

SYNTHESIS OF NOVEL SOLUBLE AROMATIC POLYPYROMELLITIMIDE
CONTAINING ORDERED 1,2,4-TRIAZINE IN THE MAIN CHAIN*Xiao-bing Yi^a, Guo-shi Wu^{a**} and Feng-cai Lu^{b**}^a Department of Chemistry, Tsinghua University, Beijing 100084, China^b Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

Abstract A new heat-resistant, soluble polymer, poly(phenyl-1,2,4-triazine imide), has been prepared via a two-step method of polycondensation of *N,N'*-bis(4-benzil)pyromellitimide and terephthalamidrazone in cresol, followed by curing at higher temperature. The rigid 1,2,4-triazine group increases the solubility of the polyimide so that the polymer is soluble in cresol, *N*-methyl-2-pyrrolidone (NMP), trifluoroacetic acid and concentrated sulfuric acid, etc. Thermogravimetric analysis (TGA) indicates that this novel polyimide has good thermal stability with a high decomposition temperature of 447°C in air and of 423°C in N₂. It has a tensile strength of 107.4 MPa with an elongation at break of around 7.6%.

Keywords Polyimides, *N,N'*-Bis(4-benzil)pyromellitimide, Rigid-rod group, 1,2,4-Triazine

INTRODUCTION

It is well known that polyimides, especially wholly aromatic polyimides, have outstanding properties, such as excellent heat resistance, dimensional stability, excellent electrical and mechanical properties. However, the inherent rigid macromolecular structures of the fully imidized form made most aromatic polyimides suffer from processing problems due to their insolubility. Numerous methods have been developed to modify the chain structures of the polyimides to counterbalance their thermal stability and processability^[1]. Among these, one effective way is to introduce some rigid-rod groups into the main chain, which have similar rigidity to the imide group. Various rigid-rod fragments such as benzimidazole, pyrrole, benzothiazole, 1,3,4-oxadiazole, benzoxazole, and quinoxaline have been shown to be effective for this purpose^[2–7]. In the present work, a bisbenzil containing a preformed imide group, *N,N'*-bis(4-benzil)pyromellitimide, was synthesized from benzoin as the starting material through a new route. Then, another rigid-rod aromatic group, phenylated-1,2,4-triazine, was introduced into the main chain of polyimide with an ordered chain structure controlled in the polymerization process of *N,N'*-bis(4-benzil)pyromellitimide with terephthalamidrazone. The resulting polymer has good solubility and thermal stability.

EXPERIMENTAL

Synthesis

The synthesis route of poly(phenyl-1,2,4-triazine imide) is shown in Scheme 1.

4-Nitroacetylbenzoin (I)

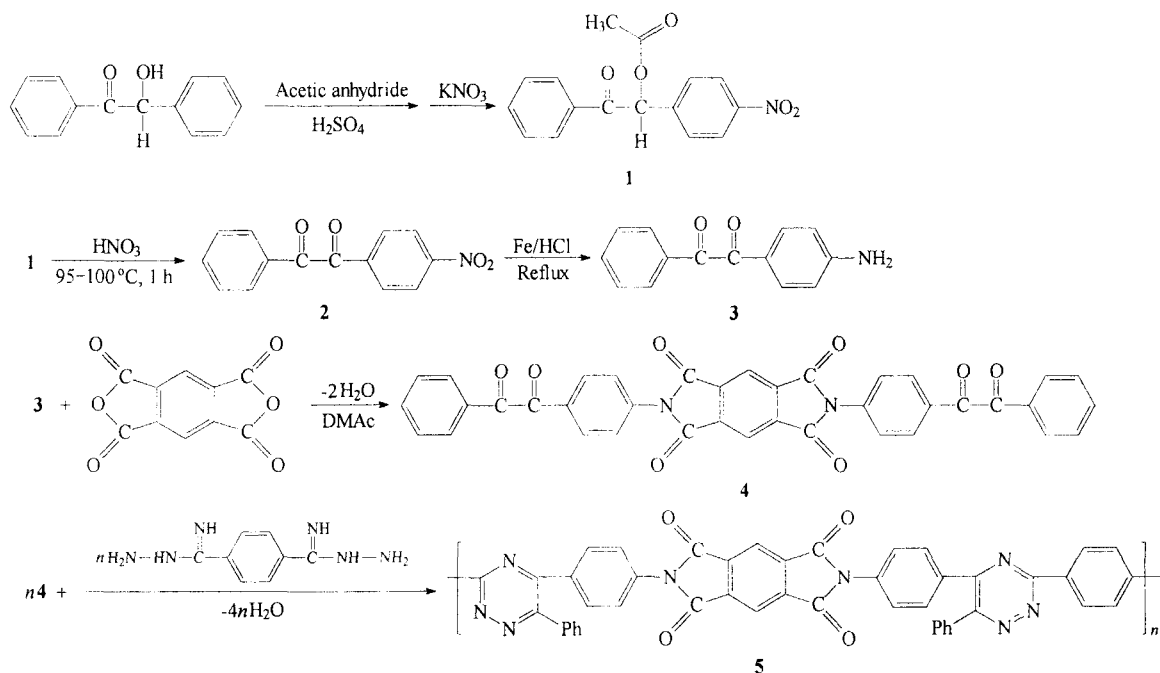
100 mL concentrated sulfuric acid was added dropwise to a mixture of 100 g (0.47 mol) benzoin and 500 g acetic anhydride with cooling by ice-water so that the temperature of the reacting system was kept below 15°C. The

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resulting solution was cooled to -15°C and then 55 g (0.54 mol) finely powdered KNO_3 was slowly added at the reaction temperature controlled below -5°C . Then the mixture was stirred at 0°C for 2 h and kept at ambient temperature for 2 days. After completion of the reaction, the mixture was poured into 1 liter of ice water to yield some white precipitate. Recrystallization from ethanol yielded a colorless and brilliant leaf-like crystalline product, yield 40%, m.p. $126\text{--}127^{\circ}\text{C}$ (lit. [8], m.p. 125°C). Elemental analysis for $\text{C}_{16}\text{H}_{13}\text{NO}_5$ (%): calcd.: C 64.20, H 4.68, N 4.68; found: C 64.03, H 4.41, N 4.63.



Scheme 1 The synthesis route of poly(phenyl-1,2,4-triazine imide)

4-Nitrobenzil (**2**)

A mixture of 10 g (0.034 mol) **1** and 28 mL (66%–68%) nitric acid was heated to $95\text{--}100^{\circ}\text{C}$ with stirring for 1 h. After completion of the reaction, the mixture was poured into cold water to yield 7.67 g of crude yellow solid which was recrystallized from 95% ethanol to give 6.29 g of product, yield 72.6%, m.p. $141\text{--}142^{\circ}\text{C}$ (lit. [8], m.p. 140°C). Elemental analysis for $\text{C}_{14}\text{H}_9\text{NO}_4$ (%): calcd.: C 65.8, H 3.53, N 5.49; found: C 65.36, H 3.60, N 5.55.

4-Aminobenzil (**3**)

A mixture of 1.91 g **2** (0.0075 mol), 1.26 g iron powder (0.0225 mol), 0.12 mL concentrated hydrochloric acid, 120 mL ethanol and 36 mL water was stirred at refluxing temperature for 1 h in a nitrogen atmosphere. After filtration of the solid residue, the hot solution was cooled to room temperature to give a slight yellow precipitate. The precipitated crude solid was recrystallized from ethanol-water (1:1) to yield 0.91 g (74.7%) of slight yellow plate crystalline, m.p. $128\text{--}129^{\circ}\text{C}$ (lit. [9], m.p. 130°C). Elemental analysis for $\text{C}_{14}\text{H}_{11}\text{NO}_2$ (%): calcd.: C 74.6, H 4.89, N 6.21; found: C 74.76, H 4.86, N 6.21.

N,N' -Bis(4-benzil)pyromellitimide (**4**)

4 was prepared from the reaction of **3** with pyromellitic dianhydride by the reported method^[10]. m.p. $366\text{--}367^{\circ}\text{C}$ (lit. [10], m.p. $365\text{--}367^{\circ}\text{C}$). IR (KBr, cm^{-1}): 3105–3051, 1779, 1721, 1665, 1596, 1356, 1090 and 724. Elemental analysis for $\text{C}_{38}\text{H}_{18}\text{N}_2\text{O}_8$ (%): calcd.: C 72.15, H 3.16, N 4.43; found: C 72.17, H 3.15, N 4.32.

Terephthalamidrazone

Terephthalamidrazone was prepared from 1,4-dicyanobenzene according to the method described by Lu *et al.*^[11].

Elemental analysis for $C_8H_{12}N_6$ (%): calcd.: C 49.98, H 6.29, N 43.72; found: C 50.36, H 6.31, N 43.36.

Polymer Synthesis

A mixture of 0.2760 g (0.436 mmol) **4**, 0.0837 g (0.436 mmol) terephthalamidrazone and 3.8 g cresol was mechanically stirred in a polymerizing reactor in a nitrogen atmosphere at 70°C for over 2 h to produce a viscous solution of the polymer precursor. After storage at room temperature for 24 h, the resulting solution was filtered. The given filtrated precursor solution exhibited an inherent viscosity (η_{inh}) of 0.63 dL/g (0.5 wt% in cresol at 30°C). Then it was spread on a clean glass plate, followed by heating on a hot plate at 70°C for 1.5–2.0 h to evaporate most of the solvent. The film on the glass plate was then put into an oven, the temperature of which was gradually raised to 300°C and kept at that point for 2 h to complete the polymerization and evaporate the remaining solvent in an argon atmosphere. Finally, the film was cooled to room temperature and removed from the glass plate by soaking in water. The average film thickness was 42 μm .

Characterization

IR spectra of the samples in KBr pellet or film forms were recorded on a Nicolet-560 spectrometer. A Hewlett Packard 8452A UV-Vis spectrophotometer with a diode array was employed for recording the spectra. Elemental analyses were carried out with a Heraeus CHN Rapid Elemental Analyzer. A TA DSC-2910 differential scanning calorimeter was used for the calorimetry measurements. Thermogravimetric analyses were performed on a TA TGA-2050 thermal analyzer at a heating rate of 10 K/min both in N_2 and in air within the temperature range of 30–800°C. The mechanical properties of the sample films were measured on an Instron 1122 extension measurement machine with a crosshead speed of 10 mm/min at room temperature.

Commercial analytical grade solvents and reagents were used throughout the experiments.

RESULTS AND DISCUSSION

Synthesis of *N,N'*-Bis(4-benzil)pyromellitimide

4-Nitroacetylbenzoin, which was synthesized from benzoin by a two-step procedure because benzil is less readily nitrated and mononitrobenzil has not been obtained from direct nitration of benzil. It was reported that dinitryl compound was produced when benzil was heated together with fuming nitric acid^[8]. Therefore, we first converted the hydroxyl group of benzoin to acetylate using acetic anhydride and then introduced the nitro-group to the *para*-position of acetylbenzoin using KNO_3 powder in an acidic environment at low temperature.

Though it was reported that 4-nitrobenzil could be formed by heating 4-nitroacetylbenzoin with nitric acid^[8], we found that the yields of the nitration reaction product increased from 54.9% to 72.6% when the reaction temperature was raised from 90 to 100°C at a nitric acid concentration of 66%–68%. On the contrary, with fuming nitric acid, no 4-nitrobenzil was obtained at temperatures of 95–100°C because it would be further nitrated with more nitro group introduced into the phenyl group in these rigorous conditions.

Augl^[10] reported a method to prepare **4** using 4-nitrodeoxybenzoin as the starting material. In our work, this compound was synthesized more conveniently from benzoin through the new route shown in Scheme 1, which avoids the use of virulent SeO_2 reagent and gives a favorable yield. The preformed imide and bis(1,2-dicarbonyl) structures in **4** were identified by IR spectra. In curve (a) of Fig. 1, corresponding to **4**, the absorptions at 1789 and 1721 cm^{-1} can be assigned as the symmetric and asymmetric C=O stretching vibrations of imide groups, respectively, while the absorptions at 1090 and 724 cm^{-1} are due to the vibrations of imide structure, and the absorption at 1356 cm^{-1} is attributed to C–N groups. In addition, the absorption bands at 1665 and 1596 cm^{-1} are related to the symmetric and asymmetric C=O stretching vibration of bis(1,2-dicarbonyl) structure.

Preparation of Rigid-Rod Polyimide

The rigid-rod polyimide containing ordered phenylated 1,2,4-triazine was synthesized by a conventional two-step method starting from the preformed imide group of **4** with terephthalamidrazone in cresol followed by thermal cyclodehydration at 300°C. As in the synthesis of any poly-1,2,4-triazine, monomer purification and drying were important in the synthesis of high molecular weight polymers. In addition, the initial polymerization rate of **4** was

much slower than that of common aromatic bis(1,2-dicarbonyl) monomers^[11], such as 1,4-bis(phenylglyoxalyl)-benzene, which readily react with terephthalamidrazone at room temperature. The electron-withdrawing imide group in **4** reduced the reactivity of the compounds with reduced polymerization rate at room temperature. Thus, the reaction temperature in the first step was raised to 70 °C. A viscous precursor solution was obtained by polymerization of **4** with stoichiometric terephthalamidrazone in cresol at 70 °C for 2 h. The resulting solution was filtered and poured onto a clean glass plate to evaporate most of solvent at 70 °C. It was then heated to 300 °C for 2 h in an argon atmosphere to complete the polymerization. Finally, a piece of creasable yellow film was obtained.

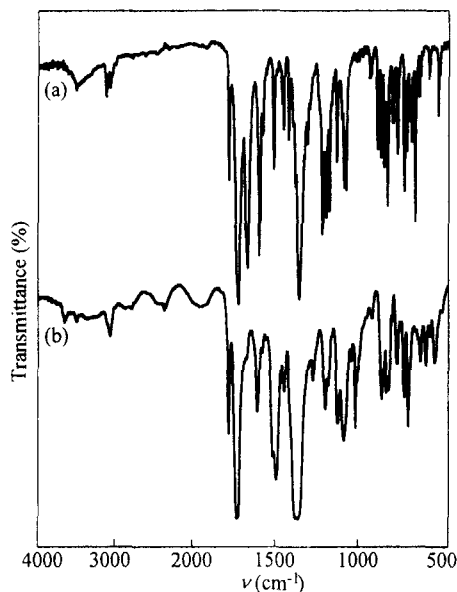


Fig. 1 FTIR spectra of (a) *N,N'*-bis(4-benzil)pyromellimide and (b) poly(phenyl-1,2,4-triazine imide)

Characterization and Properties of Product

The IR spectrum of the final product, poly(phenyl-1,2,4-triazine imide), is shown in Fig. 1(b). The absorption bands at 1779 (C=O symmetric stretching), 1728 (C=O asymmetric stretching), 1368 (C–N), 1086 and 722 cm^{−1} (vibrations of imide structure) are characteristic for the imide structures while the absorption bands at 1496, 1444, 1385–1390 (C=C, C=N, N=N) and 1016 cm^{−1} are characteristic for the 1,2,4-triazine rings. In addition, the UV-visible spectrum of this polymer in a concentrated sulfuric acid solution shows a π - π^* transition band at 334 nm, which is characteristic of 1,2,4-triazine, as shown in Fig. 2.

The solubility of poly(phenyl-1,2,4-triazine imide) in various solvents was examined and is summarized in Table 1. Though it remains insoluble in some generic organic solvents such as CH₃Cl, DMF and DMAc, it shows good solubility in NMP, cresol, trifluoroacetic acid, and concentrated sulfuric acid due to the distortion of the chain regularity by introducing of phenylated 1,2,4-triazine group into the main chain of polyimide. As is known, aromatic polyimides as a class are inherently insoluble in common solvents, this improved solubility makes the polymer more processable.

The thermal properties of this novel polymer were investigated by TGA and DSC scans. The results of the TGA analyses showed that the polymer has good thermal and thermo-oxidative stabilities because it shows little weight loss both in N₂ and in air until the temperature was higher than 400 °C. The decomposition temperatures in air for most linear aromatic polyimides are in the range of 430–575 °C. The decomposition temperature of the obtained polymer in N₂ is 423 °C and in air is 447 °C, as shown in Fig. 3.

The thermograms in Fig. 3 are similar to that of typical poly(phenyl-1,2,4-triazines) with a typical two stage decomposition steps^[11-14]. No endothermic peaks of the glass transition temperature were observed in the DSC scans from 30 to 800°C, which may be attributed to the rigidity of the repeat unit pushing the glass transition temperature of this polymer beyond the degradation temperature and precluding its observation in DSC scans^[15].

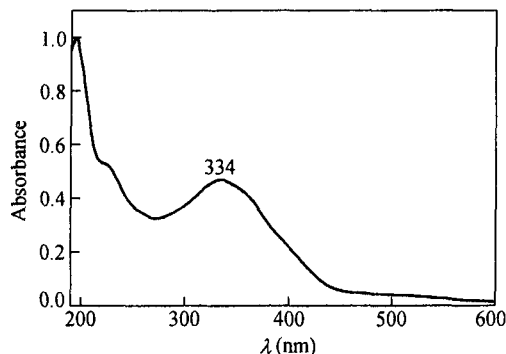


Fig. 2 UV-Vis spectrum of poly(phenyl-1,2,4-triazine imide) in concentrated sulfuric acid

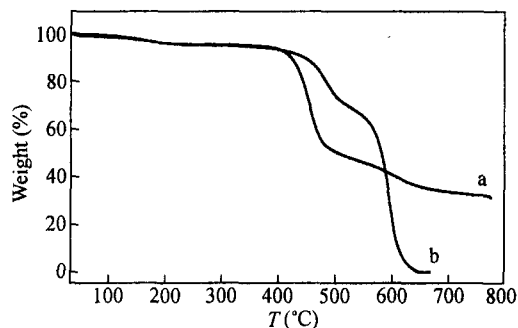


Fig. 3 Thermogravimetry of poly(phenyl-1,2,4-triazine imide) in nitrogen (a) and in air (b) at a heating rate of 10 K/min

Table 1. Solubilities of poly(phenyl-1,2,4-triazine imide) in various solvents

Temperature	Solvent							
	CH ₂ Cl	DMF	DMAc	DMSO	Cresol	NMP	CF ₃ COOH	H ₂ SO ₄
At room temperature	—	—	—	—	±	+	+	+
At 60–70°C	—	—	—	—	+	+	+	+

(+) Soluble; (–) Insoluble; (±) Slightly soluble

The poly(phenyl-1,2,4-triazine imide) film has a tensile strength of 107.4 MPa and an elongation at break of 7.6% averaged from the results of 5 samples.

CONCLUSIONS

The incorporation of ordered phenylated-1,2,4-triazine units into the main chain gave a new kind of aromatic polyimide with improved solubility as well as good thermal stability. This approach provides a new way to increase the solubility without sacrificing much of the thermal and mechanical performance of the polyimides. Unlike the preparation of most polyimides from various dianhydrides and diamines by a two-step method, the new polymer was prepared from one kind of monomer by a preformed imide group. Hence, this avoided the use of unstable poly(amic acid) solution, which is sensitive to temperature, concentration and moisture.

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