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Synthesis and Characterization of Novel Polyimides Based on Pyridine-containing Diamine

Shu Jiang ZHANG, Yan Feng LI*, Xiao Long WANG,
Da Xue YIN, Yu SHAO, Xin ZHAO

College of Chemistry and Chemical Engineering, State Key Laboratory of Applied Organic Chemistry, Institute of Biochemical Engineering & Environmental Technology, Lanzhou University, Lanzhou 730000

Abstract: A new aromatic diamine monomer containing pyridine unit, 2,6-bis (4-aminophenoxy-4'-benzoyl)pyridine(BABP), was synthesized in three steps, starting from 2,6-pyridinedicarboxyl chloride. A series of novel pyridine-containing polyimides were prepared *via* the polycondensation of BABP with various aromatic dianhydrides through poly(amic acid) precursors, and thermal or chemical imidization of the precursors. The polyimides exhibit desirable properties, *e.g.*, good solubility in N-methyl-2-pyrrolidone and *m*-cresol, excellent thermal stability and film-forming capability, as well as high inherent viscosity, indicating high molecular weight.

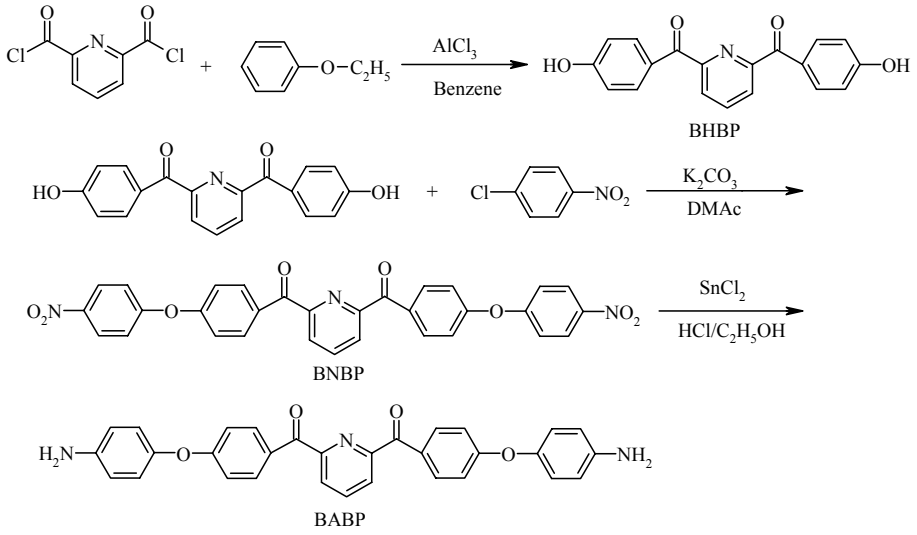
Keywords: Heteroaromatic polymer, polyimides, pyridine-containing monomer, synthesis, aromatic diamine.

Aromatic polyimides or their copolymers are well known as high performance polymers because of their excellent thermal, mechanical and electrical properties, so they have been widely employed in the fields of adhesives, composite matrices, fibers, films, foams, as well as electronic materials[1,2]. For the development of polyimides, synthesis of new monomers and related polyimides with both good processability and thermal stability would be a major research topic, and new monomers of aromatic diamine or dianhydride would play very important rules in synthesis of the imides[3,4]. Furthermore, pyridine would display excellent stabilities derived from its molecular symmetry and aromaticity, as well as polarizability resulting from the nitrogen atom in its ring [4,5], so new kinds of diamine, dianhydride or other monomers holding pyridine unit have been synthesized and employed in preparation of the polymer at elevated temperature[6,7].

In this work, a new diamine monomer, *i.e.* 2,6-bis(4-aminophenoxy-4'-benzoyl) pyridine (BABP), was synthesized in three steps, as shown in **Scheme 1**. Firstly, phenyl ethyl ether (0.32 mol) and $AlCl_3$ (anhydrous, 0.48 mol) were put into a flask with benzene, and 2, 6-pyridinedicarboxyl chloride(0.15 mol) was gradually added into the flask with stirring at 10-12℃, and heated slowly to 40℃, kept at this temperature that for 4 h, then cooled and poured into a water solution of HCl to precipitate the white solids,

* E-mail: liyf@lzu.edu.cn

Scheme 1 Synthetic route of diamine monomer containing pyridine ring



filtrated, washed with ethanol and recrystallized from methanol to get a white product, *i.e.* 2,6-bis(4,4'-dihydroxybenoxyl)pyridine (BHBP). 0.05 mol of BHBP was first dissolved in DMAc, then 0.104 mol of *p*-chloronitrobenzene and 0.105 mol of K_2CO_3 were added. The mixture was heated at 160℃ for 12 h with stirring under nitrogen then poured into a solution of ethanol and water(v/v=1), filtrated, the crude 2,6-bis(4-nitrophenoxy-4'-benzoyl)pyridine (BNBP) was recrystallized from acetone. A mixture BNBP(0.045 mol), anhydrous $SnCl_2$ (0.216 mol) and 500 mL of 95 % C_2H_5OH were put into a reaction flask and stirred, 20 mL of concentrated hydrochloric acid was added slowly, then the mixture was refluxed for 12 h. Excess ethanol was evaporated, and the remaining solution was poured into distilled water, basified with 15% NaOH solution. The precipitate was filtrated, washed with water and methanol, recrystallized from toluene to get a yellow product(BABP). The spectra analysis and exprimental data of diamine monomer BABP and its intermediate BHBP, BNBP were listed in **Table 1** and **Table 2**, respectively.

The novel polyimides were prepared by polycondensation of diamine monomer BABP with dianhydride monomer PMDA, ODPA, BTDA and 6FDA. The given amount of BABP was first dissolved in a given amount of dry NMP, then equimolar monomer of dianhydride was added slowly and reacted with the BABP dissolved in NMP, the polycondensation reaction were kept for 24 h at room temperature to form a poly (amic acid) solution, the resulting poly(amic acid)s would be changed into polyimides by either thermal imidization or chemical imidization at the final stage, as shown in **Scheme 2**. For the thermal imidization process, the obtainted poly(amic acid) solution was poured into a glass culture dish and placed in a 90℃ oven overnight for removal of the solvent to get the related film. The film was further dried and transformed into polyimide by heating at 150℃ for 30 min, 200℃ for 30 min, and 280℃ for 1 h. While

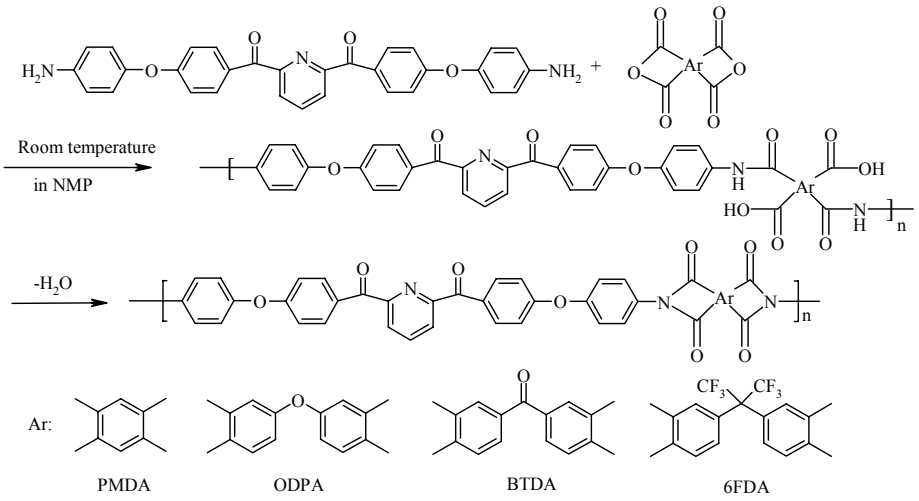
Table 1 Spectral analysis of BHBP, BNBP and BABP(δ ppm, DMSO-d_6)

Compds No.	IR(KBr)/cm^{-1}	δ_C	δ_H
BHBP	3352-3251(s) 1671 (s) 1326 (b)	190.9(2C);162.4(2C);154.2(2C); 138.8(1C);133.3(2C);126.7(2C); 125.8(2C); 115.0(2C)	10.51(s,2H); 8.28-8.20(t, 1H, J=8.4Hz); 8.09-8.06(d, 2H, J=7.4Hz);7.95-7.09(d, 4H, J=8.6Hz); 6.86-6.21 (d,4H,J=8.4Hz)
BNBP	1659 (s) 1582,1345(s) 1326 (b)	191.1(2C);161.3(2C);158.3(2C); 153.0(2C);142.9(2C);139.4(1C); 133.5(2C);132.2(4C);127.0(2C); 126.1(4C);119.2(4C);118.5(4C)	8.37-8.33(m, 3H);8.28-8.24(d, 4H, J=5.6Hz); 8.16-8.12(d, 4H, J=9.6Hz); 7.27-7.22(d, 4H, J=8.4Hz); 7.20-7.15 (d, 4H, J=11.6Hz)
BABP	3418,3345(b) 1571 (s) 1333 (s)	191.2(2C);163.3(2C);153.7(2C); 146.2(2C);144.0(2C);138.6(1C); 133.2(4C);129.0(2C);126.4(2C); 121.3(4C),115.2(4C); 114.9 (4C)	8.27-8.25(t, 1H, J=7.6Hz); 8.16-8.14(d, 2H, J=8.0Hz); 7.98-7.96(d, 4H, J=6.8Hz); 6.89- 6.87(d, 4H, J=6.8Hz); 6.81-6.80(d, 4H, J= 4.4Hz); 6.62-6.12(d, 4H, J=4.8Hz); 5.11(-NH_2)

Table 2 Experimental data of BHBP, BNBP and BABP

Compds No.	Yield (%)	m.p./℃	Molecule formula	Elemental Analysis (wt.%)			
					C	H	N
BHBP	74	279-281	$C_{19}H_{13}NO_4$	Calcd.	71.47	4.10	4.39
			(319.32)	Found	71.39	4.12	4.37
BNBP	82	196-198	$C_{31}H_{19}N_3O_8$	Calcd.	66.31	3.41	7.48
			(561.51)	Found	66.14	3.36	7.25
BABP	94	186-188	$C_{31}H_{23}N_3O_4$	Calcd.	74.24	4.62	8.38
			(501.55)	Found	73.87	4.66	8.16

Scheme 2 Synthesis of the polyimides



chemical imidization was carried out by additing mixture of equimolar pyridine and acetic anhydride into the poly(amic acid) solution with stirring at room temperature for 1 h, and then heated at 100℃ for 3 h. The resulting polyimide solution was poured into methanol to give fibrous precipitate, which was collected and dried. The FT-IR spectrum of polyimides based on the diamine monomer(BABP) indicated that absorptions at 1777, 1721cm^{-1} are the symmetric and asymmetric absorption of imide carbonyl groups respectively, there is no absorption of N-H vibration at 3418 and 3345 cm^{-1}, which indicated that imide ring was fully formed in the resulting polyimide. Meanwhile, the polyimides derived from polycondensation of BABP with PMDA, ODPA, BTDA and 6FDA hold inherent viscosity 1.02, 0.68, 0.74 and 0.54 dL/g respectively, while their degradation temperatures for 5% weight loss in air appear at 452 ℃, 507℃, 453℃ and 477℃, respectively, all of them exhibit good solubility in *m*-cresol and NMP at the same time.

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