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Polyimides from 3,3′-dioxo-[1,1′]-spirodiphthalan-5,5′,6,6′-tetracarboxylic dianhydride[1]

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Abstract

A novel dianhydride, 3,3′-dioxo-[1,1′]-spirodiphthalan-5,5′,6,6′-tetracarboxylic dianhydride, was synthesized and used as a monomer to prepare polyimides with several diamines via a conventional two-stage procedure. The intermediate poly(amic-acid)s had inherent viscosities of 0.84–1.71 dL/g and could be thermally converted into lightly yellow, transparent, flexible and tough films. Films cast from chemically imidized polyimides were transparent and colorless. The glass transition temperatures (Tg) were >400°C, and the 5% weight-loss temperatures were >420°C in N_2 and in air. The solubilities of these polyimides in various solvents were evaluated. The mechanical properties of some polyimides were also tested. © 1999 Elsevier Science Ltd. All rights reserved.

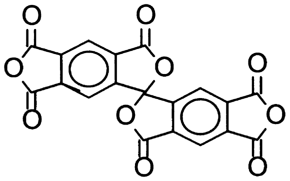
Keywords: Polyimides; Spirodilactone dianhydride; Synthesis

1. Introduction

A variety of condensation polyimides, since first discovered by Bogert and Renshaw [1] in 1908 and developed as material by Edwards and Robertson [2], have been synthesized with a great variety of monomers. They have many applications because of their outstanding performance in areas such as dielectrical and mechanical properties, thermal and chemical stability, etc. However, many researchers still design and synthesize new monomers in order to obtain polyimides possessing certain specific properties.

In recent years, spiral compounds have been paid much attention for their use as monomers in preparing polymer materials. Wang [3] at Shell Oil Co. has developed a type of polymer by introducing a spirodilactam unit, 1,6-diaza-spiro-[4,4′]-nonane-2,7-dione, into the polymer backbone. Thermal properties have been improved because of the rigidity of the spiral structure and the hindered rotation of the polymer chain. Compounds containing spirodilactone units have also been studied as comonomers in ring-opening copolymerization. Chung [4] and Sikes [6] have reported the copolymerization of spirodilactone compounds with epoxy resin. Pawlikowski [7] has reported the cross-linking reaction of spirodilactone.

Considering that spirodilactone in the polymer backbone can provide more approaches to modifying the structure of the polymer, for example, lactamization and ring-opening reactions etc., we synthesized 3,3′-dioxo-[1,1′]-spiro-diphthalan-5,5′,6,6′-tetracarboxylic dianhydride (**6**) by a convenient route (see Scheme 1). A series of polyimides were prepared from this spirodilactone dianhydride (see Scheme 2) and their properties were investigated. Also investigated was the lactamization of spirodilactone model compounds.



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2. Experiment

2.1. Materials

Bis-(3-methyl-4-aminophenyl)methane (DMMDA), 1,3-bis-(4-aminophenoxy)benzene (APB) and 2,2-bis-[4(4-aminophenoxy)phenyl]propane were prepared in our laboratory. Commercially available solvents were purified by distillation. 4,4′-oxydianiline (ODA) (>99%),

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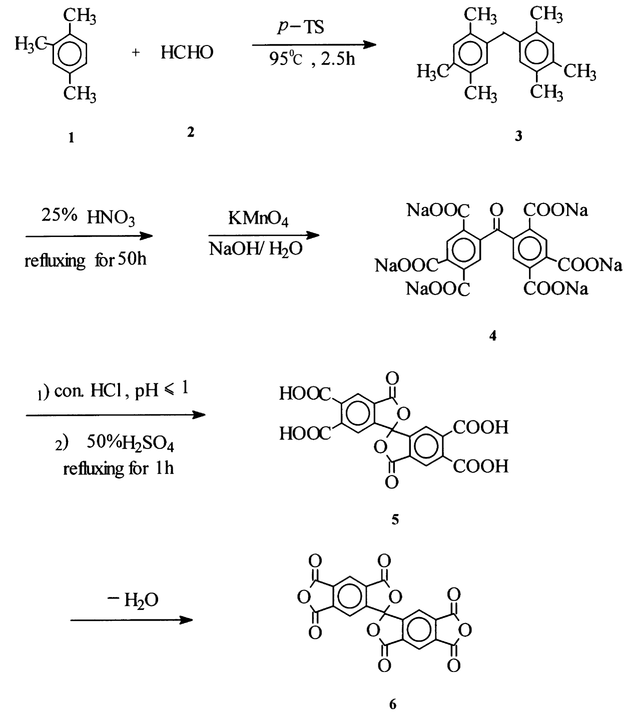


Scheme 1

1,2,4-trimethylbenzene (99%) (Aldrich), *p*-toluene sulfonic acid and paraformaldehyde were commercially available and used as received.

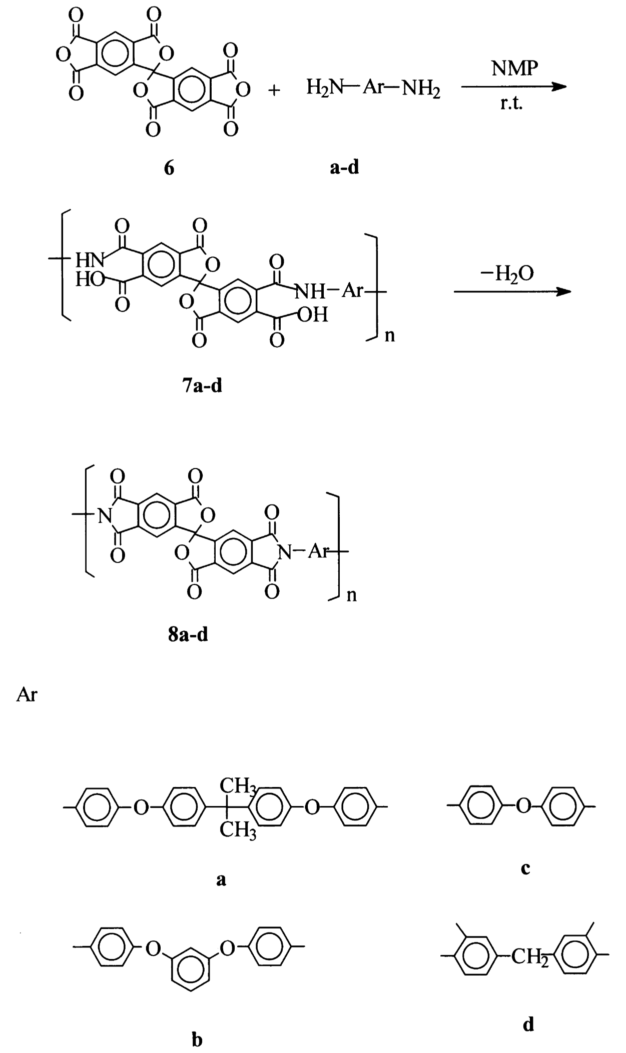
2.2. Characterization

FT-IR spectra were obtained with a Bio-Rad FTS-7 spectrometer. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Varian Unity 400 spectrometer, using tetramethylsilane (TMS) as internal standard in deuteriodimethyl sulfoxide (DMSO-d6). Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC-7 in flowing nitrogen (20 cm^3/min) at a heating rate of 20°C/min; the sample weight was about 17 mg. Thermogravimetry (TG) was tested on a Perkin-Elmer TGA-7 in flowing nitrogen or air (20 cm^3/min) at a heating rate of 10°C/min. Inherent viscosities were measured with an Ostwald viscometer at 30°C, and the concentration was 0.5 g/dL in DMAc. Mechanical properties were evaluated using an Instron-1121 materials tester. Melting points were determined by DSC in flowing nitrogen (20 cm^3/min) at a heating rate of 10°C/min.

2.3. Synthesis of monomer (**6**)

2.3.1. Bis-(2,4,5-trimethylphenyl)-methane (**3**).

1,2,4-trimethylbenzene (30.0 g, 0.25 mol), paraformaldehyde (3.0 g, 0.1 mol) and *p*-toluene sulfonic acid (3.0 g, 10 wt% of trimethylbenzene) was added to a 100 ml three-necked flask equipped with a condenser and stirred at 95°C for 2.5 h. The mixture was transferred into a 100 ml separatory funnel. The oil layer was separated and distilled under reduced pressure. A fraction at 174–176°C (6 mmHg) was collected and recrystallized twice from a mixture of ethanol and dichloromethane (v/v = 2:1). Yield 66.3%, m.p. 97–98°C (literature [8] m.p. 98°C).



Scheme 2

2.3.2. 3,3′-dioxo-[1,1′]-spirodiphthalan-5,5′,6,6′-tetracarboxylic acid (**5**) and the corresponding dianhydride (**6**).

3 (10.0 g, 0.04 mol) was added to 330 ml 20% nitric acid in a 500 ml flask equipped with a condenser and gas absorption apparatus and refluxed for 50 h. The reaction mixture was then cooled to room temperature and a slightly yellow powder was recovered by filtration and washed thoroughly with cooled water. A solution of the powder in 280 ml of 5% aqueous sodium hydroxide was heated to reflux. To the refluxing solution was added potassium permanganate (17.0 g) in small portions over a period of 10 h and the resulting mixture was refluxed for an additional 4 h. The manganese dioxide was filtered and washed thoroughly with hot water. The filtrate was evaporated to about 100 ml and carefully acidified with concentrated

Table 1
Inherent viscosities of poly(amic-acid)s and solubilities of polyimides

	η_{inh}[a] (dL/g)	Solubility[b]								
Sample		Sample	DMSO	DMAc	DMF	NMP	cresol	THF	$CHCl_3$	H_2SO_4
7a	1.71	**8a**	−	−	−	−	−	−	−	+
7b	1.34	**8b**	+	+	+	+	±	−	−	±
7c	1.06	**8c**	−	−	−	−	−	−	−	±
7d	0.84	**8d**	+	+	+	+	+	+	±	±

[a] Measured at a concentration of 0.5 g/dL in DMAc at 30.0°C using an Ostwald viscometer.

[b] Soluble (+), partially soluble (±), not soluble (−) at room temperature.

hydrochloric acid to pH ≤ 1 and refluxed for 2.5 h [9]. The mixture was cooled to room temperature and a white precipitate was collected by filtration. The resulting product was additionally boiled with 50% sulphuric acid for 1 h, and white precipitate **5** was recovered by filtration and washed thoroughly with water. Yield 86%; IR (KBr), 3517(sh), 3455(sh), 3060(w), 2949(w), 1796(vs), 1716(vs), 1618(w), 1484(w), 1425(w), 1291(s), 1244(s), 1097(s), 975(m) cm^{-1}; ^{1}H-NMR, $(\mathrm{ppm})_\delta$ 8.400(s, 2H, aromatic), 8.331(s, 2H, aromatic), 13.529(br, –COOH); ^{13}C-NMR $(\mathrm{ppm})_\delta$, 167.758, 166.991, 165.055 (carbonyl), 145.097, 140.511, 136.141, 127.933, 125.999, 124.358 (aromatic), 106.106 (central carbon of spirobilactone).

10.0 g of **5** was refluxed in a mixture of 25 ml sulfolane and 40 ml acetic anhydride for 3 h. Little solid impurity was removed by filtration, and absolute ethyl ether was added slowly to the filtrate until it was foggy, after which it was cooled in the refrigerator for 48 h. The precipitate was recovered by filtration, washed with absolute ether and dried in a vacuum oven at 250°C for 4 h, yield 89% (8.1 g). m.p. 421°C (by DSC); IR (KBr), 3057(br), 1855(sh), 1804(sh), 1620(w), 1454 (w), 1238(s), 1208(s), 1098(s), 1065(s), 981(s), 916(s) cm^{-1}. M^+:392.

2.4. Synthesis of polyimides

Polyimide **8b** was prepared from **6** and 1,3-bis-(4-aminophenoxy)benzene (APB) by a conventional two-stage procedure. To a flask of volume 25 ml was added **6** (0.7764 g, 1.98 mmol), APB (0.5787 g, 1.98 mmol) and NMP (15.6 ml). The mixture was stirred vigorously by an electromagnetic stirrer at room temperature for 2.5 h to obtain a viscous solution. The viscosity of the resulting poly(amic-acid) solution in DMAc was 1.34 dL/g, measured at a concentration of 0.5 g/dL at 30°C.

Chemical imidization was carried out by addition of a mixture of acetic anhydride (1.0 ml) and pyridine (0.5 ml) to the poly(amic-acid) solution and then stirring for 24 h at room temperature. The polyimide solution was then poured into ethanol, and the white fibrous precipitate was collected by filtration, washed with ethanol, and then dried in a vacuum oven at 40°C. Yield 99% (1.271 g); IR (Kbr), 3046(br), 1807(vs), 1784(s), 1724(vs), 1618(w), 1588(m), 1505(vs), 1477(s), 1383(s), 1262(m), 1222(vs), 1182(m), 1169(s), 1115(m), 966(m), 879(s) cm^{-1}; ^{1}H-NMR $(\mathrm{ppm})_\delta$ 8.686(s, 2H), 8.622(s, 2H), 7.596(d, 4H), 7.341(d, 4H), 6.969(m, 4H).

The poly(amic-acid)s solution was cast onto 5 cm × 10 cm glass plates and dried at 40°C for 12 h, 100°C for 2 h, and then rapidly heated to 300°C for thermal imidization. A tough and flexible film of about 0.05 mm thickness was stripped from the glass surface by soaking in water.

All other polyimides were prepared by the same procedure as mentioned above except for the 14 h stirring carried out for **d**.

3. Results and discussion

3.1. Monomer synthesis

3,3′-dioxo-[1,1′]-spirodiphthalan-5,5′,6,6′-tetracarboxylic dianhydride (**6**) has been synthesized by a five-step procedure (Scheme 1) in high yield and purity.

The oxidation of bis-(2,4,5-trimethylphenyl)methane was carried out in two stages. By boiling **3** with dilute nitric acid, a mixture of multibasic acid was obtained which was easily soluble in aqueous sodium hydroxide. The mixture was then oxidized to hexabasic acid sodium salt in 5% aqueous sodium hydroxide with potassium permanganate. The conversion of the hexabasic acid sodium salt to spirodilactone tetracarboxylic acid was effected by heating with hydrochloric acid and sulphuric acid, respectively. The additional boiling with 50% sulfuric acid was to make sure that the sodium salt could be converted completely to the corresponding carboxylic acid. Sulfolane used in the preparation of dianhydride increased the solubility of tetracarboxylic acid and dianhydride. In our experiment, we tried the alternative of one-step oxidation with dilute nitric acid and potassium permanganate, but neither of these is satisfactory because of the limited solubility of the intermediate multibasic acid in dilute nitric acid and **3** in aqueous potassium permanganate. The structure of **6** agreed well with the spectra of IR, ^{1}H-NMR, ^{13}C-NMR and mass spectra. The melting point of **6** was determined reproducibly by DSC to show as high as 421°C.

Table 2
Thermal properties of polyimides

Sample	Tg[a] (°C)	Td[b] (°C)	
		Air	N_2
8a	–	495	495
8b	–	524	530
8c	–	485	490
8d	–	420	425

[a] Assessed by DSC at a heating rate of 20°C/min in nitrogen, the samples were about 17 mg.

[b] Onset temperatures for 5% weight loss, as assessed by TG at a heating rate of 10°C/min.

3.2. Polyimides synthesis

From spirobilactone dianhydride, several polyimides have been synthesized via a conventional two-stage procedure (Scheme 2).

The poly(amic-acid)s **7a–d** had inherent viscosities ranging from 0.84–1.71 dL/g (Table 1), **7d** had the lowest viscosity because of the space hindrance of methyl in diamine **d**, which hinders the nucleophilic attack of amino to carbonyl. The structure of the polyimides was proved through IR- and ^{1}H-NMR spectroscopy, the results being consistent with the desired structure. In the IR spectra, the absorbances near 1780, 1720 and 1100 cm^{-1} are the characteristic ones of imide, while the strong band near 1800 cm^{-1} belongs to the carbonyl group of spirobilactone. The weak absorbance near 3487 cm^{-1} in IR spectra and 4.430 ppm in ^{1}HNMR spectra shows that chemical imidization was not complete.

3.3. Properties of the polyimides

The solubility of all the polyimides was tested, and the results are summarized in Table 1. For chemically imidized polyimides, **8b** and **8d** are soluble in DMSO, DMAc, DMF and NMP, especially **8d**, which is even soluble in THF and partially soluble in $CHCl_3$. When treated at 250°C for 4 h under vacuum, their solubilities became poor. All these polyimides dissolve partially in concentrated sulfuric acid.

Film cast from the soluble colorless powder **8d** in THF solvent was transparent and colorless, possibly due to the twisted structure of spirodilactone, which breaks down the conjugation of the polymer backbone.

Among the four polyimides, **8a**, **8b** and **8c** showed the highest thermal stability (Table 2) in nitrogen and in air, the 5% weight-loss temperatures being > 490°C, while that for **8d** was about 70°C lower. This may be attributed to the cleavage of methyl substitute in **8d**. The onset of weight-loss temperature of the four polyimides is about 400°C, perhaps thermolysis of lactone happening at this temperature. The thermal stability below 600°C in air for these spirodilactone-based polyimides was close to that in nitrogen. Fig. 1 shows the TG curves of polyimide **8a** in nitrogen and in air.

All four polyimides exhibited a high Tg, > 400°C (Fig. 2); this is due to the rigidity of spirobilactone in the polymer backbone. As Fig. 3 shows, there was no apparent glass transition observed for **8b**, **8c** and **8d**, probably resulting from the overlap of the glass transition temperature region and the endothermal region of decomposition.

Mechanical properties were evaluated using the slightly yellow, transparent films from thermal imidization; **8a** and **8b** were flexible and tough, while **8c** and **8d** were somewhat brittle. The tensile strength at break point, elongation to break and Young's modulus were 51 MPa, 3.2% and 2.2 GPa, respectively, for **8b**.

The early study by Wang [3] reported that a spirodilactam system, including aliphatic and aromatic, could be prepared from the reaction of the corresponding spirodilactone with amine. He considered that this reaction proceeded via a

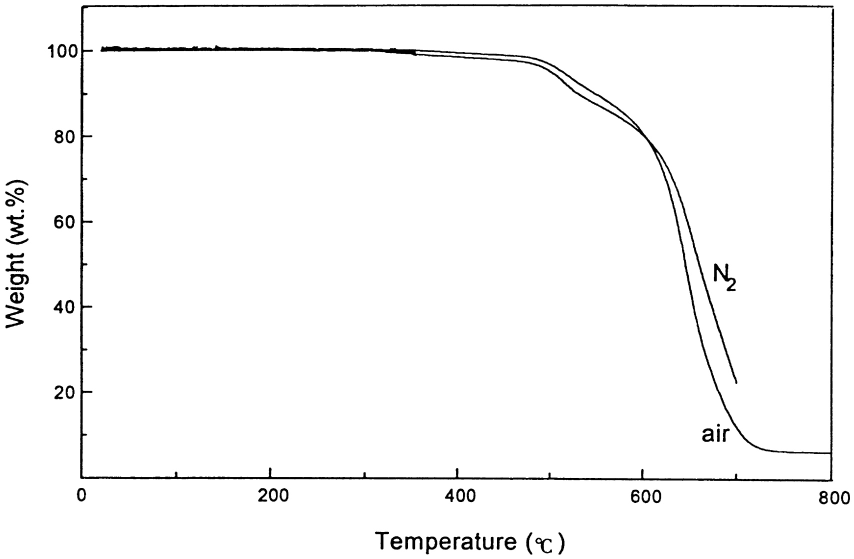


Fig. 1. Thermogravimetric analysis curves for polyimides **8a**.

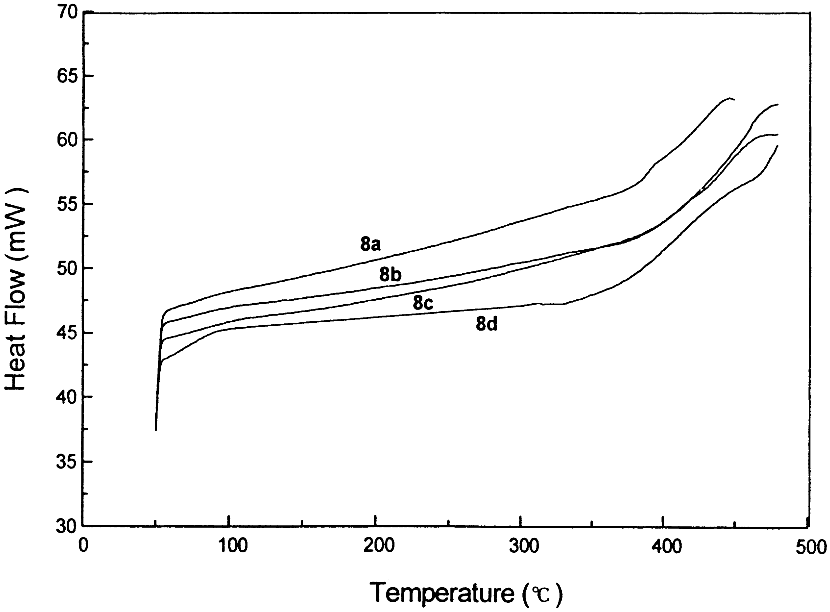


Fig. 2. Differential scanning calorimetry curves for polyimides **8a–d**.

ring-opening intermediate of spirodilactone. This procedure was achieved at a temperature ranging from 50°C to 250°C. Brady [5] also concluded that ring-opening copolymerization of dilactone could take place effectively with glycidyl ethers at temperatures from 25°C to 150°C in the presence of a tertiary amine. These results indicate that spirodilactone may react with amine under mild temperature conditions. In our work, we have studied the ring-opening behavior of spirodilactone in the presence of diamine during the polymerization. The results indicate that, for the diamines used in this paper, ring-opening products can be ignored according to the analyses we used. The details will be reported elsewhere.

4. Conclusion

A novel dianhydride, 3,3′-dioxo-[1,1′]spirodiphthalan-5,5′,6,6′-tetracarboxylic dianhydride, **6**, was prepared from 1,2,4-trimethylbenzene in high yield and purity by a five-step procedure. Four polyimides were obtained from this dianhydride. Transparent and colorless film could be obtained from the soluble polyimides. The spirodilactone-containing polyimides showed good thermal properties and high glass-transition temperatures. During the polymerization of **6** and diamines **a–d**, no ring-opening reaction could be found.

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