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Synthesis of a new aromatic diacid containing pyridine ring and related polybenzimidazole

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Abstract

A new aromatic diacid monomer containing pyridine unit, 4-phenyl-2,6-bis[4-(4-carboxyphenoxy) phenyl] pyridine **3**, was successfully synthesized in three steps, starting from 4-hydroxyacetophenone. The corresponding pyridine-containing polybenzimidazole was prepared *via* polycondensation of **3** with tetraaminodiphenyl ether (TADE) in poly(phosphoric acid) (PPA). The resulting polybenzimidazole exhibits excellent solubility, good thermal stabilities and high thermal resistance.

Keywords: Polybenzimidazoles; Pyridine-containing diacid monomer; Synthesis; Thermal stabilities

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Polybenzimidazoles (PBIs) are well known as an excellent high performance resin because of their outstanding thermal stability, thermoplastic toughness, dispersibility, and chemical stability [1]. However, their applications have been limited due to polybenzimidazoles are normally insoluble in common organic solvents and have extremely high glass-transition temperatures or melting temperatures, which preclude melting processing. For the development of polybenzimidazoles, synthesis of new monomers and related polybenzimidazoles with both good processability and thermal stability would be a major research topic, and new monomers of aromatic diacid would play important rules in synthesis of polybenzimidazoles [2,3]. Aromatic ether linkages in polymer main chains provide them significantly lower energy of internal rotation. In general, such a structural modification leads to a lower glass-transition temperature (T_g) and lower crystalline melting temperature as well as a significantly improvement in the solubility and process characteristics without greatly sacrificing thermal stability. It is generally recognized that aryl-ether linkage can impart better solubility and melt processing characteristics and improve toughness in comparison with those of polymers without aryl-ether linkage.

The PBIs are generally synthesized by the step growth polymerization of tetramine with an aromatic diacid or diacid derivate in poly(phosphoric acid) (PPA) as a reaction medium, activates both functional groups toward condensation, and reacts with the water formed by the polycondensation to effectively dehydrate the system [4]. In

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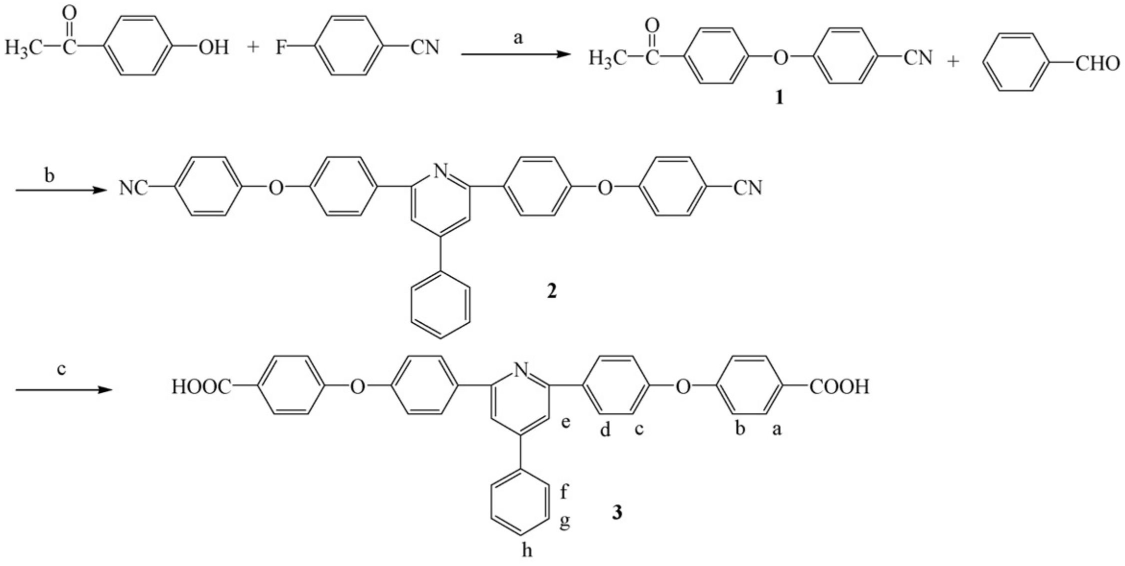


Scheme 1. Synthesis of diacid monomer **3** (a) DMF, K_2CO_3, 90 °C, 8 h;(b) HAc, NH_4Ac, reflux,24 h;(c) H_3PO_4, reflux, 2 h.

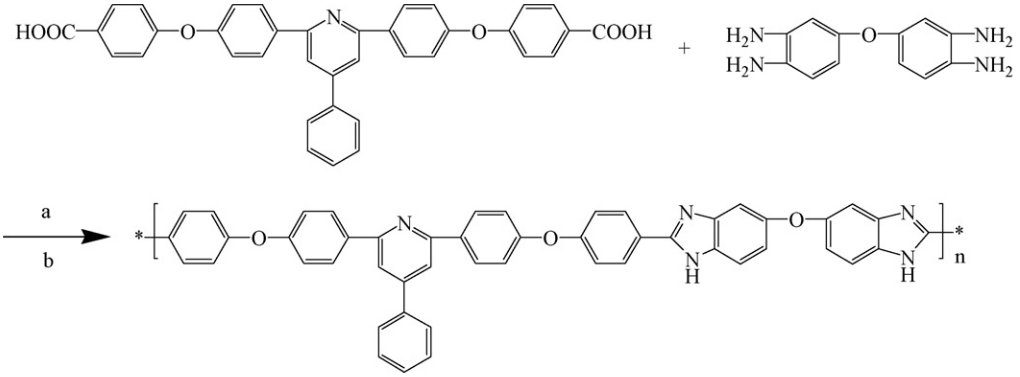
addition, the solvents of the step growth polymerization have been reported such as cresol, phenol, dimethyl sulfoxide, dimethyl formamide, sulfolane and diphenylsulfone [5,6].

In this work, a new aromatic diacid monomer containing pyridine unit, 4-phenyl-2,6-bis[4-(4-carboxyphenoxy)-phenyl] pyridine **3**, was successfully synthesized by using 4-hydroxyacetophenone as starting material, as shown in Scheme 1. Firstly, 0.05 mol of 4-hydroxyacetophenone, 0.051 mol of 4-fluorobenzonitrile and 0.1 mol of K_2CO_3 were added into a flask with 100 mL of DMF.

The mixture was heated at 90 °C for 8 h with stirring under nitrogen. After cooling down, the mixture was poured into a solution of ethanol and water (v/v = 1), the precipitation was filtrated. The crude product **1** was got and recrystallized from ethanol. A mixture **1** (0.05 mol), benzaldehyde (0.025 mol), ammonium acetate (0.625 mol) and 40 mL of glacial acetic acid were placed into a 250-mL three-necked flask equipped with a mechanical stirred and a reflux condenser. The mixture was refluxed with stirring for 24 h. Then the solid 4-phenyl-2,6-bis[4-(4-nitrilephenoxy)phenyl]pyridine **2** was filtered off and washed thoroughly with glacial acetic acid and water, respectively. Finally, in a 250-mL three-necked flask equipped with a mechanical stirrer, a thermometer, and a reflux condenser, **2** (0.01 mol) and 130 mL of 85% phosphoric acid were added and refluxed for 2 h. After cooling to room temperature, the mixture was poured into 600 mL of cold, dilute aqueous potassium hydroxide. The solution was stirred at room temperature for 6 h after modulating the pH value to 11, and then the solution was neutralized with 6 M

Table 1
Experimental data of compound.

Compounds	Yield (%)	m.p. (°C)	Molecule formula	Elemental analysis (wt.%)			
					C	H	N
1	88	81–84	$C_{15}H_{11}NO_2$ (237.08)	Calcd.	75.94	4.67	5.90
				Found	75.92	4.66	5.84
2	41	221–225	$C_{37}H_{23}N_3O_2$ (541.18)	Calcd.	82.05	4.28	7.76
				Found	81.98	4.35	7.78
3	82	136–140	$C_{37}H_{25}NO_6$ (579.17)	Calcd.	76.67	4.35	2.42
				Found	76.74	4.32	2.38



Scheme 2. Synthesis of polybenzimidazole (a) PPA, 120 °C, 3 h; (b) 200 °C, 12 h.

hydrochloric acid to pH 3–4, followed by stirring for 6 h. The product was collected by filtration and recrystallized from 50% of aqueous acetic acid using activated charcoal. Melting point of **3** is 136–140 °C. The experimental data of diacid monomer **3** and its intermediates **1**, **2** were listed in Table 1, respectively. The FABMS, *m/z*, shows M^+: 579.4 (31%). FT-IR (KBr) peaks of **3** at 2500–3500 cm^{-1} and 1235 cm^{-1} belonged to CO(O)H and C–O–C groups, respectively. ^1H NMR (200 MHz, DMSO-d_6): δ 8.44 (d, 4H, $J = 8.4$, H_a), 8.22 (s, 2H, $H_{e)}$, 8.05 (d, 4H, $J = 6.2$, H_d), 7.89 (d, 2H, $J = 8.8$, H_f), 7.57 (d, 2H, $J = 7.2$, H_g), 7.32 (d, 1H, $J = 8.6$, H_h), 7.20 (d, 8H, $J = 8.6$, H_b, H_c), and ^{13}C NMR (200 MHz, DMSO-d_6): δ 166.7, 160.6, 159.7, 156.3, 155.7, 137.6, 135.0, 131.7, 130.7, 129.1,127.4, 126.5, 125.6, 119.9, 118.7, 117.6, respectively. Elemental analysis for $C_{37}H_{25}NO_6$: calcd. C 76.67, H 4.35, N 2.42, found C 76.74, H 4.32, N 2.38. The data agree with the structure of **3**.

Related polybenzimidazole was synthesized by polycondensation of **3** and aromatic tetramine TADE *via* previously method, as shown in Scheme 2 [7]. Firstly, a 250-mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet, and an outlet $CaCl_2$ drying tube was charged with PPA (40 g) and stirred with heating under constant flow of nitrogen above 120 °C. The system was flushed with nitrogen for 10 min to remove the air then the diacid (1 mmol) and tetramine (1 mmol) was added, the temperature was slowly raised to 200 °C for 12 h. The hot solution was poured into water (150 mL) and solid polymer was filtrated and stirred in 5% aqueous sodium bicarbonate solution (5 h). The polymer was collected by filtration and washed with water until neutral. The inherent viscosity of the resulting polybenzimidazole in the NMP solution with a 0.5 g dL^{-1}concentration at 30 °C was 0.251 g dL^{-1}. FT-IR spectra of the resulting polybenzimidazole revealed strong bands at 3378 cm^{-1} due to N–H group, 1597 cm^{-1} due to C=N group and 1082 cm^{-1} due to benzimidazole. The TGA curve in nitrogen exhibited two-stage degradation processes. The value of 5% and 10% gravimetric loss in air (T_5 and T_{10}) of the resulting polybenzimidazole is 558 and 598 °C, which showed the polybenzimidazole has good thermal stability. It also exhibited good solubility in common organic solvents such as DMSO, NMP and *m*-cresol. According to the experimental results above, the new pyridine-containing aromatic diacid monomer **3** also holds good polymerizability.

Acknowledgments

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