

Synthesis of itaconimide/nadimide-functionalized benzoxazine monomers: Structural and thermal characterization



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ABSTRACT

A novel series of itaconimide/nadimide-functionalized benzoxazine monomers (I-Bz/N-Bz) from imide-terminated amines, paraformaldehyde and phenol/*m*-cresol/cardanol/4-(hydroxyphenyl) benzoxazole were synthesized and characterized by FT-IR, ¹H and ¹³C NMR and HRMS analyses. The I-Bzs exhibited lower curing temperatures compared to the N-Bzs, which may be attributable to the presence of the 1,1-disubstituted double bond in itaconimide. The poly(I-Bz)s exhibited higher glass-transition temperatures (210–216 °C) compared to the poly(N-Bz)s (151–178 °C). The itaconimide- and nadimide-functionalized benzoxazines showed comparable thermal stability, but differences in their phenolic structures affected their thermal behavior (char yield and *T*_{max}). The poly(I-Bz)s (19–47%) showed higher char yields compared to the poly(N-Bz)s (18–41%), depending on the backbone structure. The highest lap-shear strength at 200 °C was observed in I-Bz/N-Bz derived from *m*-cresol.

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1. Introduction

Polybenzoxazines have excellent mechanical and chemical properties, high glass transition temperatures, low moisture absorption, flame retardance, an absence of volatiles during polymerization and zero shrinkage upon curing. These polymers have been extensively reported in the literature [1–5]. To further improve the thermal properties of standard benzoxazine resins, monomers with varying structures have been prepared by using different phenols or amines [6–10]. These various preparations include the incorporation of functional groups such as maleimide and nadimide [11], methacryloyl [12,13], vinyl [14], allyl [15], nitrile [16], propargyl ether [17], epoxy [18], furan [19], acetylene [20], and benzoxazole [21–24] into the benzoxazine structure. The polyfunctionality of these benzoxazine monomers leads to a cross-linked network structure with improved thermal properties by reducing chain mobility.

Addition polyimides, such as maleimides and nadimides, are high-performance polymers with excellent properties. The incorporation of such units has resulted in an improved thermal stability and char yield of polybenzoxazines without an increase in the viscosity of the monomer compared to typical benzoxazine monomers. Maleimide- [11,25–28] and nadimide-functionalized [11] benzoxazines contain 1,2-disubstituted double bonds, which have a very low tendency to homopolymerize. Heating at high

temperatures is necessary for the cross-linking of maleimide- and nadimide-based resins. Conversely, itaconimides have 1,1-disubstituted double bonds, which usually cure at a lower temperature [29–31]. It is expected that the incorporation of itaconimide into benzoxazine structures can lower the curing temperature significantly. No studies have yet reported on itaconimide-functionalized benzoxazines. It was, therefore, considered to be of interest to systematically study the effect of structure on the curing characteristics and thermal stability of itaconimide-functionalized benzoxazines and to compare their thermal characteristics to those of nadimide-functionalized benzoxazine of similar structure. The synthesis, structures and letter designations of the various monomers studied in this work are depicted in Scheme 1.

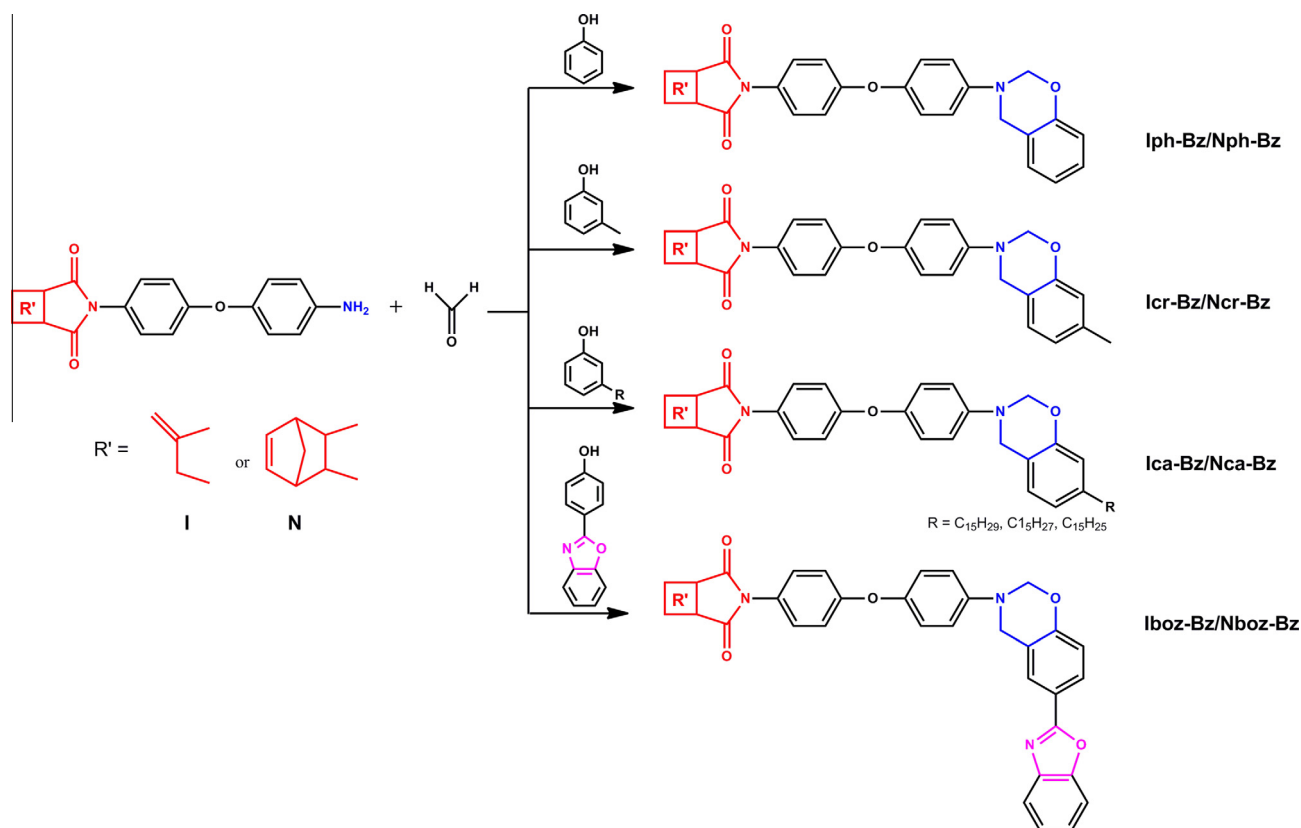
2. Experimental section

2.1. Materials

Cardanol (Satya Cashew Chemicals Pvt. Ltd., Chennai); *o*-aminophenol (Alfa Aesar, UK); poly(phosphoric acid) (PPA, with a phosphorous-pentoxide content of 80.8%) and stannous chloride (Spectrochem Pvt. Ltd., Mumbai); nadic anhydride and itaconic acid (ABR Organics, Hyderabad); *m*-cresol, phenol, *p*-aminophenol and 1-chloro-4-nitrobenzene (Loba Chemie, Mumbai); HCl (35%), hexane and ethanol (Merck, Germany); and paraformaldehyde, acetic anhydride, potassium carbonate, phosphorous pentoxide, dimethyl formamide (DMF), glacial acetic acid, sodium carbonate, sodium bicarbonate, toluene, dichloromethane, chloroform, *p*-

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Scheme 1. Synthesis, structures and letter designations of imide-functionalized benzoxazine monomers (I-Bzs and N-Bzs).

hydroxybenzoic acid, ethyl acetate, sodium sulfate and aluminum oxide were obtained from Fisher Scientific, Mumbai. Itaconic anhydride [29], 4-hydroxyphenyl benzoxazole (4-HPBO) [32] and 4-nitrophenoxy aniline (NPA) [33] were prepared according to the procedures reported in the cited works.

The acetone, glacial acetic acid and acetic anhydride were distilled before use. The other reagents were used as received.

2.2. Synthesis of imide-functionalized amine

The amines were synthesized by the reduction of the corresponding nitro compounds with stannous chloride/HCl.

2.2.1. 4-Nitrophenoxy itaconimide (NPI)

In a 250 mL two-necked round-bottomed flask equipped with a nitrogen inlet and a reflux condenser, NPA (25 g, 0.109 mol) was dissolved in 100 mL of dry acetone. Itaconic anhydride (12.21 g, 0.109 mol) was slowly added to the flask, and the contents were refluxed for 6 h. Then, sodium acetate (3 g) and acetic anhydride (22.25 g, 0.218 mol) were added to the flask, and the solution was refluxed for 12 h. The contents were then cooled and precipitated into ice water. The pale yellow precipitate was washed with a 0.5 N sodium bicarbonate solution, neutralized and finally washed with distilled water, dried and recrystallized from chloroform.

Yield: 72.8%; $^1\text{H NMR}$ (300 MHz, $\text{CDCl}_3\text{-d}_6$, δ): 8.24–8.22 (d, 2H, Ar–NO₂), 6.98–7.44 (d, 6H, ArH), 6.51 and 5.79 (s, 2H, C=CH₂), 3.55 (s, 2H, CH₂).

2.2.2. 4-Nitrophenoxy nadimide (NPN)

NPN was prepared in a single step by dissolving NPA (20 g, 0.087 mol) in glacial acetic acid (100 mL). Then, nadic anhydride (14.28 g, 0.087 mol) was slowly added while stirring continuously. The mixture was heated at 120 °C for 12 h. The imide was then

precipitated in ice-cold water, filtered, washed (first with distilled water, followed by sodium-bicarbonate solution (1 N), followed by distilled water again) and dried in a hot air oven at 60 °C and recrystallized from chloroform.

Yield: 84.9%; $^1\text{H NMR}$ (300 MHz, $\text{CDCl}_3\text{-d}_6$, δ): 8.21–8.18 (d, 2H, Ar–NO₂), 7.03–7.23 (d, 6H, ArH), 6.26 (s, 2H, CH=CH), 3.45–3.51 (d, 4H, CH–CH–C=O), 1.78–1.81 and 1.61–1.64 (d, 2H, CH₂).

2.2.3. 4,4'-Aminophenoxy itaconimide (API) or nadimide (APN)

In a 500 mL two-necked round-bottomed flask equipped with a reflux condenser and a nitrogen inlet, anhydrous stannous chloride (51.57 g, 0.272 mol), ethanol (220 mL) and 35% HCl (45.06 mL, 0.509 mol) were combined. The mixture was stirred and heated to 70 °C to become a clear solution. To this hot solution, NPI (22 g, 0.068 mol) or NPN (25.57 g, 0.068 mol) was added portion-wise while stirring continuously. The reaction was monitored by thin layer chromatography (TLC) and was completed in 4 h (APN) or 12 h (API) at 70 °C. The mixture was then cooled, and the pH was increased to 8 by the addition of a saturated solution of sodium carbonate (200 mL). The white precipitate thus obtained was filtered through a sintered funnel (grade 3) under reduced pressure to yield a white cake. The amine was extracted with dichloromethane (1 L) and dried with anhydrous sodium sulfate; the excess solvent was then evaporated off, and the resultant shiny white crystals were collected and recrystallized from chloroform/dichloromethane (1/1).

NPI: Yield: 73.3%; $^1\text{H NMR}$ (300 MHz, $\text{CDCl}_3\text{-d}_6$, δ): 3.62 (s, 2H, NH₂), 6.65–7.24 (d, 8H, ArH), 6.46 and 5.74 (s, 2H, C=CH₂), 3.49–3.50 (s, 2H, CH₂).

NPN: Yield: 80.51%; $^1\text{H NMR}$ (300 MHz, $\text{CDCl}_3\text{-d}_6$, δ): 3.64 (s, 2H, NH₂), 6.68–7.28 (d, 8H, ArH), 6.26 (s, 2H, CH=CH), 3.44–3.51 (d, 4H, CH–CH–C=O), 1.78–1.81 and 1.61–1.64 (d, 2H, CH₂).

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