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Synthesis of pyridine-based poly(*N*-arylenebenzimidazole sulfone)

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Abstract

Poly(*N*-arylenebenzimidazole pyridine sulfone) (PNABIPS) has been prepared *via* the aromatic nucleophilic displacement reaction of 2,6-bis(2-benzimidazoly)pyridine (BBP) with bis(4-fluorophenyl) sulfone. BBP was synthesized by reaction of 2,6-pyridinedicarboxylic acid with 1,2-phenylenediamine in polyphosphoric acid. The chemical structure of BBP was confirmed by FT-IR, HRMS, ^{1}H NMR and ^{13}C NMR. The characterization of the polymer was performed with FT-IR, ^{1}H NMR, elemental analysis, GPC, XRD, DSC, TGA and solubility tests. The polymer was obtained in quantitative yield with M_n value 12,600 and M_w value 28,300, respectively. DSC and TGA measurements show that the glass transition temperature (T_g) is 312 °C and 5% weight loss temperature is 434 °C in nitrogen and 545 °C in air, respectively. In addition, the novel polymer exhibits good solubility, which can be dissolved in common organic solvent at room temperature.

Keywords: Polybenzimidazoles; Poly(*N*-arylenebenzimidazole pyridine sulfone); Thermal properties; Solubility

In a wide definition poly(benzimidazole)s (PBIs) refer to a large family of aromatic heterocylic polymers containing benzimidazole units. As an amorphous thermoplastic polymer, the aromatic nuclei of PBIs provide the high thermal stability, excellent chemical resistance, retention of stiffness and toughness [1]. However, the rigid backbones of the molecules result in poor solubility in common organic solvents and limit their application. Thereby more efforts have been made to modify the polymer structures to improve the solubility without sacrificing the desirable properties [2–11]. Due to the rigidity and polarizability of pyridine rings, introducing pyridine rings into the main chain of a synthetic polymer could improve the solubility and thermal stability [12–14]. However, the synthesized polybenzimidazoles containing pyridine rings have N–H groups, and the concentration of N–H sites gradually and continuously decreases as time increases under air atmosphere at 350 °C [15].

Hay et al. firstly reported that the N–H group in benzimidazoles could undergo a C–N coupling reaction with activated halides to give linear polymers with high molecular weight under appropriate temperature, and the *N*-substituted homopolymers and copolymers have very high glass transition temperature and thermal stability [16,17]. In addition, pursuing to improve the processability of PBIs, sulfonyl groups in the PBI polymers would increase solubility and flexibility, which allow further processing, modification and production of films with good mechanical properties [18].

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Base on these, in this paper, the synthesis of 2,6-bis(2-benzimidazoly)pyridine is reported along with the preparation of poly(*N*-arylenebenzimidazole pyridine sulfone) from the N–H sites in benzimidazole ring and bis(4-fluorophenyl) sulfone. Due to the incorporation of pyridine and sulfonyl groups in the PBI backbone, the resulting polymer exhibits good thermal resistance, high glass transition temperature values and good solubility in organic aprotic solvents.

1. Experimental

The chemicals and reagents, unless otherwise specified, were purchased from Acros and TCI Chemical Co. and used as received. All the solvents were further purified before use.

Scheme 1 shows the synthesis route of 2,6-bis(2-benzimidazoly)pyridine (BBP) and poly(*N*-arylenebenzimidazole pyridine sulfone) (PNABIPS). The synthesis of BBP was performed *via* the reaction of 2,6-pyridinedicarboxylic acid with 1,2-phenylenediamine in polyphosphoric acid, PPA, as the condensation agent and solvent. PPA is a very convenient dehydration agent for the preparation of benzimidazole from acid in a single step. PNABIPS was prepared from BBP with bis(4-fluorophenyl) sulfone under the existence of anhydrous potassium carbonate at 210 °C.

BBP: white solid. Yield: 95%. mp: 353 °C. UV recorded in CH_3CN λ_{max} at 325 nm. FT-IR (KBr pellet, cm^{-1}): 3167, 3057, 1624, 1601. ^1H NMR (300 MHz, DMSO-*d*$_6$): δ 13.0 (s, 2H), 8.34 (t, 2H), 8.18 (t, 1H), 7.76 (s, 4H), 7.33 (s, 4H). ^{13}C NMR (75 MHz, DMSO-*d*$_6$): δ 150.5, 147.8, 144.2, 139.2, 134.4, 123.7, 122.2, 121.4, 119.7, 111.8. MS (MALDI-TOF): *m/z*: calcd. for $C_{19}H_{13}N_5$ 311.3402; found: 311.1175.

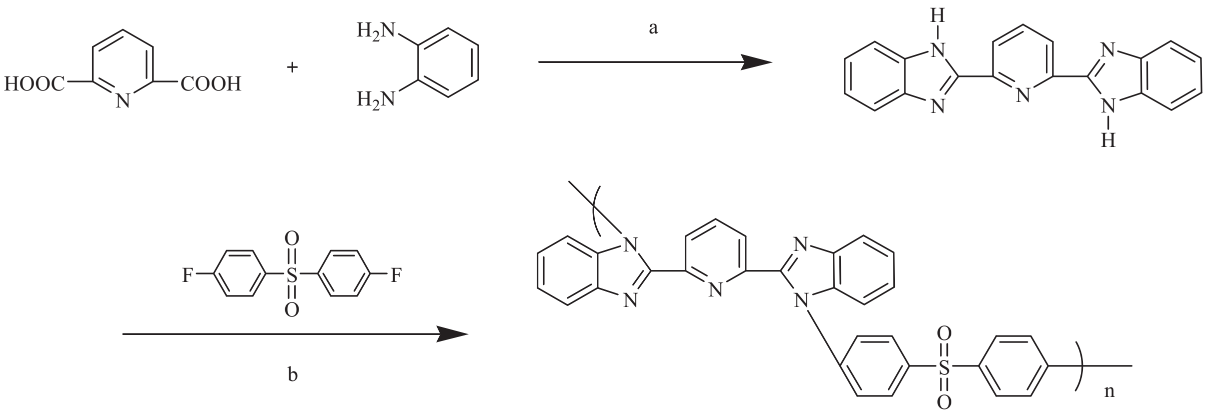
PNABIPS: dark solid. Yield: 92%. FT-IR (KBr pellet, cm^{-1}): 3057, 1624, 1601, 1188. ^1H NMR (300 MHz, DMSO-*d*$_6$): δ 8.18 (d, 2H), 7.84 (m, 1H), 7.70 (s, 4H), 7.32 (s, 4H), 6.87 (m, 4H), 6.61 (m, 4H). Anal. Calcd. for $C_{31}H_{19}N_5O_2S$ (525.142): C, 70.84; H, 3.62; N, 13.33. found: C, 70.53; H, 3.65; N, 13.30.

2. Results and discussion

The molecular weight of the reprecipitated polymer was measured by GPC (calibrated by polystyrene standards). The M_n value is 12,600 and the M_w value is 28,300, respectively. Polydispersity index (PDI) is 2.25. The wide-angle X-ray diffraction pattern of PNABIPS over the 2θ range of 5–60° is investigated. Despite the presence of the rigid phenyl ring, the polymer reveals essentially amorphous pattern. Because the polymer studied here is completely noncrystalline, any crystalline melting peaks have not been observed in the differential scanning calorimetry (DSC) study.

DSC thermogram of the polymer is shown in Fig. 1. A single glass transition temperature of PNABIPS is obtained, and the resulting polymer shows T_g is 312 °C, which lower than that of traditional PBIs ($T_g > 400$ °C) [1]. This decrease in T_g could be correlated to the elimination of hydrogen bonding after the *N*-substitution.

The synthesized polymer exhibits high thermal stability. Fig. 2 shows the primary thermogravimetric curve obtained by dynamic TGA of PNABIPS. 5% weight loss temperature is 430 °C in nitrogen and 545 °C in air, and 5%



Scheme 1. Synthesis of BBP and PNABIPS. Reagents and condition: (a) PPA, 200 °C, 6 h; and (b) K_2CO_3/sulfolane, 210 °C, 10 h.

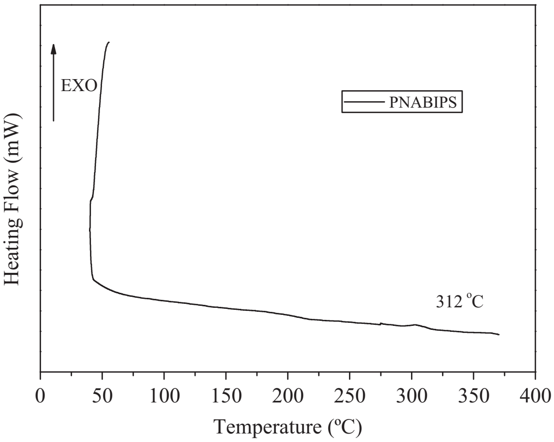


Fig. 1. DSC of polymer in nitrogen.

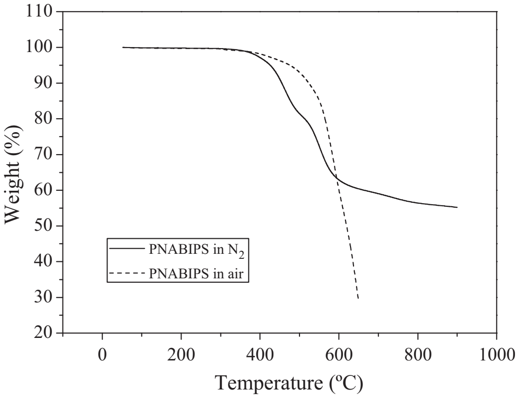


Fig. 2. TGA of polymer in nitrogen and in air.

weight loss temperature in air higher than that in nitrogen. The result may be attributed to the oxidation of PNABIPS. The end groups of PNABIPS may have N–H groups of benzimidazole rings, and hydrogen abstraction from the N–H groups initiated to form more stable quinone and benzonitrile structures in air atmosphere before decomposition [15]. TG curves reveal that the polymers is thermally stable at up to 400 °C, and the 50% weight losses take place at over 900 °C in nitrogen. Char yield is an easy and important measurement which correlates to the ability to sustain combustion. For the polymer the char yield at 600 °C is up to 60%.

PNABIPS exhibits good solubility behavior in different organic solvents. The solubility was qualitatively determined by the dissolution of 10 mg of solid polymer in 1 mL of organic solvent at room temperature. The polymer could be easily soluble in high polar solvent, such as dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP) and dimethylformamide (DMF), while partially soluble in common organic solvents, such as dimethyl sulfoxide (DMSO), dichloromethane ($CHCl_2$) and chloroform ($CHCl_3$). The polymer shows improved solubility compared with previously reported traditional PBI which is only soluble after heating in highly polar organic solvents. Compared with traditional PBIs which are only soluble after heating in highly polar organic solvents [1], PNABIPS displays the improved solubility. The difference in solubility was attributed to the presence of sulfonyl and pyridine groups in the PBI backbone, which hinder dense chain packing, thereby reducing the interchain interactions and enhancing solubility.

In conclusion, a convenient synthetic route has designed to prepare bis(benzimidazolyl) derivative containing pyridine group in high yield and high purity. It has been used as condensation monomer, in combination with bis(4-fluorophenyl) sulfone, to yield novel poly(*N*-arylenebenzimidazole pyridine sulfone) (PNABIPS). The reaction of the reactive benzimidazole N–H sites and the combination of sulfonyl and pyridine groups along with the polymer backbone remarkably endow the current polymers with some special characteristics, such as good thermal resistance, high glass transition temperature values and good solubility in common organic solvents. Intensive studies on the synthesis of poly(*N*-arylenebenzimidazole pyridine sulfone)s are in progress.

Acknowledgments

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