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# Primary Amine-Functional Benzoxazine Monomers and Their Use for Amide-Containing Monomeric Benzoxazines

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ABSTRACT: Amino-functional benzoxazine monomers have been successfully prepared. Several routes have been applied to incorporate amino group into benzoxazine structure. These approaches include reduction of the corresponding nitro-functional benzoxazines and deprotection of protected amino-functional benzoxazine monomers. Various approaches that allow primary amine groups to be prepared without damaging the existing benzoxazine groups have been evaluated. Tetrachlorophthalimide and trifluoroacetyl are found to be suitable protecting groups. In addition, a model compound of amide-functional benzoxazines is prepared from primary amine-functional benzoxazine. Fourier transform infrared spectroscopy (FTIR) and $^{1}H$ and $^{13}C$ nuclear magnetic resonance spectroscopy (NMR) are used to characterize the structure of the monomers. The polymerization behavior of amino-functional monomers and model compound are studied by differential scanning calorimetry (DSC).

## 1. Introduction

The current and vast growing interest in benzoxazine resin by academia and industry has surely been due to the wide molecular design flexibility than any other known class of resin and the excellent mechanical and physical properties. The interesting properties includes high glass transition temperature, low flammability, low absorption of water, stable and low dielectric constant, low dissipation factor, high dimensional stability, and low cost. In addition, its formation through thermally activated ring-opening polymerization of benzoxazine in the absence of an added initiator and/or catalyst does not release any volatiles, thus eliminating the formation of voids.[1a−e]

Development of new benzoxazine resins, over the past decade, has been taken in well-defined directions where, in turn, different approaches have been carried out. Blending and alloying with other polymers and reinforcing with inorganic particles are the main trend within the research on monomeric benzoxazine resins. In these approaches, benzoxazine resins have been mixed with copolymerizable resins, such as epoxy,[2a−j] urethane,[3a−e] oxazoline,[4a−d] bismaleimide,[5a,b] and cyanate ester[6] or with nonreactive polymers, including poly(ε-caprolactone),[7a−e] poly(ethylene oxide),[8] polystyrene,[9] and poly(methyl methacrylate).[10]

Benzoxazine resins are also ideally suited for composite manufacturing, and the reinforcement with glass fibers,[11a,b] cellulose fibers,[12a−e] and carbon fibers[13a−f] has been reported. Since the molecular structure of polybenzoxazines resemble that of lignin, one of the major components of wood, compatibility with cellulose is good. Incorporation of nanofillers, such as clay,[14a−l] carbon nanotube,[15a,b] polyhedral oligomeric silsesquioxane (POSS),[16a−f] SiC whisker,[17] barium titanate nanoparticles,[18] and sol−gel nanoparticles,[19] has been actively studied. Composite application requires good adhesion at the interface between the reinforcing material and matrix resin. The amphoteric nature of the polybenzoxazines can accommodate a wide variety of substrates, including such traditionally difficult fillers to adhere as calcium carbonate[20] and boron nitride.[21a,b]

Polymers containing benzoxazine is a new and attractive approach in which benzoxazine moieties are incorporated as repeating unit into the main chain of other conventional polymers. The presence of reactive benzoxazines in the main chain can partially or fully polymerize to form cross-links. By applying this concept, we can combine the typical advantages of polybenzoxazine derived from monomeric precursors to the main chain polymer backbone polymer for having a unique combination of properties. As a result, polymers that process like thermoplastics while final properties also exhibit advantages of thermosetting polymers can be developed.

The functionalization of benzoxazine monomers with reactive groups is expected to expand their applications toward further structure modifications for new functional applications in both monomeric benzoxazines and main-chain type polybenzoxazines. Property modification via synthesis of benzoxazine monomers containing functional groups, such as acetylene,[22a,b] phthalonitrile,[23a−c] allyl,[24a−g] propargyl,[25a,b] furan,[26] nitrile and maleminde,[27a−e] and carboxylic acid,[28] have been actively pursued. A systematic study of a series of monofunctional benzoxazine containing various functional groups, such as hydroxyl, carboxyl, nitro, and aldehyde, to study the effect of the introduction of these groups on the ring-opening polymerization of benzoxazine monomers has also been reported by Andreu et al.[29]

Despite the high potential of primary amine-functional benzoxazine monomers as a useful intermediate for further synthesizing various benzoxazines, no study has been reported on the synthesis due to the difficulty caused by the selectivity problems during the monomer synthesis. The current article describes various approaches to synthesize primary amine-functional benzoxazine monomers. Additionally, the synthesis and polymerization of amide-containing benzoxazine derived from the primary amine-functional benzoxazine will be discussed.

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## 2. Experimental Section

**2.1. Materials.** Aminophenol (> 98%), 4-chlorobenzene, benzyl chloride (98%), isophthalic chloride, sodium borohydride, trifluoroacetic anhydride, tetrachlorophthalic anhydride (99%), and paraformaldehyde (99%) were used as received from Sigma-Aldrich. 4,4′-Diaminodiphenylmethane (DDM) (98%) was purchased from Aldrich. Aniline was purchased from Aldrich and prurifed by distillation. Chloroform, hexane, 2-propanol, methanol, xylenes, and sodium sulfate were obtained from Fisher.

**2.2. Preparation of 6,6′-(Propane-2,2-diyl)bis(3-(4-nitrophenyl)-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazine) (1).** Into a 100 mL round flask were added 60 mL of chlorobenzene/xylene (1:1), bisphenol A (4.989 g, 0.021 mol), 4-nitroaniline (6.046 g, 0.043 mol), and paraformaldehyde (3.286 g, 0.109 mol). The mixture was stirred at 120 °C overnight. The reaction mixture was allowed to cool to room temperature, affording yellow crystals (yield ca. 90%). $^1$H NMR spectra ($CDCl_3$, ppm, $\delta$): 1.60 (s, C−$CH_3$), 4.69 (s, C−$CH_2$−N−), 5.39 (s, N−$CH_2$−O−), 6.75−8.18 (m, Ar). $^{13}$C NMR spectra (DMSO, ppm, $\delta$): 49.60 (C−$CH_2$−N−), 76.79 (N−$CH_2$−O). IR spectra (KBr, $cm^{-1}$): 1594, 1330 (C−$NO_2$ stretching), 1500 (stretching of trisubstituted benzene ring), 1232 (asymmetric stretching of C−O−C), 1193 (asymmetric stretching of C−N−C), 960 (out-of-plane C−H).

**2.3. Preparation of 4,5,6,7-Tetrachloro-2-(4-nitrophenyl)isoindoline-1,3-dione (2).** In a 1 L round-bottomed flask were added tetrachlorophthalic anhydride (41.194 g, 0.144 mol), *p*-nitroaniline (20.70 g, 0.15 mol), and 300 mL of acetic acid. The mixture was refluxed under stirring for 6 h. After cooling to room temperature, the crystals were filtered off, followed by washing repeatedly with 2 L of acetone. The crystals were dried under vacuum without any further purification to give white cotton-like crystals (yield ca. 90%). $^1$H NMR (DMSO), ppm: $\delta$ = 7.74−8.45 (4H, Ar). FT-IR $\nu$ ($cm^{-1}$) = 1776, 1722 (imide I), 1610, 1355 (C−$NO_2$ stretching), 1365 (imide II, C−N stretching), 746 (C═O bending).

**2.4. Preparation of 2-(4-Aminophenyl)-4,5,6,7-tetrachloroisoindoline-1,3-dione (3).** In a 250 mL three-necked round flask was stirred a suspension of **2** (12 g, 0.029 mol) in 150 mL of DMF at 85 °C for 30 min under a hydrogen atmosphere. To this suspension, Raney Ni (2.4 g) was added, and the reaction was continued for 4 h. Then, the Raney Ni was removed by filtration, followed by precipitation of the filtrate in water. The precipitate was collected by suction filtration, washed several times with water and cold methanol, and dried under vacuum at room temperature to afford an orange powder (mp 267 °C, yield ca. 85%). $^1$H NMR (DMSO), ppm: $\delta$ = 5.42 ($NH_2$), 6.63−7.02 (4H, Ar). FT-IR $\nu$ ($cm^{-1}$) = 3397 (N−H stretching), 1774, 1718 (imide I), 1367 (imide II, C−N stretching) 732 (C═O bending).

**2.5. Preparation of 4,5,6,7-Tetrachloro-2-(4-(6-methyl-2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-yl)phenyl)isoindoline-1,3-dione (4).** Into a 25 mL round flask were added **3** (2 g, 5.319 mmol), *p*-cresol (0.574 g, 5.319 mmol), paraformaldehyde (0.479 g, 15.957 mmol), and xylenes (15 mL) and stirred at 120 °C for 36 h. After cooling, the reaction mixture was poured into 100 mL of methanol to give an orange precipitate. The product was filtered and washed several times with methanol, followed by drying under vacuum to afford an orange powder (yield ca. 60%). $^1$H NMR (DMSO), ppm: $\delta$ = 2.2 (s, $CH_3$), 4.68 (s, $CH_2$, oxazine), 5.46 (s, $CH_2$, oxazine), 6.60−7.30 (7H, Ar). FT-IR $\nu$ ($cm^{-1}$) = 1779, 1722 (imide I), 1517 (trisubstituted benzene ring stretching), 1367 (imide II), 1205 (C−O−C asymmetric stretching), 1172 (C−N−C asymmetric stretching), 943 (C−H out-of-plane).

**2.6. Preparation of 4-(6-Methyl-2*H*-benzo[*e*][1,3]oxazin-3(4H)-yl)aniline (*p*C-a-$NH_2$).** Into a 25 mL round flask was suspended **4** (0.508 g, 1 mmol) in 15 mL of diethyl ether under a nitrogen atmosphere. The suspension was stirred for 15 min in ice bath at about 0 °C, followed by adding hydrazine monohydrate (0.15 g, 3 mmol). The suspension was stirred at −10 °C for 5 h under a hydrogen atmosphere. The reaction mixture was filtered to remove the solid residues, followed by washing the filtrate with 0.5 N aqueous NaOH (solution 3 × 15 mL) and then with water. The solution was dried over sodium sulfate anhydrous, followed by evaporation of the solvent under reduced pressure to afford a colorless viscous material (yield: 40%). $^1$H NMR (DMSO), ppm: $\delta$ = 2.18 (s, $CH_3$), 4.41 (s, $CH_2$ oxazine), 4.65 (s, $NH_2$), 5.2 (s, $CH_2$ oxazine), 6.40−6.9 (7H Ar). $^{13}$C NMR (DMSO), ppm $\delta$ = 50.35 (Ar−$CH_2$−O) and 78,66 (O−$CH_2$−N). FT-IR $\nu$ ($cm^{-1}$) = 3357 (N−H stretching), 1513 (trisubstituted benzene ring stretching), 1226 (asymmetric stretching of C−O−C), 1176 (C−N−C asymmetric stretching), 941(C−H out-of-plane).

**2.7. Preparation of 2,2′-(4,4′-(6,6′-(Propane-2,2-diyl)bis(2*H*-benzo[*e*][1,3]oxazine-6,3(4*H*)-diyl))bis(4,1-phenylene))bis(4,5,6,7-tetrachloroisoindoline-1,3-dione) (5).** Into a 50 mL round flask, **3** (2 g, 5.31 mmol), bisphenol A (0.606 g, 2.65 mmol), and excess of paraformaldehyde (0.4 g, 13.29 mmol) and 20 mL of xylenes were added and stirred at 120 °C for 4 days. After cooling, the reaction mixture was poured into methanol (100 mL), filtrated, and washed several times with fresh methanol. Removal of solvent by evaporation afforded a reddish-orange powder with a purity of 75%. Typical yield: 35%. $^1$H NMR (DMSO), ppm: $\delta$ = 1.55 (s, $CH_3$), 4.69 (s, $CH_2$ oxazine), 5.47 (s, $CH_2$ oxazine), 6.66−7.26 (14H Ar). FT-IR $\nu$ ($cm^{-1}$) =1780, 1720 (imide I), 1515 (trisubstituted benzene ring stretching), 1370 (imide II), 1215 (C−O−C asymmetric stretching), 1170 (C−N−C asymmetric stretching), 950 (C−H out-of-plane).

**2.8. Preparation of 4,4′-(6,6′-(Propane-2,2-diyl)bis(2*H*-benzo[*e*][1,3]oxazine-6,3(4*H*)-diyl))dianiline (BA-a-$NH_2$).** In a 25 mL round-bottomed flask was suspended compound **5** (0.5 g, 0.861 mmol) into 5 mL of chloroform under a nitrogen atmosphere. The suspention was stirred in an ice bath for 15 min at about 0 °C, followed by adding hydrazine monohydrate (0.258 g, 5.167 mmol). After having been stirred for 5 h under a nitrogen atmosphere, the reaction mixture was filtered, diluted with 20 mL of chloroform, and followed by washing with 0.5 N aqueous NaOH solution (3 × 15 mL) and then water. The chloroform solution was dried over sodium sulfate anhydrous, followed by evaporation of solvent under reduced pressure to afford a pinkish-white powder (yield: 90%). $^1$H NMR (DMSO), ppm: $\delta$ = 4.50 (s, $CH_2$ oxazine), 4.59 (s, $NH_2$), 5.29 (s, $CH_2$ oxazine), 6.32−7.26 (8H Ar). $^{13}$C NMR (DMSO), ppm $\delta$ = 48.93 (Ar−C−N, oxazine), 78.18 (O−C−N, oxazine). FT-IR (KBr), $cm^{-1}$: 3350 (N−H stretching), 1494 (stretching of trisubstituted benzene ring), 1231 (C−O−C asymmetric stretching), 1180 (C−N−C asymmetric stretching), 955 (out-of-plane C−H).

**2.9. Preparation of 4,5,6,7-Tetrachloro-2-(4-hydroxyphenyl)-isoindoline-1,3-dione (6).** Into a 1 L round flask were placed tetrachlorophthalic anhydride (54.985 g, 0.192 mol), *p*-aminophenol (23.0840 g, 0.2114 mol), and 500 mL of acetic acid. The mixture was stirred and refluxed for 6 h. After cooling to room temperature, the precipitate was filtered and washed with 2 L of methanol. Removal of solvent by evaporation afforded a yellow crystal; mp 310 °C (yield ca. 87%). $^1$H NMR (DMSO), ppm: $\delta$ = 6.88−7.22 (4H, Ar) 9.84 (OH). IR spectra (KBr, $cm^{-1}$) = 3455 (O−H stretching), 1766, 1708 (imide I), 1371 (imide II, C−N stretching), 732 (C═O bending).

**2.10. Preparation of 4,5,6,7-Tetrachloro-2-(3-phenyl-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazin-6-yl)isoindoline-1,3-dione (7).** Into a 1 L round flask were added 350 mL of xylenes, aniline (15 g, 0.161 mol), **6** (60.734 g, 0.161 mol), and excess of paraformaldehyde (19.351 g, 0.644 mol). The mixture was stirred at 120 °C for 36 h. The mixture was cooled to room temperature and filtrated off. The filtrate was concentrated to its half volume using a rotary evaporator. Then, the solution was added dropwise to 2 L of hexane, filtered, and washed several times with hexane. Removal of solvent by evaporation gave a yellowish-orange powder (yield ca. 60%). $^1$H NMR (DMSO), ppm: $\delta$ = 4.74 (s, $CH_2$, oxazine), 5.54 (s, $CH_2$, oxazine) 6.88−7.26 (8H, Ar). $^{13}$C NMR spectra (DMSO, ppm, $\delta$): 48.75 (Ar−C−O)

and 78.80 (O−C−N). FT-IR (KBr), $cm^{-1}$: 1781, 1722 (imide I), 1496 (stretching of trisubstituted benzene ring), 1370 (imide II), 1234 (C−O−C asymmetric stretching), 1203 (C−N−C asymmetric stretching), 937 (out-of-plane C−H).

**2.11. Preparation of 3-Phenyl-3,4-dihydro-2*H*-benzo[*e*][1,3] oxazin-6-amine (A-P-$NH_2$) by Deprotection of 7.** Into a 25 mL flask was suspended TCP-protected monofunctional benzoxazine (**7**) (0.491 g, 1 mmol) in 10 mL of diethyl ether. The suspension was cooled in an ice bath with stirring for 15 min, followed by the addition of hydrazine monohydrate (3 mmol, 0.15 g) to the suspension. The mixture was stirred for 5 h in the ice bath under a hydrogen atmosphere, followed by filtration of the solid residues. Then, the filtrate was washed by 0.5 N aqueous NaOH solution (3 × 50 mL) and then with water, followed by drying over sodium sulfate anhydrous. The solvent was removed by evaporation using a rotary evaporator under reduced pressure to give a colorless semisolid material, which was further purified by recrystallization from hexane (yield: 80%). $^1$H NMR (DMSO), ppm: $\delta$ = 4.50 (s, $CH_2$ oxazine), 4.59 (s, $NH_2$), 5.29 (s, $CH_2$ oxazine), 6.32−7.26 (8H Ar). $^{13}$C NMR (DMSO), ppm $\delta$ = 48.93 (Ar−C−N, oxazine), 78.18 (O−C−N, oxazine). FT-IR (KBr), $cm^{-1}$: 3353 (N−H stretching), 1500 (stretching of trisubstituted benzene ring), 1224 (C−O−C asymmetric stretching), 1180 (C−N−C asymmetric stretching), 950 (out-of-plane C−H).

**2.12. Preparation of 2,2′-(3,3′-(4,4′-Methylenebis(4,1-phenylene))-bis(3,4-dihydro-2*H*-benzo[*e*][1,3]oxazine-6,3-diyl))bis(4,5,6,7-tetrachloroisoindoline-1,3-dione) (8).** Into a 50 mL flask were added 20 mL of xylenes, **6** (2 g, 5.305 mmol), 4,4′-methylenedianiline (0.526 g, 2.653 mmol), and paraformaldehyde (0.3983 g, 13.2625 mmol) and stirred at 120 °C for 2 days. The reaction mixture was cooled to room temperature and precipitated into 150 mL of methanol. Removal of solvent afforded an orange-red powder (yield 51%). $^1$H NMR (DMSO), ppm: $\delta$ = 3.73 (s, $CH_2$), 4.67 (s, $CH_2$ oxazine), 5.47 (s, $CH_2$ oxazine), 6.85−7.13 (14H Ar). FT-IR (KBr), $cm^{-1}$: 1785, 1730 (imide I), 1511 (stretching of trisubstituted benzene rin), 1375 (imide II), 1228 (C−O−C asymmetric stretching), 1210 (C−N−C asymmetric stretching), 940 (out-of-plane C−H).

**2.13. Preparation of 3,3′-(4,4′-Methylenebis(4,1-phenylene))-bis(3,4-dihydro-2*H*-benzo[*e*][1,3]oxazin-6-amine) (P-ddm-$NH_2$) from Deprotection of 8.** Into a 50 mL flask was suspended TCP-protected bifunctional benzoxazine (**8**) (1 g, 2.152 mmol) in 15 mL of chloroform. The suspension was cooled in an ice bath with stirring for 15 min, followed by the addition of hydrazine monohydrate (0.645 g, 12.915 mmol) to the suspension. The mixture was stirred for 5 h in the ice bath under a hydrogen atmosphere, followed by filtration of the solid residues. Then, the filtrate was diluted with 100 mL of chloroform, washed by 0.5 N aqueous NaOH solution (3 × 50 mL) and then with water, followed by drying over sodium sulfate anhydrous. The solvent was removed under reduced pressure to give a pinkish powder. $^1$H NMR (DMSO), ppm: $\delta$ = 3.71 (s, $CH_2$), 4.44 (s, $CH_2$ oxazine), 4.57 (s, $NH_2$), 5.22 (s, $CH_2$ oxazine), 6.28−7.05 (14H Ar). $^{13}$C NMR (DMSO), ppm $\delta$ = 49.07 (Ar−C−N, oxazine), 78.45 (O−C−N, oxazine). FT-IR $\nu$ ($cm^{-1}$) = 3351 (N−H stretching), 1502 (stretching of trisubstituted benzene ring), 1222 (asymmetric stretching of C−O−C), 1182 (asymmetric stretching of C−N−C), 950 (out-of-plane C−H).

**2.14. Preparation of 2,2,2-Trifluoro-*N*-(4-hydroxyphenyl)acetamide (9).** Into a 250 mL round flask were charged *p*-aminophenol (7.709 g, 0.070 mol) and THF (100 mL) and cooled in an ice bath for 15 min. Trifluoroacetic anhydride (19.6 mL, 0.141 mol) was added dropwise with stirring in 30 min. Then, the reaction mixture was stirred in the ice bath for an additional 1.5 h. The solvent was removed by a rotary evaporator, followed by dissolving the residue in ethyl acetate (200 mL). The solution was washed with saturated aqueous sodium bicarbonate solution (3 × 200 mL) and water (3 × 100 mL). The solution was dried with sodium sulfate, filtered, and concentrated under vacuum. The product was precipitated in 500 mL of hexanes, filtered, and dried under vacuum overnight to give cotton-like crystals (mp 172 °C, 88%). $^1$H NMR (DMSO), ppm: $\delta$ = 6.75−7.44 (4H, Ar), 9.50 (s, OH), 10.99 (s, NH). $^{13}$C NMR spectra (DMSO, ppm, $\delta$): 127.88 ($CF_3$−C=O), 157.23 (q, NH−(C=O)−$CF_3$) and 155.38 (Ar−OH). FT-IR $\nu$ ($cm^{-1}$) = 3600−3100 (N−H and O−H stretching overlap), 1702 (C=O stretching).

**2.15. Preparation of 2,2,2-Trifluoro-*N*-(3-phenyl-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazin-6-yl)acetamide (10).** Into a 50 mL round flask were added aniline (1.3620 g, 14.6247 mmol), **9** (4 g, 14.6247 mmol), excess of paraformaldehyde (1.3176 g, 43.9 mmol), and 20 mL xylenes and stirred at 120 °C for 4 h. After cooling, the reaction mixture was poured into 200 mL of hexane, filtered, and washed several times with hexane. The crude product was then dissolved in 200 mL of ethyl acetate, followed by washing with 5 wt % of aqueous $Na_2CO_3$ solution (3 × 100) and water (3 × 100). The solution was dried over sodium sulfate anhydrous, followed by evaporation of solvent under vacuum to afford white powder which was used without further purification (yield 80%). $^1$H NMR (DMSO), ppm: $\delta$ = 4.67 (s, $CH_2$, oxazine), 5.46 (s, $CH_2$, oxazine), 6.70−7.60 (14H, Ar), 11.09 (s, NH). $^{13}$C NMR (DMSO), ppm: $\delta$ = 48.80 (Ar−C−N, oxazine), 78.83 (O−C−N, oxazine), 116.42 ($CF_3$−C=O) and 154.19 (q, NH−(C=O)−$CF_3$). FT-IR (KBr), $cm^{-1}$: 3286 (N−H stretching), 1700 (carbonyl stretching), 1496 (stretching of trisubstituted benzene ring), 1230 (asymmetric stretching of C−O−C), 950 (out-of-plane C−H).

**2.16. Preparation of 3-Phenyl-3,4-dihydro-2*H*-benzo[*e*]-[1,3]oxazin-6-amine (P-a-$NH_2$) by Deportation of 10.** Into a 50 mL round flask was dissolved **10** (2.034 g, 9 mmol) in a mixture of ethyl acetate and methanol at a ratio of 100:1 (100 mL:1 mL), followed by addition of $NaBH_4$ (1.7024 g, 45 mmol). The resulting mixture was stirred for 6 h at 20 °C under a nitrogen atmosphere. Then the reaction mixture was washed four times with brine and one time with water. The ethyl acetate solution was dried over sodium sulfate anhydrous. Removal of the solvent by a rotary evaporator under reduced pressure afforded a colorless viscous material (yield 85%). $^1$H NMR (DMSO), ppm: $\delta$ = 4.50 (s, $CH_2$ oxazine), 4.59 (s, $NH_2$), 5.29 (s, $CH_2$ oxazine), 6.32−7.26 (8H Ar). $^{13}$C NMR (DMSO), ppm $\delta$ = 48.93 (Ar−C−N, oxazine), 78.18 (O−C−N, oxazine). FT-IR (KBr), $cm^{-1}$: 3353 (N−H stretching), 1500 (stretching of trisubstituted benzene ring), 1224 (asymmetric stretching of C−O−C), 1180 (asymmetric stretching of C−N−C), 950 (out-of-plane C−H).

**2.17. Preparation of *N,N*′-(3,3′-(4,4′-Methylenebis(4,1-phenylene))-bis(3,4-dihydro-2*H*-benzo[*e*][1,3]oxazine-6,3-diyl))bis(2,2,2-trifluoroacetamide) (11).** Into a 50 mL round flask were added 15 mL of chlorobenzene/xylenes (1:1) and 4,4′-diaminodiphenylmethane (1.9331 g, 9.7500 mmol), **9** (4.00 g, 19.50 mmol), and excess of paraformaldehyde (1.464 g, 48.75 mmol), and the mixture was stirred at 120 °C for 3 h. The reaction mixture was poured into 200 mL of hexane, filtered, and washed twice with hexane. Then, the crude product was dissolved in 200 mL of ethyl acetate, followed by washing with 5 wt % of aqueous $Na_2CO_3$ solution (3 × 100) and water (3 × 100). The solution was dried over sodium sulfate anhydrous, followed by evaporation of solvent under vacuum to afford a white powder which was used without further (yield 87%). $^1$H NMR (DMSO), ppm: $\delta$ = 3.70 (s, $CH_2$), 4.60 (s, $CH_2$, oxazine), 5.39 (s, $CH_2$, oxazine), 6.72−7.45 (14H, Ar), 11,06 (s, NH). $^{13}$C NMR (DMSO), ppm: $\delta$ = 48.99 (Ar−C−N, oxazine), 79.09 (O−C−N, oxazine), 116.40 ($CF_3$−C=O), 154.19 (q, NH−C=O−$CF_3$). FT-IR (KBr), $cm^{-1}$: 3288 (N−H stretching), 1706 (carbonyl stretching), 1500 (stretching of trisubstituted benzene ring), 1226 (asymmetric stretching of C−O−C), 956 (out-of-plane C−H).

**2.18. Preparation of 3,3′-(4,4′-Methylenebis(4,1-phenylene))-bis(3,4-dihydro-2*H*-benzo[*e*][1,3]oxazin-6-amine) (P-ddm-$NH_2$) from Deprotection of 11.** Into a 50 mL flask was dissolved **11**

(4.1810 g, 9 mmol) in a mixture of ethyl acetate/methanol at a ratio of 100:1 (200 mL:2 mL), followed by addition of $NaBH_4$ (1.7024 g, 45 mmol). The resulting mixture was stirred for 7 h at 20 °C under a nitrogen atmosphere. Then, the reaction mixture was washed with brine (3 × 100) and with water. The solution was dried over sodium sulfate anhydrous, followed by precipitation in hexane. The precipitate was filtered and dried at room temperature to give white powder, which was stored under an inert atmosphere until use (yield 75%). $^1$H NMR (DMSO), ppm: $\delta$ = 3.71 (s, $CH_2$), 4.44 (s, $CH_2$ oxazine), 4.57 (s, $NH_2$), 5.22 (s, $CH_2$ oxazine), 6.28−7.05 (14H Ar). $^{13}$C NMR (DMSO), ppm $\delta$ = 49.07 (Ar−C−N, oxazine), 78.45 (O−C−N, oxazine). FT-IR $\nu$ ($cm^{-1}$) = 3351 (N−H stretching), 1502 (stretching of trisubstituted benzene ring), 1222 (asymmetric stretching of C−O−C), 1182 (asymmetric stretching of C−N−C), 950 (out-of-plane C−H).

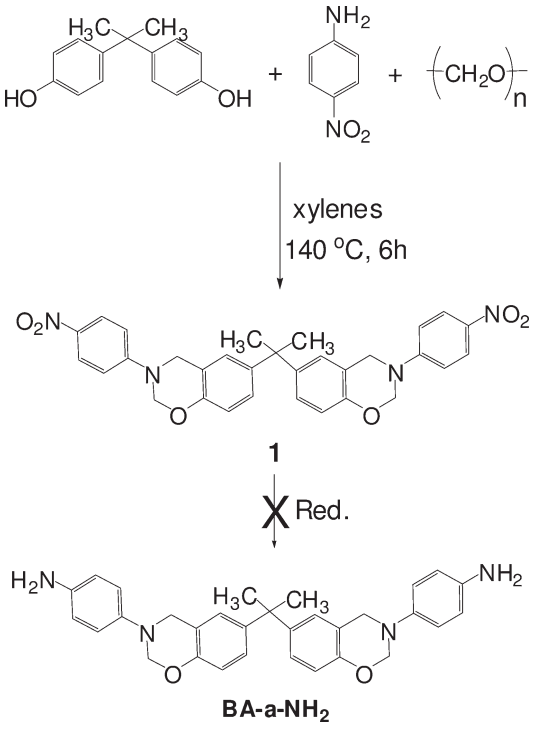
**2.19. Preparation of *N*1,*N*3-Bis(3-phenyl-3,4-dihydro-2*H*-benzo-[*e*][1,3]oxazin-6-yl)isophthalamide (12).** Into a 25 mL flask were dissolved P-a-$NH_2$ (1.157 g, 5.113 mmol) and triethylamine (4.8 mL) in 50 mL of chloroform and cooled in an ice bath. The solution was stirred for 15 min, followed by dropwise addition of the 50 mL of chloroform solution of isophthaloyl chloride (0.399 g, 1.967 mmol). The mixture was stirred for 1 h in the ice bath. The solution was washed with 0.5 N aqueous solution (3 × 100) and with water. The solution was dried over sodium sulfate anhydrous, followed by concentration and precipitation in 200 mL of hexane. The precipitate was removed by filtration and dried to give a white powder (yield 95%). $^1$H NMR (DMSO), ppm: $\delta$ = 4.67 (s, $CH_2$, oxazine), 5.44 (s, $CH_2$, oxazine), 6.72−8.47 (20H, Ar), and 10, 25 (s, NH). $^{13}$C NMR (DMSO), ppm: $\delta$ = 48.98 (Ar−C−N, oxazine), 78.71 (O−C−N, oxazine), and 130.31 (C−NH) and 164.58 (Ar−C=O−NH). FT-IR (KBr), $cm^{-1}$: 3288 (N−H stretching), 1646 (crbonyl stretching), 1496 (stretching of trisubstituted benzene ring), 1226 (asymmetric stretching of C−O−C), 1186 (asymmetric stretching of C−N−C), 954 (out-of-plane C−H).

**2.20. Measurements.** $^1$H and $^{13}$C NMR spectra were acquired on a Varian Oxford AS600 at a proton frequency of 600 MHz and its corresponding carbon frequency of 150.9 MHz. The average number of transients for $^1$H and $^{13}$C MNR measurement was 64 and 1024, respectively. A relaxation time of 10 s was used for the integrated intensity determination of $^1$H NMR spectra. Fourier transform infrared (FTIR) spectra were obtained using a Bomem Michelson MB100 FTIR spectrometer, which was equipped with a deuterated triglycine sulfate (DTGS) detector and a dry air purge unit. Coaddition of 32 scans was recorded at a resolution of 4 $cm^{-1}$. Transmission spectra were obtained by casting a thin film on a KBr plate for partially cured samples. Elemental analysis was performed by MHW Laboratories. A TA Instruments DSC model 2920 was used with a heating rate of 10 °C/min and a nitrogen flow rate of 60 mL/min for all tests of differential scanning calorimetric (DSC) study. All samples were crimped in hermetic aluminum pans with lids. Dynamic mechanical analyses were done on a TA Instruments Q800 DMA applying controlled strain tension mode with amplitude of 10 $\mu$m and a ramp rate of 3 °C/min. Thermogravimetric analyses (TGA) were performed on a TA Instruments Q500 TGA with a heating rate of 10 °C/min in a nitrogen atmosphere at a flow rate of 40 mL/min.

## 3. Results and Discussion

**3.1. Preparation of Primary Amine-Functional Benzoxazines.** Bicyclic benzoxazine monomers are typically synthesized via condensation reaction of primary amine, formaldehyde, and phenol. The one-step synthesis of primary amine-functional benzoxazines is quite difficult due to the reaction of primary amine with formaldehyde to form a triaza structure as intermediate structure of benzoxazine.[30] We have applied two approaches to synthesize primary amine-functional benzoxazines. In the first approach, novel dinitro-functional benzoxazine (**1**) was prepared from *p*-nitroaniline, bisphenol A, and paraformaldehyde as shown in Scheme 1. Our recently reported method, in which xylenes as a nonpolar, high-boiling-point solvent, was used at 140 °C.[31] The structure of the novel monomer was determined from $^1$H NMR, $^{13}$C NMR, and IR spectra. In the $^1$H NMR spectra, the typical resonances attributed to benzoxazine structure are observed at 4.69 and 5.39 ppm. The FT-IR spectra showed the characteristic absorption bands of benzoxazine structure at 1230 $cm^{-1}$ due to the stretching of C−O−C and the band at 960 $cm^{-1}$ due to the out-of-plane bending vibration of the benzene ring that is attached to the oxazine ring.[32] Also, the bands at 1594 and 1330 $cm^{-1}$ are attributed to the C−$NO_2$ group.

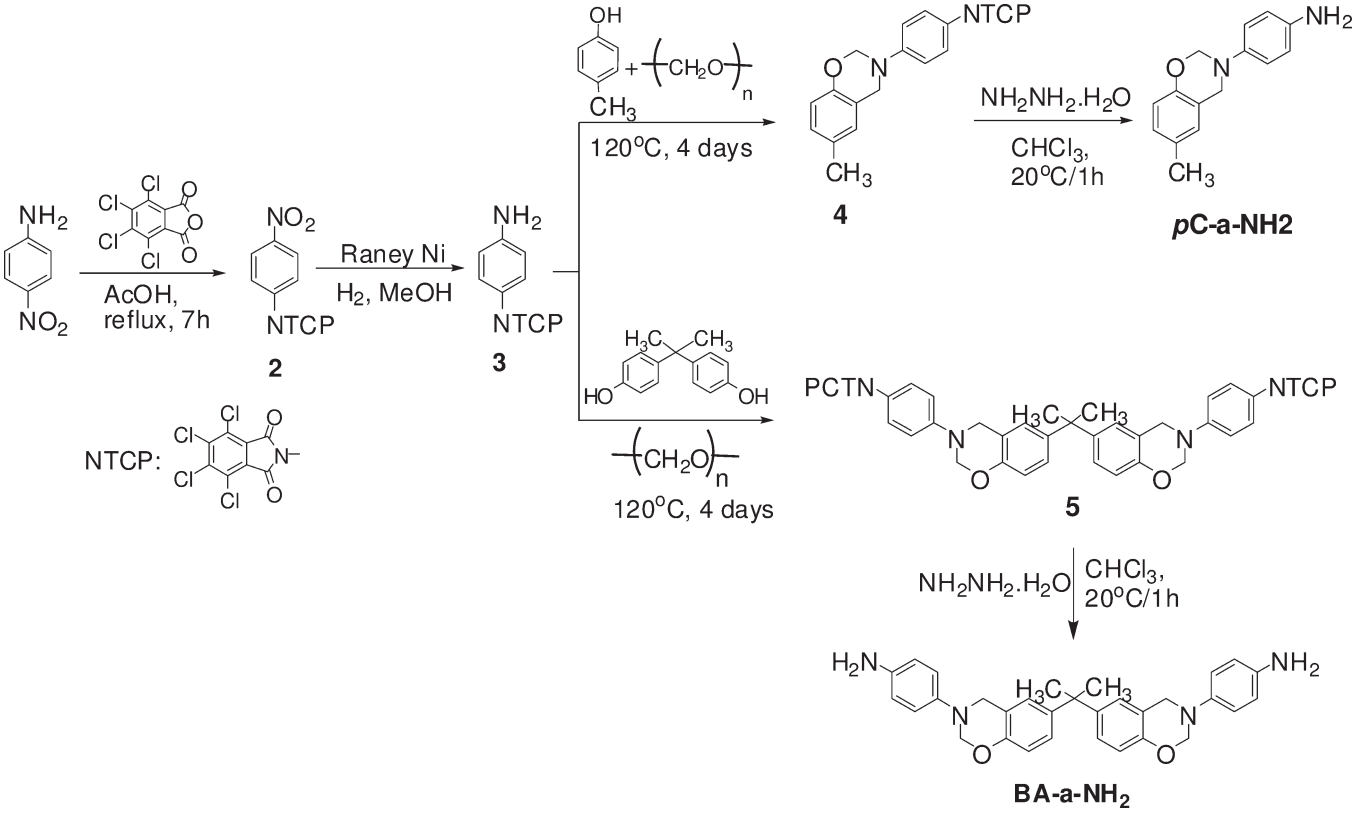
**Scheme 1. Preparation of Dinitro-Functional Benzoxazine Monomer**




Several methods have been applied for the reduction of **1** to diamino-functional benzoxazine (BA-a-$NH_2$), including hydrozinium monoformate/metal, $MH_4Cl$/metal Pd/C/$NH_2NH_2 \cdot H_2O$, Pd/C/$H_2$, Raney Ni/$NH_2NH_2.H_2O$, $FeCl_3$/charcoal/$NH_2NH_2.H_2O$, $NaBH_4$/Raney Ni, and others. However, all the methods applied for reduction were unsuccessful to afford the BA-a-$NH_2$ monomer that can be easily purified. This is attributable to many side reactions due to the instability of benzoxazine structure under the reduction conditions.

The second pathway applied for obtaining amino-functional benzoxazine was by using amine-protected phenols or amines for synthesis of benzoxazine monomers, followed by deprotection to liberate amine. The first approach in this pathway is based on the synthesis of both mono- and bifunctional benzoxazines using monoamine-protected *p*-phenylenediamine (**3**), following Scheme 2. At the first stage, tetrachlorophthalimide (NTCP)-protected *p*-nitroaniline (**2**) was prepared followed by reduction to afford **3**. The synthesis of amine protected-benzoxazines was achieved using xylenes as a nonpolar, high-boiling-point solvent at 140 °C, followed by deprotection using hydrazine hydrate at 20 °C.

**Scheme 2. Preparation of Amino-Functional Benzoxazine Monomers Using TCP-Protected *p*-Nitroaniline**




The TCP-protected monofunctional benzoxazine (**4**) was synthesized from **3**, *p*-cresol, and paraformaldehyde without any difficulties, followed by deprotection to afford amino-monofunctional benzoxazine monomer (*p*C-a-$NH_2$). The structure of *p*C-a-$NH_2$ was verified by $^1$H NMR, as shown in Figure 1. The preparation of TCP-protected bifunctional benzoxazines (A-P-$NH_2$) was slightly more difficult due to the poor solubility and heterogeneous nature of the reaction facilitates side reactions, which lead to poor yield.

TCP-protected aminophenol (**6**) was also prepared and used for preparation of primary amine-monofunctional (P-a-$NH_2$) and bifunctional (P-ddm-$NH_2$) benzoxazines, as shown in Scheme 3. Applying this pathway will save reduction step in the previous TCP-protected *p*-phenylenediamine (**3**)-based benzoxazines. TCP-protected monofunctional benzoxazine (**7**) was prepared from the reaction of **6**, aniline, and paraformaldehyde, followed by deprotection to give primary amine-monofunctional benzoxazine monomer (P-a-$NH_2$). The structure of P-a-$NH_2$ was verified by $^1$H NMR, as shown in Figure 2.

The structure P-a-$NH_2$ was further confirmed by IR, and the results are shown in Figure 3. IR spectra show the disappearance of the typical characteristic peaks of the protecting TCP group at 1781 and 1722 $cm^{-1}$ (imide I) and 1370 $cm^{-1}$ (imide II) and the presence of the typical characteristic peak at 937 $cm^{-1}$ due to the benzoxazine structure.

TCP-protected bifunctional benzoxazines (**8**) was prepared from **7** and 4,4′-methylenedianiline (DDM) and paraformaldehyde as previously mentioned. In this case of bifunctional monomer, a considerable amount of gel formation was present as a consequence of the reaction during the course of the reaction. This insoluble gel did not disappear despite applying long reaction time, leading to poor yield. The $^1$H NMR spectra of the soluble portion of the reaction mixture showed the presence of benzoxazine structure as well

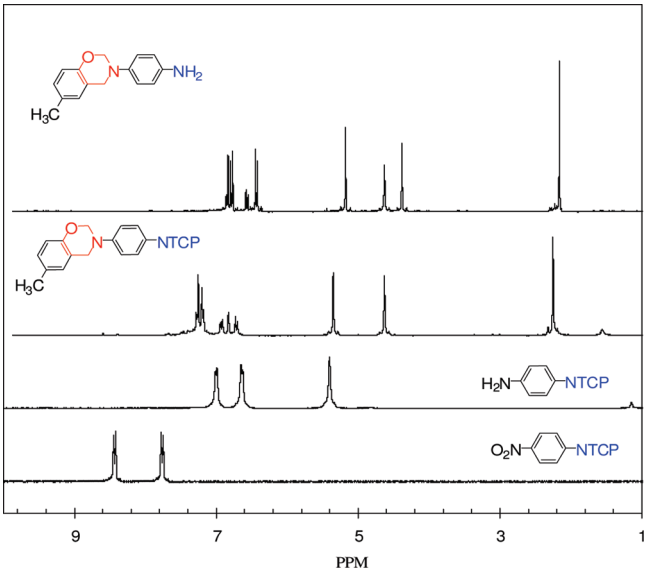
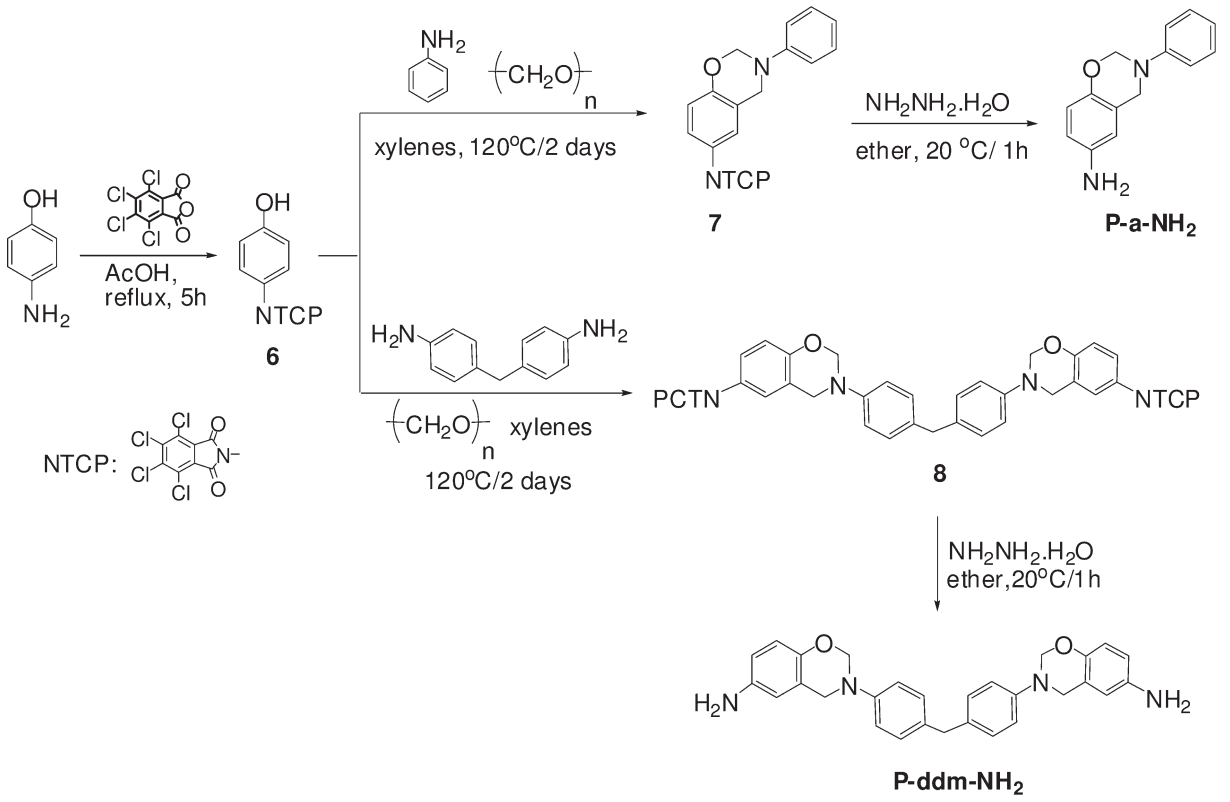



**Figure 1.** $^1$H NMR spectra of primary amine-monofunctional benzoxazine monomer (*p*C-a-$NH_2$) along with the starting materials.

as a considerable amount of side-reaction products which were, despite numerous attempts for purification, very difficult to remove. Moreover, different solvents, among the normally used for synthesis of benzoxazine monomers, were also employed, such as chloroform, dioxane, and toluene, giving equal or even worse results.

*N*-Trifluoroacetyl (TFA) was used as another amine protecting and easily leaving group. TFA-protected *p*-aminophenol (**9**) was prepared and used for the synthesis of primary amine-monofunctional and -bifunctional benzoxazines, as shown in Scheme 4.

**Scheme 3. Preparation of Amino-Functional Benzoxazine Monomers Using TCP-Protected *p*-Aminophenol**



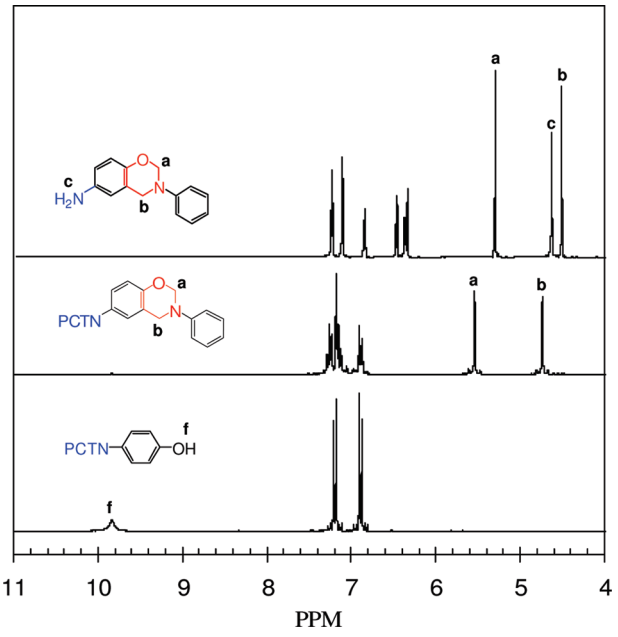




**Figure 2.** $^{1}$H NMR spectra of the primary amine-monofunctional benzoxazine monomer (P-a-$NH_2$) along with its starting materials.

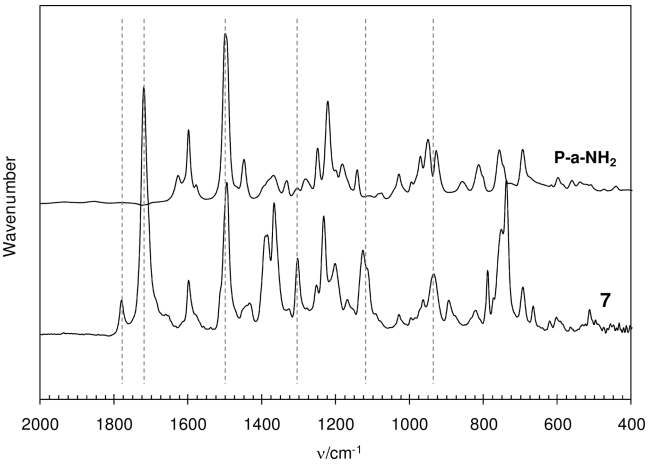
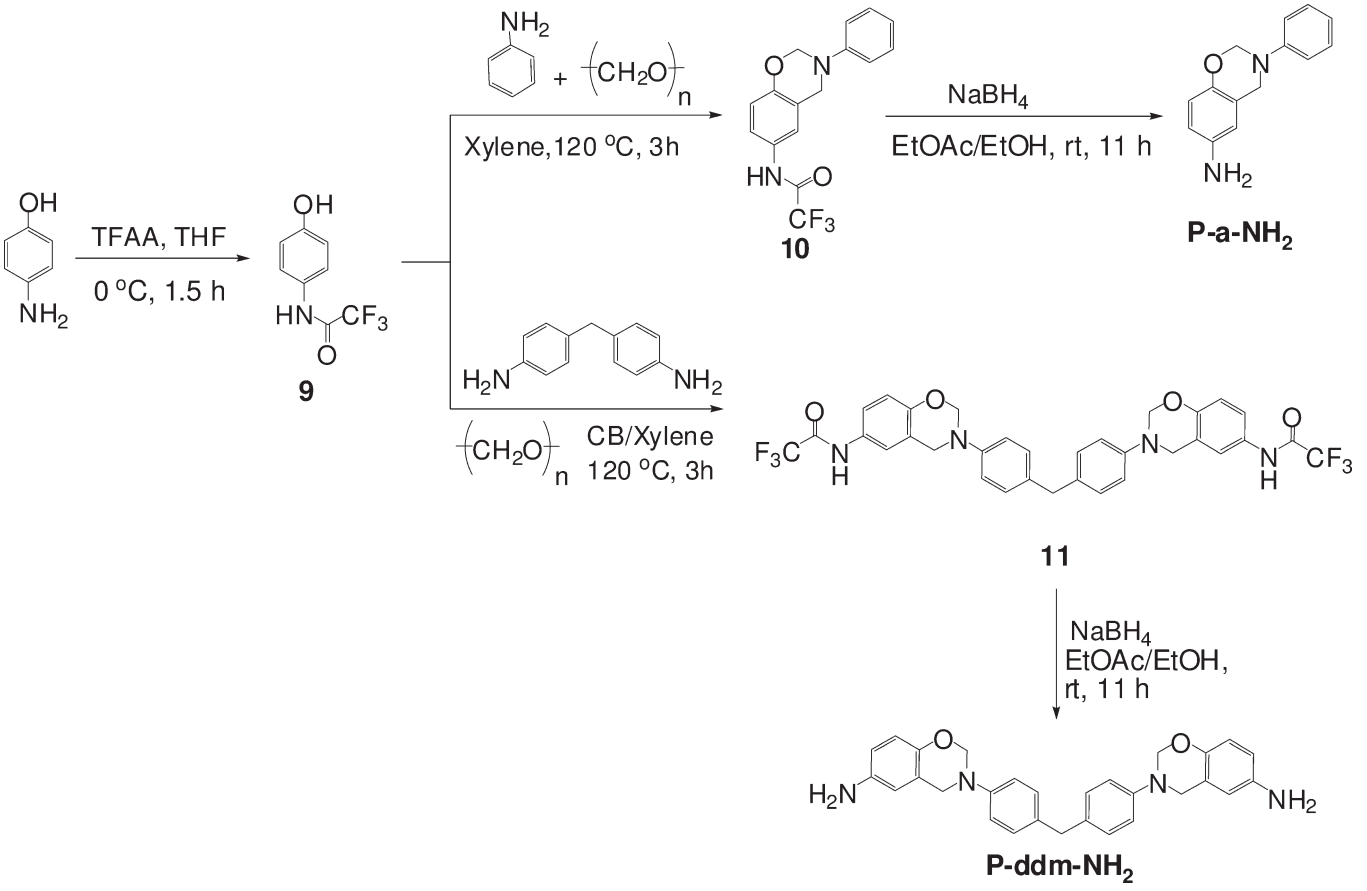



**Figure 3.** IR spectra of TCP-protected (**7**) and deprotected primary amine-monofunctional benzoxazine monomer (P-a-$NH_2$).

By using TFA-protected *p*-aminophenol, both protected monofunctional (**10**) and bifunctional (**11**) benzoxazines were prepared in good yields and short reaction times by using a new solvent system of a mixture of chlorobenzene/xylene (1:1 v/v) at 130 °C. These reactions were also carried out using different solvents such as xylene, dioxane, xylene/dioxane, DMSO, xylene/DMSO, and chlorobenzene but without having the same satisfactory results as in the case of the mixture of chlorobenzene/xylene. The deprotection to amine was easily achieved by using an ethyl acetate/methanol solution of sodium hydroxide in a reasonable high yield.

The structures of the TFA-protected benzoxazines were confirmed by $^{1}$H and $^{13}$C NMR and FT-IR analyses. Figure 4 shows the $^{1}$H NMR spectra of primary amine-functional bisbenzoxazines along with their starting materials. The $^{1}$H NMR spectra of the TFA-protected, diamino-functional benzoxazine (**11**) show the singlet NH- proton resonance at 11.06 ppm and the typical benzoxazine resonances at 4.60 and 5.39 ppm. The formation of amine-containing benzoxazines has been indicated by the frequency shift of the benzoxazine resonances from 4.67 and 5.46 ppm to 4.51 and 5.29 ppm for monofunctional monomer and from 4.60 and 5.39 ppm to 4.44 and 5.22 ppm for bifunctional monomer.

**Scheme 4. Preparation of Amino-Functional Benzoxazine Monomers Using TFA-Protected *p*-Aminophenol**



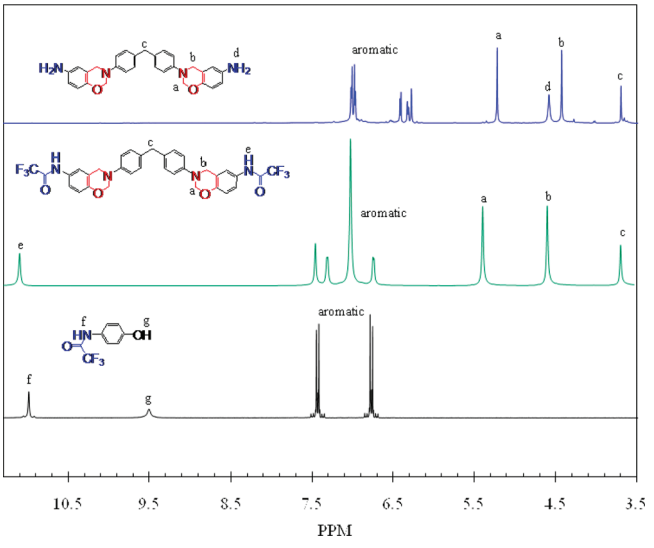




**Figure 4.** $^1$H NMR spectra of TFA-protected (**7**) and deprotected diamino-functional benzoxazine (P-ddm-$NH_2$) along with its starting materials.

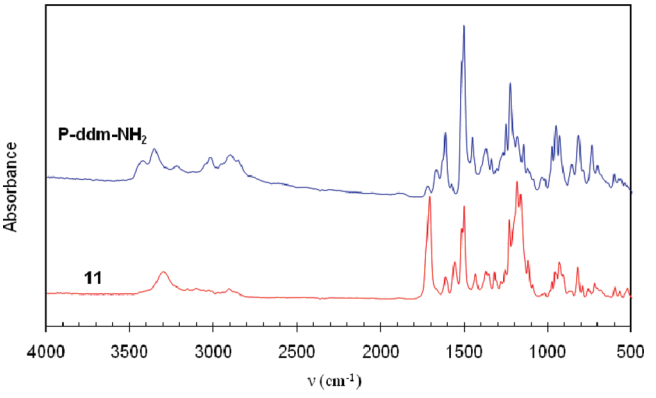



**Figure 5.** IR spectra of TCP-protected (**11**) and deprotected (P-ddm-$NH_2$)-amino-bifunctional benzoxazine monomer.

Also, new resonance appeared due to $-NH_2$ proton, at 4.52 ppm for monofunctional and 4.57 for bifunctional amino-containing benzoxazines.

The structures of two monomers were also confirmed by FT-IR. Figure 5 shows the FT-IR spectra for P-ddm-$NH_2$ as an example. In addition to the bands from the C−O−C antisymmetric stretching mode at 1230 $cm^{-1}$ for monofunctional and 1226 $cm^{-1}$ for bifunctional, and the benzene ring mode of the benzoxazine group at 950 $cm^{-1}$ in the case of monofunctional and 956 $cm^{-1}$ in the case of bifunctional, the bands corresponding to the NH stretching mode at 3286 and 3288 $cm^{-1}$ for monofunctional and bifunctional, respectively, and the carbonyl stretching mode at 1700 $cm^{-1}$ in the case of monofunctional and 1706 $cm^{-1}$ in the case of bifunctional were observed. The new characteristics bands due to the primary amine group stretching appeared at 3430, 3353, and 3224 $cm^{-1}$ for the monofunctional benzoxazine and at 3419, 3351, and 3210 $cm^{-1}$ for the bifunctional benzoxazine.

A model compound of amide-containing benzoxazine was prepared to study the reactivity of primary amine-functional benzoxazine and the properties of amide-functional

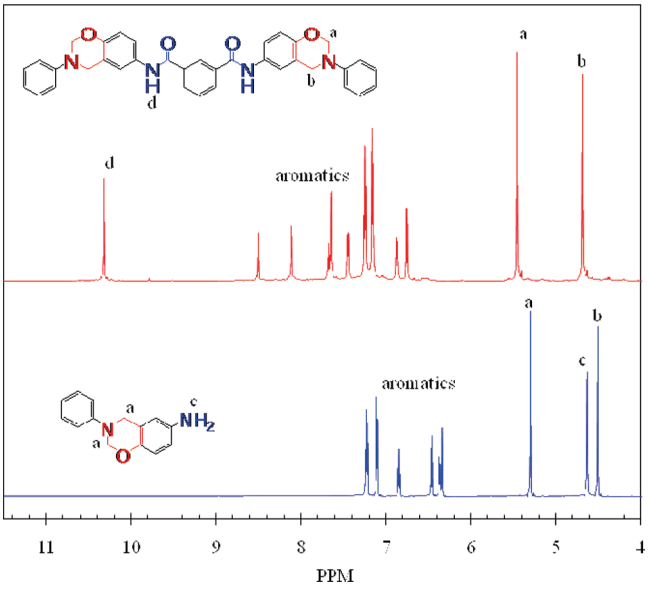
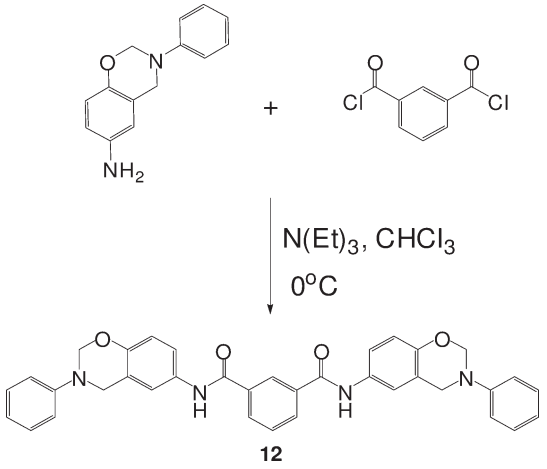



**Figure 6.** $^1$H NMR spectra of P-a-$NH_2$ and model **12**.

**Scheme 5. Preparation of Amide-Containing Benzoxazine Using Amino-Functional Benzoxazine Monomer (P-a-$NH_2$)**




**12**

benzoxazine as well. A model compound was successfully synthesized from the reaction of primary amine-containing monofunctional benzoxazine (P-a-$NH_2$) and acid chloride, as shown in Scheme 4. The structure of the model **12** was confirmed by $^1$H and $^{13}$C NMR and FT-IR analyses. Figure 6 shows the $^1$H NMR spectra of **12**. The spectra of the model compound **12** exhibit a slight increase in the chemical shifts that belong to the benzoxazine structure from 4.51 and 5.29 ppm to 4.67 and 5.44 ppm, and the appearance of the NH proton resonance of amide at 10.25 ppm, confirming the formation of an amide bond.

The structure of model compound **12** was further characterized by FT-IR, and its spectrum is shown in Figure 7. New bands appeared at 3288 and 1646 $cm^{-1}$ due to the N−H stretching and C═O stretching of amide configuration. Also, symmetric stretchings of C−O−C and C−N−C are observed at 1226 and 1186 $cm^{-1}$, respectively. The characteristic absorption benzene ring mode of benzoxazine is shown at 950 $cm^{-1}$.

**3.2. Thermal Properties of Monomers.** It is known that 1,3-benzoxazine exhibits an exothermic ring-opening polymerization reaction around 200−250 °C, which can be monitored by DSC. Figure 8 shows the DSC thermogram for the

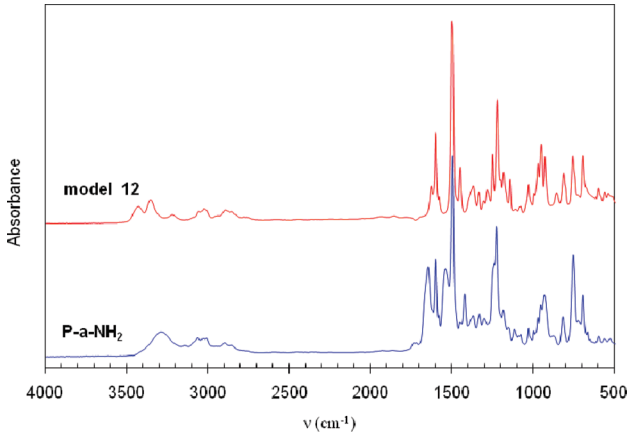



**Figure 7.** IR spectra of P-a-$NH_2$ and model **12**.

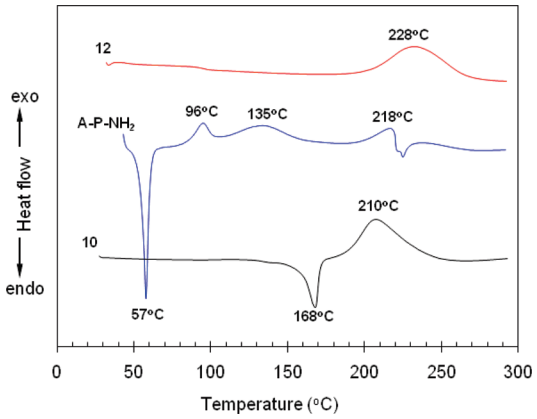



**Figure 8.** DSC thermograms of TCP-protected monofunctional amine (**10**), P-a-$NH_2$, and model **12**.

TCP-protected monofunctional benzoxazine (**10**), P-a-$NH_2$, and model **12** for comparison. Monomer **10** shows an endotherm at 168 °C due to melting and a typical DSC benzoxazine exothermic peak with onset at 184 °C and a maximum at 210 °C. However, the primary amine-functional benzoxazine shows, in addition to the sharp endotherm due to melting at 57°, multiple thermal events in the form of several exotherms. Three exothermic peaks were observed with the maxima at 96, 135, and 218 °C, attributing to the reaction between benzoxazine structure and the primary amine group along with the typical ring-opening of benzoxazine structure at higher temperature. Because of the sudden endotherms ovserved at 225 °C, which could be attributed to partial degradation, the peak position of the 218 °C was probably underestimated. The DSC profile of model **12**, which contains an amide linkage, was also studied. Unlike P-a-$NH_2$, a typical DSC benzoxazine exothermic peak was observed with onset at 194 °C and a maximum at 223 °C, attributed to benzoxazine polymerization. This cure behavior of the amide-containing benzoxazine also suggests that the presence of amide (−NH−CO−) linkage enhanced the polymerization at a relatively lower temperature in comparison with typical amine/phenol benzoxazines.

Polymerization behavior of the TCP-protected bifunctional benzoxazine (**11**) and amino-bifunctional benzoxazine (P-ddm-$NH_2$) is studied, and the DSC thermograms are shown in Figure 9. Monomer **11** shows a sharp endotherm at 216 °C, and the ring-opening reactions took place right after the melting, which is indicated with the exothermic peak at 236 °C. However, for the primary amine-functional

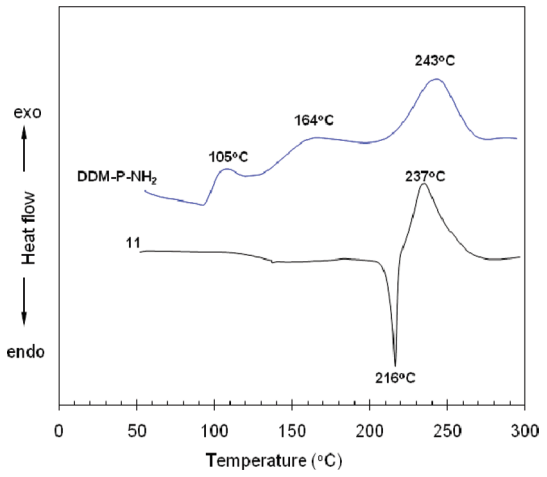



**Figure 9.** DSC thermograms of TCP-protected bifunctional amine (**11**) and P-ddm-$NH_2$.

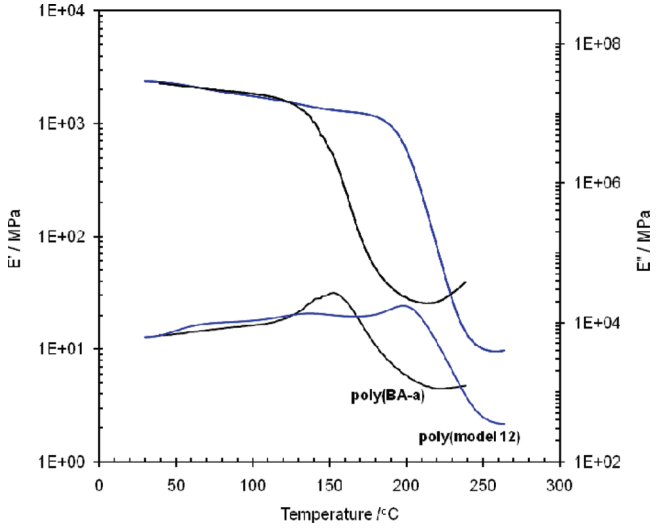



**Figure 10.** Storage and modulus moduli−temeprature relationship of of poly(BA-a) and poly(**12**).

bisbenzoxazine, P-ddm-$NH_2$, similar multithermal events were observed as P-a-$NH_2$. Three exotherms were observed with the maxima at 105, 164, and 243 °C, attributing to the interaction between benzoxazine and amino group along with the typical ring-opening of benzoxazine structure at higher temperature. The molecular mechanism of this multithermal event for the primary amine-catalyzed polymerization has not yet been studied. One possibility is that the reaction is locally heterogeneous. The other possibility is that the amine might be acting as reactant and multistage consumption of the amine may have caused the multiple thermal events. Further detailed study is needed to explain this complex phenomenon.

**3.3. Thermal Properties of Amide-Containing Benzoxazine.** Thermal properties of model compound **12** after polymerization at 240 °C for 1 h have been investigated in comparison with the typical polybenzoxazine, poly(BA-a) derived from bisphenol A/aniline bifunctional benzoxazine (BA-a). The viscoelastic properties of thermoset of poly(model **12**) and poly(BA-a) have been studied. Figure 10 shows the temperature dependence of the storage modulus and loss modulus, whereas Figure 11 shows the tan $\delta$ for the polybenzoxazine thermosets.

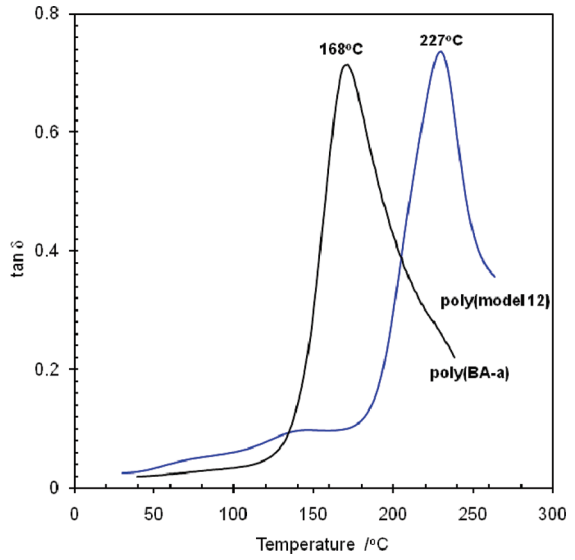



**Figure 11.** Vicolestic properties of of poly(BA-a) and poly(**12**).

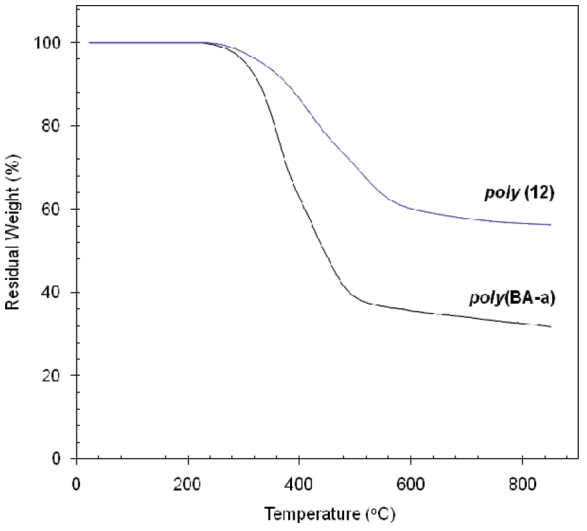



**Figure 12.** TGA thermograms of poly(BA-a) and poly(**12**).

The storage modulus ($E'$) of poly(BA-a) decreased sharply at ca. 130 °C with glass transition temeprtature ($T_g$) observed at 154 and 168 °C from the maximum of the loss modulus and tan $\delta$, respectively. For poly(model **12**), the storage modulus maintained nearly a constant value of more than 1 GPa up to 200 °C in comparison to the typical poly(BA-a) of around 140 °C. The $T_g$ shifted to as high as 198 and 227 °C from the maximum of loss modulus and tan $\delta$, respectively. The interesting properties of polybenzoxazines are generally attributed to the inter- and intramolecular hydrogen bonding between hydroxyl groups of phenolic structure and/or intramolecular 6-membered ring formation between the phenolic structure and Mannich base bridge. However, in this case of amide-containing polybenzoxazine, in addition to the typical hydrogen bonding, amide groups are expected to participate in further hydrogen bonding among polymer chains and hence induce lateral reinforcement across the polymer network structure.

Thermal stability of model compound **12** after polymerization at 240 °C for 1 h in comparison with the typical bisphenol A/aniline bifunctional benzoxazine (B-a) was investigated by TGA. TGA profiles of the polymers, poly(Ba-a) and poly(**12**), are shown in Figure 12. The 5 and 10%

weight loss temperatures ($T_{d5}$ and $T_{d10}$) for poly(BA-a) are 310 and 327 °C, respectively, whereas $T_5$ and $T_{10}$ for poly(**12**) are 341 and 380 °C, respectively. The char yield at 800 °C are 32 and 57%, for of poly(BA-a) and poly(**12**), respectively. This enhanced thermal stability of poly(**12**) as a monofunctional benzoxazine without any additional cross-linking site suggests that the presence of amide linkage play a significant role in enhancing the thermal properties.

## 4. Conclusion

Several routes have been applied to prepare amino-functional benzoxazine structure. The reduction of nitro-functional benzoxazine to the corresponding primary amine-functional benzoxazine monomers was unsuccessful due to many side reactions, owing to the instability of benzoxazine structure under reduction conditions. The most convenient approach was found to be the protection of primary amine-functional benzoxazines, followed by deprotection at mild conditions that is not harmful for benzoxazine structure. It was found that trifluoroacetyl group as the protecting group is a convenient pathway that allows easy synthesis for protected benzoxazines and can be removed easily as well. Furthermore, the reactivity of primary amine-functional bezoxazine toward further modifications has been studied by preparation of amide-functional benzoxazine as model compound, indicating the high reactivity of the benzoxazines toward further modification. The polymerization behavior of amino-functional monomers studied by DSC showed thermograms with multithermal event in the form of several exotherms at different temperature ranges.

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