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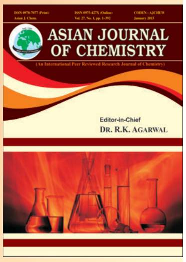

A Facile Method for the Synthesis of Benzoxazole Based Poly(2,6-pyridinylene benzobisoxazole)

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In the present study, a novel benzoxazole based rigid rod polymer poly(2,6-pyridinylene benzobisoxazole) containing pyridine unit was synthesized *via* polycondensation of 4,6-diaminoresorcinol-2,6-pyridinedicarboxylic acid salt monomer, which contains an equal number of moles of 4,6-diaminoresorcinol and 2,6-pyridinedicarboxylic acid structure. The obtained polymer was characterized by FTIR, elementary analysis, X-ray diffraction and themogravimetric analysis. The results showed that poly(2,6-pyridinylene benzobisoxazole) has an excellent thermal stability.

Keywords: Poly(*p*-phenylene benzobisoxazole), Benzoxazole, Pyridine, 4,6-Diaminoresorcinol-2,6-pyridinedicarboxylic acid salt.

INTRODUCTION

As known, the aromatic poly(*p*-phenylene benzobisoxazole) (PBO), possessing an exceptionally high specific strength and modulus, excellent thermal and oxidative stability, chemical resistance, cut and abrasion resistance, flame retardance, has received extensive attention due to its great potential applications as reinforcement fibres for advanced composites[1,2]. Significant advances have been made in the development of these high-performance fibres over the past 30 years and remarkable progress has been made in the production of so-called super organic fibre[2,3]. With development of poly(*p*-phenylene benzobisoxazole) technology, lots of work focused on poly(*p*-phenylene benzobisoxazole) property improvement and application extension[4-7]. Thus, kinds of modified poly(*p*-phenylene benzobisoxazole) with desired properties were developed, including improvement of photophysical property, compressive property, surface property and so on[8-13]. Some of the benzoxazole based rigid rod polymers were studied by introducing some unique units into the polymer chains, which are expected to show excellent properties[3,8,12].

Generally, poly(*p*-phenylene benzobisoxazole) and other similar aromatic heterocycle rigid rod polymers were prepared by direct polycondensation of diamines and diacids, whereas the polymerization process is complicated and long time is required to complete the reaction[14-18]. Many efforts were underway to improve the experimental operations. Currently, a convenient method was developed to synthesize poly(*p*-phenylene benzobisoxazole) with high molecular weight in short reaction time *via* polycondensation of 4,6-diaminoresorcinol-terephthalic acid (DAR-TA) salt monomer instead of isolated 4,6-diaminoresorcinol and terephthalic acid (TA)[19]. In DAR-TA salt structure, 4,6-diaminoresorcinol has one equivalent amount of terephthalic acid, which is expected to obtain poly(*p*-phenylene benzobisoxazole) with higher molecular weight in shorter time[19]. Although, no similar method are underway to synthesize other benzoxazole based polymer.

In present work, a facile method for a novel benzoxazole based rigid rod poly(2,6-pyridinylene benzobisoxazole) (PPBO) containing pyridine unit in the macromolecular chains synthesis has been developed *via* polycondensation of salt monomer instead of isolated diacid and diamine. More specifically, 4,6-diaminoresorcinol-2,6-pyridinedicarboxylic acid (DAR-PDA) salt is used as monomer for poly(2,6-pyridinylene benzobisoxazole) synthesis in P_2O_5/poly phosphoric acid, which is performed in short time and simple operation. Hopefully, pyridine containing polymer poly(2,6-pyridinylene benzobisoxazole) is expected to act some excellent properties.

EXPERIMENTAL

4,6-Diaminoresorcinol dihydrochloride (DAR·2HCl) was prepared from resorcinol *via* diacylation, oximation, Beckmann rearrangement and hydrolysis processes[20]. For properties discussion compared with poly(2,6-pyridinylene benzobisoxazole), poly(*p*-phenylene benzobisoxazole) was synthesized *via* polycondendation of 4,6-diamino-1,3-benzenediol-terephthalic acid salt (DAR-TA). 2,6-pyridinedicarboxylic acid

(≥ 99 %), polyphosphoric acid (PPA, content of P_2O_5 ≥ 80 %), P_2O_5 (≥ 98 %), $SnCl_2$ (≥ 98) and NaOH (≥ 96) were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received.

Fourier transform infrared (FT-IR) spectra were recorded on a Bruker VECTOR-22 IR spectrometer. The elemental analysis was determined with a CE Instruments EA-1110 elemental analyzer. X-ray diffraction (XRD) patterns were recorded by monitoring the diffractions in the range 5-60° with the scan speed 1° min^{-1} on a TTRAX3 diffractometer. CuK$_\alpha$ radiation source was operated at 40 kV and a current of 200 mA. Themogravimetric analysis (TGA) was performed on a TA SDT Q600 instrument under air or nitrogen atmosphere at a heating rate of 10 °C min^{-1} in the range 0 to 800 °C.

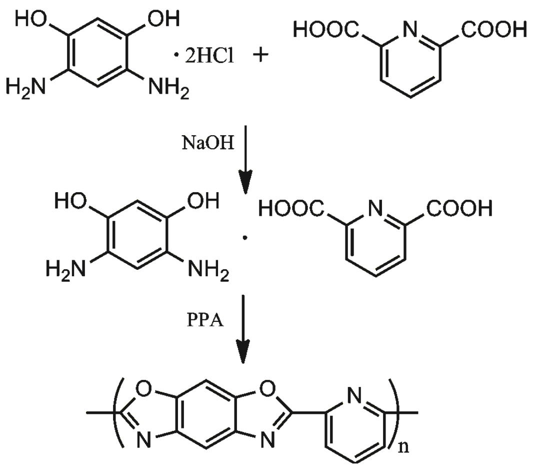
Synthesis of 4,6-diaminoresorcinol-2,6-pyridinedicarboxylic acid based salt monomer: Into a 1000 mL glass flask, equipped with a mechanical stirrer and a nitrogen inlet/outlet, were placed 400 mL water. 4,6-diaminoresorcinol dihydrochloride (4.26 g, 0.02 mol) was added. One equimolar amount of 2,6-pyridinedicarboxylic acid (0.02 mol) dissolved in NaOH (0.04 mol) aqueous solution was slowly added. Afterwards, the mixture was heated to 90 °C for 10 min and 4,6-diaminoresorcinol-2,6-pyridinedicar-boxylic acid salt solid precipitated, then the product was collected in nitrogen atmosphere. The product was dried under vacuum at 60 °C for 48 h.

Synthesis of poly(2,6-pyridinylene benzobisoxazole): Into a 100 mL reactor protected under nitrogen with a powerful and hastelloy made stirrer, were placed polyphosphoric acid (PPA; 83.69 % of P_2O_5), P_2O_5 and a small amount of tin powder. The reactor was closed and air was displaced by nitrogen by repeated evacuation and nitrogen blanketing. Then 4,6-diaminoresorcinol-2,6-pyridinedicarboxylic acid mixture was added. Afterwards, the mixture was heated to 80 °C for 2 h, then heated to 120 °C and stirred for 2 h more, following by further heating to 140 °C for 8 h and finally raised to 180 °C and held for 8 h. Finally, the product was purified by extraction of polyphosphoric acid with water and then dried under vacuum for 48 h at 80 °C.

RESULTS AND DISCUSSION

As shown in **Scheme-I**, poly(2,6-pyridinylene benzobisoxazole) was synthesized by polycondensation of the DAR-PDA salt. The monomer salt was prepared from 4,6-diaminoresorcinol dihydrochloride (DAR·2HCl) and 2,6-pyridinedicarboxylic acid (PDA) under nitrogen atmosphere, where molar quantity of the diamine is the same as the diacid. The method is expected to significantly shorten the reaction time and improve the molecular weight of the obtained copolymer, providing a convenient way for polycondensation of diamine and diacid. As expected, the polymer poly(2,6-pyridinylene benzobisoxazole) was synthesized within 20 h. Moreover, the intrinsic viscosities of the polymer poly(2,6-pyridinylene benzobisoxazole) was measured in dilute methanesulfonic acid solutions, which reaches to 10.2 dL g^{-1}.

As shown in Fig. 1, 4,6-diaminoresorcinol-2,6-pyridinedicarboxylic acid salt (I) and benzoxazole structure based polymer poly(2,6-pyridinylene benzobisoxazole) (II) containing pyridine in the polymer chains are characterized *via* FT-IR analysis,. For 4,6-diaminoresorcinol-2,6-pyridinedicarboxylic acid in Fig. 1 (I), absorbance peak at 3434 cm^{-1} is attributed to the OH vibrations, which disappears after polymerization as shown in benzoxazole based polymer(II). So do vibration peaks at 2920 and 2580 cm^{-1}, corresponding to the absorption of NH in the monomer. Band assignments in Fig. 1 (II) near 1625 cm^{-1} is attributed to the C=C stretching vibrations of aromatic rings and C=N bonds in cyclic compounds, C-O stretching vibrations is located at 1070 cm^{-1}, which indicates the formation of the oxazole rings. 1548 cm^{-1} is the asymmetric stretching vibration of an unsaturated pyridine rings, bands around 735 cm^{-1} is corresponding to the out of plane bending vibrations of pyridine rings.



Scheme-I: Strategy for synthesis of PPBO

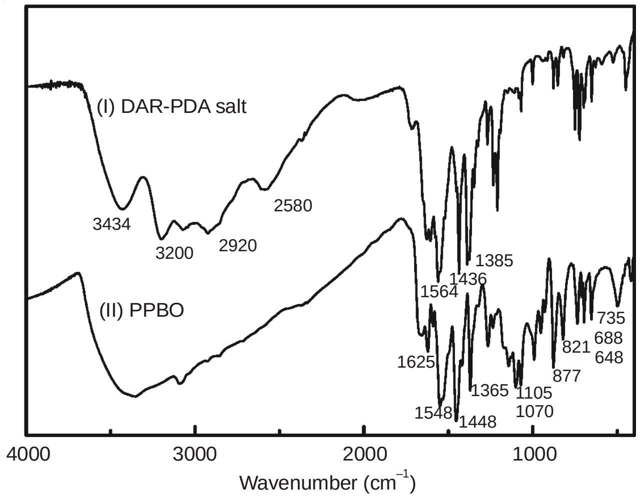


Fig. 1. FTIR spectra of 4,6-diaminoresorcinol-2,6-pyridinedicar-boxylic acid (I) and polymer poly(2,6-pyridinylene benzobiso-xazole) (II)

Further more, the elemental analysis was performed on a dry basis of 4,6-diaminoresorcinol-2,6-pyridinedicarboxylic acid and poly(2,6-pyridinylene benzobisoxazole) to investigate their chemical structure and the results are summarized in Table-1. As shown, the obtained results are in coincidence with the calculated value, further indicating the successful synthesis of 4,6-diaminoresorcinol-2,6-pyridinedicarboxylic acid and poly(2,6-pyridinylene benzobisoxazole), further implying that besides poly(*p*-phenylene benzobisoxazole), other type of polycondensation of diamine and diacid can be realized by salt monomer method.

TABLE-1
ELEMENT CONTENT (%) OF DAR-PDA SALT AND PPBO

Samples	Elemental analysis (wt. %): Calcd. (Exp.)		
	C	H	N
DAR-PDA	51.15 (50.43)	3.61 (3.25)	13.77 (13.48)
PPBO	66.38 (66.43)	2.13 (2.25)	17.87 (17.74)

Fig. 2 showed the X-ray diffraction intensity profiles of poly(2,6-pyridinylene benzobisoxazole) and poly(*p*-phenylene benzobisoxazole). It can be seem that there are only one diffraction peak around 2θ = 26.8° for polymer poly(2,6-pyridinylene benzobisoxazole) (II), while there are two strong diffraction peaks around 2θ = 16° and 26.7° for poly(*p*-phenylene benzobisoxazole) (I). The former peak for poly(*p*-phenylene benzobisoxazole) is corresponding to the "side-by-side" distance on plane between two neighboring polymer chains, whereas the latter one is related to the "face-to-face" distance on plane[8]. Poly(2,6-pyridinylene benzobisoxazole) shows a different pyridine crystalline system compared to poly(*p*-phenylene benzobisoxazole).

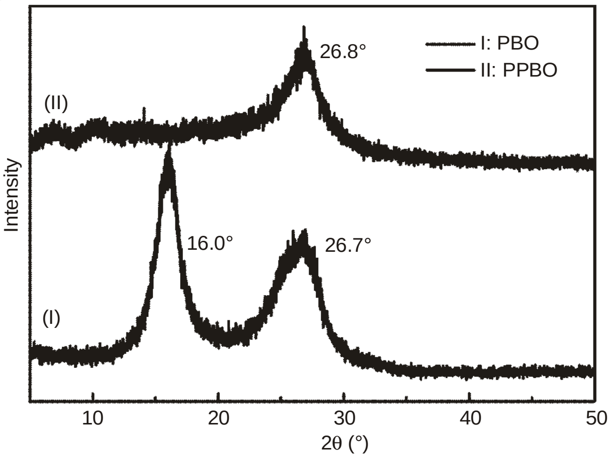


Fig. 2. XRD diffraction curves of poly(2,6-pyridinylene benzobisoxazole) and polymer poly(2,6-pyridinylene benzobisoxazole) structure

As known, poly(*p*-phenylene benzobisoxazole) shows an outstanding thermal stability. More specifically, the thermal degradation temperature of poly(*p*-phenylene benzobisoxazole) is highest in organic materials, which is nearly 650 °C in air, as shown in Fig. 3(I). Fig. 3(II) shows the thermograms of poly(2,6-pyridinylene benzobisoxazole) under air condition with a heating rate of 10 K min^{-1}. Obviously, thermal decomposition temperature of polymer poly(2,6-pyridinylene benzobisoxazole) is about 550 °C in air, which is lower than that of poly(*p*-phenylene benzobisoxazole). However, nearly 14.6 % of polymer poly(2,6-pyridinylene benzobisoxazole) is left even at 800 °C, which is much higher than that of poly(*p*-phenylene benzobisoxazole) (0 %). Degradation of poly(*p*-phenylene benzobisoxazole) and polymer poly(2,6-pyridinylene benzobisoxazole) in the air atmosphere is explained by thermo-oxidation mechanism[19]. In other word, two effects including oxidation and high-temperature degradation dominates the decomposition of polymer. In comparison with poly(*p*-phenylene benzobisoxazole), pyridine unit reduces oxidation of poly(2,6-pyridinylene benzobisoxazole), resulting in more residues left.

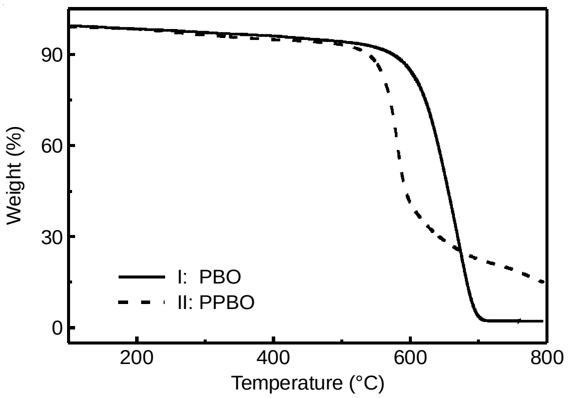


Fig. 3. TGA curves of polymer poly(2,6-pyridinylene benzobisoxazole) (II) and poly(2,6-pyridinylene benzobisoxazole) (I) under air condition with a heating rate of 10 K min^{-1}

Conclusion

In summary, based on direct polymerization of 4,6-diaminoresorcinol-2,6-pyridinedicarboxylic acid salt, a novel aromatic rigid-rod benzoxazole based poly(2,6-pyridinylene benzobisoxazole) was successfully prepared, which further provides a convenient and efficient method for polycondensation of diamines and diacids. As expected, this type of pyridine containing poly(2,6-pyridinylene benzobisoxazole) has great heat resistance in air atmospheres.

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