

Available online at www.sciencedirect.com



Chinese Chemical Letters 23 (2012) 121-122

CHINESE Chemical Letters

www.elsevier.com/locate/cclet

Novel organosoluble polyimide based on an asymmetric bis(ether amine): 3, 4'-Bis(4-aminophenoxy)-benzophenone

Qian Qian Bu, Shu Jiang Zhang, Hui Li, Yan Feng Li *

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

> Received 5 May 2011 Available online 8 November 2011

Abstract

A new kind of asymmetrical ether diamine, 3,4'-bis(4-aminophenoxy)benzophenone (BABP), was synthesized from the nucleophilic substitution reaction of 4-chloronitrobenzene and 3,4'-dihydroxybenzophenone in the presence of potassium carbonate, followed by catalytic reduction with SnCl₂·6H₂O and concentrated hydrochloric acid. The prepared diamine was employed in the preparation of a novel polyimide containing asymmetrical diaryl ether segments *via* the polycondensation of it with BTDA by a two-step method. The resulting polyimide exhibits excellent solubility, film-forming capability and high thermal resistance.

© 2011 Yan Feng Li. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.

Keywords: Asymmetrical diamine; Ether diamine; Organosoluble polyimide

It is well known that polyimides hold outstanding properties, however, 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 [1–4]. For the progress of polyimide materials, the synthesis of new aromatic monomers and related polyimides with both good solubility and maintained thermal stability would be a major research topic focused. In general, several approaches have been devoted to enhancing the solubility of polyimides, including introduction of flexible linkage and geometrically or molecularly asymmetric structures into the polymer backbone [5,6]. Introduction of aryl–ether linkage and asymmetric structure into the aromatic polyimide chains can improve the solubility without deterioration of their own excellent properties, but there are many difficulties in synthesis and purification of asymmetric diamine monomer.

In this paper, a new kind of asymmetric diamine with aryl–ether linkage, 3,4'-bis(4-aminophenoxy)-benzophenone **4** had been designed and synthesized as a potentially convenient condensation monomer to form asymmetric ether polyimides. The diamine monomer, **4**, was prepared in a high yield of 86% by the catalytic reduction of intermediate dinitro compound, **3**, which was obtained by a nucleophilic chloro-displacement reaction of 4-chloronitrobenzene (2 equiv.) with **2** (1 equiv.) in the presence of potassium carbonate in dimethylacetamide in 72% yield. **1** was synthesized through the Friedel–Crafts acylation of 3-methoxybenzoyl chloride (1 equiv.) with anisole (1 equiv.) in CH₂Cl₂ in 93%

* Corresponding author.

E-mail address: liyf@lzu.edu.cn (Y.F. Li).

^{1001-8417/\$-}see front matter © 2011 Yan Feng Li. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved. doi:10.1016/j.cclet.2011.09.014



Scheme 1. Synthesis of 3,4'-bis(4-aminophenoxy)-benzophenone (BABP).

yield, which was converted to **2** by demethylation reaction in the present of HBr and CH₃COOH in 92% yields, as shown in Scheme 1. In the FT-IR of **4**, peaks at 3442 cm⁻¹ and 3408 cm⁻¹ belonged to $-NH_2$ groups. The absorptions at 1234 cm⁻¹ were assigned to the C–O–C stretching vibration, confirming the presence of the aromatic ether linkage. In its ¹H NMR (400 MHz, DMSO-*d*₆) spectrum following signals were observed: δ 7.67 (d, 2H, *J* = 8.8 Hz, H-7), 7.42 (dd, 1H, *J* = 8.0 Hz, 8.0 Hz, H-4), 7.24 (d, 1H, *J* = 8.0 Hz, H-5), 7.11 (dd, 1H, *J* = 8.0 Hz, 2.8 Hz, H-3), 7.04 (s, 1H, H-6), 6.90 (d, 2H, *J* = 8.8 Hz, H-8), 6.79 (d, 2H, *J* = 7.8 Hz, H-9), 6.76 (d, 2H, *J* = 7.6 Hz, H-2), 6.58 (d, 2H, *J* = 7.6 Hz, H-10), 6.55 (d, 2H, *J* = 7.6 Hz, H-1), 5.05 (s, 2H, Ha), 4.97 (s, 2H, Hb), and ¹³C NMR absorption peaks appeared at δ 194.23, 163.43, 159.53, 146.75, 146.35, 145.28, 144.54, 139.45, 132.71, 130.52, 130.35, 123.35, 121.88, 121.59, 120.69, 116.63, 115.36, respectively. Elem. Anal. Calcd. for C₂₅H₂₀N₂O₃ (396.44): C 75.74%, H 5.08%, N 7.07%. Found: C 75.90%, H 4.97%, N 7.18%. The data agree with the structure of **4**.

The related polyimide was synthesized by polycondensation of BABP and aromatic dianhydride BTDA *via* previous method [7]. The inherent viscosity of the resulting polyimide in the *N*,*N*-dimethylformamide solution with a 0.5 g/dL concentration at 30 °C was 0.48 dL/g. FT-IR spectra of the resulting polyimide revealed strong bands at 1782 cm⁻¹ (asymmetrical C=O stretch), 1721 cm⁻¹ (symmetrical C=O stretch), 1375 cm⁻¹ (C–N stretch) and 1111 cm⁻¹ and 754 cm⁻¹ (imide ring deformation), which indicated that imide ring was fully formed. The values of 5% weight loss and 10% weight loss in nitrogen of the resulting polyimide is 504 °C and 536 °C, and its T_g is 248 °C, which showed the polyimide has excellent thermal stability. It also exhibited good solubility in common organic solvents such as *N*,*N*-dimethylformamide, dimethylacetamide, dimethyl sulfoxid and tetrahydrofuran. Compared with the analogous polyimide, which were prepared from a symmeric diamine, 4,4'-bis(4-aminophenoxy)-benzophenone [8], the polyimide BABP–BTDA can improve the solubility without sacrificing the thermal properties a lot. Meanwhile, a strong and flexible film could be obtained, indicting the resulting polyimide has excellent lm-forming capability. According to the above experimental results, the new ether-containing asymmetric diamine BABP holds good polymerizability.

Acknowledgments

The authors acknowledge the financial support from the Natural Science Foundation of Gansu Province (No. 096RJZA047) and the Fundamental Research Funds for the Central Universities (No. lzujbky-2011-24).

References

- [1] M.K. Ghosh, K.L. Mittal, Polyimides: Fundamentals and Applications, Marcel Dekker, New York, 1996, p. 348.
- [2] C.W. Chang, H.J. Yen, K.Y. Huang, et al. J. Polym. Sci. Part A: Polym. Chem. 46 (2008) 7937.
- [3] Z. Li, J.G. Liu, Z.Q. Gao, et al. Eur. Polym. J. 45 (2009) 1139.
- [4] C.P. Yang, Y.Y. Su, Polymer 46 (2005) 5797.
- [5] X.L. Wang, Y.F. Li, S.J. Zhang, et al. Eur. Polym. J. 42 (2006) 1229.
- [6] Y. Shao, Y.F. Li, X. Zhao, et al. J. Polym. Sci. Part A: Polym. Chem. 44 (2006) 6836.
- [7] S.J. Zhang, Y.F. Li, D.X. Yin, et al. Eur. Polym. J. 41 (2005) 1097.
- [8] C.P. Yang, F.Z. Hsiao, J. Polym. Res. 10 (2003) 181.