

SYNTHESIS AND THERMAL PROPERTIES OF POLYBENZOXAZOLE FROM SOLUBLE PRECURSOR WITH HYDROXY-SUBSTITUTED POLYENAMINONITRILE*

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Abstract Aromatic polybenzoxazole (PBO) precursor, hydroxy-substituted polyenaminonitrile, was prepared by direct polycondensation of 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene (CCB) and 4,6-diaminoresorcinol dihydrochloride (DAR) using pyridine and *N,N*-dimethylacetamide as condensing agent and solvent. The precursor has good solubility in polar aprotic solvent which is due to the strong dipolar nature of the main chain. The soluble precursor was subjected to thermal cyclization in an inert atmosphere to convert it into the corresponding PBO, which has its 5% weight loss temperature at 540 °C. The fully cyclized PBO were characterized by FT-IR and TGA. The introduction of 10% mol 1,3,5-benzenetricarboxylic chloride (BTC) into the main chain not only has little effect on the solubility of PBO precursor but also raises its 5% weight loss temperature to 552 °C and char yield at 700 °C for the cyclized PBO with BTC.

Keywords Polybenzoxazole, Precursor, Hydroxy-substituted Polyenaminonitrile, Cyclization

INTRODUCTION

The production of thermally stable organic polymers has attracted much attention during the past 30 years^[1]. Of the wide variety of thermally stable polymers which have been synthesized, the most attractive variety are aromatic, rigid rod polymers, because of their low solubility and high glass transition or melting temperature. Polybenzoxazoles (PBOs) have long been regarded as heat-resistant fibers and as matrix materials for fiber-reinforced composites^[2, 3]. The properties of PBOs that make them attractive for many applications also lead to some difficulties in synthesis and fabrication. Wholly aromatic PBOs, in fact, are soluble only in strong acids (e.g., sulfuric acid, methane sulfuric acid, and polyphosphoric acid). Therefore, some compromises should be made between thermal stability and processability.

A common approach is to synthesize a more flexible polymeric precursor, which upon subsequent heat treatment cyclizes to produce the final thermally stable polymer^[3, 4]. Polyamide is a familiar and successfully applied example of this approach^[5, 6]. On the other hand, as a part of a program to prepare processable high molecular weight polymers that cure thermally without evolution of small molecules, more effort has been made to expand the synthetic strategy related to enaminonitrile chemistry. It was found that a rather bulky and polarizable group makes the polymer more readily soluble in common solvents, and also provides a site for the thermal curing at elevated temperature^[7–10].

Recently, we have noted that polyenaminonitrile containing hydroxyl groups could be used as a soluble

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precursor for polybenzoxazoles^[11, 12]. In this work, we report some preliminary results on the soluble precursor of polybenzoxazole (PBO) by solution polycondensation from 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene and 4,6-diaminoresorcinol dihydrochloride. In addition, the effect of 1,3,5-benzenetricarboxylic chloride in the main chain on the thermal properties has been studied.

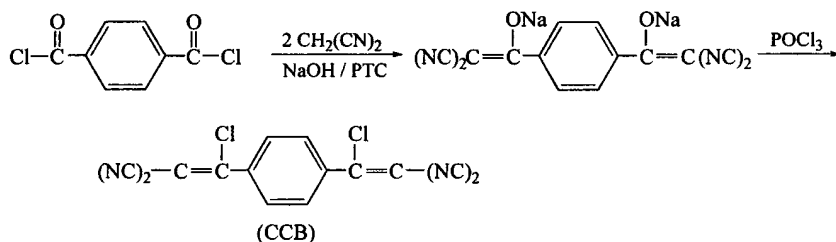
EXPERIMENTAL

Instrument

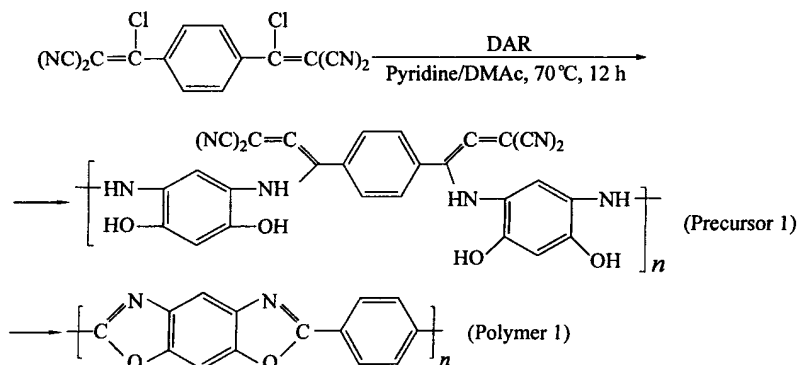
Elemental analysis was performed with an Elementar Vario EL apparatus. The FT-IR spectrum was recorded on a Nicolet IR-550 spectrometer. ¹H-NMR was conducted on a Mercury 200 spectrometer. TG analysis was carried out on a Du Pont 1090B thermal analyzer with a heating rate of 10 K/min under N₂ atmosphere.

Chemicals and Measurements

1,3,5-Benzenetricarboxylic chloride (BTC) and *p*-phthaloyl chloride (TAP) were obtained from Acros and recrystallized with dried hexane and dried under vacuum at 60°C for 24 h before use. 1,4-Bis(1-chloro-2,2-dicyanovinyl)benzene (CCB) was prepared according to the modified method^[3], as shown in Scheme 1. ¹H-NMR (CDCl₃, δ): 8.00 (s, 4H, Ar-H); Elemental analysis: Calcd. (%): C 56.30, H 1.65, N 19.03; Found (%): C 56.21, H 1.34, N 18.73; MS (*m/e*): 300 (*M*⁺), (100%). 4,6-diaminoresorcinol dihydrochloride (DAR) was purchased from Acros Company and recrystallized twice from SnCl₂/H₂O (2/10 g/g) before use. ¹H-NMR (D₂O, δ): 6.37 (s, 1H, Ar-H), 7.01 (s, 1H, Ar-H); Elemental analysis: Calcd. (%): C 33.80, H 4.73, N 13.15; Found (%): C 33.61, H 4.72, N 12.94; MS (*m/e*): 233 (*M*⁺), (20%). Other chemicals and solvents were purified by conventional methods.



Scheme 1



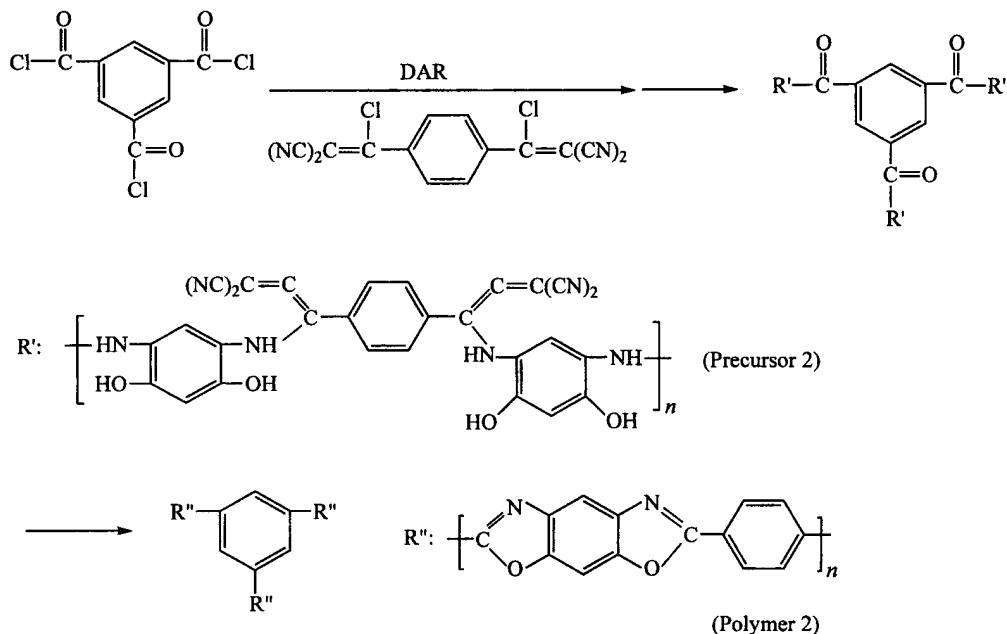
Scheme 2

Synthesis of PBO Precursor

The polymerization and cyclization reaction are shown in Scheme 2. A typical procedure for the preparation of PBO precursor 1 proceeds as follows. To a dry 50 mL three-necked flask equipped with a nitrogen inlet and magnetic stirrer was added 1.12 g (5.26 mmol) of DAR, 2.25 g of pyridine, 30 mL *N,N*-dimethylacetamide (DMAc) and the mixture was stirred for 10 min at 30°C. To the above solution was added 1.57 g CCB (5.26 mmol) and the reaction mixture was stirred for 12 h at 70°C. The brown reaction mixture was poured into a

large volume of water. The precipitate was filtered off, washed several times with water and methyl alcohol, and dried in vacuum at 80°C for 24 h to give 2.21 g of the polymer. Cyclization was completed at 400°C for 15 min under N₂ atmosphere.

Preparation of PBO precursor 2 containing 1,3,5-benzenetricarboxylic acid unit is similar to the above mentioned method^[9, 10], as shown in Scheme 3.



RESULTS AND DISCUSSIONS

Synthesis of PBO Precursor

The purity and yield of the monomer, CCB, was strongly affected by the POCl₃ purity. Usually, it is necessary to redistill the POCl₃ to use the 107–109°C distillation cut, before use in order to get high yield.

The soluble PBO precursor was synthesized from the reaction of BTC, CCB and DAR at 70°C in a pyridine/DMAc mixed solution. The cyclization reaction was monitored by FT-IR and TGA. Pyridine acts as a condensing agent and as co-solvent to increase the solubility of monomers in DMAc. The precursor 1 exhibits a broad absorption band at 3400–3100 cm⁻¹ ascribable to amino (N–H) and hydroxy (OH) groups. The nitrile absorption appears at 2215 cm⁻¹ and the cyanovinyl absorption at about 1560 cm⁻¹ in the IR spectrum as shown in Fig. 1.

Solubility

The results of qualitative solubility tests are reported in Table 1. Qualitative solubility tests were performed at room temperature on 0.1 g of precursor in 1 mL of solvent. The precursors 1 and 2, in fact, are readily soluble in organic solvents such as MSA, NMP, DMSO and DMAc. The 1,3,5-benzenetricarboxylic acid unit has little effect on the solubility of precursor 2. The solubility change of precursor is due to the polar structure of the polymer backbone with cyanovinyl amine, hydroxy groups and their strong dipolar.

Polymer Characterization

The IR spectral change of polymer 1 after heating to 400°C for 15 min is shown in Fig. 1 and is compared with precursor 1. The NH absorption band at 3200–3300 cm⁻¹, nitrile band at 2215 cm⁻¹, and the cyanovinyl band at about 1560 cm⁻¹, decrease dramatically, also the change into characteristic bands of polybenzoxazole structure

after heat treatment is obvious (Fig. 1). The thermal behavior of precursor 1 and polymer 1 under a nitrogen stream is shown in Fig. 2. As expected, two weight loss stages were found in the first scan. A broad exotherm peak was seen in the temperature range of 200–400°C, which corresponds to the loss of malononitrile. The second exotherm peak is due to the decomposition of PBO formed by the heat treatment. The second scan was performed before the precursor 1 was annealed at 400°C for 15 min to ensure the completion of the cyclization reaction. The thermal properties of the resulting PBO (polymer 1) are very good after cyclization. The temperature corresponding to 5% weight loss is 540°C and the char yield at 700°C is 56% as shown in Fig. 2. The TGA thermograms of polymer 1 and polymer 2 are shown in Fig. 3. Compared with polymer 2, the 5% weight loss temperature was increased to 552°C by the introduction 10% mol 1,3,5-benzenetricarboxylic acid unit into polymer 2 main chain. The char yield at 700°C is 83%, indicating its excellent resistance toward thermal degradation (Fig. 3). From Fig. 3, we note that weight loss of cyclized polymer depends strongly on the BTC. Since the polymer 2 with BTC should have a higher structure stability power than that without BTC, it should preferentially show thermal stability on heating.

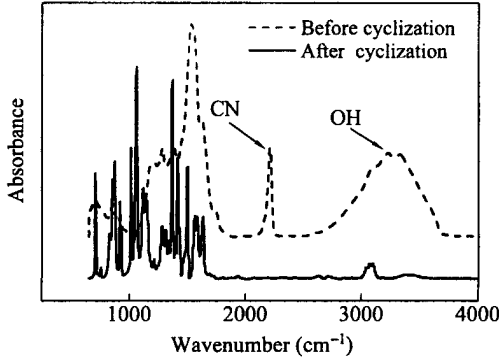


Fig. 1 IR spectrum of precursor 1 (dashed line) and polymer 1 (solid line)

Table 1. Solubility behavior of the precursor

Solvent ^a	MSA	DMAc	DMSO	NMP	THF
Solubility ^b of precursor 1	++	++	++	++	+
Solubility of precursor 2	++	++	++	++	+

^a MSA (methyl sulfonic acid), DMAc (*N,N*-Dimethylacetamide), DMSO (dimethyl sulfoxide), NMP (*N*-methyl-2-pyrrolidone), THF (tetrahydrofuran); ^b ++ (soluble), + (swelling) at room temperature

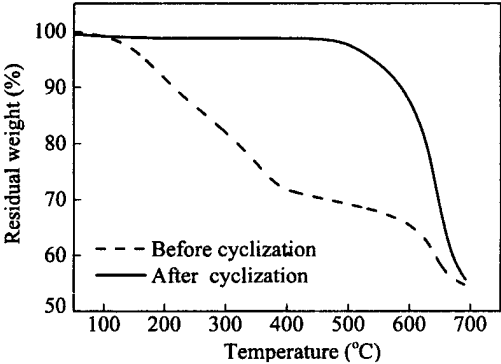


Fig. 2 TGA thermograms of precursor 1 (dashed line) and polymer 1 (solid line)

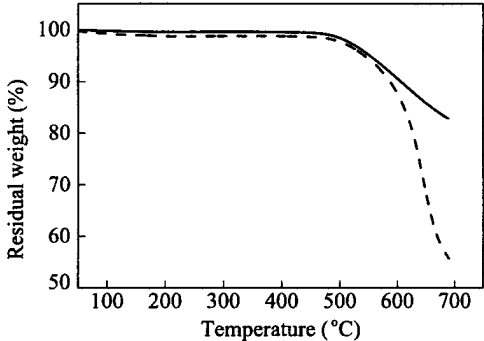


Fig. 3 TGA thermograms of polymer 2 (solid line) and polymer 1 (dashed line)

In conclusion, soluble PBO precursor was prepared by direct polycondensation of 1,3,5-benzenetricarboxylic acid chloride, 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene and 4,6-diaminoresorcinol hydrochloride

using pyridine and DMAc as condensing agent and solvent. *In situ* thermal conversion of the PBO precursor into polybenzoxazoles can provide an alternative method for generating polybenzoxazoles films and fibers. The introduction of 1,3,5-benzenetricarboxylic acid units into the main chain can increase the TG temperature and char yield while having little effect on solubility. Further studies on polybenzoxazole using soluble polybenzoxazole precursor with polyenaminonitrile containing hydroxyl groups are in progress.

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