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Polymer 48 (2007) 2250–2256
polymer
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Synthesis and properties of novel soluble polyimides having a spirobisindane-linked dianhydride unit

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Received 19 November 2006; received in revised form 7 February 2007; accepted 13 February 2007
Available online 28 February 2007

Abstract

A new synthetic procedure was elaborated allowing the preparation of semiaromatic dianhydride. *N*-Methyl protected 4-chlorophthalic anhydride was nitrated with HNO_3 to produce *N*-methyl-4-chloro-5-nitrophthalimide (**1**). The aromatic nucleophilic substitution reaction between 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethyl-1,1-spirobisindane and **1** afforded spirobisindane-linked bis(*N*-methylphthalimide) (**2**), which was hydrolyzed and subsequently dehydrated to give the corresponding dianhydride (**3**). The latter was polymerized with five different aromatic diamines to afford a series of aromatic polyimides. The properties of polyimides such as inherent viscosity, solubility, UV transparency and thermal stability were investigated to illustrate the contribution of the introduction of spirobisindane groups into the polyimide backbone. The resulting polyimides were readily soluble in polar solvents such as chloroform, THF and *N*-methyl-2-pyrrolidone. The glass-transition temperatures of these polyimides were in the range of 254–292 °C. The tensile strength, elongation at break, and Young's modulus of the polyimide film were 68.8–106.6 MPa, 5.9–9.8%, 1.7–2.0 GPa, respectively. The polymer films were colorless and transparent with the absorption cutoff wavelength at 286–308 nm.

Keywords: Organosoluble polyimide; Thermal properties; Transparency

1. Introduction

Polyimides represent a class of high performance polymers that combine high thermal stability with chemical resistance and excellent electrical and mechanical properties. While the majority of this type of materials is used as high performance engineering materials in application areas such as aerospace, some have found applications as dielectric films, interlayer dielectrics, and membranes [1,2]. For these applications it is desirable to use polyimides that are soluble in spin coating and casting processes. However, most of wholly aromatic polyimides have high melting or softening temperatures (T_s's) and are insoluble in most organic solvents because of the rigidity of the backbone and strong interchain interactions. These properties make them generally intractable or difficult to process, thus limiting their applications. Therefore, various efforts have focused on the design and preparation of processable polyimides while maintaining their excellent properties. Several approaches have been used to achieve this goal, such as the introduction of bulky substituents [3–5], flexible linkages [6–8], and twisted [9–11] or unsymmetrical structures [12–14] into the polymer chain. Copolymerization is another popular synthetic approach to obtain processable and soluble polyimides [15–17]. Recently, introducing the alicyclic structures into polymer backbone and incorporating their pendant bulky groups have been demonstrated to be a unique approach to organosoluble polyimides. For example, Chern et al. reported the synthesis of soluble polyimides containing adamantyl and diadamantyl moieties [18]. Horie et al. investigated the thermal properties, solubility and UV–vis absorption of polyimides synthesized from alicyclic diamines [19].

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doi:10.1016/j.polymer.2007.02.061

Matsumoto et al. have prepared some alicyclic dianhydride from Diels–Alder adducts and applied them to the synthesis of soluble polyimides [20]. Kudo and coworkers reported on the synthesis and properties of novel soluble polyimides having an unsymmetrical spiro tricyclic dianhydride unit [21]. Yang et al. reported on the synthesis and optical properties of polyimides based on 1,8-dimethylbicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride [22]. From the results of these works, it was known that the alicyclic unit in the polyimide backbone greatly reduces both inter- and intramolecular charge-transfer (CT) complex formation, thus improves the solubility of polyimide and makes polyimide colorless.

Spirobisindane, such as 5,5′6,6′-tetrahydroxy-3,3,3′,3′-tetramethyl-1,1-spirobisindane, which is a commercially inexpensive catechol, has been used as a rigid linker for the preparation of nanoporous network polymers by linking planar aromatic macrocycles such as phthalocyanine [23], or porphyrins [24]. The spirocentre of this linking group provides nonlinear shapes, and the fused-ring provides the required rigidity which ensures an open nanoporous structure by preventing self-association of the planar macrocycles. Most recently, Budd and coworkers reported on the syntheses of soluble non-network polymers by polycondensations of tetraphenols with activated tetrafluoro or tetrachloro aromatics [25]. This class of polymers has attracted interest as outstanding membrane materials because of the relatively rigid repeat units combined with their noncoplanar structure generating large free volume [26]. Due to such structural feature of this spirobisindane, synthesizing and characterizing polyimides, as well as incorporating spirobisindane moieties into the backbone of the polyimides, are worth proceeding. In this article, we describe the synthesis of spirobisindane-linked dianhydride and the corresponding polyimides. It was expected that the introduction of spirobisindane structure as an anhydride unit could improve the solubility of the polyimides with retention of excellent thermal stability. A spirocentre-induced noncoplanar structure is certainly responsible for lowering interchain interactions, thus improving the solubility of polyimides. Physical, thermal, and optical properties of these polyimides were also investigated.

2. Experimental

2.1. Materials

5,5′,6,6′-Tetrahydroxy-3,3,3′,3′-tetramethyl-1,1-spirobisindane, 4-chlorophthalic anhydride (99.2%), 4,4′-oxydianiline (ODA), 3,3′-dimethyl-4,4′-methylenedianiline (DMMDA), 2,3,5,6-tetramethylbenzene-1,4-diamine, 4,4′-methylenedianiline (MDA), and 1,4-bis(4-aminophenoxy)benzene were used as received from Aldrich. *m*-Cresol was distilled under reduced pressure and stored under nitrogen in the dark. *N*-Methyl-4-chlorophthalimide [27] and 1,4-bis(4-aminophenoxy)benzene (TPEQ) [28] were synthesized according to the literature. Other chemicals were used as received.

2.2. Measurement

The FTIR spectra were recorded on a Bio-Rad Digilab Division FTS-80 spectrometer. ^{1}H NMR spectra were measured at 300 MHz on an AV300 spectrometer with tetramethylsilane (TMS) as internal standard. Elemental analyses were performed on an Elemental Analyses MOD-1106. Thermogravimetric analysis (TGA) was carried out with a Perkin–Elmer TGA-2 thermogravimetric analyzer at a heating rate of 10 °C/min under both nitrogen and air atmospheres at flow rates of 30–40 mL/min. Differential scanning calorimetry (DSC) was performed on a Perkin–Elmer DSC-7 system at a heating rate of 20 °C/min under nitrogen. Tensile measurement was performed with a mechanical tester Instron-1211 instrument at a speed of 10 mm/min at 25 °C. UV–vis spectra were measured with a Shimadzu UV-2550 spectrometer in the transmittance mode. Inherent viscosities were determined on 0.5 g/dL concentration of polymer in *m*-cresol using an Ubbelohde capillary viscometer at 30.0 ± 0.1 °C. Molecular weight measurements were determined by gel permeation chromatography (GPC), the GPC measurements were conducted at 35 °C with a Waters 410 GPC instrument equipped with two Waters Styragel columns (HT6E and HT3) and a differential refractometer detector. Chloroform was used as eluent at a flow rate of 1.0 mL/min. The molecular weights were calibrated against polystyrene standards. X-ray diffractometric analysis was carried out on a Philips apparatus with a Cu Kα ($\lambda = 0.154$ nm) source. The wide-angle X-ray diffraction (WAXD) was conducted on a Philips apparatus with a Cu Kα ($\lambda = 0.154$ nm) source, operated at 40 kV and 200 mA at 293 K.

2.3. Monomer syntheses

2.3.1. N-Methyl-4-chloro-5-nitrophthalimide (**1**)

To a 100 mL three-neck flask, equipped with a mechanical stirrer, thermometer, and a condenser, was charged 19.6 g (0.10 mol) of *N*-methyl-4-chlorophthalimide and 40 mL of 98% H_2SO_4. The mixture was heated to 80 °C until the solids were dissolved completely. Fuming HNO_3 (12 mL) 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 90 °C for 5 h. Then, the reaction mixture was cooled and carefully poured into 200 mL ice/water mixture. The precipitation was filtered and washed thoroughly with water. The white product was obtained by recrystallization from xylene. Yield: 15.6 g (65%). M.p: 194–195 °C. FTIR (KBr pellet, cm^{-1}): 3039 (aromatic C–H), 2950 (NCH_3, C–H), 1704 (C=O stretching), 1545 (asymmetry NO_2 stretching), 1363 (symmetry NO_2 stretching), 1031 (Ar–Cl). ^{1}H NMR (DMSO-d_6, δ ppm): 3.07 (s, 3H, NCH_3), 8.33 (s, 1H, Ar–H), 8.55 (s, 1H, Ar–H). Anal. Calcd for $C_9H_5ClN_2O_4$ (240.60): C, 44.93%; H, 2.09%; Cl, 14.74; N, 11.64%. Found: C, 44.82%; H, 2.06%; Cl, 14.76%; N, 11.68%.

2.3.2. The bis(phthalimide) compound (**2**)

In a 100 mL round-bottom flask equipped with a Dean–Stark trap and a condenser, 3.41 g (0.01 mol) of 5,5′,6,6′-

tetrahydroxy-3,3,3′,3′-tetramethyl-1,1-spirobisindane and 3.32 g (0.048 mol) of anhydrous potassium carbonate were charged with 35 mL of *N*,*N*-dimethylacetamide (DMAc) and 15 mL of toluene. The nitrogen was bubbled into the mixture at room temperature for 10 min. The mixture was heated with stirring at 140 °C for 5 h during which time the water was azeotropically removed. After most toluene had been removed, the mixture was cooled and then 5.3 g (0.022 mol) of *N*-methyl-4-chloro-5-nitrophthalimide (**1**) was added. The reaction was carried out at 120 °C for 5 h and then the reaction mixture was precipitated into 400 mL of cold water. The precipitated yellow solid was filtered out and washed thoroughly with water. The crude product was purified by recrystallization from chloroform/methanol to give yellow product (5.4 g, 83% yield). M.p.: >300 °C. FTIR (KBr pellet, cm^{-1}): 3017 (aromatic C–H), 2953 (aliphatic C–H), 1771 (asymmetry C=O stretching), 1717 (symmetry C=O stretching), 1380 (C–N stretching), 1320 (asymmetry C–O stretching), 985 (symmetry C–O stretching), 755 (imide ring deformation). ^1H NMR (DMSO-d_6, δ ppm): 1.27 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 2.12–2.15 (d, 1H, CH_2), 2.27–2.30 (d, 1H, CH_2), 2.98 (s, 3H, NCH_3), 6.36 (s, 1H, Ar–H), 6.95 (s, 1H, Ar–H), 7.31 (s, 1H, Ar–H), 7.40 (s, 1H, Ar–H). Anal. Calcd for $C_{39}H_{30}N_2O_8$ (654.66): C, 71.55%; H, 4.62%; N, 4.28%. Found: C, 71.58%; H, 4.48%; N, 4.22%.

2.3.3. *The dianhydride compound (**3**)*

To a solution of **2** (6.55 g, 0.01 mol) in 60 mL of NMP was added slowly NaOH aqueous solution (3.2 g NaOH in 20% solution). The solution was refluxed for 48 h. After cooling to room temperature, the solution was adjusted to pH = 1.0 with 6 N HCl. The white precipitate was collected by filtration and dried in vacuum at 100 °C. The resulting tetracarboxylic acid was dissolved in 20 mL of acetic anhydride and the solution was refluxed for 6 h. The yellow solids were filtered and washed with petroleum ether after the solution was cooled to room temperature, then dried at 100 °C under vacuum to give 5.0 g of yellow product in the yield of 80%. M.p.: >300 °C. FTIR (KBr pellet, cm^{-1}): 3053 (aromatic C–H), 2953 (aliphatic C–H), 1846 (anhydride asymmetry C=O stretching), 1774 (anhydride symmetry C=O stretching), 1325 (C–O stretching). ^1H NMR (DMSO-d_6, δ ppm): 1.28 (s, 3H, CH_3), 1.36 (s, 6H, CH_3), 2.13–2.16 (d, 1H, CH_2), 2.28–2.31 (d, 1H, CH_2), 6.40 (s, 1H, Ar–H), 7.00 (s, 1H, Ar–H), 7.56 (s, 1H, Ar–H), 7.65 (s, 1H, Ar–H), Anal. Calcd for $C_{37}H_{24}O_{10}$ (628.58): C, 70.70%; H, 3.85%. Found: C, 70.96%; H, 3.78%.

2.4. *Polymer syntheses*

Polyimide **4a** is given as an example. Diamine **a** (0.1983 g, 1.0 mmol) and dianhydride **3** (0.6286 g, 1.0 mmol) were first dissolved in 10 mL of *m*-cresol in a 100 mL three-neck round-bottom flask. The flask was purged with nitrogen and then the reaction mixture was stirred at room temperature for 30 min until complete dissolution of solids. After adding a few drops of isoquinoline, the mixture was heated with stirring at 190 °C for 24 h. Water formed during the imidization was continuously removed by the steady flow of nitrogen. At the end of the reaction, the mixture was cooled and precipitated into 50 mL of ethanol. The polymer that precipitated was collected by filtration, washed with ethanol for several times and dried in a vacuum oven at 90 °C for 24 h. The yield was 97% (0.77 g).

2.5. *Spectroscopic data of the polymers*

2.5.1. *Polyimide **4a***

^1H NMR ($CDCl_3$, δ ppm): 7.35–7.32 (8H, m, Ar), 7.29–7.26 (4H, m, Ar), 6.72 (2H, s, Ar), 6.38 (2H, s, Ar), 4.06 (2H, s, CH_2), 2.35–2.31 (2H, d, CH_2), 2.20–2.16 (2H, d, CH_2), 1.38 (6H, s, CH_3), 1.32 (6H, s, CH_3). FTIR (KBr pellet, cm^{-1}): 1778 (asymmetry C=O, str), 1726 (symmetry C=O, str), 1360 (C–N, str), 744 (imide ring deformation). Anal. Calcd for $C_{50}H_{34}N_2O_8$ (790.83): C, 75.94; N, 3.54; H, 4.33. Found: C, 76.02; N, 3.62; H, 4.21.

2.5.2. *Polyimide **4b***

This polyimide was synthesized from 4,4′-oxydianiline (ODA) and dianhydride (**3**). The yield was 98%. ^1H NMR ($CDCl_3$, δ ppm): 7.39–7.37 (8H, m, Ar), 7.18–7.16 (4H, m, Ar), 6.75 (2H, s, Ar), 6.41 (2H, s, Ar), 2.36–2.32 (2H, d, CH_2), 2.25–2.21 (2H, d, CH_2), 1.40 (6H, s, CH_3), 1.35 (6H, s, CH_3). FTIR (KBr pellet, cm^{-1}): 1778 (asymmetry C=O, str), 1725 (symmetry C=O, str), 1357 (C–N str), 743 (imide ring deformation). Anal. Calcd for $C_{49}H_{32}N_2O_9$ (792.8): C, 74.24; N, 3.53; H, 4.07. Found: C, 73.98; N, 4.03; H, 4.08.

2.5.3. *Polyimide **4c***

This polyimide was synthesized from 3,3′-dimethyl-4,4′-methylenedianiline (DMMDA) and dianhydride (**3**). The yield was 98%. ^1H NMR ($CDCl_3$, δ ppm): 7.39 (2H, s, Ar), 7.31 (2H, s, Ar), 7.23–7.12 (6H, m, Ar), 6.76 (2H, s, Ar), 6.42 (2H, s, Ar), 4.04 (2H, s, CH_2), 2.40–2.36 (2H, d, CH_2), 2.25–2.21 (2H, d, CH_2), 2.20 (6H, s, CH_3), 1.42 (6H, s, CH_3), 1.36 (6H, s, CH_3). FTIR (KBr pellet, cm^{-1}): 1780 (asymmetry C=O, str), 1726 (symmetry C=O, str), 1370 (C–N, str), 747 (imide ring deformation). Anal Calcd for $C_{52}H_{38}N_2O_8$ (818.88): C, 76.27; N, 3.42; H, 4.68. Found: C, 76.05; N, 3.62; H, 4.61.

2.5.4. *Polyimide **4d***

This polyimide was synthesized from 1,4-bis(4-aminophenoxy)benzene and dianhydride (**3**). The yield was 94%. ^1H NMR ($CDCl_3$, δ ppm): 7.36–7.34 (8H, m, Ar), 7.10–7.08 (8H, m, Ar), 6.72 (2H, s, Ar), 6.38 (2H, s, Ar), 2.35–2.31 (2H, d, CH_2), 2.22–2.18 (2H, d, CH_2), 1.38 (6H, s, CH_3), 1.33 (6H, s, CH_3). FTIR (KBr pellet, cm^{-1}): 1778 (asymmetry C=O, str), 1725 (symmetry C=O, str), 1358 (C–N, str), 742 (imide ring deformation). Anal. Calcd for $C_{55}H_{36}N_2O_{10}$ (884.9): C, 74.65; N, 3.17; H, 4.10. Found: C, 74.70; N, 3.15; H, 4.18.

2.5.5. *Polyimide **4e***

This polyimide was synthesized from 2,3,5,6-tetramethylbenzene-1,4-diamine and dianhydride (**3**). The yield was

94%. ^{1}H NMR (CDCl$_3$, δ ppm): 7.41 (2H, s, Ar), 7.33 (2H, s, Ar), 6.78 (2H, s, Ar), 6.44 (2H, s, Ar), 2.40–2.36 (2H, d, CH$_2$), 2.24–2.20 (2H, d, CH$_2$), 2.10 (12H, s, CH$_3$), 1.43 (6H, s, CH$_3$), 1.37 (6H, s, CH$_3$). FTIR (KBr pellet, cm^{-1}): 1780 (asymmetry C=O, str), 1723 (symmetry C=O, str), 1357 (C–N, str), 745 (imide ring deformation). Anal. Calcd for $C_{47}H_{36}N_2O_8$ (756.82): C, 74.59; N, 3.70; H, 4.80. Found: C, 74.64; N, 3.65; H, 4.78.

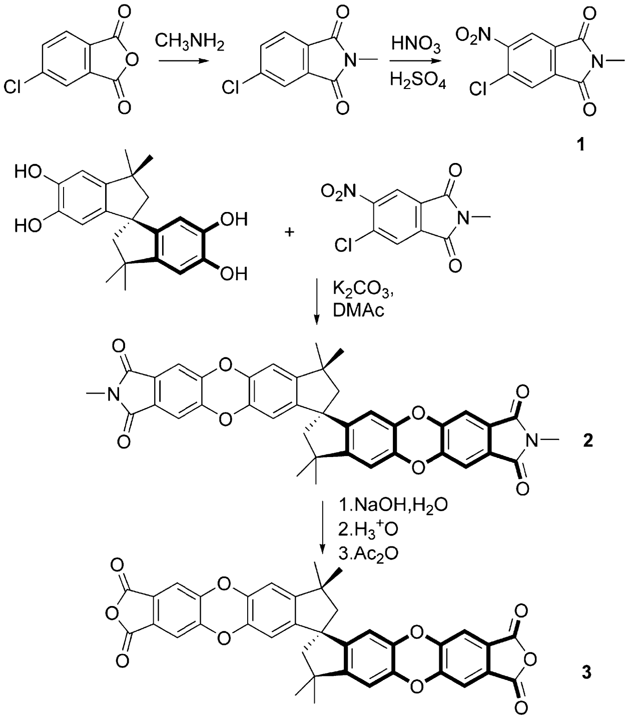
2.6. Preparation of film

A 5–7 wt% solution of polymer in 1,1′,2,2′-tetrachloroethane (TCE) was prepared and filtered through a 0.2 μm syringe filter. The solution was then poured on a leveled clean glass plate. The casting process took about 5 h at 50 °C. The casting film was dried in a vacuum oven at 100 °C and 200 °C for additional 12 h.

3. Results and discussions

3.1. Monomer synthesis

The synthetic procedure for the target dianhydride **3** is shown in Scheme 1. *N*-Methyl-4-chlorophthalimide was dissolved in 98% H_2SO_4 at 80 °C before fuming HNO_3 is dropped in. The nitration reaction was carried out with HNO_3/98% H_2SO_4 at the temperature of 85–90 °C to produce *N*-methyl-4-chloro-5-nitrophthalimide (**1**) in the yield of 65%. No nitration reaction occurred below 80 °C due to lack of reactivity, because the strong electron-withdrawing effect of two carbonyl groups would deactivate the aromatic rings toward electrophilic substitution. Raising the temperature to above 110 °C causes product to hydrolyze to yield 4-chloro-5-nitrophthalic acid. FTIR and ^{1}H NMR confirmed the chemical composition and structure of the product.



Scheme 1. Synthesis of dianhydride monomer containing a rigid spirocyclic linking groups.

Bis(phthalimide) (**2**) was prepared in high yield (85%) using the aromatic nucleophilic substitution reaction between **1** and 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethyl-1,1-spirobisindane. The high reactivity of *N*-methyl-4-chloro-5-nitrophthalimide toward nucleophilic substitution is due to the strong electron-withdrawing effect of two carbonyl groups. The dibenzodioxane forming reaction has to 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 bis(phthalimide) (**2**) with sodium hydroxide and subsequent acidification with hydrochloric acid gave tetra acid, which was cyclodehydrated with acetic anhydride to generate a 87% yield of dianhydride (**3**). Elemental analyses, IR, and ^{1}H NMR spectroscopic techniques were used to identify the structures of the intermediate compound **2** and the target dianhydride monomer **3**. The ^{1}H NMR spectrum of the dianhydride monomer is illustrated in Fig. 1. Assignment of each proton is also given in this figure and this spectrum agrees well with the proposed molecular structure of **3**.

The new anhydride monomer was polymerized with five different diamines in *m*-cresol with a catalytic amount of isoquinoline (Scheme 2). Polyimides are commonly synthesized via low temperature polycondensation of diamines and dianhydrides in aprotic dipolar solvents, e.g., DMAc and NMP. In this study, the polycondensation of the dianhydride monomer **3** and various diamines did not give high molecular weight polyimides under this condition. This is due to the low reactivity of the dianhydride containing two electron-donating oxygen atoms in each anhydride moieties. Therefore, a one-step method at a high temperature using *m*-cresol as the solvent was adopted in this study. All of the polymers **4** were synthesized by the dissolution of dianhydride **3**, an aromatic diamine in *m*-cresol, before isoquinoline was added as an enhancer at room temperature 30 min later. Then, the reaction mixture was heated to 190 °C and kept there for 24 h. Water formed during the imidization was continuously removed with a stream of nitrogen. The polyimide products were

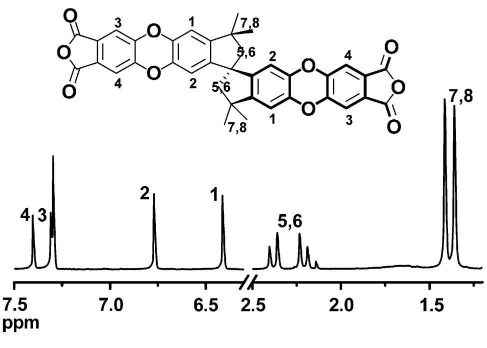
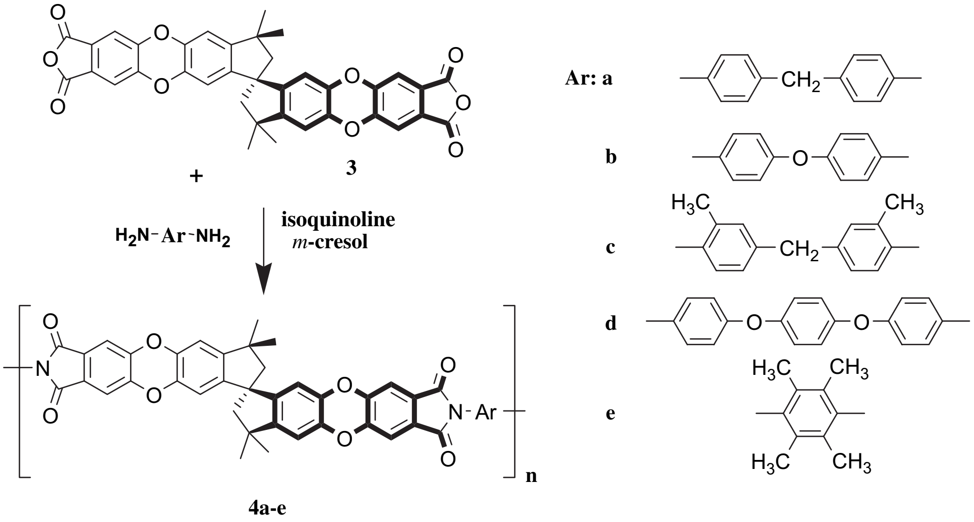


Fig. 1. ^{1}H NMR spectrum of dianhydride (**3**) in CDCl$_3$.



Scheme 2. Synthesis of polyimides derived from dianhydride (**3**).

isolated by precipitation in ethanol. The polymer was purified by continuous washing with ethanol and dried at 90 °C under vacuum for 24 h. As shown in Table 1, all polyimides (**4a**–**e**) had inherent viscosities in the range of 0.42–0.63 dL/g in *m*-cresol. The weight-average molecular weights of polyimides (**4a**–**e**) were recorded in the range of $3.4–5.4 \times 10^4$ g/mol based on polystyrene standard. The polymers were characterized by elemental analysis, FTIR and ^1H NMR spectroscopic techniques. FTIR spectra of these polyimides showed imide carbonyl peaks at around 1778 and 1725 cm^{-1} and did not show an amide carbonyl peak at 1650 cm^{-1}, indicating complete imidization during polycondensation. The ^1H NMR spectrum of polyimide **4e**, as shown in Fig. 2, was consistent with its expected structure.

3.2. Polymer properties

The solubility of the polymers was tested in various solvents and the results are summarized in Table 2. All the polyimides were readily soluble with a 10% solid content both in strong dipolar solvents and in common organic solvents such as NMP, CH_2Cl_2, $CHCl_3$, and THF. In general, these polymers revealed an enhanced solubility as compared with conventional aromatic polyimides. This can be attributed in part to the incorporation of bulky alicyclic units into polymer backbone, which retards dense chain packing and leads to a decreased chain–chain interaction. The packing-disruptive spiro noncoplanar structure in the bis(ether anhydride) moiety also contributed to the enhancement of solubility. As shown in Scheme 1, the two adjacent planar components are orthogonally arranged and are connected to the spirocentre (i.e., a single tetrahedral carbon atom shared by two rings). Thus, the resulting polymers should have a periodically twisted polymer backbone, and this would lower the chain packing and increase the solubility. The good solubility of these polymers in low boiling point solvents is a benefit to prepare the polymer films or coatings at low processing temperature. The dense films of these polyimides were prepared (whenever possible) by the re-dissolution of powdered samples in NMP, followed by the standard casting procedures.

The thermal properties of these polymers were assessed with DSC and thermogravimetric analysis (TGA). Table 3

Table 1
Inherent viscosity, molecular weight and elemental analysis of polyimides

Polymer	η_{inh}[a] (dL/g)	Mn[b] ($\times 10^{-4}$)	Mw[b] ($\times 10^{-4}$)	Empirical formula	Elemental analysis (%)			
						C	H	N
4a	0.56	2.7	5.3	$(C_{50}H_{34}N_2O_8)_n$	Calcd	75.94	4.33	3.54
					Found	76.02	4.21	3.62
4b	0.53	2.3	4.9	$(C_{49}H_{32}N_2O_9)_n$	Calcd	74.24	4.07	3.53
					Found	73.98	4.08	4.03
4c	0.63	3.2	5.4	$(C_{52}H_{38}N_2O_8)_n$	Calcd	76.27	4.68	3.42
					Found	76.05	4.61	3.62
4d	0.59	2.8	5.1	$(C_{55}H_{36}N_2O_{10})_n$	Calcd	74.65	4.10	3.17
					Found	74.70	4.18	3.15
4e	0.42	1.9	3.4	$(C_{47}H_{36}N_2O_8)_n$	Calcd	74.59	4.80	3.70
					Found	74.64	4.78	3.65

[a] Inherent viscosity measured was at a concentration of 0.5 g/dL in *m*-cresol at 30 °C.

[b] With respect to polystyrene standards, with $CHCl_3$ as the eluent.

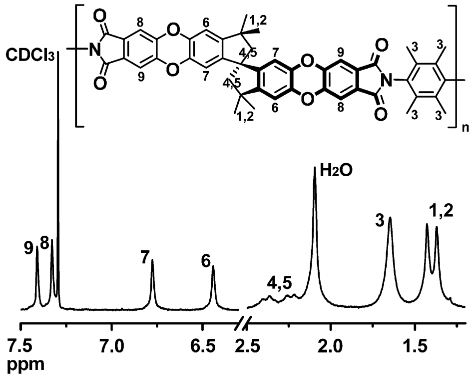


Fig. 2. ^{1}H NMR spectrum of polyimide **4e** in $CDCl_3$.

shows the thermal properties of polyimides with the onset decomposition temperature (T_d) and the temperature at 10% weight loss (T_{10}). The 10% weight loss temperatures (T_{10}) in nitrogen were observed at 395–430 °C. These results show that the thermal stability is lower than that of aromatic polyimides, whereas it is enough for microelectronics applications.

The glass-transition temperature (T_g) was determined by DSC at a heating rate of 20 °C/min under an atmosphere of nitrogen. The T_g values of these polyimides ranged from 254 °C to 292 °C, depending on the diamine monomers used. Among all the polyimides synthesized, polymer **4a** showed the highest T_g of 292 °C, which can be attributed to the rigid diamine moieties in the polymer backbone. Polymer **4e** had relatively lower T_g (254 °C) due to the presence of extra methyl groups in the *ortho*-position of the imide nitrogen which hinder the rotation of C–N imide bond and force the two phenyl rings into a non-coplanar conformation. This, in turn, leads to an increase in the free volume and the decrease in the T_gs of polymers. Cella and Faler reported a spirobisindane dietheranhydride (SBIDA) synthesized from 5,5′-dihydroxy-3,3,3′,3′-tetramethyl-1,1″-spirobisindane and 4-nitro-*N*-methylphthalimide [29]. Chao and Barren reported on the synthesis and properties of polyimides based on SBIDA [30]. It was found that the polyimide made from SBIDA and an aromatic diamine had a higher glass-transition temperature than the polyimide made from bisphenol A dietheranhydride and the same diamine. It is conceivable that the structural rigidity of SBIDA contributes to the increase in the glass-transition temperature of those polyimides. In comparison with SBIDA, the spirobisindane tetraetheranhydride (**3**) is more rigid due to the rotation around carbon–oxygen bond being restricted for the formation of dibenzodioxane. Therefore, the polyimides from **3** showed an increased T_g than those from SBIDA. For example, the T_g value of polyimide **4b** (280 °C) is about 30 °C higher than that of polyimide from SBIDA and ODA (252 °C).

The optical properties of the polyimide films are studied using UV–vis spectroscopy. Two quantities, the transmission onset and the 80% transmission wavelength, are used to evaluate the transparency of these films. The UV–vis spectrum of three polyimide films is displayed in Fig. 3 together with the UV–vis spectrum of Kapton [poly(4,4′-oxydiphenylene pyromellitimide)] film for comparison. The onset and 80% transmission wavelengths for the polyimides films are listed in Table 4. They range from 286 nm to 308 nm for the onset wavelength and 312–328 nm for the 80% transmission wavelength. These values are lower than that of Kapton. This may be interpreted by the reduction of intermolecular charge-transfer

Table 2
Solubility of polyimides[a]

Polymer	Acetone	THF	CH_2Cl_2	$CHCl_3$	TCE[b]	DMAc	DMSO	NMP	*m*-Cresol
4a	−	+	+	+	+	−	−	+	+
4b	−	+	+	+	+	−	−	+	+
4c	−	+	+	+	+	−	−	+	+
4d	−	+	+	+	+	−	−	+	+
4e	−	+	+	+	+	−	−	+	+

[a] The solubility was determined at 10% solid content. +: soluble; the solid polymer was completely dissolved in the solvent to afford a clean, homogenous solution. −: insoluble; the solid polymer did not dissolve in the solvent.

[b] 1,1′,2,2′-Tetrachloroethane.

Table 3
Thermal properties of polyimides

Polymer code	T_g[a] (°C)	T_d[b] (°C)		T_{10}[c] (°C)	
		Air	N_2	Air	N_2
4a	292	392	402	406	418
4b	280	408	422	421	428
4c	286	396	399	412	420
4d	266	401	415	422	430
4e	254	378	382	392	395

[a] From the second trace of DSC measurements conducted at a heating rate of 20 °C/min.

[b] Onset decomposition temperature in TGA at 10 °C/min heating rate.

[c] Ten percent weight loss temperature in TGA at 10 °C/min heating rate.

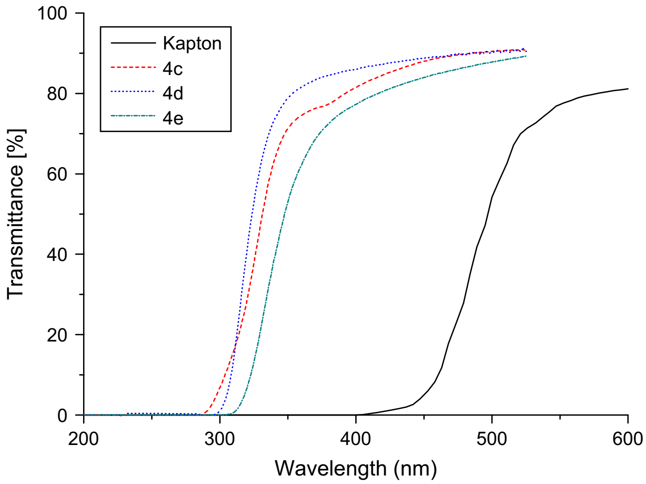


Fig. 3. UV–vis spectrum of three polyimide films and Kapton film.

Table 4
The onset and 80% transmission wavelengths for three polyimides films and Kapton

Polymers	Transparency onset (nm)	80% Transmission (nm)
4c	286	314
4d	295	312
4e	308	328
Kapton	408	472

Table 5
Mechanical properties of polyimide films

Polymers	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (GPa)
4c	98.4	8.1	1.9
4d	106.6	9.8	2.0
4e	68.8	5.9	1.7

complex (CTC) between alternating electro-donor (diamine) and electron-acceptor (dianhydride) moieties. The aliphatic spiro structure in the dianhydride moiety is not sterically favorable for the electronic interaction. The electron-donating ether groups in the dianhydride moiety also contribute somewhat toward decreasing the overall electron affinity of the phthalimide units and subsequently lower the intermolecular CT interaction. In addition, the introduction of the spiro alicyclic structures would greatly break the conjugation along the backbone and decrease the chromophore length.

The crystallinity of the prepared poly(ether imide)s was determined by wide-angle X-ray diffraction (WAXD) scans. All the polymers showed almost completely amorphous diffraction patterns. This is reasonable because the presence of spirocyclic linking groups induces looser chain packing. The mechanical properties of the polymer films are summarized in Table 5. They had tensile strengths of 68.8–106.6 MPa, elongation at break of 5.9–9.8%, and tensile modulus of 1.7–2.0 GPa. Most of the polymers showed tough and strong behavior.

4. Conclusions

A novel dianhydride having spirobisindane unit was synthesized, characterized and applied to polyimide preparation. The polyimides showed good solubility toward organic solvents and could be cast into colorless and strong films. They also exhibited moderately high T_gs and good thermal stability. Thus, this series of polyimides demonstrated a good combination of properties and may be of interest for microelectronics, optoelectronics and gas separation membrane applications.

Acknowledgements

We thank the National Basic Research Program of China (No. 2003CB615704) and the National Science Foundation of China (Nos. 20474061 and 50683087) for the financial support.

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