SYNTHESIS OF POLY (BIBENZIMIDAZOLE-P-PHENYL- BENZOBISOXAZOLE)

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ABSTRACT

A diacid monomer of benzobisoxazole 2, 6-di(p-phenylene-carboxylic) acid (BBODPA) was synthesized in a simple procedure, and characterized by means of FTIR, ¹H NMR and ¹³C NMR. The resulting BBODPA was polymerized with 3, 3'-diaminobenzidine tetrahydrochloride (DAB) to prepare poly (bibenzimidazole-p-phenyl-benzobisoxazole) (PBBIBBO) in polyphosphoric acid. The inherent viscosities values of PBBIBBO indicated that it was a kind of high molecular weight polymer. The structure of PBBIBBO was confirmed by ¹H NMR, ¹³C NMR and FTIR. Thermal properties and dissolubility of PBBIBBO were also investigated. These results showed that PBBIBBO exhibited good thermal stability.

Key words: Copolymer, polybenzimidazole, polybenzoxazole, thermal stability

INTRODUCTION

Polybenzimidazole (PBI) and polybenzoxazole (PBO) have received considerable attention since 1960s, due to their chemical resistance, thermal stability and good mechanical properties at high temperature.^{1,2} Fibers,^{3,4} foams,^{5,6} membrane^{7,8} and structural materials^{9,10} of PBI and PBO have been extensively investigated. Melt polycondensation^{2,11} and solution polycondensation¹²⁻¹⁶ have been frequently used to synthesize PBI and PBO. Attempts have been made to combine polybenzimidazole with polybenzoxazole, in order to obtain more thermal stable and tractable polymers. For example, copolymers containing both PBI and PBO segments have been prepared.^{17,18} The authors claimed that phase separation reaction would not easily take place compared with the solution mixture of polybenzimidazole and polybenzoxazole.

In the present study, homopolymer of poly (bibenzimidazole-p-phenyl-benzobisoxazole) (PBBIBBO) was synthesized. Benzobisoxazole 2, 6-di(p-phenylene-carboxylic) acid (BBODPA) was firstly synthesized using 4, 6-Diaminoresorcinol Dichloride (DAR) and paraphthaloyl chloride (PPC), as described in Scheme 1. Then the resulting BBODPA polymerized with 3, 3'-diaminobenzidine tetrahydrochloride (DAB) in polyphosphoric acid (PPA) to prepare PBBIBBO (Scheme 2). The compound of PBBIBBO which combined both benzoxazole groups and benzimidazole groups on the polymer chain was expected to find a place in preparing fiber and membrane materials.

Scheme 1. Synthesis of BBODPA.

Scheme 2. Synthesis of PBBIBBO.

EXPERIMENTAL

Materials

DAB and DAR were prepared by the procedures of Herward and Marvel.² Benzidine, m-phenylene diamine, paraphthaloyl chloride, polyphosphoric acid, phosphorus pentoxide and acetic acid were obtained from commercial sources and used as received.

Methods

A Bruker AV-400 type superconducting magnetic resonance spectrometer (400 MHz, using H₂SO₄-d₂ as solvents) was performed to record the ¹H-nuclear

magnetic resonance spectra (¹H NMR) and ¹³C-nuclear magnetic resonance spectra (¹³C NMR). Fourier transform infrared (FTIR) spectra were obtained with a Bruker IFS66v/S Fourier transformation spectrophotometer (KBr discs). Thermal gravimetric analysis (TGA) was performed using a STA449C device (NETZSCH, Germany). The samples for TGA were placed in 75 µl Al₂O₃ pans and heated from 25 °C to 1000 °C at a heating rate of 10 °C/min, under a constant N₂ flow of 20 ml/min. Inherent viscosities ($\eta_{inh} = \ln \eta_{ra}/C$) of polymers were determined for solution of 0.5 g/dl in H₂SO₄ (98%) at 30 °C using a Ubbelohde viscometer.

Synthetic procedure for the monomer of BBODPA

In a three necked 2000 ml round bottom flask equipped with a mechanical stirrer and nitrogen inlet was placed 500 ml of PPA, 54.46 g (0.40 mol) of PPC and 2.5 g of SnCl₄·2H₂O. In to this flask 49.82 g (0.20 mol) of DAR (C₆H₈N₂O₂·2HCl·2H₂O) was added gradually and dissolved to prevent the carry-over of the reactant by the emitting HCl under 105 °C. Once that the addition was finished the temperature was raised to 200 °C and kept at this temperature for 7 h. The product was isolated by pouring the hot solution into water, washing with water, dipping in dilute KOH overnight and drying in a vacuum oven at 50 °C for 24 h. The yield of BBODPA was 95%.

Preparation of PBBIBBO

A 2000 ml three-necked flask equipped with a stirrer and nitrogen inlet was charged with 1000 ml of PPA (P₂O₅ ≥ 85%) and 2 g of SnCl₄·2H₂O. The flask was then placed into a silicone oil bath preheated to 105 °C. Into this flask, 40.8035 g (0.1030 mol) of DAB (C₁₂H₈N₄·4HCl·2H₂O) was added gradually and dissolved to prevent the carry-over of the reactant by the emitting HCl. To the resulting mixed solution 43.60 g (0.10 mol) of BBODPA (C₂₂H₁₂N₂O₆·2H₂O) were added. Under a thin stream of nitrogen, the solution was heated at 200 °C for 12 h. The polymeric target product was isolated by pouring the hot solution into water, washing with water by decantation, dipping in dilute KOH overnight, washing thoroughly with water and CH₃OH, and drying in a vacuum oven at 50 °C, generating 46.42 g of PBBIBBO.

RESULTS AND DISCUSSION

Monomer syntheses

We have attempted to use benzobisoxazole 2, 6-di carboxylic acid (BBODPA) (Figure 1) as the monomer to synthesize PBBIBBO. However, BBODPA decomposed under 140 °C. Leonard and Kaimierczak suggested that the 2-carboxyl acid in benzoxazole or benzimidazole molecular were thermally unstable.¹⁹ These results agreed with our research. It seems that the carboxylic acid on the 2-benzoxazole or 2-benzimidazole was thermally unstable. The phenyl carboxylic acid like BBODPA was more thermally stable and selected as the monomer to synthesize the PBBIBBO.

Fig. 1. Molecular structures of (a) BBODPA and (b) BBODPA.

The monomer of BBODPA was prepared by solution method, as depicted in Scheme 1. The resulting BBODPA is confirmed by FTIR and ^1H NMR and ^{13}C NMR. Figure 2 shows the FTIR spectrum of BBODPA. It is observed that a broad O-H stretch is presented at $2000\text{--}3700\text{ cm}^{-1}$, 20 carbonyl group at 1688 cm^{-1} (C=O acidic, stretching), asymmetric C=C at 1610 cm^{-1} (C=C, stretching) and CN of benzoxazole at 1268 cm^{-1} (C=N, stretching).

Fig. 2. FTIR spectra of (a) PBBIBBO and (b) BBODPA.

The ^1H NMR spectrum of BBODPA was obtained in deuterated sulfuric acid. The aromatic proton was observed at 7.9–8.5 ppm. It should be noted that BBODPA was almost insoluble in DMSO and CHCl_3 . $\text{H}_2\text{SO}_4\text{-d}_2$ was used as solvent to acquire the ^1H NMR spectrum. The proton of carboxylic acid (COO-H) was not observed, which was attributed the proton-exchange between $\text{H}_2\text{SO}_4\text{-d}_2$ and carboxylic acid group of BBODPA.

^1H NMR ($\text{H}_2\text{SO}_4\text{-d}_2$, δ ppm): 7.95 (benzobisoxazole, 1H), 8.20 (benzene, 2H), 8.39 (benzene, 2H), 10.5 (H_2SO_4 , solvent).

^{13}C NMR ($\text{H}_2\text{SO}_4\text{-d}_2$, δ ppm): 111.0, 120.5, 125.3, 127.4, 128.4, 129.4, 145.3, 163.3, 170.4.

Polymer synthesis

The obtained PBBIBBO was a high molecular weight polymer, as evidenced from its inherent viscosities (η_{inh}) values of 4.2 dL/g for the polymer. Figure 2 show the FTIR spectrum of PBBIBBO. As can be seen, there is no strong O-H stretch at $2000\text{--}3700\text{ cm}^{-1}$ and carbonyl group at 1689 cm^{-1} , indicating that complete closure of the oxazole rings in the polymerization has been achieved. The characteristic peaks of BBODPA and PBBIBBO in FTIR spectra are listed in Table 1.²¹

Table 1. Summary of FTIR spectra of BBODPA and PBBIBBO.

Assignment	Frequency (cm^{-1})	
	BBODPA	PBBIBBO
C=O stretch	1689	
Asym. C=C stretch	1610	1618
Hetero-ring stretch (vs)	1498	1480
1, 4- C_6H_4	1409	1413
Hetero-ring stretch (vs)	1365	1364
Hetero-ring 'breathing' (vs)	1108	1110
1, 2, 4, 5- C_6H_2 (s)	864	848

The ^1H NMR spectrum of PBBIBBO was obtained in deuterated sulfuric acid. The proton of aromatic was observed at 7.6–8.5 ppm. The proton of

benzimidazole was not observed, like that of BBODPA, which was attributed the proton-exchange between $\text{H}_2\text{SO}_4\text{-d}_2$ and benzimidazole moiety.

The characterization by ^1H NMR, ^{13}C NMR and FTIR confirmed that the resulting PBBIBBO have the expected chemical structures.

^1H NMR ($\text{H}_2\text{SO}_4\text{-d}_2$, δ ppm): 7.63 (benzobisoxazole, 2H), 7.71 (benzimidazole, 1H), 8.09 (benzene, 4H), 8.27 (benzimidazole, 1H), 8.42 (benzimidazole, 1H), 10.5 (H_2SO_4 , solvent).

^{13}C NMR ($\text{H}_2\text{SO}_4\text{-d}_2$, δ ppm): 110.8, 114.6, 115.7, 120.5, 122.9, 128.0, 130.6, 131.0, 134.5, 137.2, 139.4, 152.8, 162.7.

Thermal properties

The weight vs. temperature curves for PBBIBBO and BBODPA are shown in Figure 3. BBODPA displayed three-step thermal degradation processes, namely, desorption of water, decomposition of carbonyl group and aromatic group. The initial 6–8 wt.% weight loss of BBODPA below $145\text{ }^\circ\text{C}$ is mainly due to the volatilizing of water, which corresponds to about 2 crystal water molecules per unit of BBODPA ($\text{C}_{22}\text{H}_{12}\text{N}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$). The degradation of carbonyl group of BBODPA begins at $200\text{ }^\circ\text{C}$ and the decomposition of aromatic group begins at $410\text{ }^\circ\text{C}$.

It can be observed in Figure 3 that the initial decomposition temperature of PBBIBBO is about $590\text{ }^\circ\text{C}$. When temperature reached $770\text{ }^\circ\text{C}$, there is still about 50 wt.% of residual left. These values show that PBBIBBO has reasonably good thermal stability. It is also shown that PBBIBBO exhibit better thermal stability than its monomer of BBODPA and DAB.

Fig. 3. TGA results of (a) PBBIBBO and (b) BBODPA.

Dissolubility of BBODPA and PBBIBBO was examined in different solvents and the results are summarized in Table 2. They are soluble in sulfuric acid. BBODPA is insoluble in other hot solvents except in hot DMF. PBBIBBO is soluble in hot DMF, DMAc and NMP.

Table 2. Dissolubility of BBODPA and PBBIBBO (++: soluble at room temperature; soluble in hot; -: insoluble).

	H_2SO_4	DMSO	DMF	DMAc	NMP
BBODPA	++	-	+	-	-
PBBIBBO	++	-	+	+	+

CONCLUSIONS

The diacid monomer of BBODPA was synthesized from DAR and PPC, and was characterized in this work. BBODPA was then used as monomers for the synthesis of new PBBIBBO.

Investigation of dissolubility of PBBIBBO showed that it was insoluble in polar aprotic solvents but soluble in H_2SO_4 at room temperature. Thermal stability of BBODPA and PBBIBBO were also studied with TGA. The result showed temperature of 5% weight loss of PBBIBBO stayed in the range of $590\text{--}600\text{ }^\circ\text{C}$, indicating good thermal stabilities of the polymer.

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