Polyimides Derived from 1,4-Bis [3-oxy-(*N*-aminophthalimide)] Benzene

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ABSTRACT: A novel diamine, 1,4-bis [3-oxy-(*N*-amino-phthalimide)] benzene (BOAPIB), was synthesized from 1,4-bis [3-oxy-(*N*-phenylphthalimide)] benzene and hydrazine. Its structure was determined via IR, ^{1}H NMR, and elemental analysis. A series of five-member ring, hydrazine-based polyimides were prepared from this diamine and various aromatic dianhydrides via one-step polycondensation in *p*-chlorophenol. The inherent viscosities of these polyimides were in the range of 0.17–0.61 dL/g. These polymers were soluble in polar aprotic solvents and phenols at room temperature. Thermogravimetric analysis (TGA) showed that the 5% weight-loss temperatures of the polyimides were near 450°C in air and 500°C in nitrogen. Dynamic mechanical thermal analysis (DMTA) indicated that the glass-transition temperatures (T_gs) of these polymers were in the range of 265–360°C. The wide-angle X-ray diffraction showed that all the polyimides were amorphous. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 1226–1234, 2009

Key words: polyimides; polycondensation; structure–properties relationship; thermal properties

INTRODUCTION

Aromatic polyimides are a class of polymers that have unique high temperature stability, excellent mechanical and electrical properties, and outstanding chemical resistance. Therefore, they are widely used in the aerospace, transportation, electrical and microelectronic industries. However, in many cases, their applications are restricted because of their inability to dissolve in common organic solvent and lack of melt processability.[1–3] To overcome these limitations, considerable efforts have been placed in design to synthesize various dianhydride and diamine monomers to improve their processability without sacrificing the other excellent properties. At present, the introduction of aromatic ether segments into polyimides has been attracting great attention, because the presence of flexible ether links is believed to improve the processability of the polyimides.

Hydrazine is the simplest diamine, but only a few reports on hydrazine-based polyimides can be found in the literature. In 1990's, Hay and coworkers prepared high-molecular-weight polyimides from monomers with six-member-ring *N*-amino imide by the introduction of flexible moieties from dianhydride or copolymerization with other diamine monomers. These polyimides had very high T_gs, excellent thermal stability, and good solubility.[4–10] Recently, we have reported that a series of five-member-ring, hydrazine-based polyimides can be derived from 3,3'-bis(*N*-aminophthalimide) with high solubility, thermal stability, and T_gs; some of them also showed high optical transparency.[11] As the continuing work of our research on hydrazine-based polyimides, we herein report the synthesis and properties of a series of polyimides derived from 1,4-bis [3-oxy-(*N*-amino-phthalimide)] benzene.

EXPERIMENTAL

Materials

3-Chlorophthalic anhydride (97%), 1,4-bis(3,4-dicarboxyphenoxy) benzene dianhydride (4,4'-HQDPA), and 3,3',4,4'-biphenyltetracarboxylic acid dianhydride (4,4'-BPDA) were afforded by our laboratory. 1,4-bis(2,3-dicarboxyphenoxy) benzene dianhydride (3,3'-HQDPA),[12] 2,2',3,3'-biphenyltetracarboxylic acid dianhydride (3,3'-BPDA),[13] 2,2',3,3'-benzophenone-
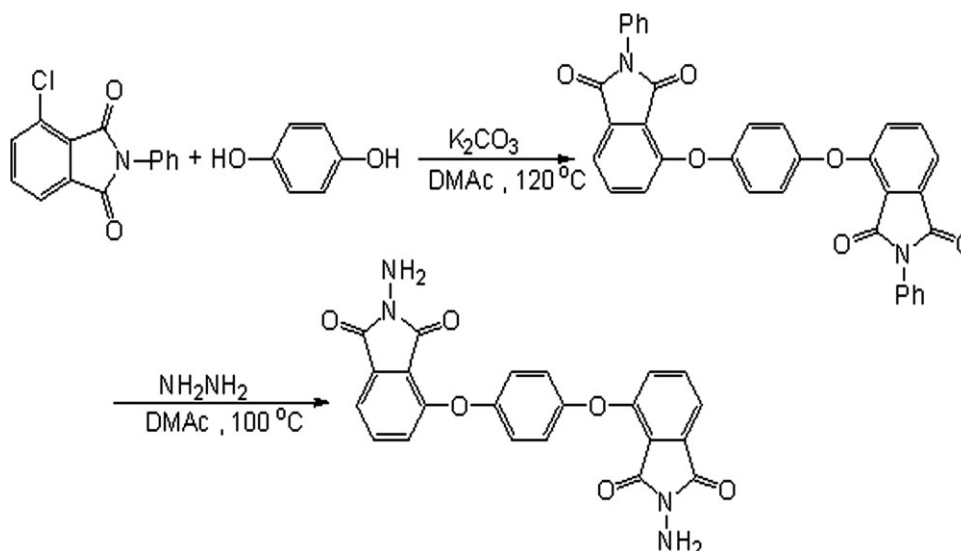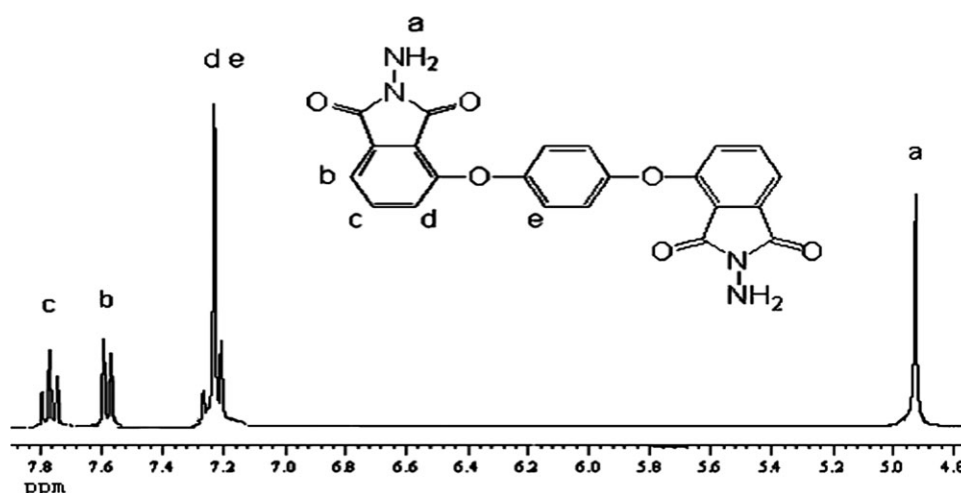
Scheme 1 Synthesis of BOAPIB.

tetracarboxylicacid dianhydride (3,3′-BTDA),[14] and 2,2′,3,3′-oxy(diphthalic anhydride) (3,3′-ODPA)[15] were synthesized in our laboratory. 3,3′,4,4′-benzophenonetetracarboxylicacid dianhydride (4,4′-BTDA), Hydroquinone and Hydrazine monohydrate (80)% were purchased from Aldrich Chemical. Bis [4-(3,4-dicarboxyphenoxy) phenyl]propane dianhydride (BPADA) and 3,3′,4,4′-oxy (diphthalic anhydride) (4,4′-ODPA) were purchased from Shanghai Research Institute of Synthetic Resins. All other reagents used in this work were purchased from Beijing Chemical Reagent Plant. 4,4′-BPDA, 4,4′-BTDA, 4,4′-ODPA, and 3,3′-BPDA, 3,3′-BTDA, 3,3′-ODPA were purified by sublimation under vacuum. BPADA was purified by recrystallizing in toluene. N,N′-Dimethylacetamide (DMAc) was dried over phosphorus pentoxide, distilled under reduced pressure, and then stored over 4 Å molecular sieves. p-Chlorophenol was used after distillation under reduced pressure. Sulfolane was distilled over KOH under reduced pressure. N-Methylpyrrolidinone (NMP) was stirred over phosphorus pentoxide overnight at room temperature, and then vacuum-distilled. 3-Chloro-N-phenylphthalimide was prepared from 3-chlorophthalic anhydride and aniline, and recrystallized in ethanol. All other reagents were of analytical grade and used as received unless otherwise stated.

Measurements

FTIR spectra were obtained with a Bio-Rad Digilab-Division FTS-80 spectrometer. Elemental analyses were performed on an Elemental Analyzer MOD-1106 (Italyd). ^{1}H NMR spectra were recorded on a Varian Unity spectrometer at 300 MHz with

Figure 1 ^{1}H NMR spectrum of BOAPIB in DMSO-d_6.
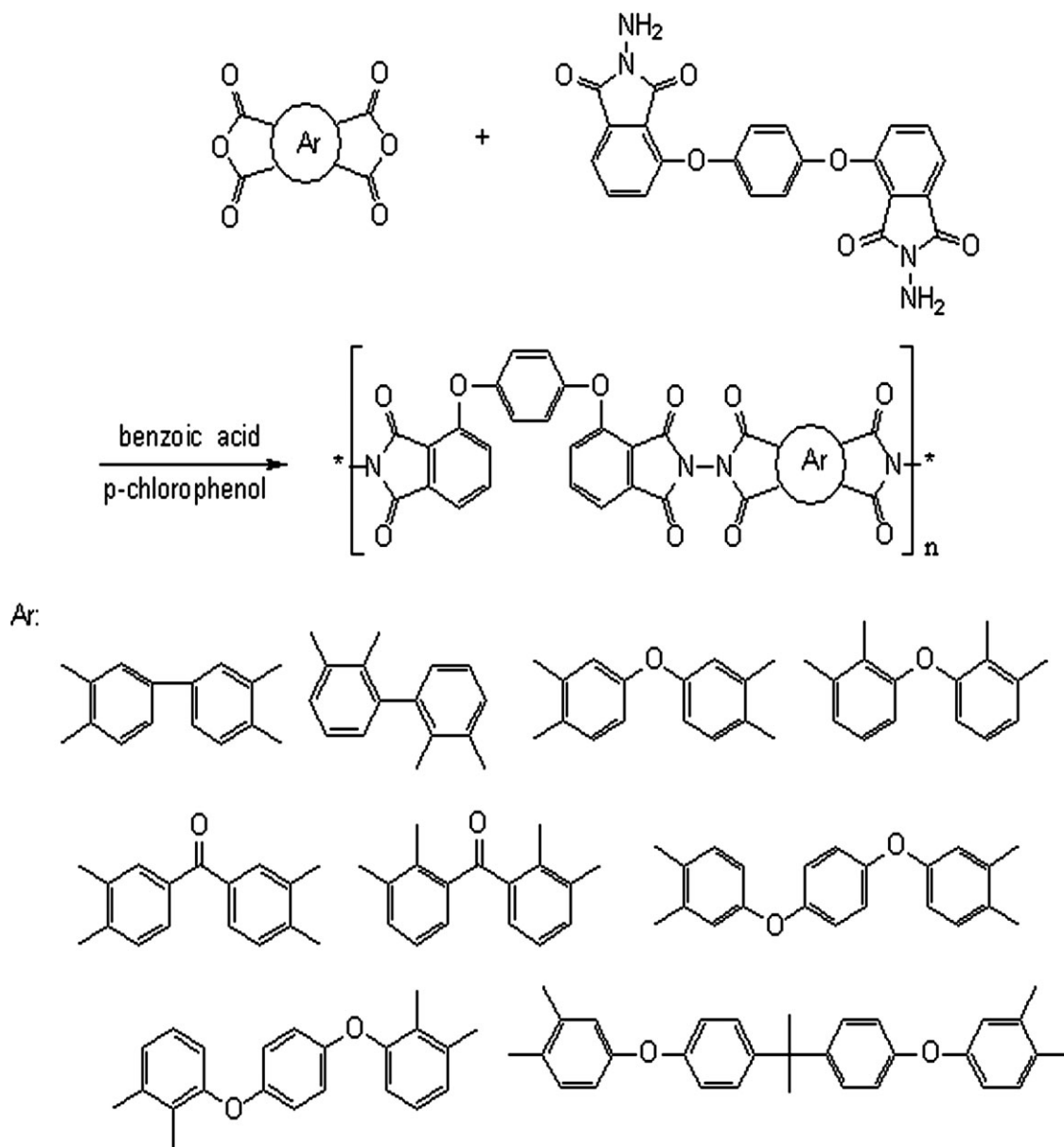
Scheme 2 Synthesis of polyimides.

tetramethylsilane as an internal standard. Melting points were determined on a RY-1 (Beijing Taike Apparatus Limited Corp.) melting point apparatus, and were uncorrected. Inherent viscosities were determined at 30°C with an Ubbelodhe viscometer and the concentration was 0.5 g/dL in DMAc or *m*-cresol. DMTA thermograms were obtained from a dynamic mechanical thermal analyzer (Rheometric Scientific, USA) in a tension mode at a frequency of 1 Hz and a heating rate of 5°C/min from room temperature to 400°C. TGA analysis was carried out at a heating rate of 10°C/min in air and nitrogen with a Perkin-Elmer TGA-2 thermogravimetric analyzer. The tensile measurements were carried out on a tensometer; Instron Model 1122 at room temperature. The differential scanning calorimetry (DSC)

experiments were carried out on a Perkin–Elmer DSC-7 system at a heating rate of 10°C/min under nitrogen atmosphere. The wide-angle X-ray diffraction (WAXD) measurements were undertaken on a Philos X-ray diffractometer with Cu-K radiation (40 kV, 30 mA) from 5–40° with a scanning rate of 2°/min.

MONOMER SYNTHESIS

The synthesis procedure is showed in Scheme 1.

1, 4-bis [3-oxy-(*N*-phenylphthalimide)] benzene

32.21 g (0.125 mol) of 3-chloro-*N*-phenylphthalimide, 6.87 g (0.0625 mol) of hydroquinone, 17.25 g

TABLE I
The Yields, Inherent Viscosities, and Elemental Analysis Data of Polyimides

| | | | Elemental analysis data | | | | | |
| | | | C | | H | | N | |
Polymer codes	η_{inh} (dL/g)[a]	Yield (%)	Calcd	Found	Calcd	Found	Calcd	Found
4,4′-BPDA	0.61	95	66.28	66.42	2.34	2.25	8.14	8.02
3,3′-BPDA	0.32	95	66.28	66.30	2.34	2.32	8.14	8.15
4,4′-ODPA	0.46	96	64.78	64.89	2.29	2.41	7.95	7.58
3,3′-ODPA	0.26	95	64.78	64.83	2.29	2.35	7.95	7.62
4,4′-BTDA	0.57[b]	97	65.37	65.20	2.25	2.50	7.82	7.69
3,3′-BTDA	0.17	92	65.37	65.17	2.25	2.44	7.82	7.71
4,4′-HQDPA	0.59	98	66.34	66.51	2.53	2.50	7.03	6.98
3,3′-HQDPA	0.47	97	66.34	66.58	2.53	2.52	7.03	6.95
BPADA	0.45	96	69.58	69.86	3.31	3.56	6.12	6.05

The polymer codes in the tables and figures were all replaced by the abbreviation of dianhydrides for the same diamine.

[a] Inherent viscosity measured with 0.5 g/dL in DMAc at 30°C.
[b] Inherent viscosity measured with 0.5 g/dL in *m*-cresol at 30°C.

(0.125 mol) of anhydrous K_2CO_3, and 150 mL of DMAc were placed in a 500-mL of three-necked, round-bottomed flask with a magnetic stirrer. The mixture was heated at 120°C for 15 h under nitrogen atmosphere. After cooled to room temperature, the reaction mixture was poured into 1000 mL of ethanol, and then stirred for 1 h. The precipitate was filtered and washed with 250 mL of water for three times. The product was obtained as white crystals after purified by sublimation under vacuum (24.51 g, yield 71%), mp 312–313°C (lit.[16] 311–312°C).

IR: 1770 (asym C=O stretching), 1721 (sym C=O stretching), 1390 (asym C—N stretching) 1370 (sym C—N stretching), and 1254 (C—O—C stretching) cm^{-1}. ^{1}H NMR (300 MHz DMSO): 7.77–7.70 (t, 2H) 7.62–7.57 (d, 2H) 7.47–7.39 (t, 4H) 7.38–7.35 (d, 4H) 7.34–7.31 (d, 2H) 7.21–7.15 (m, 6H). Elem. Anal. Calcd for $C_{34}H_{20}N_2O_6$: C, 73.91%; H, 3.65%; N, 17.37%. Found: C, 73.85%; H, 3.69%; N, 17.38%.

1, 4-bis [3-oxy-(*N*-aminophthalimide)] benzene (BOAPIB)

The reaction path is the second step in the Scheme 1. 22.10 g (0.04 mol) of 1, 4-bis [3-oxy-(*N*-phenyl-phthalimide)] benzene, 10 g (0.08 mol) of hydrazine hydrate (80%), and 200 mL of DMAc were placed in a 500-mL of three-necked, round-bottom flask with a magnetic stirrer. The mixture was heated to 100°C while stirring for 4 h. After cooled to room temperature, the yellow precipitate was collected by filtration. It was washed with 200 mL of ethanol and then with aqueous ammonium (150 mL, 0.25 mol/L) for three times, and dried in air. 1,4-bis [3-oxy-(*N*-aminophthalimide)] benzene was further purified by

recrystallizing in DMAc (10.62 g, total yield 62%), mp 314–316°C.

IR (KBr): 3360 (asym N—H stretching), 3333 (sym N—H stretching), 1775 (asym C=O stretching), 1728 (sym C=O stretching), 1407 (C—N stretching), 1098 (N—N stretching), 739 (C=O bending) cm^{-1}. ^{1}H NMR (300 MHz, DMSO) (Fig. 1): ä (ppm) 7.81–7.72 (t, 2H), 7.61–7.56 (d, 2H), 7.29–7.19 (d, d, 2H, 4H), 4.92 (s, 4H). Elem. Anal. Calcd for $C_{22}H_{14}N_4O_6$: C, 61.40%; H, 3.28%; N, 13.02%. Found: C, 61.35%; H, 3.29%; N, 13.04%.

POLYMER SYNTHESIS

In this work, all polyimides were prepared via a conventional one-step procedure in *p*-chlorophenol. A representative polymerization procedure is presented as follows: 1,4-bis [3-oxy-(*N*-aminophthali-mide)] benzene (0.4304 g, 0.001 mmol), BPADA (0.5201 g, 0.001 mmol), *p*-chlorophenol (2.5 g), and a catalytic amount benzoic acid were placed into a 50-mL of three-necked flask equipped with a mechanical stirrer. The mixture was heated at 100°C for 4 h and then at 190°C for 24 h under nitrogen atmosphere. The water formed during imidization was removed with a slow stream of nitrogen passing through the solvent. After cooled to 50°C, the viscous mixture was poured slowly into 150 mL of ethanol to obtain fiber-like precipitate and then filtrated. The precipitate was extracted with ethanol in a Soxhlet extractor for 24 h, and then dried at 200°C for 4 h under vacuum to afford the polyimide with the yield of 96%. Subsequently, respective films were cast from polymer NMP or polymer (only for 4,4′-BTDA/BOAPIB)-sulflane solutions, on a clean
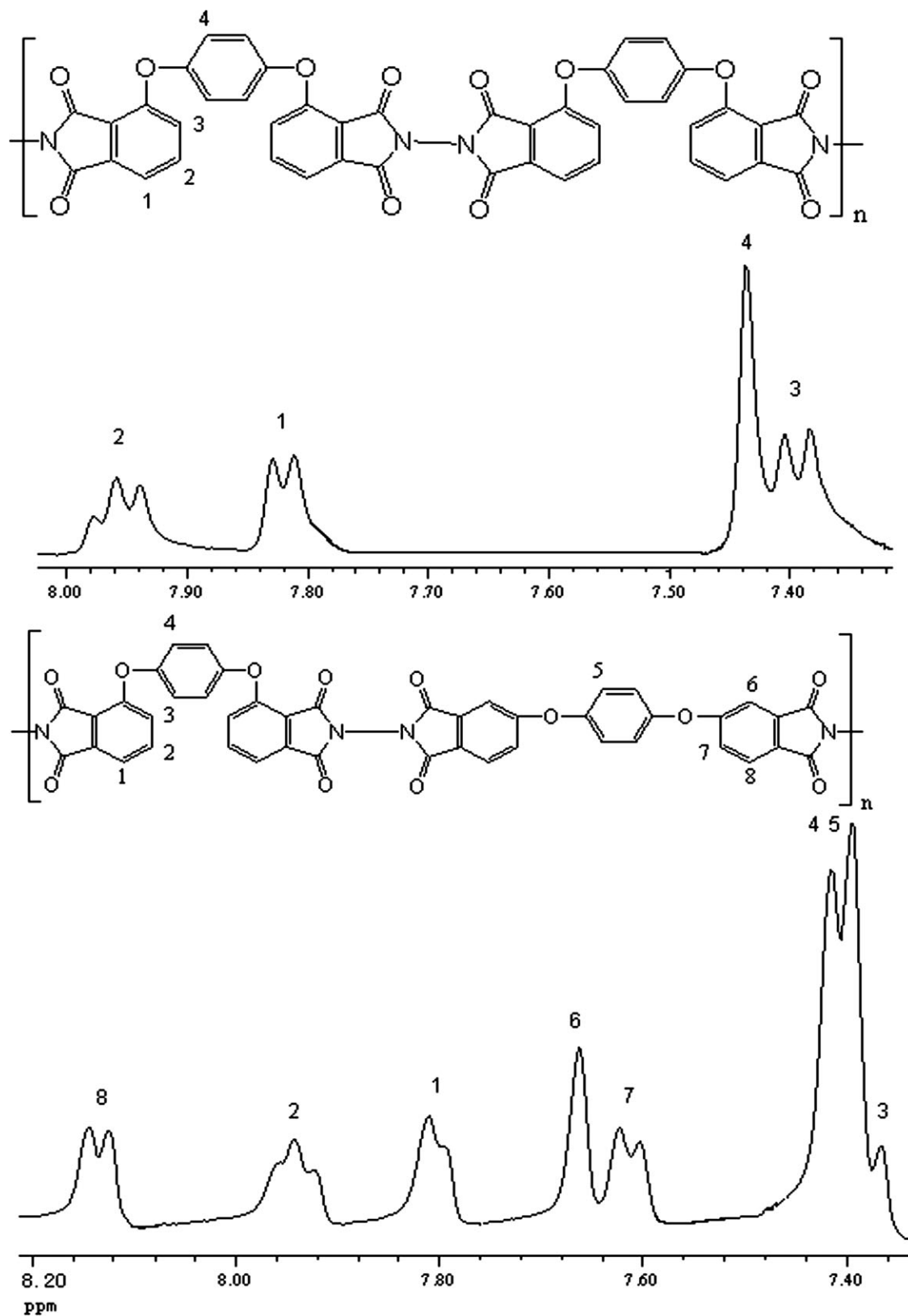
Figure 2 ^{1}H NMR spectrums of the polyimides derived from 4,4′-HQDPA and 3,3′-HQDPA in DMSO-d_6.
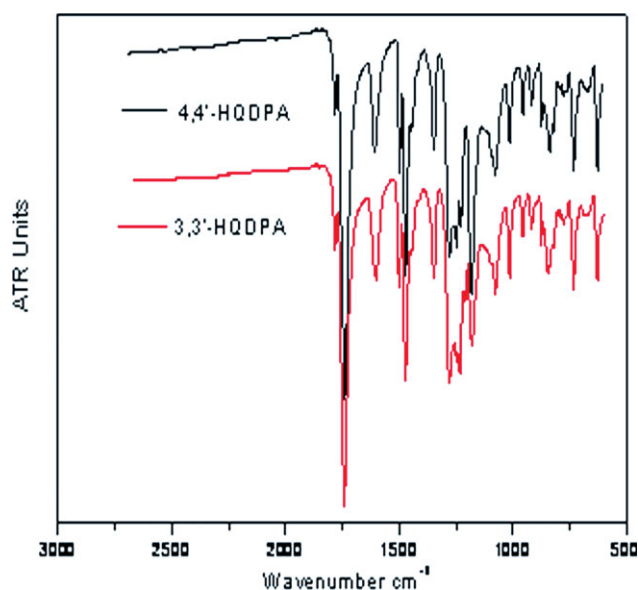
Figure 3 FTIR spectrums of the PI films derived from 4,4′-HQDPA and 3,3′-HQDPA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

dry glass plate, and then dried at 80°C (8 h), 150°C (4 h), and 260°C (4 h) under vacuum.

RESULTS AND DISCUSSION

Synthesis of monomer

N-aminophthalimide and phthalhydrazide were obtained via reaction between hydrazine and phthalic anhydride or its derivatives. The ratios of *N*-aminophthalimide to phthalhydrazide depend greatly on the intrinsic properties and positions of the substituents in phenyl ring. Displacement of hydrogen atom in 3- or 3,6-position by chlorine atom or amino groups leads to high yield of *N*-aminophthalimide. Dine-Hart reported[17] that the *N*,*N*′-diaminopyromellitimide was not stable enough to prepare high-molecular-weight polyimide. In our

case, 3,3′-bis (*N*-aminophthalimide) from 3,3′-bis (*N*-phenylphthalimide) and hydrazine could be obtained in good yield. This compound was stable during purification and polymerization thus, making it possible to get the five-member-ring, hydrazine-based polyimides.

As shown in Scheme 1, 1,4-bis [3-oxy-(*N*-aminophthalimide)] benzene was prepared from 1,4-bis [3-oxy-(*N*-phenylphthalimide)] benzene and hydrazine in DMAc. The peaks assigned for the aniline segments in ^{1}H NMR spectrum disappeared, and a new peak was observed at 4.92 ppm (assigned for the protons of the amino group). Furthermore, new bands in FTIR spectrum appeared around 3360 and 1098 cm^{-1}, which were the characteristic bands for N—H and N—N bonds. Combined with the elemental analysis, the structure of 1,4-bis [3-oxy-(*N*-aminophthalimide)] benzene could be confirmed. The by-product, six-member-ring bis (phthalhydrazide), was removed by washing with aqueous ammonium (0.25 mol/L). In spite of the lack of steric hindrance in 1,4-bis [3-oxy-(*N*-phenylphthalimide)] benzene, the yield of 1,4-bis [3-oxy-(*N*-aminophthalimide)] benzene was moderate. The by-product phthalhydrazide was collected by acidifying the filtrated original reaction solvent with hydrochloric acid. The ratio of the main-product to the by-product was about 3 : 1.

Synthesis of polymer

As illustrated in Scheme 2, a series of polyimides were synthesized via a conventional one-step procedure in *p*-chlorophenol.[2,11] The polymerization was carried out at 100°C for 4 h, and then heated to 190°C and maintained for 24 h under nitrogen atmosphere. During the synthesis of the polyimides from 4,4′-BTDA or 4,4′-ODPA, the precipitates formed at 100°C, and then disappeared above 120°C. The reason for this phenomenon was related to the solubility of those polymers varying with temperature. The inherent viscosities of the resulted

TABLE II
Solubility of the Polyimides

Polymer codes	CHCl$_3$	TCE^a	THF	DMAc	DMF	DMSO	NMP	*m*-cresol
4,4′-BPDA	−	+	−	+ +	+ +	+ +	+ +	+ +
3,3′-BPDA	−	−	−	+ +	+	+ +	+ +	+ +
4,4′-ODPA	−	+ +	−	+ +	+ +	+ +	+ +	+ +
3,3′-ODPA	−	+ +	−	+ +	+ +	+ +	+ +	+ +
4,4′-BTDA	−	+ −	−	b	b	+ +	b	+
3,3′-BTDA	−	+ +	−	+ +	+ +	+ +	+ +	+ +
4,4′-HQDPA	+ −	+ +	−	+ +	+ +	+	+ +	+ +
3,3′-HQDPA	+ −	+	−	+	+	+	+	+
BPADA	+ +	+ +	+ −	+ +	+ +	+	+ +	+ +

++, soluble at room temperature; +, soluble on heating; +−, partially soluble on heating; −, insoluble on heating.
^{a} TCE, 1,1,2,2-tetrachlotoethane.
^{b} Gelation.

TABLE III
Thermal and Mechanical Properties of the Polyimides

Polymer codes	T_g (°C)		$T_{5\%}$ (°C)[a]		Tensile strength (MPa)	Modulus (GPa)	Elongation (%)
	DMTA[b]	DSC[c]	Air	N_2			
4,4′-BPDA	360	320	460	510	92	1.64	9.1
3,3′-BPDA[d]		345	500	510			
4,4′-ODPA	330	315	470	500	85	1.33	8.3
3,3′-ODPA[d]		290	460	485			
4,4′-BTDA	330	315	440	500	75	1.30	9.8
3,3′-BTDA[d]		290	390	400			
4,4′-HQDPA	300	290	455	500	103	1.33	13.1
3,3′-HQDPA	270	270	455	500	84	1.13	11.0
BPADA	265	270	450	480	91	1.41	11.8

[a] 5% weight loss in air obtained from TGA at a heating rate of 10°C/min in air.
[b] Obtained from DMTA at a heating rate of 3°C/min at 1 Hz.
[c] Obtained from DSC at a heating rate of 10°C/min in air.
[d] Films were both brittle.

polyimides were in the range of 0.17–0.61 dL/g in DMAc or m-cresol at 30°C, depending on the dianhydrides used (Table I).

Representative ^{1}H NMR and FTIR spectrums of the polyimides from 3,3′-HQPDA/BOAPIB and 4,4′-HQPDA/BOAPIB were given in Figures 2 and 3. All the polymers showed characteristic absorption bands near 1782 (asym C=O str), 1740 (sym C=O str), 1350 (C—N str), 1100 (N—N str), and 730 cm^{-1} (imide ring deformation), but not the characteristic absorptions of polyamide, which indicated the completion of imidization. The elemental analysis data agreed with our proposed structures in general (Table I).

Polymers characterization

As listed in Table II, all the polyimides showed good solubility in polar aprotic solvents and phenols at room temperature. The enhanced solubility was attributed to the introduction of ether linkage and the bent chain structure. The solubility of polyimides from 4,4′-aromatic dianhydrides was better than those were made from 3,3′-aromatic dianhydrides, especially for the polymers based on HQDPAs. This result did not agree with the previous report about the isomer effect on the polyimides.[12–15,18–24] Generally speaking, polyimides from 3,3′-dianhydrides exhibited higher solubility in organic solvents than those were made from 4,4′-dianhydrides owing to the more bent structure that hinders packing of the
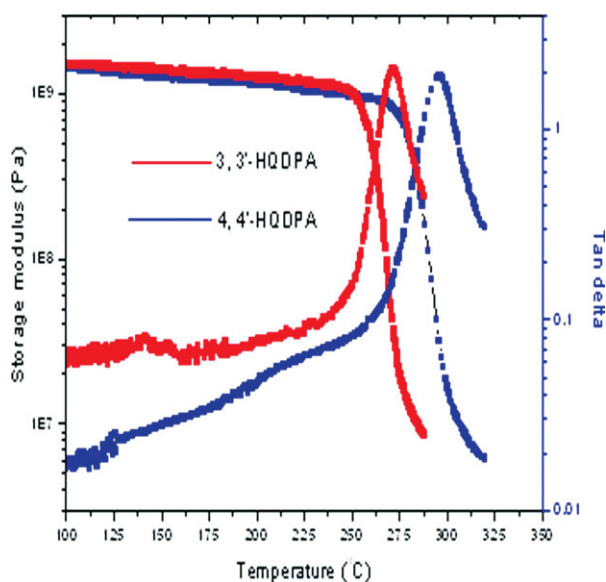

Figure 4 DMTA curves of polyimides derived from 4,4′-HQDPA and 3,3′-HQDPA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
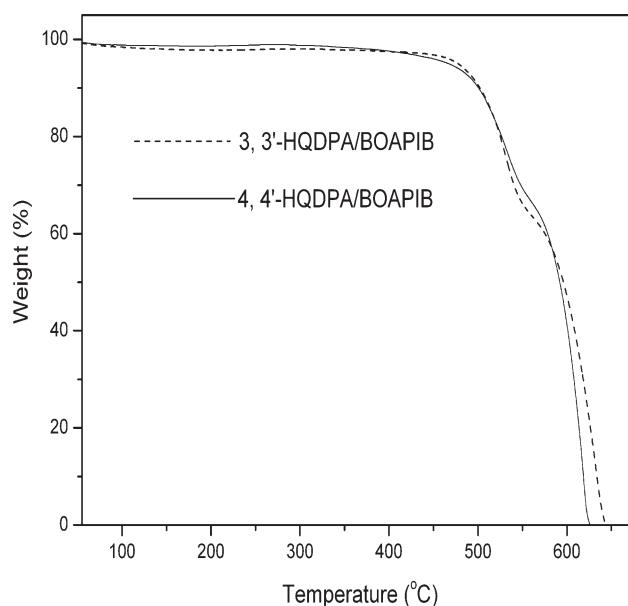

Figure 5 TGA curves of polyimides derived from 4,4′-HQDPA and 3,3′-HQDPA.

TABLE IV
Hydrolytic Stability of Hydrazine-Contained Polyimides

Polymer codes	10% Sodium hydroxide solution (30°C)	10% Hydrogen chloride solution (boiling)	Water (boiling for a week)
4,4'-BPDA	Brittle after 2 h	Brittle after 48 h	Flexible
4,4'-ODPA	Brittle after 3 h	Brittle after 56 h	Flexible
4,4'-BTDA	Brittle after 2 h	Brittle after 26 h	Flexible
4,4'-HQDPA	Viscoelasticity after 30 h	Brittle after 130 h	Flexible
3,3'-HQDPA	Brittle after 12 h	Brittle after 140 h	Flexible
BPADA	Brittle after 110 h	Brittle after 148 h	Flexible

macromolecular chains. But, the reason for this result still remains unclear.

The thermal and mechanical properties of the polyimide films were summarized in Table III. The films had tensile strength of 75–103 MPa, elongation at break of 5–13.1%, and tensile modulus of 1.13–2.77 GPa.

T_gs of these polyimides were determined by both DMTA and DSC, and the results were listed in Table III. The tan delta peak values were regarded as the T_gs of these polyimides. The representative DMTA thermograms of 4,4'-HQDPA/BOAPIB and 3,3'-HQDPA/BOAPIB were given in Figure 4. The T_g values of polymers from 4,4'-dianhydrides were higher than those were made from 3,3'-dianhydrides, except for the polyimides synthesized from isomeric BPDAs. This phenomenon agreed with our previously reported polyimides derived from and 3,3'-BAPI,[11] but did not agree with most studies conducted on isomeric polyimides.[12–15,18–24] It can be assumed that the molecular structure interaction between chains and molecular weight have contribution to the observed thermal stability (i.e., T_gs) of the polymer. Usually, the T_gs of polyimides from 3,3'-dianhydrides are higher than those derived from 4,4'-dianhydrides, owing to the higher rotation barrier of the bond from 3-carbon at phthalimide ring than that from 4-carbon. On the other hand, the interaction between molecular chains also plays important role in the contribution to T_gs. Polyimide based on 3, 3'-dianhydride has more bent chain than that from 4,4'-dianhydride, so the packing between the molecular chains of the latter may be tighter than that of the former. The balance of two factors determined the T_g values of the polyimides. Furthermore, the lower molecular weight of polyimides based on 3,3'-dianhydrides, especially for polyimides from isomeric BTDA and ODPA, may also influence the T_gs. In addition, we assumed the result, which is contrary with previous report on isomeric polyimides,[25] should be a complement to the isomeric effect of polyimides based on isomeric dianhydrides. The TGA thermograms showed that the temperatures of 5% weight loss ($T_{5\%}$) of the polyimides

ranged from 390 to 500°C in air (Fig. 5), and from 400 to 510°C in nitrogen. The polymer synthesized from 3,3'-BTDA showed relatively lower thermal stability to oxidation than others.

The hydrolytic stability of hydrazine-based polyimides was measured under acid, basic, and neutral conditions and the results were summarized in Table IV. In general, the order of hydrolytic stability was BTDA < BPDA < ODPA < 3,3'-HQDPA < 4,4'-HQDPA <BPADA. Because the hydrolysis of imide groups was mainly resulted from the nucleophilic attack of the water molecule onto the carboxyl carbon atoms, the dianhydrides with higher electron density in carboxyl carbon atoms should produce polyimides with higher hydrolytic stability. Therefore, polyimides from the dianhydrides with electron-withdrawing groups (such as BTDA and BPDA) showed poorer stability when compared with polyimides from the dianhydrides with electron-donating groups (such as ODPA, HQDPA, and BPADA).
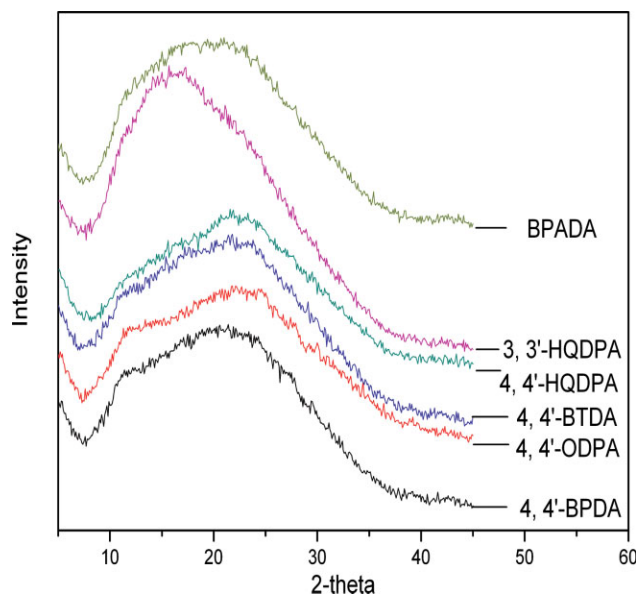

Figure 6 WAXD of polyimides. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The crystallinity of the polyimides was examined by wide-angle X-ray diffraction (refer to Fig. 6), and the results indicated that all the polyimides were amorphous in nature.

CONCLUSIONS

A novel diamine, five-member ring hydrazine-containing 1,4-bis [3-oxy-(*N*-amino phthalimide)] benzene, was synthesized from 1,4-bis [3-oxy-(*N*-phenylphthalimide)] benzene and hydrazine. A series of polyimides were prepared from this diamine and various aromatic dianhydrides via a conventional one-step method in *p*-chlorophenol. These polyimides have good solubility in polar aprotic solvents and phenols at room temperature, which is attributed to the introduction of flexible aromatic ether, and rigid but noncoplanar *N,N*-bisphthalimide segments. Tough and flexible films could be cast from the polymer solutions, except for those from 3,3′-BPDA, 3,3′-BTDA, and 3,3′-ODPA. The T_gs of the polyimides were in the range of 265–360°C. The T_g values of the polymers based on 4,4′-dianhydrides were higher than those based on 3,3′-dianhydrides, except for the polymers from isomeric BPDA. These polyimides showed good thermooxidative stability, and their $T_{5\%}$ ranged from 390 to 500°C in air and from 400 to 510°C in nitrogen.

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