Crosslinked Polyamide Based on Main-Chain Type Polybenzoxazines Derived from a Primary Amine-Functionalized Benzoxazine Monomer

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ABSTRACT: Two types of main-chain type polybenzoxazines with amide and benzoxazine groups as repeating units in the main chain, termed as poly(amide-benzoxazine), have been synthesized. They have been prepared by polycondensation reaction of primary amine-bifunctional benzoxazine with adipoyl and isophthaloyl dichloride using dimethylacetamide as solvent. Additionally, a model reaction is designed from the reaction of 3,3'-(4,4'-methylenebis(4,1-phenylene))bis(3,4-dihydro-2H-benzo[e][1,3]oxazin-6-amine) with benzoyl chloride. The structures of model compound and polyamides are confirmed by Fourier transform infrared (FTIR) and proton nuclear mag-

INTRODUCTION Polybenzoxazine is a novel phenolic-type thermoset, which has attracted much interest in recent years due to its outstanding properties. Despite having a few good properties and wide industrial use of traditional phenolic resins, the shortcomings associated with these materials are well known. For example, volatiles such as water or formaldehyde are released during polymerization process due to condensation reaction. Thus, these volatiles lead to poor mechanical properties due to the formation of microvoids, not to mention about the health concern the reaction byproducts cause. Another shortcoming is the use of base or acid catalyst for polymerization, which results in corrosion of the processing equipment. In this manner, properties belonging to polybenzoxazines, such as near-zero volumetric shrinkage and no byproduct release on polymerization, low water absorption, excellent electrical thermal properties, and good chemical resistance, low flammability,¹⁻⁷ and very good molecular design flexibility, make polybenzoxazines attractive for numerous applications. Polybenzoxazines are obtained by thermally activated cationic ring-opening polymerization of the corresponding benzoxazines without any added initiator¹ and without generating any byproducts. Benzoxazine resins can also be polymerized with initiators. Depending on the type of initiators used, the resultant polymer takes either the phenolic or arylether type.^{8,9} However, thermal treatment of the aryl ether-type polybenzoxazine leads to the phenolic type.⁹ The

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Materials Views

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netic resonance (¹H NMR) spectroscopies. Differential scanning calorimetry and FTIR are also used to study crosslinking behavior of both the model compound and polymers. Thermal properties of the crosslinked polymers are also studied by thermogravimetric analysis. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 4335–4342, 2011

KEYWORDS: crosslinked polyamide; main chain benzoxazine polymer; polymerization behavior; primary amine-functional benzoxazine

benzoxazine ring-containing monomers are easily prepared from a phenolic derivative, a primary amine, and formaldehyde.^{1,10,11} For some applications, brittleness, necessity of moderately high temperature for the ring-opening polymerization, and difficulty of processing into thin film from the typical monomers need to be overcome. Such needs lead to the recent approaches in polybenzoxazine research. One of the approaches consists of designing main-chain type polymers incorporating benzoxazine moieties as a repeating unit either as pendant groups or in the main chain.^{12–26} In this manner, this class of benzoxazine polymers can be processed into tough films, thereby behaving as thermoplastics. In addition, the product can be fully or partially crosslinked by thermal treatment, adding typical advantages of thermosets to the final product.

Although many benzoxazine resins have been reported,⁷ no successful attempt has been reported until recently²⁷ on the synthesis of primary amine-functional benzoxazines despite its great potential to be the raw materials for many benzoxazine monomers and polymers.

Polyamides, as a major class of polymers, find applications in fibers and film technology due to their inherent flame retardance, thermal and chemical resistances, and good mechanical properties. Having realized this versatile applicability of polyamides, it appears worthwhile to study the effect

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of incorporating benzoxazine into polyamide structure. However, the common weakness of polyamide is its sensitivity of the properties to moisture content as well as poor creep resistance, as is usually the case for many thermoplastic polymers. On the other hand, the problem usually raised for thermosetting polymers is their brittleness. By combining the thermoplastic nature of polyamide and thermosetting nature of the crosslinked polybenzoxazine, we created thermoplastic/thermoset crossover molecules that offer processibility, ductility, and film formability advantages of thermoplastics while adding to them are the improved thermal, chemical, and creep resistances as well as dimensional stability of thermosetting resins. Reduced moisture sensitivity was an added advantage. Thus, developing the current crosslinked polyamide has various advantages, in particular to balance various mechanical and physical properties that was lacking in traditional pure thermoplastics and thermosetting resins.

In this study, a primary amine-bifunctional benzoxazine, which was recently developed in our laboratory,²⁷ was used for the synthesis of aliphatic and aromatic benzoxazine-containing polyamides, which are collectively abbreviated as poly(amide-benzoxazine). In addition, a model amide-containing bifunctional benzoxazine monomer was also studied. The preparation, characterization, and properties of model compound and main-chain type polybenzoxazines as well as their thermosets will be discussed.

EXPERIMENTAL

Materials

Adipoyl chloride, *p*-aminophenol, benzoyl chloride, 4-chlorobenzene, isophthaloyl chloride, sodium borohydride, trifluoroacetic anhydride, and paraformaldehyde were used as received from Sigma-Aldrich. 4,4'-Diaminodiphenylenemethane (DDM) was purchased from Johnson Matthey Catalog. Dimethylacetamide (DMAc), chloroform, ethyl acetate, hexane, methanol, triethylamine, xylenes, sodium hydroxide, and sodium sulfate were obtained from Fisher.

Characterization

A Varian Oxford AS600 at a proton frequency of 600 MHz and a corresponding carbon frequency of 150.9 MHz was used to acquire ¹H and ¹³C NMR spectra in deuterated dimethylsulfoxide (DMSO). Tetramethylsilane was used as an internal standard. Thermal stability was examined with a TA Instruments Model 2920 differential scanning calorimeter (DSC) using a heating rate of 10 $\,^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. Fourier transform infrared (FTIR) spectra were acquired on a Bomem Michelson MB100 equipped with a deuterated triglycine sulfide detector and a dry air purging unit at a resolution of 4 cm^{-1} using KBr plates. Dynamic mechanical analysis (DMA) was done on a TA Instruments Model Q800 DMA applying controlled strain tension mode with amplitude of 10 μ m and a ramp rate of 3 °C/min. Thermogravimetric analysis (TGA) was performed on a TA Instruments Model Q500 TGA with a heating rate of 10 °C/min under a nitrogen atmosphere.

Preparation of 3,3'-(4,4'-Methylenebis(4,1phenylene))bis(3,4-dihydro-2H-benzo[e][1,3]oxazin-6amine)

Primary amine-bifunctional benzoxazine (3,3'-(4,4'-methyle-nebis(4,1-phenylene))bis(3,4-dihydro-2H-benzo[e][1,3]oxazin-6-amine), P-ddm-NH₂) was prepared following the method developed in our laboratory, which is published elsewhere.²⁷

¹H NMR (DMSO-*d*₆), ppm: δ = 3.71 (s, CH₂), 4.44 (s, Ar-CH₂—N, oxazine), 4.57 (s, NH₂), 5.22 (s, N—CH₂—O, oxazine), 6.28–7.05 (14H Ar). ¹³C NMR (DMSO-*d*₆), ppm: δ = 49.07 (Ar-C—N, oxazine), 78.45 (O—C—N, oxazine). FTIR *v* (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).

Preparation of *N*,*N*'-(3,3'-(4,4'-Methylenebis(4,1phenylene))bis(3,4-dihydro-2H-benzo[e][1,3]oxazine-6,3diyl))dibenzamide, Model Compound

P-ddm-NH₂ (0.4 g, 0.861 mmol) and triethylamine (2 mL) were dissolved in 13 mL of DMAc, cooled in an ice bath, and stirred for 15 min. Then, a solution of benzoyl chloride (0.254 g, 1.808 mmol) in 15 mL chloroform was added dropwise for 15 min. After addition of acid chloride, the mixture was stirred for 1 h in the ice bath. After diluting with chloroform, the crude product was washed three times with 0.5 N NaOH aqueous solution and additional three times with water. The solution was dried over sodium sulfate anhydrous, followed by precipitation in hexanes. Removal of solvent by evaporation afforded a white powder (Yield 95%).

¹H NMR (DMSO-*d*₆), ppm: δ = 3.70 (s, CH₂), 4.60 (s, Ar-CH₂—N, oxazine), 5.37 (s, N—CH₂—O, oxazine), 6.70–7.94 (24H, Ar) and 10.08 (s, NH). ¹³C NMR (DMSO-*d*₆), ppm: δ = 49.13 (Ar-C—N, oxazine), 78.95 (O—C—N, oxazine), 131.32 (C—NH) and 164.58 (Ar-(C=O)—NH). FTIR (KBr), cm⁻¹: 3311 (N—H stretching), 1646 (carbonyl stretching), 1498 (stretching of trisubstituted benzene ring), 1226 (asymmetric stretching of C—O—C), 1186 (asymmetric stretching of C—N—C), 946 (out-of-plane C—H).

Preparation of Main-Chain Type Aliphatic Poly(amide-benzoxazine)

In a three-necked, round-bottomed flask with a rubber septum and stirring magnet, a solution of P-ddm-NH₂ (1 g, 2.152 mmol) in DMAc (13 mL) and triethylamine (1 mL) was added. The flask was cooled to -5 °C using an ice/ ethanol bath, and a solution of adipoyl chloride (0.394 g, 2.152 mmol) in DMAc (7 mL) was dropwise syringed to the reaction mixture for 15 min. The reaction mixture was then allowed to warm to room temperature and stirred for 24 h under nitrogen atmosphere. Then, the crude product was filtrated to remove the formed salt, followed by precipitation into ethyl acetate (~100 mL). The solid was filtered, washed with ethyl acetate, and dried overnight in vacuum oven at room temperature to give a white solid (yield 85%).

¹H NMR (DMSO- d_6), ppm: $\delta = 1.58$ (CO–CH₂–CH₂), 2.26 (CH2-CH2-CH2), 3.68 (Ar-CH2-Ar), 4.53(Ar-CH2-N, oxazine), 5.31 (O–CH₂–N, oxazine), 6.5–7.5 (Aromatics) and 9.68 (NH). FTIR (KBr) (cm⁻¹): 3272 (N-H stretching), 1660 (carbonyl stretching), 1500 (stretching of trisubstituted benzene ring), 1226 (asymmetric stretching of C-O-C), 1187 (asymmetric stretching of C—N—C), 935 (out-of-plane C—H).

Preparation of Main-Chain Type Aromatic Poly(amide-benzoxazine)

This polymer was prepared similarly as the aliphatic polymer from P-ddm-NH₂ (1 g, 2.152 mmol) in DMAc (13 mL), triethylamine (1 mL), and isophthaloyl chloride (0.437 g, 2.152 mmol) in DMAc (7 mL). The solid was filtered, washed with ethyl acetate, and dried in vacuum oven at 50 $^\circ\text{C}$ overnight to give a white solid (yield 85%).

¹H NMR (DMSO- d_6), ppm: $\delta = 3.69$ (CH₂), 4.59 (Ar-C-O, oxazine), 5.36 (O-C-N, oxazine), 6.69-8.46 (Aromatics) and 10.26 (NH). FTIR (KBr), cm⁻¹: 3253 (N-H stretching), 1660 (carbonyl stretching), 1502 (stretching of trisubstituted benzene ring), 1228 (asymmetric stretching of C-O-C), 1191 (asymmetric stretching of C—N—C), 931 (out-of-plane C—H).

Crosslinking of Poly(amide-benzoxazine)s

A solution of polymers in DMAc (30% solid content) has been prepared. The solution has been cast over dichlorodimethylsilane-treated glass plates. The solvent films have been dried at 70 °C for 24 h under vacuum. Thereafter, the film as fixed on glass plate has been thermally treated using the following heating schedule: 100, 120, 150, 180, 200, and 240 °C for 2 h each, unless otherwise indicated, to afford film of reddish brown color and thickness of about 100 μ m. The highest polymerization temperature for the aliphatic sample was at 220 °C for 2 h, instead of 240 °C for 2 h of the aromatic polymer. Films obtained under these polymerization conditions were used for the dynamic mechanical analysis. However, for the DSC study, the highest temperature for both linear and aromatic polymers was set at 250 °C for 1 h.

RESULTS AND DISCUSSION

Preparation of Model Compound

In order to study the reactivity of primary amine-bifunctional benzoxazine (P-ddm-NH₂) and the properties of amide-containing benzoxazine, a model compound was synthesized from the reaction of P-ddm-NH₂ with benzoyl chloride, as shown in Scheme 1. The chemical structure was con-



SCHEME 1 Preparation of an amide-containing model compound. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



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FIGURE 1 ¹H NMR spectra of P-ddm-NH₂ and the amide-containing model compound.

firmed by ¹H NMR, ¹³C NMR, and FTIR spectroscopies. ¹H NMR spectra shown in Figure 1 for the model compound exhibit a slight increase in the chemical shifts of the methylene proton resonances of the oxazine ring from that of P-ddm-NH₂ benzoxazine structure from 4.44 and 5.22 ppm to 4.60 and 5.37 ppm, respectively. In addition, the appearance of the NH-proton due to the amide bond at 10.08 ppm and the disappearance of the resonance at 4.57 ppm due to the primary amine of P-ddm-NH₂ were observed, indicating successful formation of the amide groups.

Figure 2 shows FTIR spectra of model compound and P-ddm- NH_2 . The characteristic peaks due to the N-H and C=0 stretching modes of amide linkage are observed at 3311 and



FIGURE 2 IR spectra of P-ddm-NH₂ and the amide-containing model compound. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



SCHEME 2 Preparation of aliphatic and aromatic main-chain type poly(amide-benzoxazine)s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

1,646 cm⁻¹, respectively. In addition, characteristic absorptions assigned to benzoxazine structure due to the C-O-C and C-N-C stretching, and the benzene ring mode of benzoxazine at 1,226, 1,186, and 946 cm⁻¹, respectively, were also observed. Both NMR and IR spectra suggest the formation of model amide-containing benzoxazine in high yield.

Preparation of Main-Chain Type Poly(amide-benzoxazine)

Similar conditions as for the model compound were applied for the synthesis of both aliphatic and aromatic poly(amidebenzoxazine)s as shown in Scheme 2. Main-chain type polybenzoxazines were synthesized by solution polycondensation of P-ddm-NH₂ with both adipoyl and isophthaloyl dichloride in DMAc as a solvent at room temperature, using triethylamine as a base catalyst. Isolated yields of polymers were about 85%, and the products were soluble in aprotic organic solvents, such as dimethylformamide, *N*-methylpyrrollidone, DMAc, and DMSO, at room temperature with \sim 20% solid content.



FIGURE 3 ¹H NMR spectra of P-ddm-NH₂ and aliphatic and aromatic poly(amide-benzoxazine)s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The molecular structure of the polymers was confirmed by ¹H NMR and FTIR spectroscopies. Figure 3 shows the ¹H NMR spectra of both aliphatic and aromatic poly(amide-benzoxazine)s along with the primary amine-bifunctional benzoxazine (P-ddm-NH₂). The spectrum of aliphatic poly(amidebenzoxazine) exhibits a slight increase in the chemical shifts of the methylene groups of the oxazine ring from 4.44 and 5.22 ppm to 4.53 and 5.31 ppm, respectively, besides the appearance of the characteristic resonance at 9.68 ppm representing N—H proton from the amide linkage. Similarly, in case of the aromatic poly(amide-benzoxazine), the chemical shifts of benzoxazine structure are observed at 4.59 and 5.36 ppm, and a new resonance of the amide N-H is shown at 10.26 ppm. The NMR data of the polymers are in accordance with that of model compound. Common to both polymers is the $-CH_2$ of ddm unit at 3.70 ppm. The multiplets in the range of 7.0-7.1 ppm are due to the aromatic protons of the ddm unit. The multiplets of the aromatic protons of P-ddm-NH₂ in the range of 6.3-6.5 ppm shifted to the range of 6.3-6.9 ppm on main-chain polymer formation. Multiple singlets in the



FIGURE 4 IR spectra of P-ddm-NH₂ and amide-containing polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 5 DSC of thermograms of P-ddm-NH₂, model compound, and heat-treated model compound at 175 °C for 10 s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

range of 7.3–8.5 ppm of both aliphatic and aromatic polymers are due to the aromatic protons of the isophthalamide unit introduced on aromatic main-chain formation.

The structure of the poly(amide-benzoxazine)s was further confirmed by FTIR. Figure 4 shows the spectra of the polymers. The band assignments were as per Bellamy²⁸ and Dunkers and Ishida.²⁹ The characteristic band due to the N—H stretching mode of the amide group was observed at 3,272 cm⁻¹ for polymers, whereas the characteristic absorption at 3,351 cm⁻¹ due to the N—H stretching mode of the primary amine has disappeared. In addition, characteristic band attributed to the Amide I band was also observed at 1,660 cm⁻¹ in both polymers. Furthermore, the benzene ring mode of the benzoxazine group in the main chain was observed at 935 and 931 cm⁻¹ for the aliphatic and aromatic poly(amide-benzoxazine)s, respectively. Thus, both NMR and IR spectra indicate the formation of poly(amidebenzoxazine)s.

Study of Polymerization Behavior by DSC and FTIR

The effect of the presence of aromatic amide linkage on the ring opening of benzoxazine in model compound was studied by DSC. Figure 5 shows DSC thermographs of P-ddm-NH₂ and model compound. As has been reported previously, the polymerization behavior of P-ddm-NH₂ consists of multithermal events, suggesting the catalytic interaction of the primary amine group with the benzoxazine structure [28]. The DSC thermogram of model compound shows an exotherm with the sharp maximum at 163 °C, immediately after the initial endothermic peak at 154 °C. Such a phenomenon, later confirmed by ¹H NMR and FTIR (not shown), suggests the enthalpic relaxation caused by partially ordered rearrangement of the molecules probably due to a favorable molecular structure at such a temperature assisted by the hydrogen bonding among amide groups. This rearrangement

would result in the disappearance of the first exothermic event as shown in the second scan after the treatment of the model compound at 175 °C for 10 s. On heat treatment, the softening event around 110 °C is clearly observed, further supporting the destruction of the partial order. The exotherm with the maximum centered at 244 $^\circ\text{C}$ is attributed to the ring-opening polymerization of benzoxazine. This is the typical temperature where ring-opening reaction is observed without the presence of initiator, catalyst, or any special structural effect, such as the influence of the orientation. The heat treatment at 175 °C did not influence at all the main exothermic behavior, including the exotherm peak temperature and heat of polymerization. As no clear melting behavior is observed for the nonheat-treated model compound, despite its rather high purity, it is possible that the packing structure of this model compound resembles metamorphic structure of polyamide, whose ordered structure is between amorphous and crystalline structures. Although aliphatic polyamide, such as nylon 6, forms metamorphous structure very easily³⁰ and only with special conditions the amorphous structure can be observed, the relaxation of model compound may be slow due to the steric hindrance in packing by the oxazine ring that is not coplanar to the benzene ring.³¹

The structure of model compound was studied after the heat treatment. FTIR analysis shown in Figure 6 before and after the thermal treatment indicates no changes in the structure. This supports the claim that the first exotherm centered at 163 °C is not due to any configurational changes of the benzoxazine structure.

DSC of Poly(amide-benzoxazine) as a Function of Heat Treatment

The thermally activated crosslinking behavior of the mainchain type poly(amide-benzoxazine)s through ring-opening



FIGURE 6 FTIR spectra of model compound before and after the heat treatment at 175 °C for 10 s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 7 DSC of the aliphatic poly(amide-benzoxazine) after various thermal treatment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reaction was also studied by DSC and FTIR. Figures 7 and 8 show the DSC thermograms of the main-chain type poly(amidebenzoxazine)s after thermal treatments at 100, 150, 200, and 250 $^{\circ}$ C for 1 h at each temperature.

It was observed that the onset of exothermic peak, which is attributed to the ring-opening polymerization of benzoxazine in the main chain, took place at about 181 °C with the maximum at 236 °C for the aliphatic poly(amide-benzoxazine). However, the onset of the exothermic peak of aromatic poly(amide-benzoxazine) started at slightly higher temperature of 204 °C with maximum at 245 °C. This can be attributed to the flexiblizing effect of the aliphatic chain in aliphatic poly(amide-benzoxazine), which assisted the segmental mo-



FIGURE 8 DSC of the aromatic poly(amide-benzoxazine) after various thermal treatment.



FIGURE 9 FTIR spectra of the aliphatic poly(amide-benzoxazine) after various thermal treatment.

bility for ring opening polymerization to take place easier than the whole aromatic structure.

In both poly(amide-benzoxazines)s, the exothermic peak decreased after each treatment temperature. The exotherm practically disappeared at 250 °C, thereby showing the completion of the ring-opening reaction. The completeness of the crosslinking via ring-opening polymerization of benzoxazine was also confirmed by FTIR. Figure 9 shows the FTIR spectra of the aliphatic poly(amide-benzoxazine) as an example. The characteristic bands are seen due to the benzoxazine structure at 1,500 cm⁻¹ (the trisubstituted benzene ring mode), 1,226 cm⁻¹ (the C—O—C antisymmetric stretching mode of oxazine), 1,187 cm⁻¹ (the C—N—C antisymmetric stretching mode of benzoxazine). By the end of thermal treatment



FIGURE 10 Dynamic mechanical spectra of the crosslinked poly(amide-benzoxazine)s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 11 TGA thermograms of the crosslinked poly(amidebenzoxazine)s after thermal treatment at 250 °C for 30 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

at 250 °C, the characteristic bands attributed to the benzoxazine structure disappeared, supporting the conclusion obtained by the DSC analysis.

Thermal Properties of Crosslinked Poly(amide-benzoxazine)s

The results of dynamic mechanical analysis of the thermoset obtained from the heat treatment of the poly(amide-benzoxazine) at 250 °C are shown in Figure 10 for the storage (E')modulus, loss (E'') modulus, and tan δ for the two polymers. The $T_{\rm g}$ was observed from the maxima of E'' at 236 and 169 °C for aromatic and aliphatic crosslinked poly(amide-benzoxazine)s, respectively. In addition, a very weak transition was observed under 100 °C from the maxima of E'' for both aliphatic and aromatic polymers. As described elsewhere, 3,22 β transition has been observed in crosslinked polybenzoxazine resulting from a monomeric benzoxazine based on bisphenol-A and aniline, abbreviated as poly(BA-a), around 90 °C, whereas the corresponding $T_{\rm g}$ was 170 $\,^{\circ}\text{C}.$ It is therefore possible that for crosslinked aromatic poly(amide-benzoxazine), this transition is due to the β -transition, taking into consideration that even though T_{g} of the current polymer is higher than poly(BA-a), the presence of an aliphatic segment in the repeating unit makes possible a β -transition at such a value. Crosslinked aromatic polyamides³²⁻⁴⁰ have been studied in the past. However, the majority of the studies relate to the reverse osmosis membrane development and either the degradation as a result of crosslinking and permeation properties were of interest. Very little studies have been published on the thermal property improvement of crosslinked polyamide, in particular aliphatic polyamide.

The thermal stability of crosslinked poly(amide-benzoxazine) has been studied by TGA. Figure 11 shows the TGA thermograms of the polymers after thermal treatment at 250 $^{\circ}$ C for 30 min. As expected, the crosslinked aromatic poly(amidebenzoxazine) exhibits higher thermal stability than the polymer containing aliphatic segment. For aliphatic poly(amidebenzoxazine), the initial decomposition temperatures of 5 and 10% weight losses (T_5 and T_{10}) and the char yield at 800 °C are 259 °C and 312 °C and 41%, respectively. For the aromatic poly(amide-benzoxazine), the initial decomposition temperatures of 5 and 10% weight losses (T_5 and T_{10}) and the char yield at 800 °C are 347 °C and 403 °C and 57%, respectively. The uncrosslinked aromatic amide reported by Behniafar and Khosrani-borna showed excellent thermal stability in the temperature range of 300-500 °C. However, the weight quickly reduced in the 600-700 °C range, showing the char yield at 700 °C less than 35%. Yet, another uncrosslinked aromatic polyamide based on sulfone group studied by Zulfiqar and Sarwar⁴² reported the char yield at 600 °C to be about 40%. Our crosslinked poly(amide-benzoxazine)s, even the aliphatic material, showed much higher char yield at 800 °C, indicating significant improvement in char formation by crosslinking through the oxazine reactions.

CONCLUSIONS

A novel approach has been developed to synthesize thermosetting polyamides by incorporating benzoxazine structure as a repeating unit in the main chain. For better understanding of the polymerization reaction, a model compound was synthesized from the primary amine-bifunctional benzoxazine with benzoyl chloride in high purity. The main-chain type polymers have also been prepared by polycondensation reaction of the primary amine-bifunctional benzoxazine with adipoyl and isophthaloyl dichloride in dimethylacetamide as solvent. The structures of model compound and polyamides are confirmed by FTIR and ¹H NMR. The crosslinking of aliphatic poly(amide-bezoxazine) took place at slightly lower temperature than the aromatic polymer due to the flexiblizing effect of the aliphatic segment in the main chain. The polymers after crosslinking showed good thermal stability appointing these materials as a good candidate for high performance applications.

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