Synthesis, curing kinetics and thermal properties of a novel self-promoted fluorene-based bisphthalonitrile monomer

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ABSTRACT

A novel amino-containing fluorene-based bisphthalonitrile monomer, 9,9-bis(4-aminophenyl)-2,7-(3,4-dicyanophenoxy)-fluorene (AFPN), was successfully synthesized via the nucleophilic displacement of the nitro-substituent from 4-nitrophthalonitrile. The structure of AFPN was confirmed by Fourier transform infrared (FT-IR), ^{1}H and ^{13}C nuclear magnetic resonance (NMR). Its curing behavior and curing kinetics were investigated using differential scanning calorimetry (DSC) and FT-IR techniques. Isoconversional method based on Starink was applied to analyze the curing process of AFPN. The thermal and mechanical properties of the cured product were evaluated by thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA). The AFPN showed a self-promoted curing behavior, whereas the introduction of the amino groups increased its curing rate and lowered its curing temperature. Additionally, its cured polymer showed an excellent thermal and thermo-oxidative stability, since its char yield reached 76.5% at 800 °C in nitrogen and 83.4% at 600 °C in air, respectively.

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1. Introduction

Phthalonitriles as a unique class of high-performance thermosetting resins have attracted more attention due to their outstanding thermal stability, good mechanical properties, high glass transition temperature and excellent flame resistance [1–4]. These unique characteristics give the phthalonitrile resins a wide range of applications in marine, aerospace and microelectronic industries [5–7]. However, the polymerization of the neat phthalonitrile monomer is extremely difficult, requiring several days at elevated temperature before the gelation process occurs, which limits their wide uses and exaggerates its cost. A variety of curing additives are manipulated in phthalonitrile curing reaction to increase its polymerization degree such as phenols [8], organic amines [9–11], and strong organic acid/amine salts [12]. However, these additives generally release volatiles during the curing reaction, resulting in the creation of many voids within their crosslinked networks. In order to produce a highly crosslinked polymerization system, organic amines have drawn much attention. However, this phthalonitrile/amine composition exhibits a narrow processing window because of its high melting point (∼230 °C) [10]. To overcome this problem, much effort has been conducted via the concept of the molecular design. The phthalonitrile monomers containing hydroxyl and amino group show a self-promoted curing behavior even in the absence of the curing additives [13,14]. The high temperature of melting transition is also a common shortcoming for phthalonitrile monomers [15,16]. Therefore, development of a new phthalonitrile resin system having self-promoted curing behavior with low melting temperature would be an attractive issue for both academia and industrial applications.

Fluorene molecule contains two benzene rings linked with a five-membered ring provides a high overlaps of π-orbitals [17]. Polymers containing a fluorenyl structure in their backbone (so-called 'Cardo-type polymers') have various excellent properties, such as good heat-resistance, high char yield, high limited oxygen index, good flame-retardance and an excellent solubility in common organic solvents [18,19]. So, the incorporation of cardo groups in the backbone of polymers can impart a significant increase in both their T_g and thermal stability by restricting their segmental mobility. Two bisphthalonitrile monomers containing fluorene have been synthesized by the nucleophilic displacement of the nitrosubstituent from 4-nitrophthalonitrile with 9,9-bis(4-hydroxyphenyl) fluorene and 9,9-bis(3,5-dimethyl-4-

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hydroxyphenyl) fluorene in the presence of potassium carbonate [20]. As a result, the development of such polymers has been the focus of an extensive research interest over the last few years [21–24]. Owing to their rigid molecular structure, the introduction of thermally stable fluorene group into their main chain could be an effective approach to improve the thermal stability of these polymers.

In this work, a novel amino-containing self-promoted fluorene-based bisphthalonitrile compound was successfully synthesized. Chemical structure of the monomer was confirmed by FT-IR, ^{1}H and ^{13}C NMR. The rheological behavior of the monomer was also discussed. Non-isothermal DSC was used to investigate the curing kinetics of AFPN. The curing behavior of the bisphthalonitrile monomer and the thermal and mechanical properties of its cured polymer were discussed by DSC, FT-IR, TGA and DMA.

2. Experimental

2.1. Materials

9,9-bis[(3,4-dicyanophenoxy) phenyl]fluorene (BPF) was synthesized according to literature [20]. 2,7-dihydroxy-9-fluorenone, methylsulfonic acid, aniline, and anhydrous potassium carbonate were obtained from Shanghai Jingchun Reagent Co., Ltd. (China). 4-nitrophthalonitrile was supplied by Alpha (Shijiazhuang) Chemical Co., Ltd. (China). All solvents were purchased from Tianjin Kermel Chemical Reagent Co., Ltd. (China), and used without further purification.

2.2. Synthesis of the novel bisphthalonitrile containing amino (AFPN)

Scheme 1 illustrates the synthesis of 9,9-bis(4-aminophenyl)-2,7-dihydroxy-fluorene (AHF) and 9,9-bis(4-aminophenyl)-2,7-(3,4-dicyanophenoxy)-fluorene (AFPN).

2.2.1. Synthesis of AHF

Aniline (111.6 g, 1.2 mol), 2,7-dihydroxy-9-fluorenone (42.4 g, 0.2 mol), and methylsulfonic acid (9.6 g, 0.1 mol) were added into a 250 mL three neck round bottom flask equipped with a mechanical stirrer and refluxing condenser. The reaction mixture refluxed at 150 °C for 14 h under nitrogen atmosphere. After that, the reaction mixture was cooled down to 110 °C, and then poured into triethylamine and stirred at 110 °C for 20 min. The precipitated product was isolated by suction filtration and washed thoroughly with ethanol and distilled water several times at room temperature before drying in a vacuum oven. The pale yellow powder (AHF) was afforded (69.16 g, 91% yield). FT-IR (KBr, cm^{-1}): 1587 cm^{-1}, 1510 cm^{-1}, 1466 cm^{-1} (C=C), 3310 cm^{-1} and 3380 cm^{-1} (−NH$_2$), ^{1}H NMR (500 MHz, DMSO-d$_6$, ppm): 9.24 (s, 2H), 7.44 (d, 2H, J = 8.11 Hz), 6.71 (d, 4H, J = 8.48 Hz), 6.65 (d, 2H, J = 8.11 Hz), 6.63 (s, 2H), 6.40 (d, 4H, J = 8.48 Hz), 4.92 (s, 4H). ^{13}C NMR (500 MHz, DMSO-d$_6$, ppm): 156.45, 153.98, 147.35, 133.94, 131.47, 128.77, 120.08, 114.44, 113.97, 113.21, 63.70. Elem. Anal. Calcd for C$_{25}$H$_{20}$N$_2$O$_2$: C 78.93%, H 5.30%, N 7.36%. Found: C 78.65%, H 5.12%, N 7.63%.
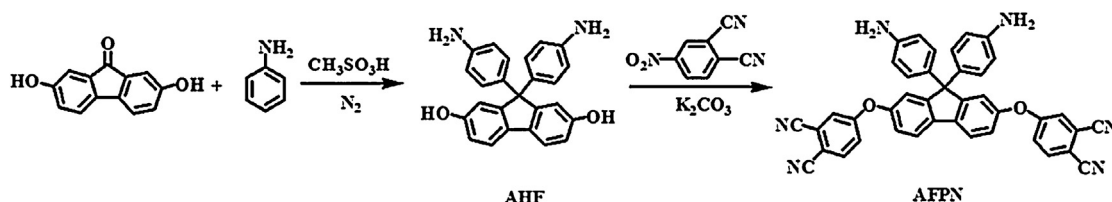
2.2.2. Synthesis of AFPN

AHF (11.4 g, 0.03 mol), 4-nitrophthlonitrile (10.38 g, 0.06 mol), potassium carbonate (8.28 g, 0.06 mol), and DMSO (80 mL) were added to a 250 mL three neck round bottom flask equipped with a mechanical stirrer and refluxing condenser. The reaction mixture refluxed at 90 °C for 14 h under nitrogen atmosphere. The reactant was poured into hot distilled water (60–70 °C). The precipitate was collected by filtering and washing the product with hot distilled water until the pH value of water was neutral. The precipitate was collected and dried in a vacuum oven at 80 °C for 24 h. The AFPN powder (16.49 g, 87% yield) was obtained. FT-IR (KBr, cm^{-1}): 3450 and 3372 (stretch, N−H), 2232 (stretch, −CN), 1486–1596 (stretch, C=C), 3033 (stretch, C=CH), 1251 (stretch, C−O−C). ^{1}H NMR (500 MHz, DMSO-d$_6$, ppm): 8.07 (d, 2H, J = 8.92 Hz), 7.99 (d, 2H, J = 8.20 Hz), 7.79 (d, 2H, J = 2.59 Hz), 7.41 (dd, 2H, J = 8.92, 2.59 Hz), 7.18 (d, 2H, J = 8.20 Hz), 7.14 (s, 2H), 6.78 (d, 4H, J = 8.63 Hz), 6.42 (d, 4H, J = 8.63 Hz), 4.97 (s, 4H). ^{13}C NMR (500 MHz, DMSO-d$_6$, ppm): 161.86, 155.64, 153.74, 147.82, 136.70, 136.50, 132.28, 128.74, 123.05, 122.40, 119.80, 118.43, 117.14, 116.38, 115.80, 114.20, 108.56, 64.30. Elem. Anal. Calcd for C$_{41}$H$_{24}$N$_6$O$_2$: C 77.84%, H 3.82%, N 13.28%. Found: C 77.58%, H 3.61%, N 13.53%.

2.3. Preparation and curing of bisphthalonitrile monomer

The amino-containing fluorene-based bisphthalonitrile powders were placed into a sheet steel mold, and were degassed under vacuum oven at 120–130 °C for 4 h to remove embedded gases. Then, the specimens were cured without adding any initiator or extra catalyst according to the following schedule: 220 °C/3 h, 250 °C/3 h and 280 °C/6 h in an air-circulating oven. The thickness of the cured samples was limited to 2 mm via a polishing process.

2.4. Characterization

Fourier transform infrared (FT-IR) spectra were recorded by a PerkinElmer Spectrum 100 spectrometer using KBr optics in the range of 4000–450 cm^{-1}. Transmission spectra were obtained at a resolution of 4 cm^{-1} after averaging two scans by casting a thin film on a KBr plate for monomers and cured samples. ^{1}H and ^{13}C NMR characterizations were obtained using a Bruker AVANCE-500 NMR spectrometer with DMSO-d$_6$ as the solvent and tetramethylsilane (TMS) as an internal standard. The average number of transients for ^{1}H and ^{13}C NMR spectroscopy was 16 and 1024, respectively. A relaxation delay time of 1 s was used for the integrated intensity determination of ^{1}H NMR spectra. Elemental analysis was carried out with a Vario EL cube (Elementar Analysensysteme GmbH). DSC analysis was performed on a TA Q200 differential scanning calorimeter using 3–5 mg of the sample under a constant flow of a nitrogen atmosphere of 50 mL/min. The instrument was calibrated with a high purity indium standard, and α-Al$_2$O$_3$ was used as the reference material. The sample was weighed into a hermetic aluminum sample pan at 25 °C, which was then sealed, and the sample was scanned at heating rate of 20 °C/min from 20 to 350 °C. The dynamic rheological measurements were carried out using TA Instruments AR-2000ex Rheology at an angular frequency

Scheme 1. Synthesis of AFPN monomer.