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Synthesis and Characterization of N-Substituted Polybenzimidazoles

Yewei Xu[1], Jie Tang[2], Guanjun Chang[1], Xuan Luo[1], Fanghua Zhu[1] and Lin Zhang[1,*]

[1]Research Centre of Laser Fusion, China Academy of Engineering Physics, Mianyang, P.R. China
[2]School of Chemistry and Chemical Engineering, Mianyang Normal University, Mianyang, P.R. China

*Corresponding author: Fax: +86 816 2493148; Tel: +86 816 2484234; E-mail: xywchem@sina.com

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Soluble N-substituted polybenzimidazoles have been prepared by aromatic nucleophilic displacement reaction of N-H sites in 1,3-*bis*(2-benzimidazolyl)benzene (mBBIB) with activated aromatic difluorides containing sulfonyl and carbonyl groups in sulfolane at 210 ºC in the presence of anhydrous potassium carbonate. 1,3-*Bis*(2-benzimidazolyl)benzene was synthesized from isophthalic acid and 1,2-phenylenediamine in polyphosphoric acid. The structure of 1,3-*bis*(2-benzimidazolyl)benzene was confirmed by FT-IR, HRMS, ^{1}H and ^{13}C NMR. The characterizations of the resulting polymers were performed with FT-IR, ^{1}H NMR, elemental analysis, GPC, DSC, TGA and solubility tests. DSC and TG measurements showed that polymers had high glass transition temperatures (Tg > 210 ºC) and good thermal stability with high decomposition temperatures (T_D > 430 ºC). These novel polymers also showed good solubility.

Key Words: N-Substituted, Polybenzimidazole, Thermal properties, Solubility.

INTRODUCTION

Due to outstanding physical properties, high performance polymers were considered the most promising class of polymers for special applications to automotive, aircraft and spacecraft industries[1]. However, only a few types have been commercialized because of their high production costs. Polybenzimidazoles (PBIs) is one example. They are materials with high thermal stability, excellent chemical resistance, retention of stiffness and toughness[2,3]. However, the poor solubility of polybenzimidazoles, a resulting of their highly rigid backones, is a major barrier to their application. Thereby persistent efforts have been made to improve the solubility by modifying the polymer structures of polybenzimidazoles while maintaining their desirable properties. These modifications are accomplished in two ways, either by synthetically modifying the monomers prior to polymerization or by the post-polymerization substitution of the polymer at the reactive benzimidazole N-H sites[4-8]. However, few papers were published on modifying the monomers prior to polymerization at the reactive benzimidazole N-H sites[9]. In air at 350 ºC, the concentration of N-H groups gradually and continuously decreases over time. Hay *et al.*[10,11], first reported that the N-H group in benzimidazoles could undergo a C-N coupling reaction with activated halides to produce linear polymers with high molecular weight at appropriate temperature and these N-substituted homopolymers and copolymers showed very high glass transition temperatures and pronounced thermal stability. In addition, pursuing to explore higher molecular weight polybenzimidazoles with different structures, sulfonyl and carbonyl groups in the polybenzimidazole polymers would be increased solubility and flexibility[12].

In this paper, the synthesis of 1,3-*bis*(2-benzimidazolyl)-benzene (mBBIB) is reported along with the preparation of N-substituted polybenzimidazoles from the N-H sites in benzimidazole ring and *bis*(4-fluorophenyl) sulfone or 4,4'-difluorobenzophenone. Because of the incorporation of sulfonyl and carbonyl groups in the polybenzimidazole backbone and the reaction of the reactive benzimidazole N-H sites, the resulting polymer exhibited good thermal resistance, high glass transition temperature values and good solubility in organic aprotic solvents.

EXPERIMENTAL

All chemicals and reagents, except where otherwise specified, were purchased from Aldrich, Acros and TCI Chemical Co. and used as received. All solvents were further purified before use.

FT-IR spectra were recorded on a Nicolt 6700 FT-IR spectrometer for the measurement of infrared absorption spectra for monomers and polymers. NMR spectra were recorded using a Brucker NMR spectrometer in DMSO-d_6. Mass spectra were recorded on VG Autospec 3000 for ESI MS. Elemental analyses were performed using a Vario EL III analyzer. The molecular weights and molecular weight distributions were estimated by gel permeation chromatography (GPC) on a Wyatt DAWN HELEOS using DMF as an eluent. Differential scanning calorimetry (DSC) was recorded on a 910-TA instrument in a nitrogen atmosphere at a heating rate of 10 ºC/min. Thermogravimetric analysis (TGA) was conducted using a TA-SDT Q600 thermal analysis in air or nitrogen atmosphere at a heating rate of 10 ºC/min.

Synthesis of 1,3-*bis*(2-benzimidazolyl)benzene (mBBIB): A 25 mL three-neck round-bottomed flask equipped with a magnetic stirrer, a water cooled condenser and an argon inlet and outlet was charged with 1,2-phenylenediamine 0.454 g (4.2 mmol), isophthalic acid 0.332 g (2 mmol) and 10 mL polyphosphoric acid (PPA). The temperature was slowly raised to 200 ºC and the reaction mixture was heated for 6 h. The resulting solution was allowed to slowly cool to room temperature and subsequently poured into cold water. Following drop 15 % NaOH solution and neutralize to pH = 8. Then filtered through celite, water washed and dried. The obtained crude product was re-crystallized from ethanol and dried in vacuum at 60 ºC. The yield is 94 %.

Synthesis of N-substituted polybenzimidazoles: A 25 mL three-necked round-bottom flask was equipped with a magnetic stirrer, a water cooled condenser and an argon inlet and outlet. To this, we added 2 mmol of 1,3-*bis*(2-benzimidazolyl)-benzene, 2 mmol of difluoride derivative and 4 mmol of anhydrous potassium carbonate in 10 mL of sulfolane and 3 mL of chlorobenzene. The reaction mixture was heated to azeotrope off the resulting water and the chlorobenzene. The chlorobenzene was then removed and the reaction mixture was brought up to 210 ºC for 10 h. The reaction mixture was cooled down and the solution was poured into water to precipitate out the polymer. Then the polymer was collected by filtration and dried in a vacuum at 80 ºC for 24 h.

RESULTS AND DISCUSSION

Monomer synthesis: As shown in **Scheme-I**, the synthesis of 1,3-*bis*(2-benzimidazolyl) benzene (mBBIB) is performed *via* the reaction of isophthalic acid with 1,2-phenylenediamine in polyphosphoric acid (PPA), as the condensation agent and solvent. Polyphosphoric acid is a very convenient dehydration agent for the preparation of benzimidazole from acid in a single step.

The structure of mBBIB was confirmed by FT-IR, HRMS, ^{1}H and ^{13}C NMR. Fig. 1 presents the FT-IR spectrum of mBBIB. No residual carbonyl absorption was observed between 1780 and 1650 cm^{-1}, suggesting the nearly complete closure of the imidazole rings under the reaction condition and the characteristic benzimidazole bands were clearly observed at 1630 cm^{-1} (C=N/C=C stretching), 1570 cm^{-1} (ring vibration of conjugation between benzene and imidazole rings) and 1530 cm^{-1} (in-plane ring vibration of 2-substituted benzimidazole). The bands at 3167 cm^{-1} were ascribed to the stretching vibration of the isolated non-hydrogen bonded N-H groups of benzimidazole ring. The characteristic absorptions for aromatic C-H groups were detected at 3064 cm^{-1}. Fig. 2 shows the signal assignments of the ^{1}H NMR spectrum of mBBIB. The spectrum reveals aromatic protons at 7.0-9.1 ppm and imidazole N-H protons at 13 ppm. Furthermore, the m/e of the fragments in high resolution mass measurements and the signal assignments of the ^{13}C NMR spectrum were in agreement with the predicted structures of the monomer.

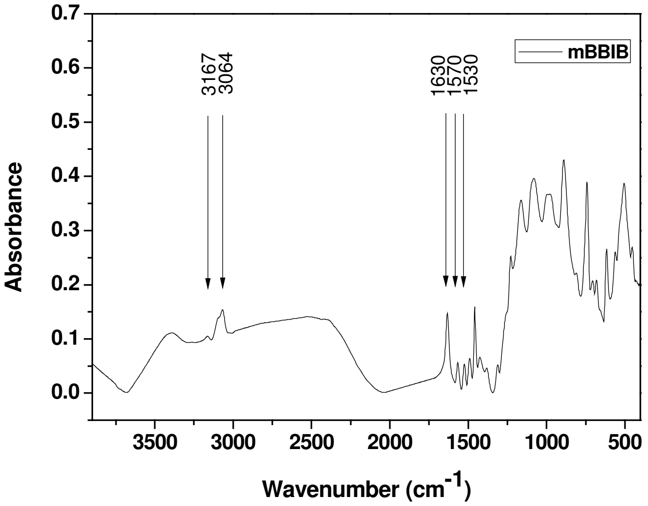


Fig. 1. FTIR spectrum of mBBIB

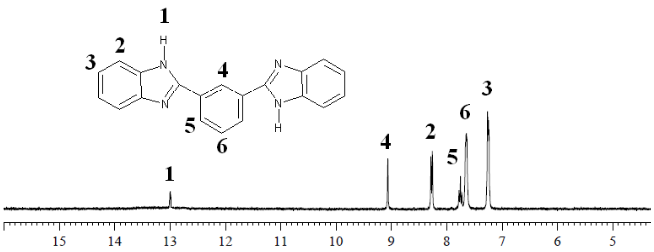
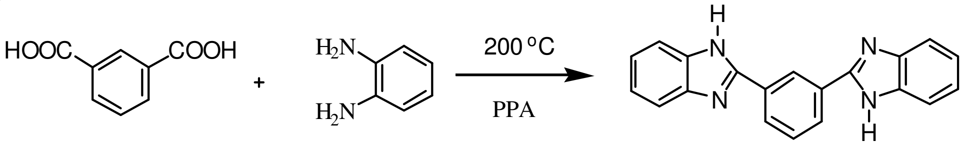


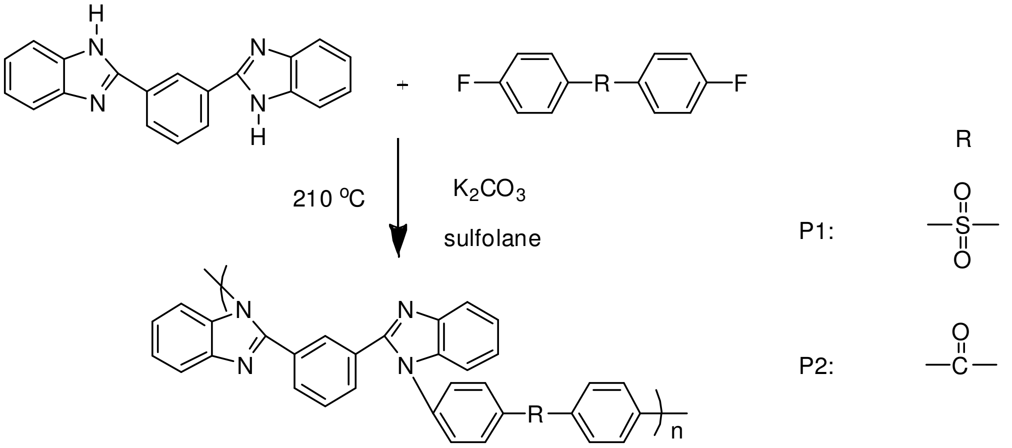
Fig. 2. ^{1}H NMR spectrum of mBBIB

Polymer synthesis: N-substituted polybenzimidazoles were prepared from mBBIB with *bis*(4-fluorophenyl) sulfone or 4,4'-difluorobenzophenone under the existence of anhydrous potassium carbonate at 210 ºC. The detailed prepared process is shown in **Scheme-II** and the yields of the polymerization reactions were above 92 % (Table-1).

The structures of N-substituted polybenzimidazoles were confirmed by FT-IR, ^{1}H NMR and elemental analysis. The FT-IR spectra of the synthesized polymers are shown in Fig. 3. The characteristic benzimidazole bands and characteristic absorptions for aromatic C-H groups could also be observed. The characteristic absorption bands for sulfonyl groups at around 1070 cm^{-1} and carbonyl groups at around 1660 cm^{-1} appeared and the stretching vibration of the isolated non-



Scheme-I: Synthesis of mBBIB



Scheme-II: Synthesis of N-substituted polybenzimidazoles

TABLE-1
CHARACTERIZATION OF N-SUBSTITUTED POLYBENZIMIDAZOLES

Polymer code	Mn[a]	Mw[a]	Mw/Mn[a]	T_5 (°C)[b] N_2	T_5 (°C)[c] air	Tg (°C)[d]	Yield (%)
P1	12000	26400	2.2	439	468	211.3	92
P2	13500	41900	3.1	519	543	230.2	94

[a]The soluble fraction in DMF calibrated by GPC polystyrene standards. [b]5 % weight loss temperature under N_2 with heating rate 10 °C/min. [c]5 % weight loss temperature under air with heating rate 10 °C/min. [d]Obtained by DSC under N_2 with heating rate 10 °C/min.

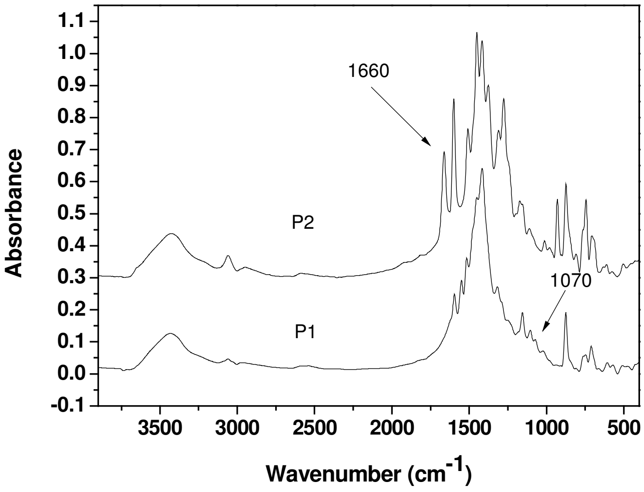


Fig. 3. FT-IR spectra of P1 and P2

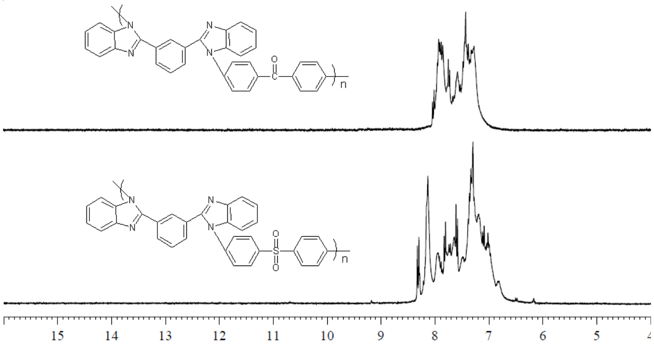


Fig. 4. ^1H NMR spectra of P1 and P2

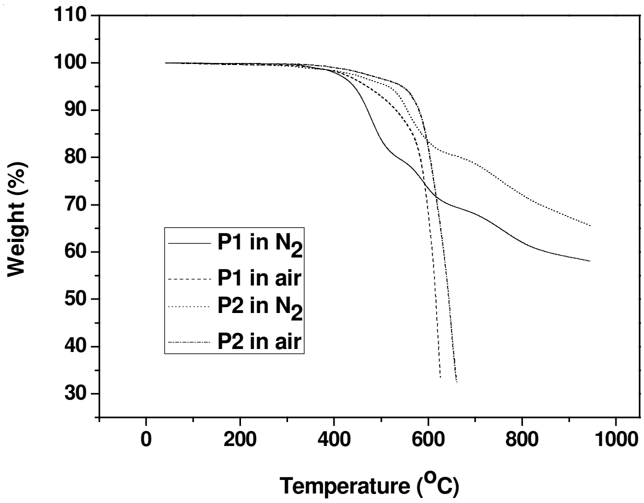


Fig. 5. TGA of P1 and P2 in nitrogen and in air

hydrogen bonded N-H groups at 3175 cm^{-1} disappeared. Fig. 4 shows the ^1H NMR spectroscopic data of P1 and P2. The spectra show the disappearance of imidazole N-H protons at around 13 ppm in the case of unsubstituted mBBIB. The integration of the aromatic protons (between 7.0 and 8.5 ppm) belonging to the added phenylsulfonyl and benzophenone groups indicated successful aromatic nucleophilic displacement reaction. Furthermore, the elemental analysis data were in agreement with the predicted structures of P1 and P2.

The molecular weights of the reprecipitated polymers were measured by GPC (calibrated by polystyrene standards). Mn and Mw/Mn of P1 were 12000 and 2.2, respectively. P2 was 13500 and 3.1.

Thermal behaviours: The synthesized polymers showed notable thermal stability and a high char yield in nitrogen at 500 °C. Fig. 5 shows the primary therogravimetric curves of P1 and P2 obtained by dynamic TGA. TG curves reveal that the polymers are thermally stable at up to 440 °C in nitrogen and 510 °C in air, respectively (Table-1). The 50 % weight losses take place at over 900 °C in nitrogen. Char yield is an important indicator. It is correlated to the ability to sustain combustion. For these polymers, the char yields in nitrogen at 800 °C were up to 60 %.

TABLE-2
SOLUBILITY OF N-SUBSTITUTED POLYBENZIMIDAZOLES [a]

Polymer code	DMAc	DMF	NMP	DMSO	CH_2Cl_2	$CHCl_3$	THF	H_2SO_4
P1	++	++	++	++	+-	+-	--	++
P2	++	++	++	+-	+-	+-	--	++

[a] ++: Solid polymer was completely dissolved at room temperature; +-: Solid polymer was partly dissolved at 50 ºC; --: Solid polymer could be swelled at 50 ºC.

A differential scanning calorimeter was used to determine the glass transition temperatures (Tgs) of N-substituted polybenzimidazoles. Obvious Tgs were observed upon the second DSC heating traces. DSC thermograms of P1 and P2 are shown in Fig. 6. The thermograms of the P1 and P2 reveal them to have almost the same differential scanning calorimetry characteristics. A single glass transition temperature was obtained and Tgs of P1 and P2 were 211.3 and 230.2 ºC, respectively (Table-1). Tgs of the resulting polymers were found to lower than that of traditional PBIs (Tg > 400 ºC)[2]. This decrease in Tg could be correlated to the elimination of hydrogen bonding after the N-substitution.

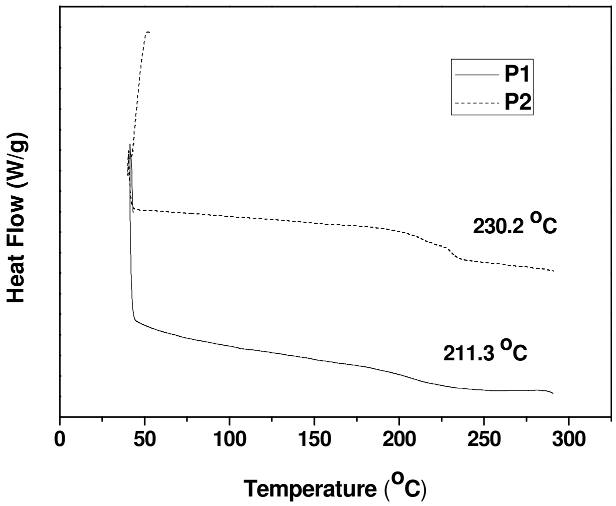


Fig. 6. DSC of the polymers in nitrogen atmosphere

Solubility: N-Substituted polybenzimidazoles showed different solubility behaviours in different organic solvents (Table-2). The solubility was qualitatively determined by the dissolution of 10 mg of solid polymer in 1 mL of organic solvent at room temperature. The polymers were readily soluble in highly polar solvents, such as dimethylacetamide (DMAc), dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP). They were only partially soluble in common organic solvents, such as dimethyl sulfoxide (DMSO), dichloromethane ($CHCl_2$) and chloroform ($CHCl_3$). Unlike traditional polybenzimidazoles which are only soluble after heating in highly polar organic solvents[2], all synthesized polymers displayed the improved solubility. The difference in solubility was attributed to the presence of sulfonyl and carbonyl groups in the polybenzimidazole backbone and the disappearance of the N-H sites from the benzimidazole rings, which hinders dense chain packing, thereby reducing the interchain interactions and enhancing solubility.

Conclusion

A convenient synthetic route has designed to prepare 1,3-*bis*(2-benzimidazolyl) benzene in high yield and high purity. It has been used as condensation monomer, in combination with *bis*(4-fluorophenyl) sulfone or 4,4'-difluorobenzophenone, to yield novel soluble N-substituted polybenzimidazoles. The reaction of the reactive benzimidazole N-H sites and the combination of sulfonyl and carbonyl 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. The synthesized polymers may have potential as one of the new solution-tolerant, high-temperature polymeric material.

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