High water and thermal stability of a novel 1,1',8,8'-binaphthalimide-containing polyimide

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Abstract: 4,4'-Binaphthyl-1,1',8,8'-tetracarboxylic Dianhydride(BNTDA) was synthesized from 4-bromo-1,8-naphthalic anhydride and polymerized with 4,4'-diaminodiphenyl ether(4,4'-ODA) in m-cresol. The structure of the BNTDA was characterized by IR and ^1H NMR. The thermal performance of the polyimide was studied with DSC and TGA. Furthermore, the hydrolytic stability of the polyimide membranes were evaluated by immersing the membranes into 10% NaOH or 10% H_2SO_4 aqueous solution, respectively refluxing for 24h. The polyimides that incorporated with six-membered naphthalene anhydrides exhibited better hydrolytic stability than that with five-membered benzene anhydrides. Polyimide membranes showed excellent water and good thermal stabilities.

Key Words: Polyimides, Hydrolytic stability, Six-membered naphthalene anhydrides

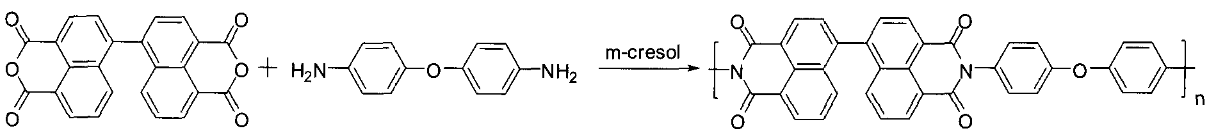
1. Introduction

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[1-3]. A large number of polyimides have been widely used in industrial applications such as microelectronics[4-6]. However, many of the polyimides containing a phthalimide structure (five-membered imide ring) in the polymer backbone showed a bad hydrolytic stability and these results in the degradation of the polymer main chain and a dramatic drop in the mechanical strength for polyimides membranes. In order to investigate the relationship between water stability and chemical structure of polyimides and achieve high water stability, many great efforts have been made. It's well known that the stability of six-membered is better than five-membered. Therefore, many workers have widely used a six-membered dianhydride 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA) for polyimides and the hydrolytic stability has improved accordingly. There is a conventional rule that is the hydrolysis of imide groups was mainly resulted from the nucleophilic attack of the water molecule on the carbonyl carbon atoms, the dianhydrides with higher electron density in carbonyl carbon atoms should produce polyimides with higher hydrolytic stability. It has been reported that the electron density of the carbonyl carbon atoms can be characterized by their electron affinity(E_a), and the lower values of E_a is, the higher the electron density is in the carbonyl carbon atoms[5]. In a paper, the author has made many works on the E_a of 4,4'-Binaphthyl-1,1',8,8'-tetracarboxylic Dianhydride(BNTDA) and NTDA, they found that the BNTDA has a lower electron affinity(3.7790) than NTDA(4.0102)[6]. Therefore, we can predict that the polyimides synthesized from BNTDA should show superior water stability. Furthermore, the polyimides containing naphthalene ring structure is beneficial to the thermal properties. In our paper, we has discussed the water and thermal stability of polyimides synthesized from BNTDA and 4,4'-ODA respectively.

2. Experiment

Synthesis of polyimides based on BNTDA

A representative polymerization procedure is described as follow: 3.9433g(10mmol) of BNTDA, 2.0024g(10mmol) 4,4'-ODA, 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 then heated to 180 °C for 9h, a few 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 polyimide with the yield of 95%.



Scheme 1. The synthesis of polyimide derived from BNTDA

Membrane preparation

A series of tough, ductile polyimdies membranes were prepared with a controlled thickness of 30-50μm. The polyimides were redissolved in m-cresol to form an 8-10% solution at room temperature. The solution was filtered and cast onto glass plates at 80°C for 10h, 120 °C 10h, 180 °C 5h, 250 °C 1h, 300 °C 1h.

Hydrolysis stability in base and acid environments

The hydrolysis stability tests of the polyinide films were performed by immersing the films into deionized water, 10% NaOH or 10% H_2SO_4 aqueous solution, and refluxing for 24h. Then, the mechanical properties of the treated films were compared with the untreated ones.

3. Results and discussion

Thermal properties of the polyimide

The thermal property of the polyimide was measured by DMA and TGA. Fig.1 and Fig. 2 shows the DMA and TGA curves of the polyimide respectively. In fig. 1, a super high glass transition temperature was observed. Glass transition temperature of the polyimide is about 430°C. In Fig. 2 we found that the 5% weight loss temperature (T_{d5}) in N_2 is about 560°C. From these two Figures, it can be seen that the polyimide synthesized from BNTDA and 4,4'-ODA showed excellent thermal properties. As the polyimide obtained from dianhydride containing naphthalene rings, and also due to the rigid chain structure, the thermal properties are superior as we expected.

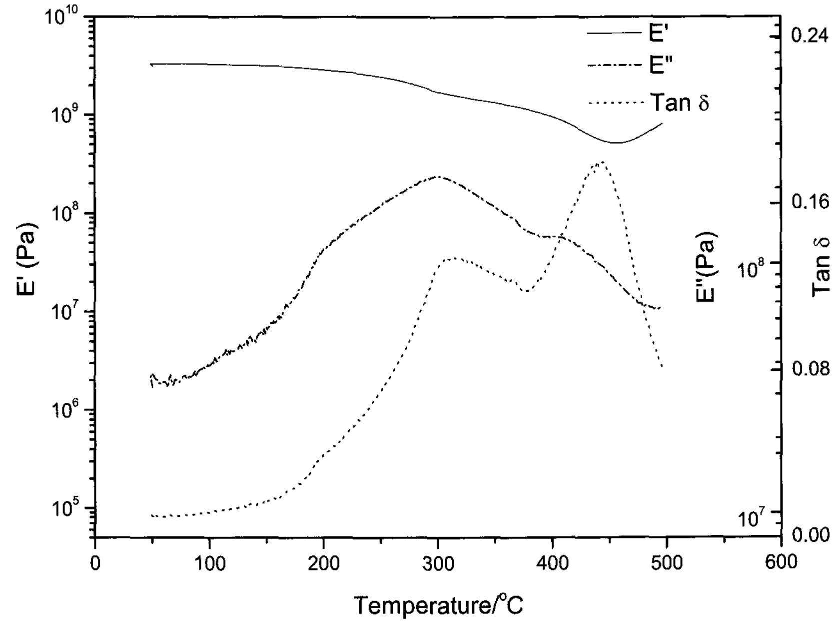


Fig. 1. DMA curves of the polyimide based on BNTDA

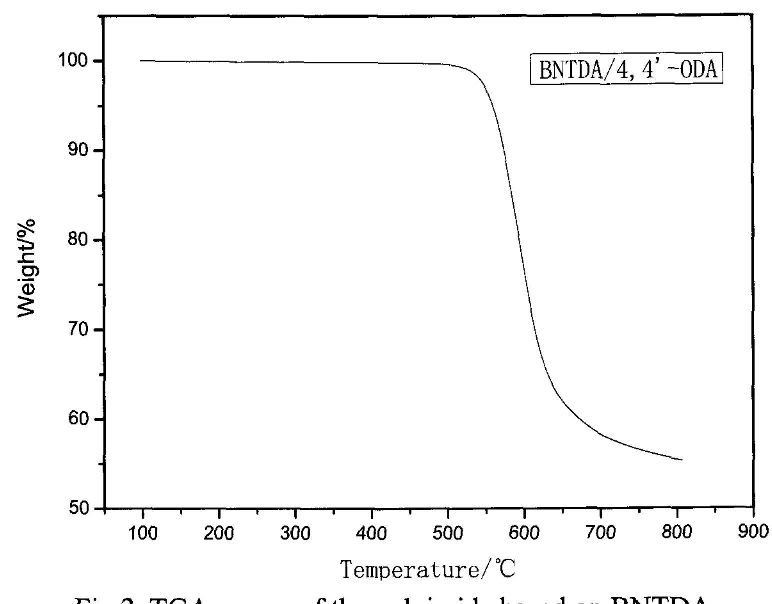


Fig.2. TGA curves of the polyimide based on BNTDA

Hydrolytic stability of the polyimide membranes

The hydrolysis stability tests of the polyimide films were performed by immersing the films into deionized water, 10% NaOH or 10% H_2SO_4 aqueous solution, and refluxing for 24h. Then, the mechanical properties of the treated films were compared with the untreated ones and listed in Table 1. As can be seen from Table 1, the film 2-4 showed 5% reduction in tensile strength and nearly no reduction in tensile modulus, from which we can see that the piolyimide showed super water stability. The reason is that the naphthalene anhydrides contained a six-membered ring structure is stable than benzene anhydrides contained five-membered.

Table 1. Mechanical properties of the polyimide membrane before and after hydration

Treatment[a]	Tensile properties		
	Strength(MPa)	Modulus(GPa)	Elongation(%)
1	161	2.40	13.7
2	153	2.39	12.1
3	153	2.40	12.0
4	140	2.40	8.2

[a] Treatment 1: without any treatment; 2: refluxing in 10% NaOH aqueous solution for 24h; 3: refluxing in 10% H_2SO_4 aqueous solution for 24h; 4: refluxing in deionized water for 24h.

4. Conclusions

We have successfully synthesized the polyimide derived from BNTDA and 4,4'-ODA. The obtained polyimide was studied by DMA and TGA, and the results show that the polyimide exhibits excellent thermal properties. Furthermore, the hydrolysis stability tests suggest that the polyimide membrane possess super water stability.

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