

Preparation and Properties of Novel Polyimides Derived from 1,1-bis[4-(5-amino-2-pyridinoxy)phenyl]cyclohexane

Jianan YAO(姚佳楠), Zhao ZHANG, Daming WANG, Chunhai CHEN, Hongwei ZHOU*(陈春海)

Alan G. MacDiarmid Institute, College of Chemistry, Jilin University, Changchun, 130012, P.R. China

ABSTRACT: A novel aromatic diamine pyridine-containing monomer 1,1-bis[4-(5-amino-2-pyridinoxy)phenyl]cyclohexane (BAPDC) was synthesized. BAPDC reacted with five different commercial dianhydrides via traditional two-step polymerization to prepare polyimides. PI films have good thermal stability and high temperature of glass transition ($T_g > 240^\circ\text{C}$). PI-2 derived from ODPDA and PI-4 derived from 6FDA showed high transparency with an UV-visible absorption cut-off wavelength at 355 and 359nm. Meanwhile, the polyimides exhibited high tensile modulus of 1.9-2.8GPa.

Keywords: Polyimides; Cyclohexane; Pyridine; High performance

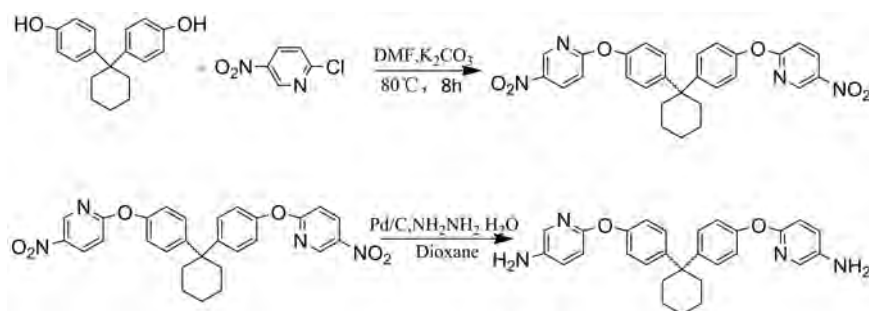
1. Introduction

Aromatic polyimides are well known as their high thermal stability, excellent mechanical strength, good chemical resistance and so on [1-4]. Due to their outstanding properties, polyimides as high performance polymers are widely used in the fields of electrical materials, coating, adhesives, films, fibers and composites [5-8]. Fully aromatic polyimides have rigid chains and strong interchain interactions, which lead to polymers having poor solubility and difficult to process[9, 10].

This work explores the introduction of pyridine and cyclohexane to polyimide to improve the optical property. In this study, a series of novel polyimides based on BAPDC and various commercial aromatic dianhydrides were synthesized and characterized.

2. Experimental

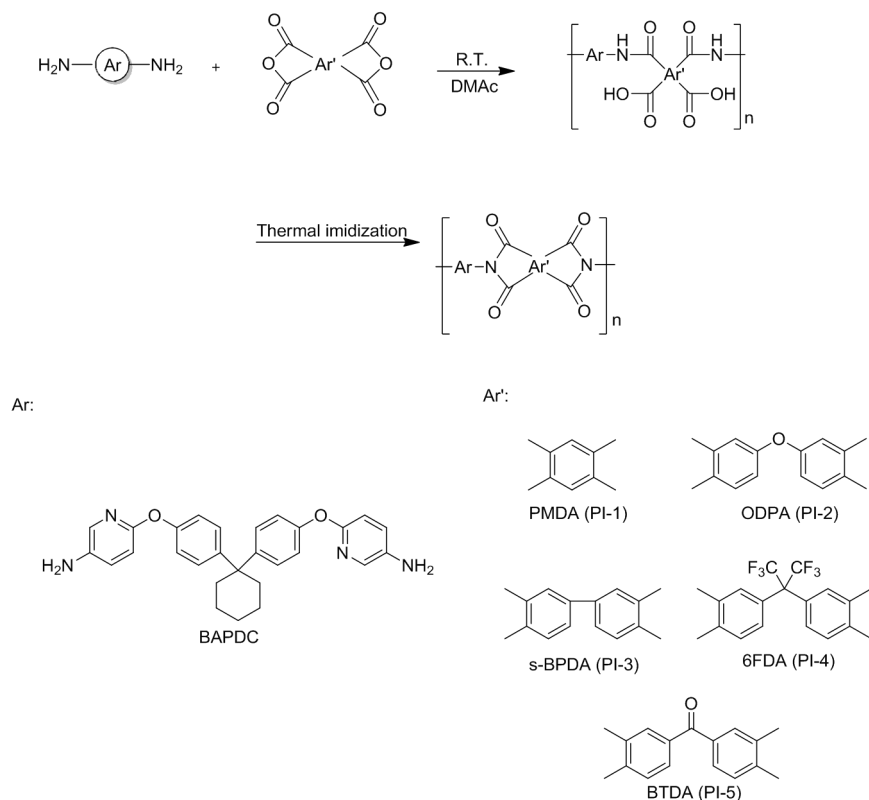
Monomer synthesis



Scheme 1. Synthesis route of diamine monomer

Polymer synthesis

PI films were prepared via a traditionally two-step polymerization process. The diamine monomer (BAPDC) was reacted with five kinds of commercially dianhydrides, PMDA, ODPDA, BPDA, BTDA, 6FDA, to give the synthetic route is shown in **Scheme2**.



Scheme 2. Synthesis route of the polyimides

3. Result and discussion

Thermal properties of polyimide films

The thermal behavior of polyimide films were determined by DSC, TGA, DMA and TMA and all results were in **Table 1**. The thermal analysis indicated a high thermal stability of the synthesized polyimides. The T_g s of the polyimides were found to be in the range of 243-327°C and 242-294°C, as obtained by DSC and DMA, respectively.

Table 1. Thermal properties of polyimides

	T_g (°C)		$T_{5\%}$ (°C) ^c		$T_{10\%}$ (°C) ^c		R_w ^d (%)	CTE ^e (ppm/K)
	DSC ^a	DMA ^b	N ₂	Air	N ₂	Air		
PI-1	327	294	477	445	490	479	35	49
PI-2	243	242	480	476	492	493	45	70
PI-3	268	258	490	472	503	498	51	57
PI-4	269	268	493	476	507	503	54	67
PI-5	259	255	474	463	488	490	51	59

Optical properties of polyimides

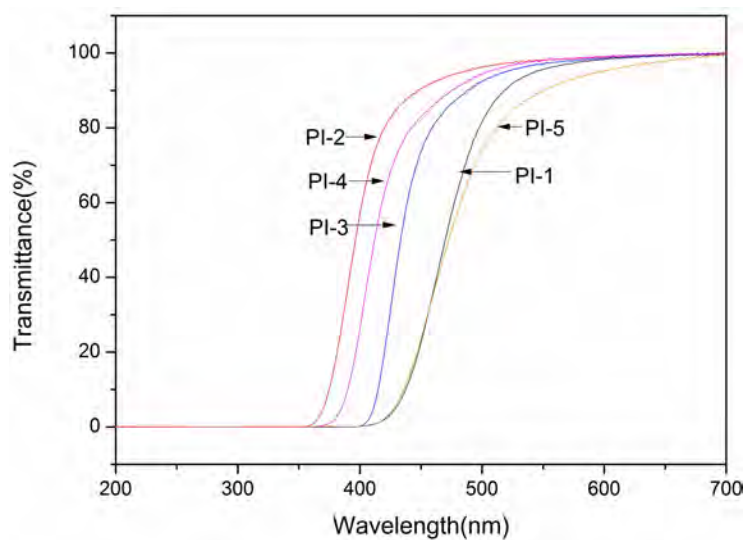


Fig 1. UV-visible spectra of the polyimides

The optical properties of polyimides were detected by UV-vis spectroscopy, and the results are presented in **Fig1**. All of polyimides show good transparency at the cut-off wavelength ($\lambda_{\text{cut-off}}$) of 355-398nm and the transmittances at 500nm.

Mechanical properties of polyimides

Table 2. Mechanical properties of polyimides

	T _S ^a (MPa)	T _M ^b (GPa)	E _B ^c (%)
PI-1	73±1.2 ^d	2.1±0.30	2.10±0.30
PI-2	95±3.4	2.0±0.09	10.90±2.06
PI-3	81±5.6	2.0±0.25	9.25±2.32
PI-4	89±4.3	1.9±0.14	7.90±0.83
PI-5	102±1.3	2.3±0.11	12.16±2.90

^a Tensile strength; ^b Tensile modulus; ^c Elongation at break; ^d 4.8 standard deviation.

The mechanical properties of PI films are summarized in **Table 2**. All of polyimides showed good mechanical properties with the tensile strength of 72-102MPa, tensile modulus of 1.9-2.3GPa and elongations at breakage of 2.1-12.16%.

Conclusions

A novel aromatic pyridine diamine was synthesized and characterized, which were employed to react with five various aromatic dianhydrides, through a traditional two-step polymerization method. The PIs containing pyridine were exhibited high transparency and the thermal stability did not deteriorate. The PIs are also given good mechanical properties, T_S of 73-102MPa, T_M of 1.9-2.3GPa, and E_B of 2.10-12.16%. The combination of pyridine and bulky group demonstrated a promising application of the polyimides.

REFERENCES

1. Liaw, D.-J., et al., *Advanced polyimide materials: syntheses, physical properties and applications*. Progress in Polymer Science, 2012. **37**(7): p. 907-974.
2. Sroog, C., *History of the invention and development of the polyimides*. PLASTICS ENGINEERING-NEW YORK-, 1996. **36**: p. 1-6.
3. Ohya, H., V. Kudryavsev, and S.I. Semenova, *Polyimide membranes: applications, fabrications and properties*. 1997: CRC Press.
4. Mittal, K.L., *Polyimides and other high temperature polymers: synthesis, characterization and applications*. Vol. 3. 2005: CRC Press.
5. Hergenrother, P.M., *The use, design, synthesis, and properties of high performance/high temperature polymers: an overview*. High Performance Polymers, 2003. **15**(1): p. 3-45.
6. Vandezande, P., L.E. Gevers, and I.F. Vankelecom, *Solvent resistant nanofiltration: separating on a molecular level*. Chemical Society Reviews, 2008. **37**(2): p. 365-405.
7. Périchaud, A., et al., *Auto-repairment of polyimide film coatings for aerospace applications challenges & perspectives*. 2012: INTECH Open Access Publisher.
8. Ma, X., et al., *Synthesis and gas transport properties of hydroxyl-functionalized polyimides with intrinsic microporosity*. Macromolecules, 2012. **45**(9): p. 3841-3849.
9. Guo, Y., et al., *Fluorinated bismaleimide resin with good processability, high toughness, and outstanding dielectric properties*. Journal of Applied Polymer Science, 2015. **132**(46).
10. Yokota, R., et al., *Molecular design of heat resistant polyimides having excellent processability and high glass transition temperature*. High Performance Polymers, 2001. **13**(2): p. S61-S72.