

A Novel Synthesis Method for the Preparation of Aromatic Poly(imide benzoxazole) from Trimellitic Anhydride Chloride and Bis(*o*-aminophenol)

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ABSTRACT: A poly(imide benzoxazole) was prepared directly from trimellitic anhydride chloride and 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (BisAPAF) monomers in a two-step method. In the first step, a poly(hydroxyamide amic acid) precursor was synthesized by the low-temperature solution polymerization in an organic solvent. Subsequently, thermal cyclodehydration of the poly(hydroxyamide amic acid) precursor at 350°C produced the corresponding poly(imide benzoxazole). The inherent viscosity of the precursor polymer was 0.22 dL/g. The cyclized poly(imide benzoxazole) showed a glass transition temper-

ature (T_g) at 329°C and a 5% weight loss temperature at 530°C in nitrogen and at 525°C in air. The poly(imide benzoxazole) is amorphous as evidenced by the wide-angle X-ray diffraction measurement. The structures of the precursor polymer and the fully cyclized polymer were characterized by Fourier transform infrared (FTIR) and proton nuclear magnetic resonance spectroscopy (¹H NMR). © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2388–2391, 2003

Key words: polyimides; synthesis; high temperature materials

INTRODUCTION

Aromatic polyimides and polybenzoxazoles are heterocyclic polymers with excellent thermal stability, high mechanical properties, good electrical properties, and superior chemical resistance. They are widely used in high-performance applications, such as buffer coatings and interlayer dielectric materials in the semiconductor industry.^{1–5} The synthesis of poly(imide benzoxazole)s has been reported in a few papers and patents.^{6–8} In these reports, the poly(imide benzoxazole)s were prepared by the condensation reaction of a pre-synthesized diamine monomer containing benzoxazole moiety with a dianhydride monomer or a pre-synthesized diacid chloride monomer containing imide moiety with a bis(*o*-aminophenol) monomer. These synthesis methods involved complex monomer synthesis and purification procedures, which are tedious and expensive.

In our study, we used a commercially available monomer, trimellitic anhydride chloride, to react with a bis(*o*-aminophenol) monomer and successfully created the poly(imide benzoxazole) in a simple way. The synthetic routes used in this study for the preparation of the poly(imide benzoxazole) are shown in Scheme

1. The structure of the poly(imide benzoxazole) polymer can be further modified by the incorporation of a diacid chloride monomer to form a copolymer. By carefully choosing the type and amount of monomers, it is possible to modify the properties of the poly(imide benzoxazole) polymer, such as flexibility, solubility, processability, etc. In this paper, we focus on the synthesis and characterization of the poly(imide benzoxazole) polymer.

EXPERIMENTAL

Materials

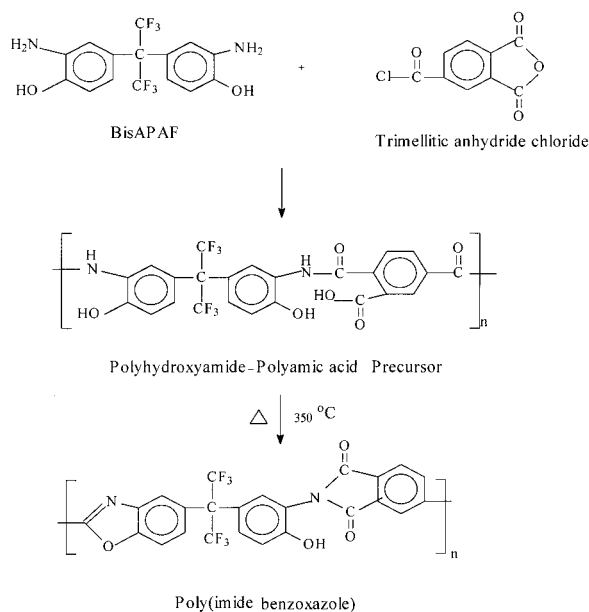
2,2-Bis(3-amino-4-hydroxyphenyl)hexafluoropropane (BisAPAF) was purchased from Chriskev (Leawood, KS). Trimellitic anhydride chloride was obtained from Aldrich (Saint Louis, MO) and dried under vacuum at 60°C for 24 h before use. Anhydrous *N*-methylpyrrolidinone (NMP) and pyridine were obtained from Aldrich (Saint Louis, MO) and used without further purification. Other chemicals and solvents were used as received.

Polymer synthesis

A typical preparation of the poly(hydroxyamide amic acid) precursor proceeds as follows: To a dry 250-mL three-necked flask equipped with a nitrogen inlet and mechanical stirrer were added 5.21 g (14.24 mmol) of BisAPAF, 1.24 g (15.68 mmol) of pyridine, and 50 g of

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Scheme 1 Poly(imide benzoxazole) synthesis.

anhydrous NMP. After the BisAPAF was completely dissolved, the solution was cooled to 5°C with ice water. Then, 3 g (14.24 mmol) of trimellitic anhydride chloride was added slowly into the solution. After complete addition, the reaction mixture was stirred at room temperature for 16 h. The resulting viscous solution was added in a dropwise manner to 1 L of stirring deionized water. The precipitated polymer was collected by filtration, washed with deionized water three times, and then dried in a vacuum oven at 60°C for 24 h.

Preparation of poly(hydroxyamide amic acid) film and thermal conversion to poly(imide benzoxazole)

First, 7 g of poly(hydroxyamide amic acid) polymer powder was dissolved in 17 g of NMP to make a 26% (w/w) solution. A film was cast from the viscous solution on a glass plate with a doctor's knife. The film was dried at 100°C for 1 h, 200°C for 1 h, and 350°C for 1 h in a heating oven under nitrogen flow to convert the poly(hydroxyamide amic acid) to poly(imide benzoxazole). The film was yellow and transparent. The results of elemental analysis for this poly(imide benzoxazole) are as follows:

ANAL. Calcd for
 $(C_{24}H_{10}F_6N_2O_4)_n$: C, 57.14%; H, 1.98%;
 N, 5.55%.
 Found: C, 57.35%; H, 2.14%;
 N, 5.80%

Characterization

Fourier transform infrared (FTIR) spectra were recorded on a Bio-Rad (Hercules, CA) Model 155 FTIR

Spectrometer. Proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectra were recorded on a Bruker (Rheinstetten, Germany) Advance 600 Spectrometer in DMSO-d_6 . The inherent viscosities were measured with a Cannon-Ubbelohde No. 100 viscometer at a concentration of 0.5 g/dL in NMP at 30°C. Thermal stability was analyzed with a Seiko Exstar (Tokyo, Japan) Model 6000 Thermogravimetric Analyzer (TGA) at a heating rate of 10°C/min under air and nitrogen. The glass transition temperature (T_g) was determined on a TA Instruments (New Castle, DE) Model 2920 Differential Scanning Calorimeter (DSC) at a heating rate of 10°C/min under nitrogen. Wide-angle X-ray diffraction (WAXD) experiments were conducted with a Rigaku (Tokyo, Japan) D/MAX-IIIIV X-ray diffractometer using $\text{Cu-K}\alpha$ radiation.

RESULTS AND DISCUSSION

Polymer synthesis

Trimellitic anhydride chloride has been used to synthesize poly(amide imide) by the low-temperature polycondensation reaction of trimellitic anhydride chloride with diamines.^{9–13} In our research, we used bis(*o*-aminophenol) instead of diamine to react with trimellitic anhydride chloride to prepare poly(imide benzoxazole). The polymer was prepared in a two-step method, as shown in Scheme 1. In the first step, the poly(imide benzoxazole) precursor, poly(hydroxyamide amic acid), was synthesized from the reaction of trimellitic anhydride chloride and BisAPAF at 5°C in anhydrous NMP. In this reaction, the BisAPAF monomer was dissolved in NMP first and then the trimellitic anhydride chloride monomer was added to react with BisAPAF. The physical state of trimellitic anhydride chloride monomer affected the inherent viscosity of the resulting polymer, as shown in Table I. A higher inherent viscosity polymer was always obtained when the trimellitic anhydride chloride was added in a solid state than when it was added in an NMP solution. The reason for this result could be that

TABLE I
Poly(hydroxyamide amic acid) Synthesis from Trimellitic Anhydride Chloride and BisAPAF

Batch	Polymerization Condition	Yield (%)	η_{inh}^a (dL/g)
1	Trimellitic anhydride chloride was dissolved in NMP and added in a dropwise manner to BisAPAF solution	Quantitative	0.17
2	Trimellitic anhydride chloride was added in a solid state to BisAPAF solution	Quantitative	0.22

^a Measured at 30°C in NMP at a concentration of 0.5 g/dL.

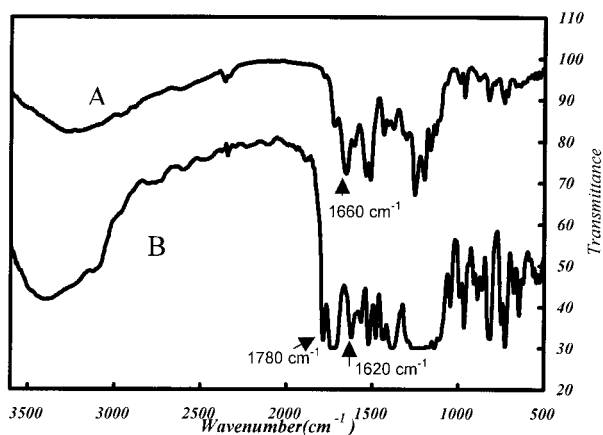


Figure 1 Infrared spectra of (A) poly(hydroxyamide amic acid) precursor and (B) poly(imide benzoxazole).

the trimellitic anhydride chloride monomer is moisture sensitive and will react with moisture in NMP and in the atmosphere.

The formation of poly(hydroxyamide amic acid) was confirmed by FTIR and $^1\text{H-NMR}$ spectra, as shown in Figures 1 and 2, respectively. The polymer exhibited a broad absorption band at $3400\sim 3100\text{ cm}^{-1}$ due to the amino (N—H), hydroxyl (OH), and carboxyl (COOH) groups and a strong carbonyl (amide) absorption at 1660 cm^{-1} in the FTIR spectrum. The $^1\text{H-NMR}$ spectrum of the polymer also showed the hydroxyl (OH) and carboxyl (COOH) (10.4 ppm) and amino (N—H) (9.7 and 9.9 ppm) groups.

In the second step, the film of poly(hydroxyamide amic acid) obtained from the solution casting was heated in an oven at 350°C under nitrogen for 1 h to convert it to poly(imide benzoxazole). The dehydrative cyclization of poly(hydroxyamide amic acid) to form a benzoxazole ring and a imide ring was con-

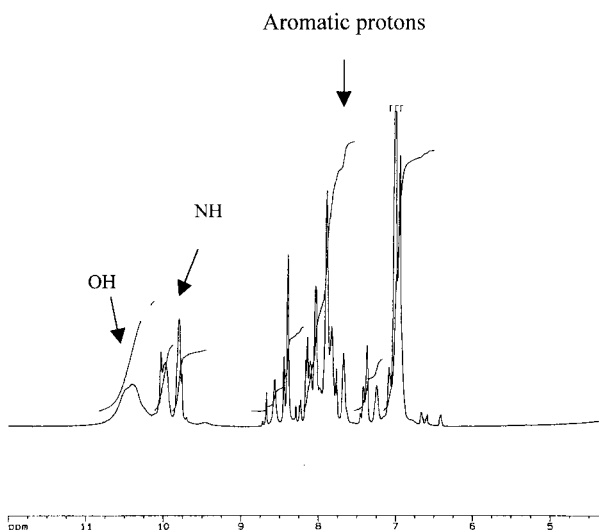


Figure 2 $^1\text{H-NMR}$ of poly(hydroxyamide amic acid) precursor.

TABLE II
Solubility of Poly(hydroxyamide amic acid) and Poly(imidebenzoxazoic)

Solvent	Poly(hydroxyamide amic acid)	Poly(imidebenzoxazole)
NMP	+ ^a	— ^b
DMAC ^c	+	—
DMSO ^d	+	—
DMF ^e	+	—
THF ^f	+	—
Acetone	+	—
Ethanol	+	—

^a +, soluble.

^b —, insoluble.

^c DMAC, dimethylacetamide.

^d DMSO, dimethyl sulfoxide.

^e DMF, dimethylformamide.

^f THF, tetrahydrofuran.

firmed by the disappearance of absorption at 1660 cm^{-1} (amide C=O) and by the appearance of a new characteristic absorption of benzoxazole ring at 1620 cm^{-1} and a new characteristic absorption of imide ring at 1780 cm^{-1} in the FTIR spectrum (Figure 1). The elemental analysis values of poly(imide benzoxazole) are in good agreement with the calculated values of the structure of the polymer.

Polymer characterization

The qualitative solubility of the poly(hydroxyamide amic acid) and the corresponding poly(imide benzoxazole) is summarized in Table II. The poly(hydroxyamide amic acid) precursor was soluble in many solvents, but the poly(imide benzoxazole) did not dissolve in any organic solvents. Therefore, the poly(imide benzoxazole) polymer can only be processed in the precursor state and then converted to the final poly(imide benzoxazole) state by thermal cycliza-

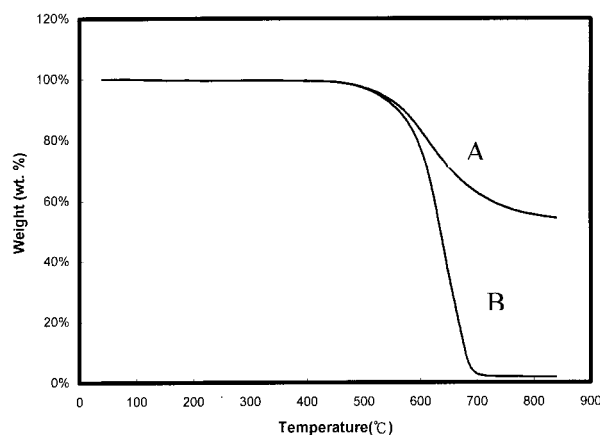


Figure 3 TGA thermograms of poly(imide benzoxazole) in (A) nitrogen and (B) air.

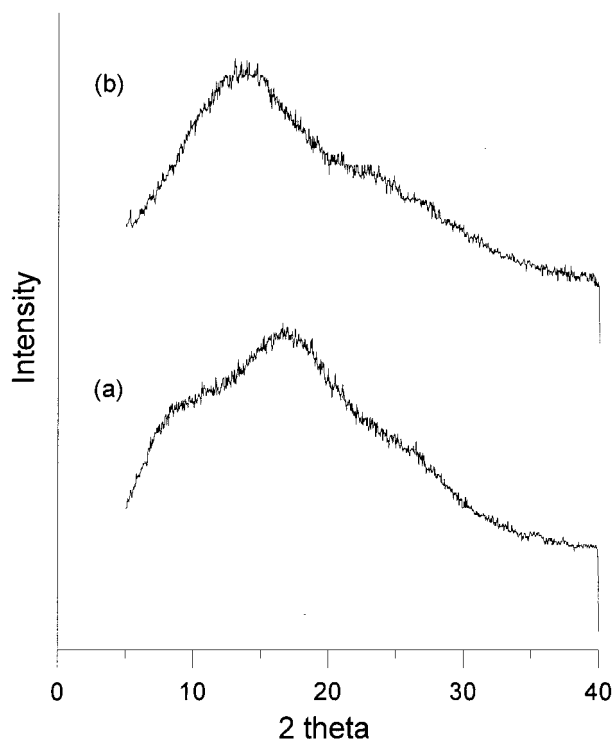


Figure 4 Wide-angle X-ray diffraction patterns of (a) poly-(hydroxyamide amic acid) precursor and (b) poly(imide benzoxazole).

tion. The product made from this poly(imide benzoxazole) should have good chemical resistance.

The thermal properties of the poly(imide benzoxazole) were studied by DSC and TGA techniques. The poly(imide benzoxazole) had a high T_g at 329°C. The polymer displayed excellent thermal and thermooxidative stabilities. The TGA thermograms, which were obtained with a heating rate of 10°C/min, showed a 5% weight loss at 530°C in nitrogen and at 525°C in air (Figure 3). The polymer had a high char yield of 58% at 800°C in nitrogen, which indicated it could be an excellent flame-retardant material.

To study the morphology of both poly(hydroxyamide amic acid) precursor and poly(imide benzoxazole), the films prepared from these two polymers were examined by WAXD. The WAXD patterns of the films are shown in Figure 4. A broad amorphous halo appeared in both polymers indicated the absence of crystallinity, which could be due to the bulky $-(CF_3)_2$ groups in the backbone and the asymmetrical molecular structures.

CONCLUSIONS

Using trimellitic anhydride chloride monomer, we prepared a poly(imide benzoxazole) with BisAPAF in a direct and simple way. The poly(imide benzoxazole) is amorphous in nature. The polymer film had a T_g at 329°C and showed high thermal and thermooxidative stabilities and good chemical resistance. Thus, this poly(imide benzoxazole) can be used in high-performance applications. Future work will include the modification of the poly(imide benzoxazole) with the incorporation of a diacid chloride monomer onto the polymer backbone to modify its properties.

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