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Synthesis and properties of organosoluble polyimides based on 2,2′-diphenoxy-4,4′,5,5′-biphenyltetracarboxylic dianhydride

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Abstract

A novel method for the preparation of 2,2′-diphenoxy-4,4′,5,5′-biphenyltetracarboxylic dianhydride have been investigated. This new dianhydride contains flexible phenoxy side chain and a twist biphenyl moiety and it was synthesized by the nitration of an *N*-methyl protected 3,3′,4,4′-biphenyltetracarboxylic dianhydride and subsequent aromatic nucleophilic substitution with phenoxide. The overall yield was up to 75%. The dianhydride was polymerized with five different aromatic diamines to afford a series of aromatic polyimides. The polyimide properties such as inherent viscosity, solubility, UV transparency and thermaloxidative properties were investigated to illustrate the contribution of the introduction of phenoxy group at 2- and 2′-position of BPDA dianhydride. The resulting polyimides possessed excellent solubility in the fact that the polyimide containing rigid diamines such as 1,4-phenylenediamine and 4,4′-oxydianiline were soluble in various solvents such as *N*-methyl-2-pyrrolidone, *N*,*N*-dimethylacetamide, dimethyl sulfoxide and chloroform. The glass-transition temperatures of the polymers were in the range of 255–283 °C. These polymers exhibited good thermal stability with the temperatures at 5% weight loss range from 470 to 528 °C in nitrogen and 451 to 521 °C in air, respectively. The polyimide films were found to be transparent, flexible, and tough. The films had a tensile strength, elongation at break, and Young's modulus in the ranges 105–168 MPa, 15–51%, 1.87–2.38 GPa, respectively.

Keywords: Polyimides; High solubility; Polycondensation

1. Introduction

Aromatic polyimides generally possess excellent thermal and mechanical, electrical, and chemical properties. Therefore, they are being used in many applications such as electrics, coatings, composite materials, and membranes [1,2]. However, the commercial use of these materials is often limited because of their poor solubility and high softening or melting temperatures. Consequently, polyimide process is generally carried out from soluble poly(amic acid) solution then subsequently converted to intractable polyimide through thermal treatment. Problems often arise because the poly(amic acid)s is thermally and hydrolytically unstable. The water released during imidization also tends to cause void in the final materials [3,4]. The high curing temperatures could also cause serious damage to devices that are thermally sensitive, such as thin-film-transistor-driven active-matrix liquid-crystal devices (TFTAM-LCDs) [5].

To overcome problems, much effort has been concentrated on the design and preparation of processable polyimides based on new dianhydrides [6–12] and diamines [13–22] with the purpose of obtaining certain advantageous properties.

One of the most successful approaches to attaining solubility without sacrificing their excellent properties is to introduce twisted biphenyl structures in polyimide backbones through the synthesis and polymerization of appropriately substituted dianhydrides and diamines.

Harris et al. [23,24] have demonstrated that polyimides from 2,2′-disubstituted biphenyltetracarboxylic dianhydride(2,2′-disubstituted BPDAs) exhibit excellent

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solubility and high transparency in the visible–UV region. Kwon [25] reported high oxygen permeability of the polyimides synthesized from two dianhydride monomers composed of noncoplanar twisted biphenyl unit containing *tert*-butylphenyl or trimethylsilylphenyl groups. The improvement in properties can be attributed to the incorporation of twist-biphenyl-imide structures in these 2,2′-disubstituted-BPDAs. The introduction of 2,2′-substituted pendant group was carried out by the chemical modification of the BPDA or its precursor. The used approach involved the bromination of BPDA or tetramethyl substituted biphenyl and subsequent Suzuki cross-coupling reaction with phenylboric acid. The yield of bromination of BPDA was lower (20%) and the expensive palladium complex was consumed in the coupling reaction [23].

In this paper, we report a feasible synthetic method to introduce phenoxy group in the 2- and 2′-positions of 4,4′,5,5′-biphenyltetracarboxylic dianhydride by the nitration of 3,3′,4,4′-biphenyltetracarboxylic dianhydride, then the nitro displacement with phenoxide. The resulting dianhydride was polymerized with several aromatic diamines and the polyimides obtained were to be thoroughly characterized. We believe this is a facile synthetic method to modify polyimide. It opens the way to introduce functional group into polyimide chain, such as –CN, –OH, –OR, –SR, –F group, by this approach.

2. Experimental

2.1. Materials

N,*N*-dimethyacetamide (DMAc) was dried over P_2O_5 and then over 4 Å molecular sieves, distilled under reduced pressure, and stored under nitrogen in the dark. *m*-Cresol was distilled under nitrogen before use. 3,3′-4,4′-Biphenyltetracarboxylic dianhydride (BPDA) (purchased from TCI), 4,4′-oxydianiline (ODA) 1,4-phenylenediamine (PDA) and 1,3-phenylenediamine (mPDA) were purified by sublimation under vacuum. 4,4′-Methylenedianiline (MDA) and 2,2-dimethylbiphenyl-4,4′-diamine (DMB) were purified by recrystallization from ethanol prior to use. Other chemicals were used as received.

2.2. Measurement

The FTIR spectra were recorded on a Bio-Rad digilab Division FTS-80 spectrometer. Thermogravimetric analysis (TGA) was carried out with a Perkin–Elemer TGA-2 thermogravimetric analyzer at a heating rate of 10 °C/min under nitrogen. Differential scanning calorimetry (DSC) was performed on a Perkin–Elemer DSC-7 system at a heating rate of 20 °C/min under a nitrogen atmosphere. 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. Intrinsic viscosities were determined on 0.5 g/dL concentration of polymer in DMAc using an Ubbelohde capillary viscometer at 30.0 ± 0.1 °C. ^{1}H NMR and ^{13}C NMR spectra were measured at 300 MHz on an AV300 spectrometer with tetramethylsilane (TMS) as an internal standard. Molecular weight measurements were determined by gel-permeation chromatography (GPC) using a refractive index detector. Polymer samples were dissolved in stabilized THF (30 mg/mL) and filtered through a 0.20 μm Teflon filter. All the molecular weights are measured relative to polystyrene standards. UV–visible spectra were measured with a SHIMADZU UV-2550 spectrometer in the transmittance mode.

2.3. Monomer synthesis. 4,4′-Bis(N-methylphthalimide) (**1**)

BPDA (29.4 g, 0.10 mol) and xylene (100 mL) were charged into a three-necked round-bottom flask, equipped with a mechanical stirrer. A 25 wt% aqueous solution of methylamine was added dropwise. The mixture was stirred at room temperature for 1 h, and then heated at reflux until no visible traces of water could be seen in the Dean–Stark trap. The mixture was cooled to room temperature. Filtrated and dried overnight at 100 °C under reduced pressure to give (31.7 g, 99%) white powder. The crude product was used in the next reaction without purification. FT-IR (KBr pellet) 1767 (asym C=O str), 1720 (sym C=O str), 1385 (C–N str), 736 cm^{-1} (imide ring deformation). ^{1}H NMR (DMSO-d$_6$): δ 2.99 (s, 6H, NCH_3), 7.88–7.90 (d, 2H, Ar–H), 8.17–8.21 (d, 4H, Ar–H). Anal. Calcd for $C_{18}H_{12}N_2O_4$ (320.31): C, 67.50; H, 3.78; N, 8.75. Found: C, 65.93; H, 3.66; N, 8.84.

2.4. 4,4′-Bis(2,2′-dinitro-N-methylphthalimide) (**2**)

To a three-neck round-bottom flask equipped with a mechanical stirrer was added **1** (20 g, 62.5 mmol) and 98% H_2SO_4 (30 mL). The solution was warmed to 70 °C under vigorous stirring until **1** was dissolved. Fume HNO_3 was added at a rate that kept the internal temperature between 80 and 90 °C. After complete addition, the mixture was allowed to react at 80 °C for 2 h. The reaction mixture was cooled, poured onto 100 g ices, and 100 mL cold water was added. The yellow precipitate was separated by filtration, washed thoroughly with water and dried. The yield was 23.4 g (91%). FT-IR (KBr pellet) 1537,1346 (NO_2), 1772 (asym C=O str), 1713 (sym C=O str), 1386 (C–N str), 739 cm^{-1} (imide ring deformation). ^{1}H NMR (DMSO-d$_6$): δ 3.11 (s, 6H, NCH_3), 8.15 (s, 2H, Ar–H), 8.63 (s, 2H, Ar–H). Anal. Calcd for $C_{18}H_{10}N_4O_8$ (410.30): C, 52.69; H, 2.46; N, 13.66. Found: C, 51.27; H, 2.37; N, 14.12.

2.5. 4,4′-Bis(2,2′-diphenoxy-N-methylphthalimide) (**3**)

In a three-necked flask equipped with a Dean–Stark trap and a mechanical stirrer, phenol (5.2 g, 55 mmol) was dissolved in 50 mL DMAc. NaOH (2.3 g, 57.5 mmol) and toluene (20 mL) were added. The nitrogen was bubbled into the mixture at room temperature for 1 h. The mixture was stirred and heated under nitrogen for 3 h during which time the water was azeotropically removed. Toluene was then removed, and the reaction was cooled to 80 °C. Compound **2** (10.3 g, 25 mmol) was added, and the reaction was maintained for 2 h at 80 °C. The solution was precipitated in water (200 mL) and the product was thoroughly washed with water. A crude product (10.6 g, 96% yield) was isolated by filtration and washed with water, then dried in vacuum at 100 °C. FT-IR (KBr pellet) 1250 (asym), 1040 (sym) (OPh), 1772 (asym C=O str), 1713 (sym C=O str), 1386 (C–N str), 739 cm^{-1} (imide ring deformation). ^{1}H NMR (DMSO-d_6): δ 3.01 (s, 6H, NCH_3), 7.04–7.06 (d, 4H, Ar–H), 7.08 (s, 2H, Ar–H), 7.25 (m, 2H, Ar–H), 7.41–7.45 (m, 4H, Ar–H), 8.03 (s, 2H, Ar–H). Anal. Calcd for $C_{30}H_{20}N_2O_6$ (504.50): C, 71.42; H, 4.00; N, 5.55. Found: C, 70.31; H, 3.75; N, 5.83. Mp: 258–260 °C.

2.6. *2,2′-diphenoxy-4,4′, 5,5′-biphenyltetracarboxylic dianhydride (5)*

To a solution of **3** (12.6 g, 25 mmol) in 50 mL H_2O was added slowly KOH (8.4 g, 0.15 mol). The solution was heated at reflux for 24 h, and made acidic by the addition of 6.5 N HCl to pH of 1.0. The white precipitate was collected by filtration and dried in vacuum at 100 °C. Then the teracarboxylic acid was dissolved in 20 mL acetic anhydride at refluxed for 4 h. After the solution was cooled to room temperature, the product was filtered and wash with toluene and dried at 100 °C under vacuum, the crude product was recrystallized from acetic anhydride. The yield was 10.4 g (87%). FT-IR (KBr pellet) 1250 (asym), 1040 (sym) (OPh), 1840, 1778 (anhydride); ^{1}H NMR (DMSO-d_6): δ 7.09 (m, 4H, Ar–H), 7.17 (s, 2H, Ar–H), 7.30–7.33 (m, 2H, Ar–H), 7.47–7.49 (m, 4H, Ar–H), 8.36 (s, 2H, Ar–H). ^{13}C NMR (DMSO-d_6): δ 111.2, 120.3, 124.7, 125.9, 129.2, 130.7, 133.3, 133.9, 154.1, 161.5, 162.2. Anal. Calcd for $C_{28}H_{14}O_8$ (478.42): C, 70.30; H, 2.95. Found: C, 70.61; H, 2.86. Mp: 223–224 °C.

2.7. *Polymer synthesis*

A general procedure for the synthesis of polyimide is as follows: to a 50-mL three-necked round bottom flask was added diamine (1.00 mmol), dianhydride (1.00 mmol), five drops of isoquinoline as a catalyst and newly distilled m-cresol. The flask was purged with nitrogen and the solution was stirred for 3 h under a nitrogen atmosphere at room temperature. The reaction system was heated slowly to reflux with stirring for 3 h at the same time the water removed by nitrogen. The mixture was cooled and precipitated into a large excess of ethanol. The polymer was separated by filtration, washed with ethanol for several times and dried in a vacuum oven at 80 °C for 24 h.

2.8. *Spectroscopic data of the polymers*

2.8.1. *Polyimide **6a***

^{1}H NMR (DMSO-d_6): 7.11–7.29 (12H, br, Ar), 7.48 (8H, br, –CH2–), 8.20 (2H, s, Ar). FT-IR (KBr pellet) 1241 (asym), 1070 (sym) (OPh), 1777 (asym C=O str), 1720 (sym C=O str), 1375 (C–N str), 743 cm^{-1} (imide ring deformation).

2.8.2. *Polyimide **6b***

^{1}H NMR (DMSO-d_6): 4.04 (2H, s, $–CH_2–$), 7.06–7.09 (4H, br, Ar), 7.14 (2H, s, Ar), 7.24 (2H, br, Ar), 7.32–7.43 (10H, br, Ar), 8.13 (2H, s, Ar). FT-IR (KBr pellet) 1218 (asym), 1070 (sym) (OPh), 1776 (asym C=O str), 1723 (sym C=O str), 1354 (C–N str), 743 cm^{-1} (imide ring deformation).

2.8.3. *Polyimide **6c***

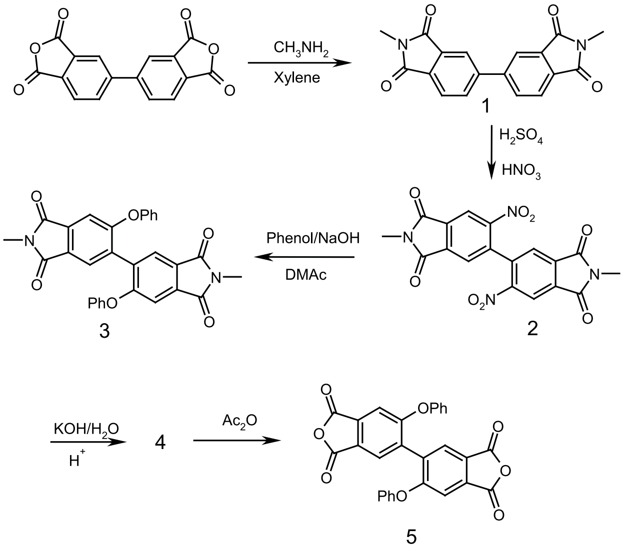
^{1}H NMR (DMSO-d_6): 2.07 (6H, s, $–CH_3$), 7.10–7.16 (6H, br, Ar), 7.24–7.33 (8H, br, Ar), 7.41–7.46 (4H, br, Ar), 8.20 (2H, s, Ar). FT-IR (KBr pellet) 1241 (asym), 1070 (sym) (OPh), 1777 (asym C=O str), 1720 (sym C=O str), 1369 (C–N str), 743 cm^{-1} (imide ring deformation).

2.8.4. *Polyimide **6d***

^{1}H NMR ($CDCl_3$): 7.03–7.10 (4H, br, Ar), 7.23–7.29 (2H, br, Ar), 7.38–7.40 (6H, br, Ar), 7.53 (4H, br, Ar), 8.10 (2H, s, Ar). FT-IR (KBr pellet) 1218 (asym), 1021 (sym) (OPh), 1777 (asym C=O str), 1724 (sym C=O str), 1354 (C–N str), 743 cm^{-1} (imide ring deformation).

2.8.5. *Polyimide **6e***

^{1}H NMR ($CDCl_3$): 6.98–7.00 (4H, br, Ar), 7.20–7.26 (2H, br, Ar), 7.34–7.37 (6H, br, Ar), 7.49–7.51 (2H, br, Ar),



Scheme 1. Synthesis of 2,2′-diphenoxy-4,4′-5,5′-biphenyltetracarboxylic dianhydride.

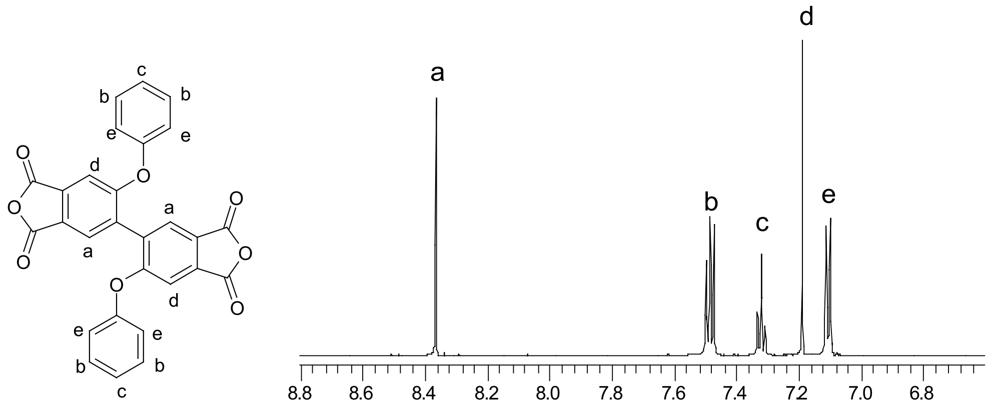


Fig. 1. ^{1}H NMR spectrum of 2,2′-diphenoxy-4,4′-5,5′-biphenyltetracarboxylic dianhydride in DMSO-d_6 solution.

7.59–7.65 (2H, br, Ar), 8.03 (2H, s, Ar). FT-IR (KBr pellet) 1216 (asym), 1070 (sym) (OPh), 1778 (asym C=O str), 1724 (sym C=O str), 1353 (C–N str), 742 cm^{-1} (imide ring deformation).

2.9. Preparation of dense film

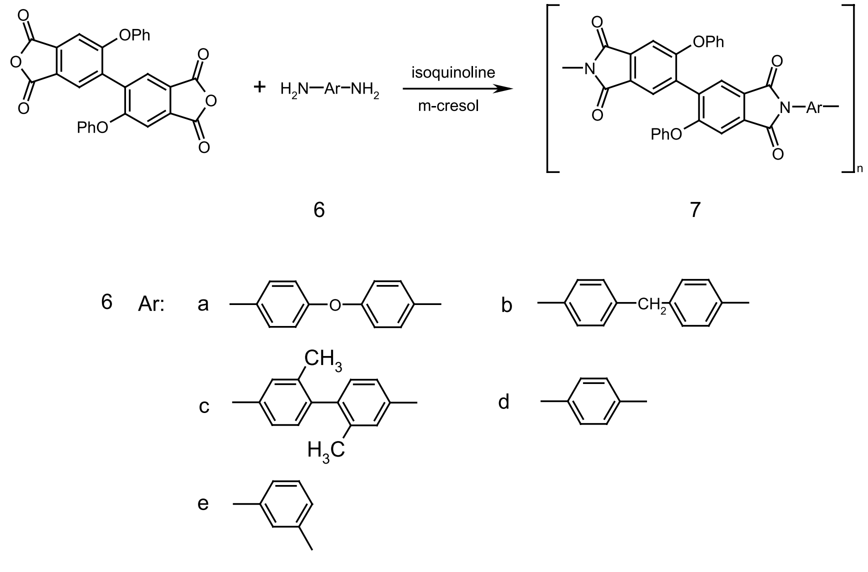
A 7–10 wt% solution of polymer in chloroform was stirred overnight and filtered. Film cast onto the glass plate from the clear solution and dried at room temperature for 5 h. Then putting into a vacuum oven and heated at 60 °C for 2 h, at 100 °C for 10 h to ensure complete removal of solvent, and then cooled to room temperature slowly.

3. Results and discussion

3.1. Monomer syntheses

New dianhydride monomer with phenoxy group attached to the 2,2′-positions of BPDA, was successfully prepared via consecutive reactions, as shown in Scheme 1. The overall yield based on BPDA as a starting material, was 75%. The compound **1** was dissolved in 98% H_2SO_4 at 70 °C before 95% HNO_3 is dropped in. The nitration reaction was carried out with 95% HNO_3/98% H_2SO_4 at the temperature of 80–90 °C to give 4,4′-*Bis*(2,2′-dinitro-*N*-methylphthalimide) (**2**) in yield of 91%. No nitration reaction occurred below 60 °C due to lack of reactivity, because the strong electron-withdrawing effect of two carbonyl groups would deactivate the aromatic rings towards electrophilic substitution. Rising the temperature to above 110 °C causes product hydrolyze to yield 2,2′-dinitro-4,4′,5,5′-biphenyltetracarboxylic acid.

The dinitro phthalimide (**2**) was converted to the diphenoxy phthalimide (**3**) by reaction with phenoxide in DMAc, and the yield was 96%. The high reactivity of N-substituted nitrophthalimides towards nucleophilic substitution is from the strong electron-withdrawing effect of two carbonyl groups. The displacement reactions have to



Scheme 2. Syntheses of PI**6a**–**e**.

Table 1
Polyimides from various diamines

PI	$[\eta]^{a}$ (dL/g)	$M_n \times 10^{-4b}$	$M_w \times 10^{-4b}$	T_g (°C)[c]	T.g.a.[d] (°C)	
					Air	N_2
6a	1.13	5.5	11.1	270	510	521
6b	0.82	3.2	5.8	255	468	470
6c	1.02	4.3	9.7	258	451	476
6d	1.15	[e]	e	283	521	528
6e	1.04	e	e	262	511	508

[a] Inherent viscosity was measured in *N*,*N*-dimethylacetamide (DMAc) solution at a concentration of 0.5 g/dL at 30±0.1 °C.

[b] GPC (30 mg/mL THF solution), polystyrene standards.

[c] Glass transition temperation (T_g) measured on DSC at a heat rate of 20 °C/min.

[d] Temperature at which a 5% weight loss occurred when the polymers were placed to t.g.a with a heating rate of 10 °C/min.

[e] Polymer is partially soluble in THF.

be carried out under anhydrous conditions because the imide's rings of nitrophthalimides are sensitive to a base catalyzed hydrolytic ring opening reaction.

Hydrolysis of the 2,2′-diphenoxyphthalimide (**3**) with sodium hydroxide in water and subsequent acidification with hydrochloric acid give 2,2′-diphenoxy-4,4′, 5,5′-biphenyltetracarboxylic acid, which was cyclodehydrate with acetic anhydride to generate a 87% yield of 2,2′-diphenoxy-4,4′, 5,5′-biphenyltetracarboxylic dianhydride (DPOBPDA). Elemental analyses, IR, and ^{1}H NMR spectroscopies confirmed the structures of the monomers (**4**). ^{1}H NMR spectrum of the monomers (**4**) is give in Fig. 1.

3.2. Polymers syntheses

DPOBPDA (**4**) was polymerized with five different diamines in m-cresol containing a catalytic amount of isoquinoline (Scheme 2). The polymerizations, which were carried out with 10% (w/v) solids concentrations, were initially run at ambient temperature for 2 h. The resulting

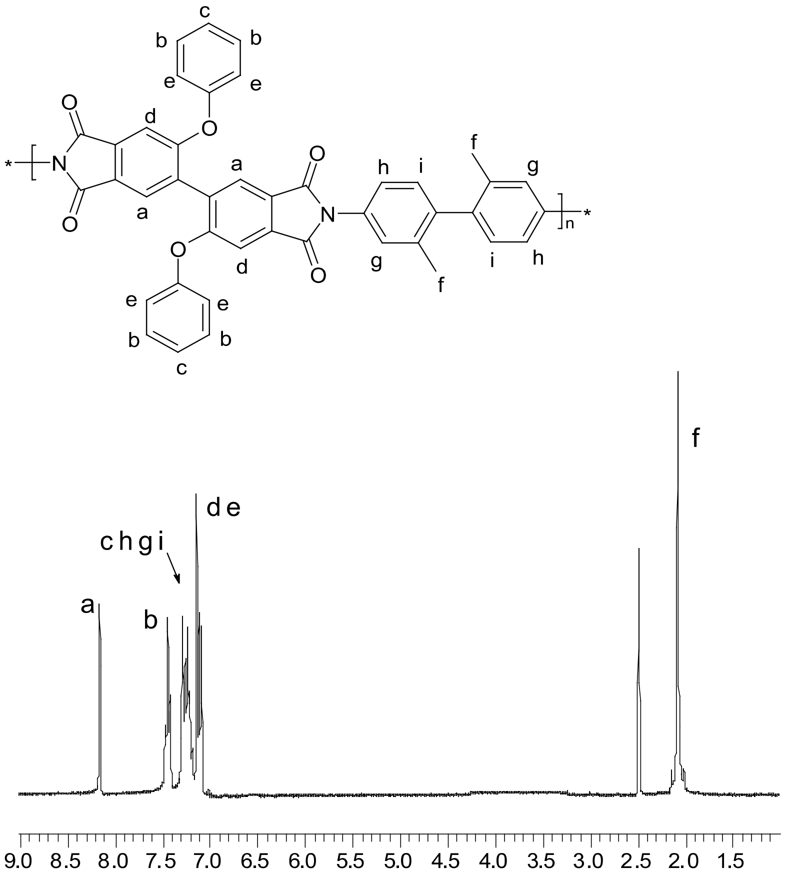


Fig. 2. ^{1}H NMR spectrum of PI 6c in DMSO-d_6 solution.

Table 2
Elemental analysis of polyimide

Polymer	Experiment formula		Elem. anal. (%)		
			C	H	N
6a	$(C_{40}H_{22}N_2O_7)_n$	Calcd	74.76	3.45	4.36
	$(642.63)_n$	Found	73.50	3.38	4.33
6b	$(C_{41}H_{24}N_2O_6)_n$	Calcd	76.87	3.78	4.37
	$(640.66)_n$	Found	75.53	3.64	4.22
6c	$(C_{42}H_{26}N_2O_6)_n$	Calcd	77.06	4.00	4.28
	$(654.69)_n$	Found	75.68	3.83	4.30
6d	$(C_{34}H_{18}N_2O_6)_n$	Calcd	74.18	3.30	5.09
	$(550.53)_n$	Found	72.80	3.19	4.83
6e	$(C_{34}H_{18}N_2O_6)_n$	Calcd	74.18	3.30	5.09
	$(550.53)_n$	Found	72.86	3.16	5.01

poly(amic acid) solutions were then heated at reflux for 5 h. Water formed during the imidization was continuously removed with a stream of nitrogen. In all of the reactions, homogeneous solutions were obtained. The polyimide products were isolated by precipitation in ethanol. The polymer was purified by continuous washed with ethanol and dried at 80 °C under vacuum for 24 h. The yields of polymerization were 92–97%.

According to Table 1, the polymerization of diamines with DPOBPDA gave moderate-to-high inherent viscosities of 0.82–1.15 dL/g in DMAc. The molecular weights of the soluble polyimides (**6a–c**) were measured by GPC (10 mg/mL tetrahydrofuran solution as an eluent) after calibration with the standard polystyrens, except for polymer **6d–e**, which was partially soluble in tetrahydrofuran. These polymer had number-average molecular weight (M_n) in the range from 3.7×10^4 to 11.2×10^4. The polymers were identified by elemental analysis, IR and ^{1}H NMR spectra (Fig. 2). The elemental analysis results of these polymers are listed in Table 2. The IR spectra supported the formation of polyimides. The characteristic absorption bands of the polyimides rings appeared near 1778 (asym C=O str), 1724 (sym C=O str), 1353 (C–N str), and 742 cm^{-1} (imide ring deformation).

3.3. Polymer properties

The solubility behaviour of these polyimides is summarized in Table 3. The polymers **6a–e** showed good solubility in organic solvents such as, chloroform, DMF, DMSO, DMAc and NMP. The polyimides **6d**, **e** were partially soluble in THF. Compared with polyimide derived from BPDA and 4,4′-oxydianiline (ODA) [26], polyimides **6a** derived from DPOBPDA and ODA are significantly more soluble in organic solvents. Apparently, such an improvement in solubility can be attributed to the bulky phenoxide substituents introduced at the 2- and 2′-positions of the biphenyl moiety, which appears to force the two phenyl rings into adopting a noncoplanar conformation. This, in turn, disrupts the crystal packing and provides enhanced solubility.

The UV–visible spectra of polymer, which possessed a thickness 6 μm, are displayed in Fig. 3. The onset and 80% transmission wavelengths are listed in Table 4. The films exhibit onset wavelength from 313 to 364 nm and 80% transmission of light from 402 to 424 nm. The values of polyimide **6b**, **c** based on 2,2-dimethylbiphenyl-4,4′-diamine(DMB) and 1,4′-methylenedianiline(MDA) are comparable with that of polyimides based 2,2′-diphenyl- and 2,2′-ditrifluoromethylBPDAs and DMB, [9] but are about 10 nm longer that of the corresponding polyimide **6a**, **d**, **e**. This indicates that the methyl group of DMB and methylene moiety of MDA is effective at breaking the conjugation along the backbone. It may decrease the chromophore length.

The thermal properties of the polyimides were investigated by thermogravimetric analysis (TGA) (Table 1) and differential scanning calorimetry (DSC) (Fig. 4). Film samples of polyimides underwent 5% weight losses at 470–528 °C in nitrogen and at 451–521 °C in air when

Table 3
Solubility of polyimides

Polymer	Acetone	THF	DMF	DMSO	DMAc	NMP	$CHCl_3$
6a	−	+	+	+	+	+	+
6b	−	+	+	+	+	+	+
6c	−	+	+	+	+	+	+
6d	−	−	+	+	+	+	+
6e	−	−	+	+	+	+	+

+, soluble; −, insoluble.

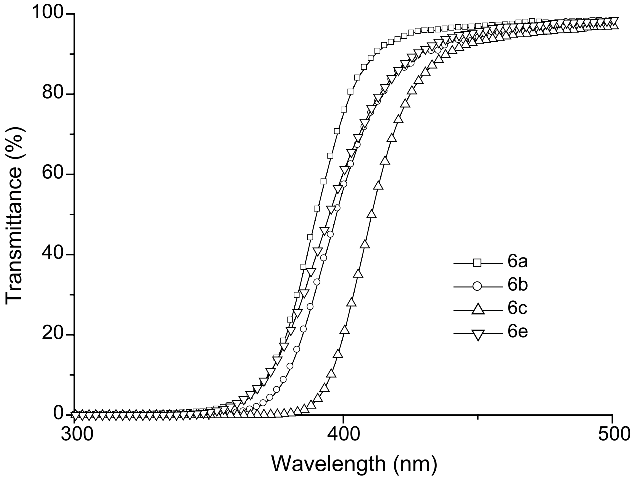


Fig. 3. Ultraviolet-visible absorption spectra of PI **6a**–**c**, **e**.

subjected to TGA with a heating rate of 10 °C/min. Thus, the polymers based on DPOBPDA dianhydride displayed lower thermooxidative stability than analogous polymers based on BPDA [26]. This is most likely due to the strong electron-donating effect of the phenoxy group and the weaker bonding of C–O bond. The bond energies of carbon–oxygen and carbon–hydrogen bonds are 359 and 413 kJ/mol, respectively [27].

Thermal transitions were investigated by DSC in the temperature range from 100 to 400 °C at a heating rate of 20 °C/min. T_g values of **6a**–**e** ranged from 255–283 °C. DSC curve of polyimide 6**a** is show in Fig. 4. In generally, both molecular packing and chain conformation (chain rigidity and linearity) affected T_gs of polymers. The introduction of phenoxy group into 2- and 2′-positions of BPDA hinders the rotation of the two phenyls rings and further increases the chain rigidity. The resulting effect should increase T_gs of polymers dramatically. However, the introduction of phenoxy group also lowers T_gs because of the increase in the free volume of polymers and the flexible property of phenoxy group. In the fact, the T_gs of the polyimides obtained from DPOBPDA and ODA (**6a**, 270 °C), and DMB (**6c**, 258 °C) are lower than that of the polyimide prepared from BPDA and ODA (273 °C), and DMB (287 °C) [28].

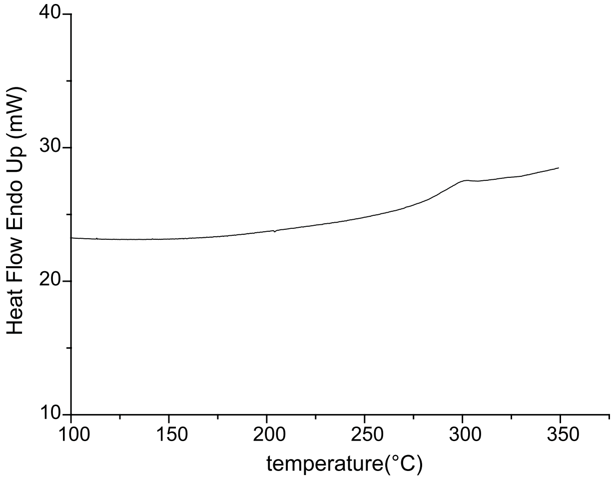


Fig. 4. DSC curve of PI **6a**.

Table 4
A set of UV-VIS spectra of PI **6** films

Polymers	Transparency onset (nm)	80% transmission (nm)
6a	332	413
6b	364	424
6c	344	414
6e	313	402

The mechanical properties of the polyimide films were examined at room temperature in air with a constant drawing rate of 2 mm/min (sample size: 30-mm length, 8-mm width, about 20-μm thick). The results are summarized in Table 5. The films had tensile strength, elongation at break, and Young's modulus in the ranges 105–168 MPa, 15–51%, 1.87–2.38 GPa, respectively. Polyimide **6a**, **b** containing flexible ODA, MDA diamines show much higher values of elongation than the other PIs based on rigid diamines. This indicates that the presence of linking group –O– and $–CH_2–$ will contribute much in imparting chain flexibility and hence in elongation of the films than the other PIs [29].

4. Conclusions

By means of specific synthetic routes, suitable methods for the synthesis of novel dianhydrides containing phenoxy groups in the 2,2′-posion of BPDA have been outlined. In our work, the synthesis of novel monomer 2,2′-diphenoxy-4,4′, 5,5′-biphenyltetracarboxylic dianhydride and its polymerization with several diamines was reported for the first time. The resulting polyimides had good solubility in conventional organic solvent. The inherent viscosity was measured at 0.82–1.15 dL/g. The flexible and tough polyimide films were found to be transparent. The films had a tensile strength, elongation at break, and Young's modulus in the ranges 105–168 MPa, 15–51%, 1.87–2.38 GPa, respectively. The polyimides containing a rigid BPDA moiety and a large phenoxy pendant group could be a good candidate for membrane application. The investigation of their gas separation properties is in progress.

Table 5
Mechanical properties of polyimides films

Polymers	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (GPa)
6a	168	51	2.38
6b	112	45	2.02
6c	105	15	1.96
6e	106	30	1.87

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References

[1] Wilson D, Stenzenberger HD, Hergenrother PM, editors. Polyimides. New York: Chapman and Hall; 1990.
[2] Ghosh MK, Mittal KL, editors. Polyimides fundamentals and applications. New York: Marcel Decker; 1996.
[3] Becker KH, Schmidt HW. Macromolecules 1992;25:6784.
[4] Huang SJ, Hoyt AE. Trends Polym Sci 1995;3:262.
[5] Kazuyuki H, Qing HL, Sung HL, Rikio Y. Proceedings of second China–Japan Seminar on Advanced Aromatic Polymer, Guilin, China, 1998, 29.
[6] Liaw DJ, Liaw BY. Chem Mater 1998;10:734.
[7] Eastmond GC, Paprotny J. Eur Polym J 1999;35:2097.
[8] Ayala D, Lozano AE, de Abajo J, de la Campa JG. J Polym Sci Part A: Polym Chem 1999;37:805.
[9] Li F, Ge JJ, Honigfort PS, Fang S, Chen JC, Harris FW, Cheng SZD. Polymer 1999;40:4987.
[10] Hsiao SH, Yang CP, Chu KY. Macromolecules 1997;30:165.
[11] Liu JG, He MH, Zhou HW, Qian ZG, Wang FS, Yang SY. J Polym Sci Part A: Polym Chem 2002;40:110.
[12] Yang CP, Hsiao SC, Tsai CY, Liou GS. J Polym Sci Part A: Polym Chem 2004;42:2416.
[13] Huang W, Yan D, Lu Q, Tao P. J Polym Sci Part A: Polym Chem 2002;40:229.
[14] Tamai S, Yamaguchi A, Ohta M. Polymer 1996;37:3683.
[15] Li F, Fang S, Ge JJ, Honigfort PS, Chen JC, Harris FW, et al. Polymer 1999;40:4571.
[16] Spiliopoulos IK, Milkrayannidis JA. Macromolecules 1998;31:515.
[17] Hsiao SH, Li CT. Macromolecules 1998;31:7213.
[18] Liaw DJ, Liaw BY, Yang CM. Acta Polym 1999;50:332.
[19] Chou CH, Reddy DS, Shu CF. J Polym Sci Part A: Polym Chem 2002; 40:3615. Part A: Polym Chem 2002, 40, 524.
[20] Yang CP, Su YY, Hsiao FZ. Polymer 2004;45:7529.
[21] Liaw DJ, Chen WH. Polymer 2003;44:3865.
[22] Yang CP, Hsiao SH, Wu KL. Polymer 2003;44:7067.
[23] Harris FW, Lin SH, Cheng SZD. Polymer 1996;37:5049.
[24] Lin SH, Li F, Cheng SZD, Harris FW. Macromolecules 1998;31: 2080.
[25] Ahn SK, Kim HS, Kim YH, Kwon SK. Macromolecules 2003;36: 2327.
[26] Rozhanskii I, Okuyama K, Goto K. Polymer 2000;41:7057.
[27] Dickerson RE, Gray HB, Darensbourg MY, Darensbourg DJ. Chemical priciples. 4th ed. Menlo Park, CA: Benjamin Cummings; 1984, p. 565.
[28] Arnold Jr FE, Cheng SZD, Hsu SL-C, Lee CJ, Harris FW. Polymer 1992;33:5179.
[29] Khatua SC, Maiti S. Eur Polym J 2002;38:537.