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Synthesis of a new pyridine-containing diamine and related polyimide

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Abstract

A new kind of aromatic diamine monomer containing pyridine unit, 2,6-bis[4-(4-aminophenoxy)phenoxy]pyridine (BAPP), was synthesized in three steps, using hydroquinone as starting material. A novel pyridine-containing polyimide was prepared from the resulting diamine BAPP with 4,4′-oxydiphthalic anhydride (ODPA) via a conventional two-step thermal imidization method. The resulting polyimide exhibits excellent solubility, film-forming capability and high thermal resistance.

Keywords: Pyridine; Aromatic polyimide; Pyridine-containing diamine

Aromatic polyimides have been widely used in aerospace, electrical and electronic applications, composite material and optoelectronical industries because of their excellent thermal, mechanical and electrical properties as well as outstanding chemical resistance [1–3]. Despite their outstanding properties, most of them have high melting temperatures or softening temperatures and limited solubility in most solvents because of their rigid backbones and strong interactions between chains, which restrict their application in corresponding fields [4]. To overcome these problems, much research effort has been focused on the synthesis of soluble and processable polyimides in fully imidized form without deterioration of their own excellent properties. Several approaches to soluble polyimides including introduction of flexible linkage and heteroaromatic rings into the polymer backbone have been developed in the past decade [5,6]. The pyridine rings with heteroaromatic structure have excellent stabilities derived from its molecular symmetry and aromaticity, introduction of aryl–ether linkage into the polymer chains can improve the solubility, so the incorporation of aryl–ether linkage and pyridine rings into polyimide backbone would improve the solubility without deterioration of their own excellent properties.

In this work, a new pyridine-containing diamine, 2,6-bis[4-(4-aminophenoxy)phenoxy]pyridine (BAPP) **3**, was synthesized by a three step procedure, as shown in Scheme 1. Firstly, 4-(4-nitrophenoxy)phenol **1** was synthesized through the nucleophilic etherification of 4-chloronitrobenzene (0.8 equiv.) with potassium phenolate of hydroquinone (1.0 equiv.) in dimethylformamide (DMF). Then the dinitro compound, 2.6-bis[4-(4-nitrophenoxy)phenoxy]pyridine **2** was synthesized by nucleophilic substitution reaction of **1** (2.1 equiv.) and 2.6-dichloropyridine

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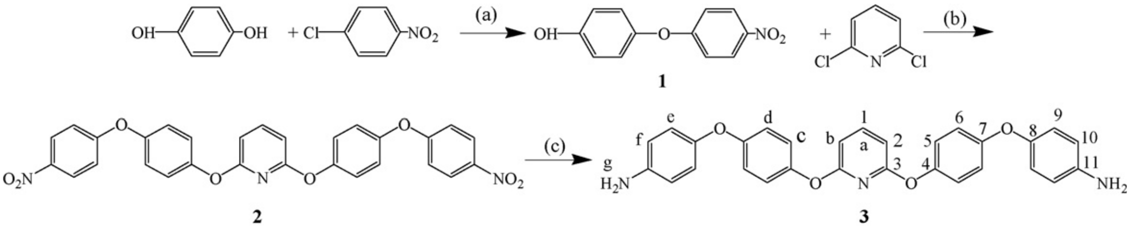

Scheme 1. Synthesis of 2,6-bis[4-(4-aminophenoxy)phenoxy]pyridine (BAPP). (a) DMF, K_2CO_3, 100 °C, 10 h; (b) DMAC, K_2CO_3, 150 °C, 24 h; (c) $NH_2NH_2{\cdot}H_2O$, Pd/C, CH_3CH_2OH, 80 °C, 6 h.

(1.0 equiv.) in the presence of anhydrous potassium carbonate (2.1 equiv.) in dimethylacetamide (DMAc). Finally **2** was converted to the corresponding diamine monomer **3** by hydrazine Pd/C-catalyzed reduction, the corresponding yield was 66%, 50% and 95%. The MS(ESI) of **3**, *m/z*, shows $(M+1)^+$: 478.1. Its ^{1}H NMR (400 MHz, $CDCl_3$, δ) data were at δ 7.60 (t, 1H, $J = 8.0$ Hz, H-a), 7.01 (d, 4H, $J = 9.2$ Hz, H-c), 6.87 (m, 8H, H-d, H-e), 6.65 (d, 4H, $J = 8.8$ Hz, H-f), 6.47 (d, 2H, $J = 8.0$ Hz, H-b), 3.40 (broad, 4H, H-g), and ^{13}C NMR (400 MHz, $CDCl_3$, δ) absorption peaks appeared at δ 162.68(C^3), 155.43(C^7), 148.86(C^4), 148.32(C^8), 142.60(C^{11}), 141.99(C^1), 122.27(C^5), 120.76(C^6), 118.02(C^9), 116.22(C^{10}), 103.63(C^2). Elem. Anal. Calcd. for $C_{29}H_{23}N_3O_4$ (477.17): C 72.94%, H 4.85%, N 13.40%. Found: C 72.90%, H 4.87%, N 13.38%. The data agree with the structure of BAPP.

The related polyimide was synthesized by polycondensation of BAPP and aromatic dianhydride ODPA via previous method [7]. The inherent viscosity of the resulting polyimide in the DMF solution with a 0.5 g/dL concentration at 30 °C was 0.46 dL/g. FT-IR spectra of the resulting polyimide revealed strong bands at 1776 cm^{-1} (asymmetrical C=O stretch), 1717 cm^{-1} (symmetrical C=O stretch), 1376 cm^{-1} (C–N stretch) and 1111 and 745 cm^{-1} (imide ring deformation), which indicated that imide ring was fully formed. The value of 5% gravimetric loss and 10% gravimetric loss in nitrogen of the resulting polyimide is 501 °C and 527 °C, and its *Tg* is 274 °C, which showed the polyimide has excellent thermal stability. It also exhibited good solubility in common organic solvents such as DMF, DMAc, dimethyl sulfoxide and tetrahydrofuran. Meanwhile, the resulting polyimide has excellent film-forming capability; a strong and flexible film could be obtained. The polyimide film has tensile strength of 101.2 MPa, elongation at break of 9.6%, and tensile modulus of 1.43 GPa. According to the above experimental results, the new pyridine-containing diamine BAPP holds good polymerizability.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2009.11.004.

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