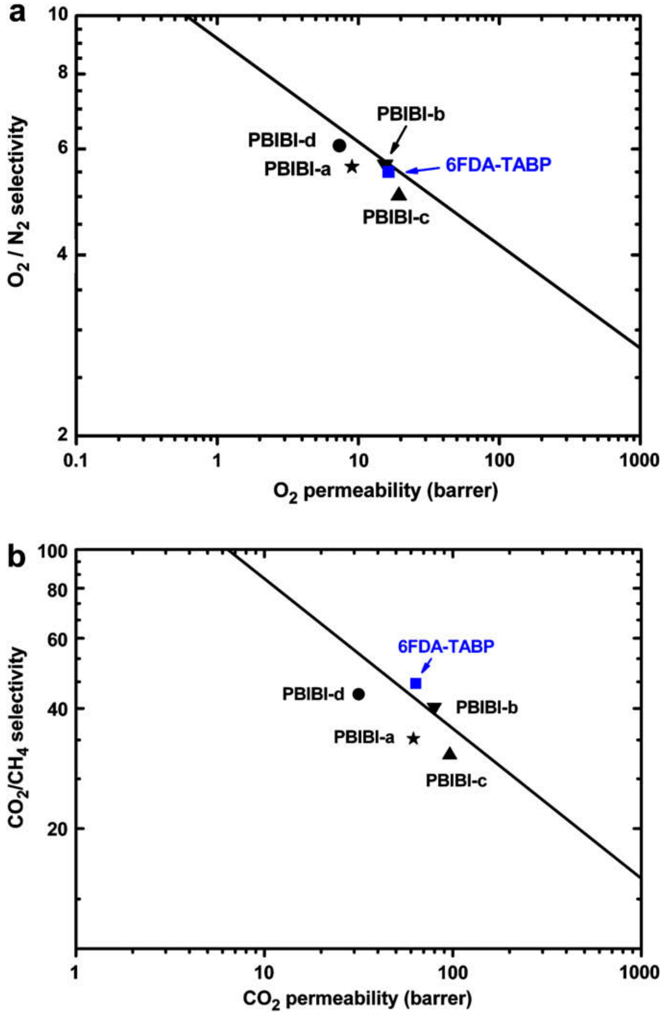


Fig. 4. Permeability/permselectivity diagrams for the O_2/N_2 (a) and CO_2/CH_4 (b) gas pair, respectively.

was consistent with the well-known tradeoff. To provide some perspective on the performance of these polymers, the permeability/selectivity maps are present in Fig. 4 for O_2/N_2 and CO_2/CH_4 pairs, respectively. The solid lines represent the upper bound lines of Robeson [17]. All the experimental ideal gas selectivities for the PBIBIs were seen to lie on or slightly below the upper bound limit. Furthermore, **PBIBI-b** demonstrates excellent CO_2/CH_4 separation performance, surpassing the CO_2/CH_4 separation limitation. The gas-separation performance of the PBIBIs was similar to that of the polypyrrolone 6FDA-TABP, from 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and 3,3′,4,4′-tetraaminobiphenyl (TABP) as is shown in Fig. 4 [18]. The results suggest that these novel polymers are attractive materials for industrial gas separation.

4. Conclusions

Novel ether linked aromatic tetraamines were synthesized via a straightforward, high-yielding, two-step route from readily available reagents. With these monomers, the high molecular weight poly[bis(benzimidazobenzisoquinolinones)](PBIBIs) were obtained by a one-step, high-temperature solution polycondensation. The resulting polymers had good solubility in phenolic solvents and could be cast into transparent and strong films due to the introduction of twist non-coplanar naphthalene rings and flexible ether linkages. They also exhibited high glass transition temperatures that were below their corresponding decomposition temperature values while preserving a relatively high thermal and oxidative stability. Furthermore, these polymer membranes showed high gas permeabilities and gas separation properties lying on or above the upper bound trade off limit. The good combination of properties and solubility exhibited in this series of poly[bis(benzimidazobenzisoquinolinones)] demonstrated their potential for future high performance materials.

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