



Synthesis, curing behavior and thermal properties of fluorene-containing benzoxazines based on linear and branched butylamines



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ABSTRACT

A series of fluorene-containing benzoxazine monomers based on linear and branched butylamines were successfully synthesized in high purity and good yield through a facile one-pot procedure by the reaction of 9,9-bis-(4-hydroxyphenyl)-fluorene with paraformaldehyde and isomeric butylamines. The chemical structures of the target monomers were characterized by Fourier transform infrared (FT-IR), Elemental analysis, ¹H and ¹³C nuclear magnetic resonance (NMR). The curing behavior of benzoxazine monomers was studied by differential scanning calorimetry (DSC) and FT-IR. The thermal properties of cured polybenzoxazines were measured by DSC and thermogravimetric analysis (TGA). The results reveal that the polarity of solvent and the basicity of butylamines produce clear effects on the synthesis of the butylamine-based benzoxazine monomers. Also, the basicity and steric effect of butylamines exhibit significant effects on the curing behavior of benzoxazine monomers and the thermal properties of their polymers. The glass transition temperature and thermal stability of branched butylamine-based polybenzoxazines are higher than those of the corresponding linear butylamine-based polybenzoxazine and traditional bisphenol A-based polybenzoxazines.

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1. Introduction

Polybenzoxazines, as a class of thermosetting phenolic resins formed by the cationic ring-opening of the corresponding benzoxazine monomers without any added initiator, have demonstrated various attractive properties such as high thermal stability, high char yields, high glass transition temperature (T_g), near-zero volumetric change upon curing, good mechanical and dielectric properties, low water absorption, and low flammability [1–5]. These unique characteristics make polybenzoxazines a better candidate over epoxies and traditional phenolic resins in the electronic encapsulation, high-performance composite matrices, coating, adhesion, and fire resistant materials, etc. [6–17]. Meanwhile, difunctional polybenzoxazines are especially outstanding as their additional molecular design flexibility, which were required to construct an infinite network structure through synthesis process utilizing a difunctional phenolic compound with a monofunctional amine and formaldehyde. A plenty of studies have been conducted in order to improve the heat resistance of polybenzoxazine by increasing the crosslink density of the cured benzoxazine resin or

by introducing some specific functional groups such as allyl, propargyl, diacetylene, nitrile, phthalonitrile, maleimide, oxazoline, benzimidazole, and trimethoxysilane [1–3,18–28]. The multiple curing processes are also another positive alternative to modify polybenzoxazine by blending with other materials such as epoxy, novolac, polyurethane, bismaleimide, polyimide, clays, carbon nanotubes, and graphene [1–3,12,29,30]. Moreover, polybenzoxazines derived from various bisphenols and linear aliphatic amines or various phenols and linear aliphatic diamines show more outstanding mechanical properties by incorporating a flexible chain into the polybenzoxazine backbone. However, the thermal properties of linear aliphatic amine-based polybenzoxazines generally exhibit low T_g values and poor thermal stabilities, and decrease with the length of the aliphatic chains [31–34]. The influence of steric effect of branched-chains in the aliphatic amine-based polybenzoxazines on the thermal properties of polymers attracted seldom attention.

Fluorene molecule contains two benzene rings linked with a five-membered ring which provides a high overlaps of π -orbitals [35]. Polymers containing fluorenyl structure in their backbones (so-called ‘Cardo-type polymers’) have various excellent improved properties, such as good heat-resistance, high char yield, high limited oxygen index, good flame retardancy, and excellent solubility in common organic solvents. Therefore, the development of these polymers, such as polyimide, polyamide, epoxy resin, and

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polycarbonate has attracted extensive research interests during the past few years [36–38]. Recently, some researches on synthesis, polymerization behavior, curing kinetics, and thermal properties of fluorene-based benzoxazines derived from 9,9-bis-(4-hydroxyphenyl)-fluorene (BHPF) and 9,9-bis-(4-aminophenyl)-fluorene (BAPF) have been reported [39–44]. The results showed that fluorene-based polybenzoxazines display higher T_g and better thermal stability than traditional bisphenol A-based polybenzoxazines. In our previous study, the mixed solvents of 1,4-dioxane and ethanol were used in the synthetic process by two step approach [39]. However, the crude products contained a certain amount of ring-opening compounds as impurities, which were eliminated by washing them several times with NaOH aqueous solution. As a result, the yields of all fluorene based benzoxazine monomers, including aromatic and aliphatic amine-based benzoxazines, were less than 60%. The reasons of the formation of oligomers and occurrence of side reactions were mainly attributed to the presence of polar solvents and water in the mixture, as well as the high reaction temperatures selected [45]. Nevertheless, nonpolar solvents, such as chloroform, carbon tetrachloride, dioxane, or *n*-hexane, helped ring closure of the open Mannich base, and reduced the chances of ring opening [9]. In Liu's work, a relatively long reaction time (36 h) was needed for a furan-terminated fluorene-based benzoxazine in dioxane system and the sample loss even reached about 25% after recrystallizing [40]. Moreover, a high post-cure temperature was needed for fluorene-based benzoxazines to achieve higher thermal properties, which in turn could result in thermal decomposition of polybenzoxazines at elevated temperature. Therefore, it is necessary to further investigate the synthetic methodology and relationship between structure and properties of branched-chains aliphatic amine-based polybenzoxazines.

In the current study, a series of fluorene-based benzoxazine monomers with high purity were prepared from BHPF, paraformaldehyde, and four butylamine isomers by facile one-pot procedure. Chemical structures of the monomers were confirmed by FT-IR, elemental analysis, ^1H and ^{13}C NMR, and X-ray diffractometer (XRD). The curing behavior of the benzoxazine monomers and the thermal properties of its cured polymers were discussed by DSC, FT-IR, and TGA.

2. Experimental

2.1. Materials

BHPF (99.3%) was synthesized according to literature [36]. *n*-Butylamine (99.5%), *iso*-butylamine (99.5%), (\pm)-*sec*-butylamine (99%), *tert*-butylamine (99%), and paraformaldehyde (AR grade) were purchased from Shanghai Jingchun Chemical Co., Ltd. (China). All the manipulated solvents and other chemicals were of reagent grade or better, and used without any further purification.

2.2. Synthesis of benzoxazine monomers

A series of fluorene-containing benzoxazine monomers were prepared using BHPF, paraformaldehyde, and butylamine isomers including *n*-butylamine, *iso*-butylamine, (\pm)-*sec*-butylamine, and *tert*-butylamine. The reaction route and the abbreviations of benzoxazine monomers derived from isomeric butylamines are shown in Scheme 1.

2.2.1. Synthesis of BF-*n*-b

BHPF (7.0 g, 20 mmol), *n*-butylamine (3.0 g, 41 mmol), paraformaldehyde (2.7 g, 90 mmol) and 20 mL 1,4-dioxane were added to a 50 mL three neck flask equipped with a magnetic stirrer, reflux condenser and thermometer. The mixtures were then heated at

90 °C for 5 h. The reaction was allowed to cool to room temperature and then poured into water. The crude product was isolated by filtration and washed with water followed by drying under vacuum at 60 °C overnight. The obtained white powder was dissolved in methylene chloride, washed with 0.3 N NaOH solution and then with water. The organic phase was dried over sodium sulfate anhydrous, filtered, followed by evaporation of methylene chloride to afford white crystals (86.3% yield, m.p.: 173 °C). FT-IR (KBr, cm^{-1}): 1496 (C–H in-plane bending), 1380 (C–H deformation), 1322 (CH_2 wagging), 1234 (C–O–C asymmetric stretching), 1158 (C–N–C asymmetric stretching), 1078 (C–O–C symmetric stretching), 940 (C–H out-of-plane bending), 860 (C–N–C symmetric stretching), 821,740 (C–H out-of-plane bending). ^1H NMR (500 MHz, CDCl_3 , ppm): 6.65–7.75 (m, 14H, Ar–H), 4.77 (s, 4H, O– CH_2 –N), 3.80 (s, 4H, Ar– CH_2 –N), 2.67 (t, 4H, N– CH_2 –), 1.49 (m, 4H, CH_2 – CH_2 – CH_2), 1.30 (m, 4H, CH_2 – CH_2 – CH_3), 0.89 (t, 6H, – CH_3). ^{13}C NMR (125 MHz, CDCl_3 , ppm): 116.16–152.99 (24C, the carbons of benzene rings), 82.37 (2C, O– CH_2 –N), 64.36 (1C, quaternary carbon in the fluorene ring), 51.20 (2C, N– CH_2 –Ar), 50.51 (2C, N– CH_2 –), 30.28 (2C, CH_2 – CH_2 – CH_2), 20.41 (2C, CH_2 – CH_2 – CH_3), 14.07 (2C, – CH_3). Elem. Anal. Calcd for $\text{C}_{37}\text{H}_{40}\text{N}_2\text{O}_2$: C 81.58%, H 7.40%, N 5.14%. Found: C 81.24%, H 7.49%, N 5.21%.

2.2.2. Synthesis of BF-*i*-b

BHPF (7.0 g, 20 mmol), *iso*-butylamine (3.0 g, 41 mmol), paraformaldehyde (2.7 g, 90 mmol) and 20 mL 1,4-dioxane were added to a 50 mL flask. The reactants were then heated at 100 °C for 3 h. The next steps were the same as the procedure of BF-*n*-b. White powder was obtained (81.3% yield, m.p.: 173 °C). FT-IR (KBr, cm^{-1}): 1494, 1384 and 1366 (C–H deformation), 1321, 1230, 1156, 1076, 940, 860, 820, 738. ^1H NMR (500 MHz, CDCl_3 , ppm): 6.63–7.75 (m, 14H, Ar–H), 4.76 (s, 4H, O– CH_2 –N), 3.78 (s, 4H, Ar– CH_2 –N), 2.46 (d, 4H, N– CH_2 –), 1.75 (m, 2H, – CH – CH_3), 0.89 (d, 12H, – CH_3). ^{13}C NMR (125 MHz, CDCl_3 , ppm): 116.13–153.05 (24C, the carbons of benzene rings), 83.11 (2C, O– CH_2 –N), 64.32 (1C, quaternary carbon in the fluorene ring), 59.61 (2C, N– CH_2 –Ar), 50.83 (2C, N– CH_2 –), 26.73 (2C, – CH – CH_3), 20.62 (4C, – CH_3). Elem. Anal. Calcd for $\text{C}_{37}\text{H}_{40}\text{N}_2\text{O}_2$: C 81.58%, H 7.40%, N 5.14%. Found: C 81.32%, H 7.32%, N 4.98%.

2.2.3. Synthesis of BF-*s*-b

BHPF (7.0 g, 20 mmol), *sec*-butylamine (3.0 g, 41 mmol), paraformaldehyde (2.7 g, 90 mmol) and 10 mL toluene were added to a 50 mL flask. The reactants were then heated at 90 °C for 1 h. The reaction was allowed to cool to room temperature and then poured into hexane. The crude product was isolated by filtration and washed with hexane followed by dried under vacuum at 60 °C for 24 h. White powder was obtained (73.5% yield, m.p.: 172 °C). FT-IR (KBr, cm^{-1}): 1496, 1382, 1321, 1233, 1161, 1076, 948, 860, 820,743. ^1H NMR (500 MHz, CDCl_3 , ppm): 6.60–7.75 (m, 14H, Ar–H), 4.89–4.82 (m, 4H, O– CH_2 –N), 3.89–3.82 (m, 4H, Ar– CH_2 –N), 2.81 (m, 2H, N– CH –, the protons of chiral carbon), 1.58 and 1.37 (m, 4H, – CH_2 –), 1.05 (d, 6H, CH – CH_3), 0.86 (t, 6H, CH_2 – CH_3). ^{13}C NMR (125 MHz, CDCl_3 , ppm): 116.26–153.70 (24C, the carbons of benzene rings), 80.96 (2C, O– CH_2 –N), 64.37 (1C, quaternary carbon in the fluorene ring), 57.05 (2C, N– CH_2 –Ar), 47.18 (2C, N– CH –, chiral carbon), 27.73 (2C, – CH_2 –), 17.70 (2C, CH – CH_3), 10.71 (2C, CH_2 – CH_3). Elem. Anal. Calcd for $\text{C}_{37}\text{H}_{40}\text{N}_2\text{O}_2$: C 81.58%, H 7.40%, N 5.14%. Found: C 81.38%, H 7.37%, N 4.95%.

2.2.4. Synthesis of BF-*t*-b

BHPF (7.0 g, 20 mmol), *tert*-butylamine (3.0 g, 41 mmol), paraformaldehyde (2.7 g, 90 mmol) and 10 mL toluene were added to a 50 mL flask. The reactants were then heated at 100 °C for 1 h. The next steps were the same as the procedure of BF-*s*-b. Finally,

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