

# Synthesis and properties of novel aromatic polynaphthalimides derived from dianhydride containing three ether linkages

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**Abstract:** A novel dianhydride monomer 4, 4'-Bis (1, 8-naphthalic anhydride) diphenyl ether (**I**) was prepared from 4-bromo-1, 8-naphthalic anhydride and 4, 4'-Dihydroxydiphenyl ether. Then the dianhydride was polymerized with 4, 4'-Diaminodiphenylmethane (**a**) and 1, 3-bis (4-aminophenoxy) benzene (**b**) in *m*-cresol via a conventional one-step procedure, respectively. BNDE (**I**) was characterized by <sup>1</sup>H NMR, IR, MS and DSC. The polymer **I a-b** were soluble in many polar organic solvents, such as *m*-cresol, N-methylpyrrolidone and chloroform, **I b** can also swell in N,N-dimethylacetamide, but none of them was soluble in THF. All the polyimides own thermal stability associated with high T<sub>g</sub> in the range of 264-324°C, 5% weight loss temperatures in excess of 500°C, and char yields at 800°C in nitrogen higher than 50%. Tensile measurements showed polymer **I a-b** possessed high modulus (2.3~2.4GPa) and elongation(7-13%).

**Key Words :** Polyimides, Six-membered naphthalene anhydrides, ether linkage

## Introduction:

Aromatic polyimides are considered to be one of the most important classes of high-performance polymers because of their excellent thermal, mechanical, and electrical properties as well as outstanding chemical resistance, polynaphthalimide as a member of polyimides exhibits more excellent properties because of the naphthalic dianhydride structures. However, they also suffer from the more difficult processability problem simultaneously, inasmuch as they are more insoluble and infusible<sup>1-4</sup>. These properties make them difficult to fabricate by means of conventional techniques.

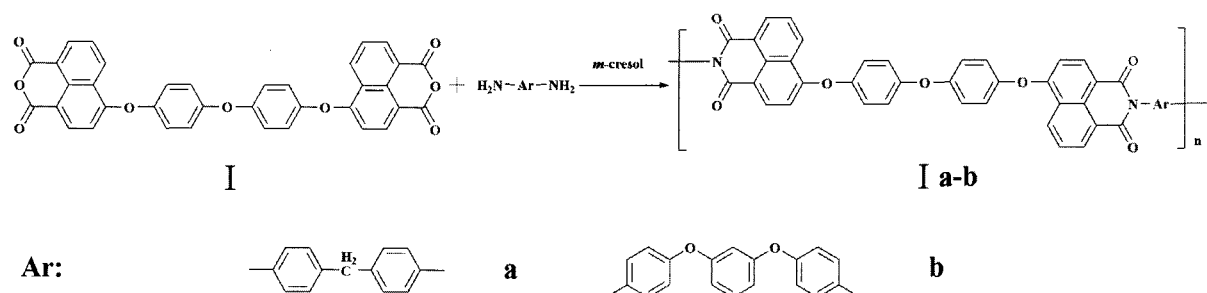
In order to overcome these limitations, several kinds of structural modifications have been adopted. One is to lower molecular weight polyimides terminated with reactive group, for example, maleimide and nadimide<sup>5, 6</sup>. Alternatively, structural modifications of the polymer backbone such as the addition of bulky lateral substituents<sup>7-10</sup>, flexible alkyl side chains<sup>11</sup>, non-coplanar biphenylene moieties<sup>12</sup>, and kinked comonomers<sup>13</sup> have been utilized to modify the polymer properties. Overall, the most practical approach is to introduce flexible linkages between the aromatic ring in the diamine and dianhydrides. Modified polyimides with flexible bonds that provide improved solubility have successfully improved the processing properties.

In the present investigation, the authors we describe the synthesis of polyimides derived from 4, 4'-Bis (1, 8-naphthalic anhydride) diphenyl ether contained three ether linkages between two naphthalene rings and commercial diamines. These polynaphthalimides are all amorphous and readily soluble in organic solvents at room temperature, they also have outstanding thermal stability and excellent mechanical properties.

## Experiment

## Synthesis of polynaphthalimides based on BNDE

A representative polymerization procedure is described as follows: 5.9452g(10mmol) of BNDE, 1.9626g(10mmol) 4, 4'-Diaminodiphenylmethane, 2.4424g(20mmol) benzoic acid, and 35ml m-cresol were placed in a three-necked, 100ml round-bottom flask equipped with a mechanical stirrer, nitrogen inlet and outlet. The mixture was stirred at room temperature for a few minutes, and heated to 180 °C for 9h, then several drops of isoquinoline added; the reaction was continued for another 9h. After cooling to 100 °C, additional 10ml m-cresol was added to dilute the viscous solution. Then it was poured into 300ml of ethanol with stirring. The fiberlike precipitate was collected by filtration and extracted with ethanol in a Soxhlet extractor for 24h, and then dried in vacuum for 4h to afford power of polynaphthalimide with the yield of 95%. The above mentioned procedures were followed by the synthesis of other polynaphthalimide **I b**.



Scheme 1. The synthesis of polynaphthalimides derived from BNDE

## Membrane preparation

A series of tough and ductile polymer membranes were prepared with a controlled thickness of 30-50  $\mu\text{m}$ . The polyimides powders were dissolved in *m*-cresol to form 6-8% solutions at room temperature. The solutions were filtered and cast onto glass plates at 60 °C for 5 h, 120 °C for 10 h, 150 °C for 5 h, and then in vacuum 200 °C for 5 h, 250 °C for 1 h, 300 °C for 1 h, respectively.

## Measurements

**Differential scanning calorimetry (DSC)** of the polyimides were performed using a Mettler Toledo DSC 821<sup>e</sup> apparatus at a heating rate of 20 °C  $\text{min}^{-1}$  under a nitrogen atmosphere at a flow rate of 200  $\text{cm}^3 \text{min}^{-1}$ . The glass transition temperature ( $T_g$ ) was taken at the mid-point of the heat flow versus temperature curve. **The infrared (IR) spectra** of the KBr powder-pressed pellets were performed with Bruker Vector22 spectrometer. **Dynamic mechanical analysis (DMA)** was performed on thin film specimen (4×0.6×0.004  $\text{cm}^3$ ) on a TA DMA Q800 at a heating rate of 3 °C  $\text{min}^{-1}$  and at a load frequency of 1 Hz in  $\text{N}_2$  environment. The peak on the  $\tan\delta$  as a function of temperature curves was regarded as  $T_g$  of the polyimides film. **Tensile properties** such as the tensile modulus, tensile strength and elongation of the films at break were measured as the average using specimens on a Shimadzu AG-I tensile apparatus. Sample size: 4×0.3×0.003  $\text{cm}^3$ , strain rate: 8  $\text{mm s}^{-1}$ . The thermal properties of the membranes were evaluated using a Perkin-Elmer **thermogravimetric analyzer (TGA-7)** with Pyris data collection and analysis software. Film samples were heated at a constant rate of 5 °C  $\text{min}^{-1}$  in air or nitrogen (25  $\text{cm}^3 \text{min}^{-1}$ ) atmosphere.

## Results and discussion

### Polymer synthesis

A typical procedure is outlined in Scheme 1. Polymerizations of the dianhydrides BNDE with aromatic diamines were carried out via a one-step method in *m*-cresol in the presence of catalytic amount of benzoic acid for 9 h and then isoquinoline 9 h at 190 °C. All polyimides remained fully soluble during the course of the polymerization. Fibrous high molecular weight polyimides could be isolated upon precipitation into methanol. Fig. 1 shows the FT-IR spectra of the polyimide membranes. The typical absorption bands for naphthalene imide rings are found around 1712  $\text{cm}^{-1}$  (symmetric stretching of carbonyl group), 1670  $\text{cm}^{-1}$  (asymmetric stretching of carbonyl group), 1361  $\text{cm}^{-1}$  (C-N stretching), and 784  $\text{cm}^{-1}$  (carbonyl group bending).

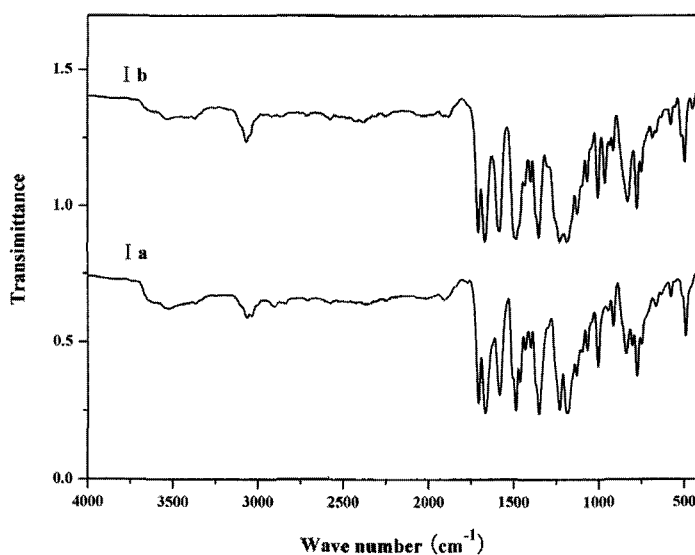


Fig. 1. The FT-IR spectra of polynaphthalimides

### Solubility properties of polyimides

The solubility of all the polyimides was investigated and the results are summarized in Table 1. As shown in Table 1, all the polyimides studied were soluble in *m*-cresol, concentrated  $\text{H}_2\text{SO}_4$  (98 wt %) and NMP.

Table 1. Solubility<sup>1</sup> of polynaphthalimides I a-b

PI	$\text{H}_2\text{SO}_4$	<i>m</i> -cresol	NMP	DMAc	DMF	$\text{CHCl}_3$	THF
I a	+	+	+	—	—	+	—
I b	+	+	+	±	±	+	—

<sup>1</sup>: Qualitative solubility was tested with 1mg of a sample in 1mL of stirred solvent.

+: Fully soluble at room temperature.

±: partially soluble on heating.

—: Insoluble on heating.

The polymer **I b** was partially soluble in DMAc and DMF, whereas the polynaphthalimide **I a** was insoluble in these two solvents. All of them were insoluble in THF. According to the results, the solubility of **I b** was better than **I a**, the possible reason is the more flexible chain structure caused by the ether linkages and the *meta*-structure of **I b**. Overall, these two polynaphthalimides are more soluble than other ordinary ones, and this is primarily due to the inserting in of the three ether linkages between two naphthalene rings which provide them with a significantly lower energy of internal rotation.

### Thermal properties of polyimides

The glass transition of temperatures ( $T_g$ ) of the polyimides **I a-b** was detectable below 400 °C by differential scanning calorimetry under nitrogen. The Fig. 2 showed that the transitions on DSC thermo grams of these two polymers were above 260 °C. All polymers were determined by DMA, The glass transition temperature of polyimide films and the data is listed in Table 2. Fig. 3 showed the DMA curves (modulus as a function of temperature) of films, which present that all the polymers exhibited high  $T_g$ , and the results are consistent with the test of DSC.

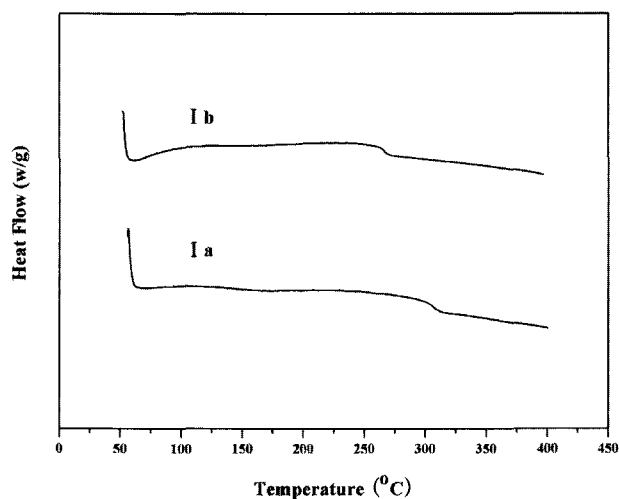


Fig. 2. The DSC curves of polyimides

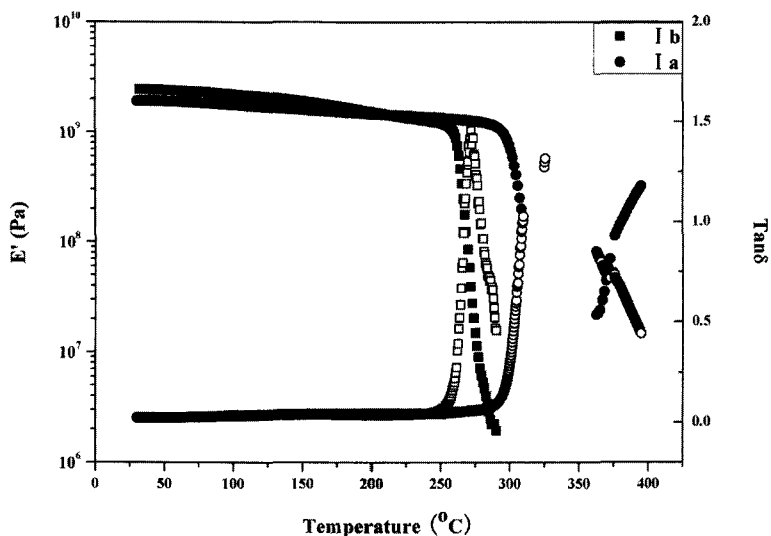


Fig. 3. The DMA curves of polyimides

The polymers demonstrated excellent thermal and thermo-oxidative stabilities as assessed by thermogravimetric analysis in N<sub>2</sub> and air atmospheres at a heating rate of 5 °C min<sup>-1</sup>. The data are listed in Table 2 and the thermal stability behavior was illustrated in Fig. 4. The temperatures of 5% weight loss were all above 503 °C in N<sub>2</sub>, the char yields reported at 800 °C in N<sub>2</sub> are above 53%.

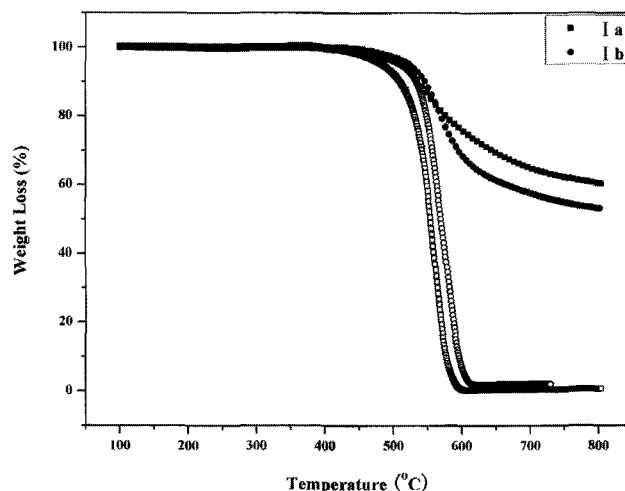


Fig. 4. The TGA curves of polyimides

Table 2. Thermal properties of polyimides I a-b

PI	T <sub>g</sub> <sup>1</sup> (°C)	T <sub>g</sub> <sup>2</sup> (°C)	T <sub>d</sub> (5%) <sup>3</sup> (°C)		Char yield <sup>4</sup> (wt %)
			In Air	In N <sub>2</sub>	
I a	300	324	480	503	60
I b	264	272	513	523	53

### Tensile properties

The mechanical properties (tensile, modulus and elongation at break) of the film were tested at room temperature. The results appear in Table 3, from which we can see that all the polyimides film exhibit excellent mechanical properties.

Table 3. Mechanical properties of polyimides

PI	Tensile properties		
	Strength (MPa)	Modulus (GPa)	Elongation (%)
I a	112.9	2.4	6.9
I b	113.4	2.3	12.7

### Conclusions

A series of polyimides were readily prepared by the one-step method starting from dianhydride BNDE with two commercial diamines MDA and 1, 3, 4-APB. The experimental results indicated that these two (Next see p146)