Preparation and Properties of Some Thermosets Derived from Allyl-Functional Naphthoxazines

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ABSTRACT: A series of novel naphthoxazine monomers containing allyl functionalities were synthesized from the reaction of 1-naphthol, 2-naphthol, and 1,5-dihdroxynaphthalene with allylamine and formalin. Another series of naphthoxazines were similarly prepared by using aniline instead of allylamine for comparison. The chemical structures of these novel monomers were confirmed by IR, ^{1}H NMR, and elemental analysis. DSC of the aniline- based naphthoxazines showed an exotherm due to the ring-opening polymerization of oxazine. For allylamine-based naphthoxazines, two exotherms were observed. The first exotherm is attributed to the thermal crosslinking of the allyl group and the second is due to the ring- opening polymerization of oxazine. The thermal cure of the allylamine-based naphthoxazine monomers gave thermoset resins with novel structure comprising of polynaphthoxazine with extended network via the polymerization of allyl functionalities. Dynamic mechanical analyses and thermogravimetric analyses showed that the thermosets derived from allyl- functional naphthoxazines have high T_g's and stable storage moduli to higher temperature as well as better thermal stability than that of aniline-based naphthoxazines. J Appl Polym Sci 100: 3769–3777, 2006

Key words: naphthoxazine; allyl group; novel thermosets; thermal properties

INTRODUCTION

The ease of handling and processability of benzoxazine monomers along with the attractive properties of their polymers endow this class of thermosets a promising future as a novel candidate of phenolic resin. The availability and the low cost of the starting raw materials, including phenols and primary amines needed for the preparation of benzoxazine monomers, offer flexibility in designing varieties of polybenzoxazines. Benzoxazine monomers are characterized by a low melt viscosity, which makes them easily processable in comparisons with other resins such as typical phenolics or bismaleimides. Additionally, the monomers can be easily polymerized through the ring-opening polymerization of benzoxazine ring to afford the corresponding polybenzoxazine, without using any strong acid or basic catalyst and without generating any byproducts. Polybenzoxazines possess similar characteristics to the traditional phenolic resins, such as good heat resistance and flame retardance. Furthermore, they provide some additional interesting characteristics that are not found in the traditional phenolic resins, such as low water absorption and excellent dimensional stability due to the near-zero volumetric shrinkage upon cure.[1–5]

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The aforementioned advantageous characteristics of polybenzoxazines have been attracted much attention. Thus, various approaches have been recently adopted for the production of polybenzoxazine-based materials with superior thermal and mechanical properties, aiming at expanding their applications.[6–10] The modification of benzoxazine structure by the incorporation of another curable group has received much attention as a powerful approach to obtain high performance polybenzoxazines having better thermal and physical properties. Several polymerizable groups such as ethynyl,[11] nitrile,[12] propargyl,[13] allyl,[14] and maleimide[15] were incorporated into benzoxazine structure.

This approach has successfully afforded polybenzoxazines with high glass transition (T_g) temperature and thermal stability in comparison with typical polybenzoxazines.

Polymers containing condensed polynuclear aromatic structure, such as naphthalene, are known to have excellent thermal stability because of their extent of double bond conjugation. Naphthalene ring has been incorporated into the backbone of many polymers such as epoxy,[16,17] bismaleimides,[18] phenolic resin,[19,20] polyester,[21] polyamides,[22] poly(ester amide),[23] poly(ester-imide),[24] polyimides,[25,26] poly(amide-imide),[27–29] and poly(aryl ether ketone).[30] Recently, Shen and Ishida reported the preparation of aniline-based bifunctional naphthoxazines with improved thermomechanical properties.[31]

We are interested in obtaining high performance polybenzoxazines and their composites having high

thermal stability in a wide range of service environment. Encouraged by our promising results on allylamine-based benzoxazine,[10] we report herein the preparation of a series of novel allylamine-based naphthoxazines, and therefrom, the properties of the thermosets. Aniline-based naphthoxazines were also prepared for comparison.

EXPERIMENTAL

Materials

1-naphthol, 2-naphthol, 1,5-dihrdroxynaphthalene, allylamine, aniline, and formaldehyde (37% in water) were used as received from Tokyo Kasei (Japan). Dicumylperoxide (DCPO) was used as received from Tokyo Kasei.

Preparation of 3-allyl-3,4-dihydro-2*h*-1,3-naphthoxazine (1-N-ala)

Into a 300-mL round flask in an ice bath, formaldehyde (37% in water) (200 mmol, 16.232 g) and 20 mL dioxane were charged. Then, allylamine (100 mmol, 5.709 g) in 30 mL dioxane was added dropwise using dropping funnel, with the temperature kept below 10°C. The reaction mixture was stirred for 15 min at that temperature. To this solution, 1-naphthol (100 mmol, 14.417 g) dissolved in 100 mL dioxane was added portionwise at that temperature. The temperature was then raised gradually, and the solution was kept stirring at 100°C for 4 h. Thereafter, the solvent was removed by rotary evaporator. The residue was dissolved in 300 mL of ethyl acetate and washed three times with 1 L of aqueous 2*N* sodium hydroxide, and finally two times with 500 mL of distilled water. The solution was dried with anhydrous sodium sulfate, followed by the evaporation of ethyl acetate to afford a brown crystalline residue. The residue was further purified by recrystallization from isopropanol to afford pale brown crystals (16 g, 71%, m.p. 67–68°C).

Elemental analysis ($C_{15}H_{15}NO$): Calc.; C, 79.97%; H, 6.71%; N, 6.22%. Found; C, 79.47%; H, 6.69%; N, 6.22%. ^{1}H NMR spectra ($CDCl_3$), ppm: δ = 3.45 (d, —CH_2—), 4.15 (s, —CH_2—), 5.15 (s, —CH_2—), 5.20–5.30 (m, ═CH_2), 5.95–6.05 (m, —CH═), 7.05–8.15 (m, Ar, H). IR spectra (KBr, cm^{-1}): 954 (C—O—C), 1028–1036 (C—O—C), 1240 (Ar—O—C), 1340 (CH2 wag. oxazine), 1644 (str. of C═C) and 3082 (str. of ═C—H.

Preparation of 2-allyl-2,3-dihydro-1*H*-1,3-naphthoxazine (2-N-ala)

2-N-ala was prepared from formaldehyde (37% in water) (200 mmol, 16.232 g), allylamine (100 mmol, 5.709 g) and 2-naphthol (100 mmol, 14.417 g) similar to the previous method for 1-N-ala. The resulting yellowish crystalline product was further purified by recrystallization from methanol to afford colorless crystals (17 g, 75%, m.p. 40–41°C).

Elemental analysis ($C_{15}H_{15}NO$): Calc.; C, 79.97%; H, 6.71%; N, 6.22%. Found; C, 79.72%; H, 6.74%; N, 6.27%. ^{1}H NMR spectra (DMSO), ppm: δ = 3.25 (d, —CH_2—), 4.25 (s, —CH_2—), 4.90 (s, —CH_2—), 5.15–5.30 (m, ═CH_2), 5.80–6.00 (m, —CH═), 7.00–7.95 (m, Ar, H). IR spectra (KBr, cm^{-1}): 954 (C—O—C), 1028 (C—O—C), 1240 (Ar—O—C), 1340 (CH2 wag. oxazine), 1644 (str. of C═C) and 3082 (str. of ═C—H).

Preparation of bis(4,5-dihydro-5-allyl-oxazinyl)naphthalene (15-N-ala)

15-N-ala was prepared from formaldehyde (37% in water) (400 mmol, 32.432 g), allylamine (200 mmol, 11.418 g), and 15-dihydroxynaphthalene (100 mmol, 16.005 g), similarly. However, for 15-N-ala, the product was precipitated from the reaction solution at the initial stage of reflux at 100°C. Then, the reaction mixture was cooled down to room temperature and filtered to give yellowish green precipitate. The precipitate was repeatedly washed with distilled water and dried under vacuum to yield 28 g of yellowish green powder. The powder was purified by recrystallization from dioxane to afford pale yellow needle crystals (23 g, 71%, m.p. 155–156°C).

Elemental analysis ($C_{20}H_{22}N_2O_2$): Calc.; C, 74.51%; H, 6.88%; N, 8.69%. Found; C, 74.27%; H, 6.79%; N, 8.62%. ^{1}H NMR spectra ($CDCl_3$), ppm: δ = 3.25 (d, —CH_2—), 4.15 (s, —CH_2—), 5.05 (s, —CH_2—), 5.15–5.25 (m, ═CH_2), 5.85–6.05 (m, —CH═), 7.05–7.65 (m, Ar, H). IR spectra (KBr, cm^{-1}): 954 (C—O—C), 1036 (C—O—C), 1240 (Ar—O—C), 1340 (CH2 wag. oxazine). 1644 (str. of C═C) and 3082 (str. of ═C—H).

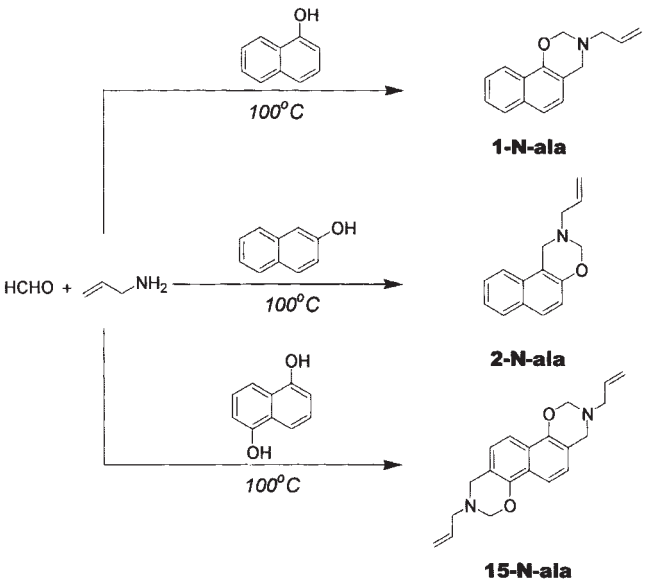
Preparation of 3-phenyl-3,4-dihydro-2*H*-1,3-naphthoxazine (1-N-a)

1-N-a was prepared from formaldehyde (37% in water) (200 mmol, 16.232 g), aniline (100 mmol, 9.313 g), and 1-naphthol (100 mmol, 14.417 g) similarly. The resultant reddish crystalline product was further purified by recrystallization from benzene/hexane to afford orange crystals (19 g, 73%, m.p. 63–62°C).

Elemental analysis ($C_{18}H_{15}NO$): Calc.; C, 82.73%; H, 5.79%; N, 5.36%. Found; C, 81.86%; H, 5.85%; N, 4.72%. ^{1}H NMR spectra ($CDCl_3$), ppm: δ = 4.85 (s, —CH_2—), 5.30 (s, —CH_2—) and 6.95–7.85 (m, Ar, H). IR spectra (KBr, cm^{-1}): 1028–1036 (sym. C—O—C), 1230–1236 (asym. C—O—C) and 1327–1340 (CH_2 wagging).

Preparation of 2-phenyl-2,3-dihydro-1*H*-1,3-naphthoxazine (2-N-a)

2-N-a was prepared from formaldehyde (37% in water) (200 mmol, 16.232 g), aniline (100 mmol, 9.313 g),



Scheme 1. Preparation of 1-N-ala, 2-N-ala, and 15-N-ala monomers.

and 2-naphthol (100 mmol, 14.417 g) similarly. The yellowish crystalline product was further purified by recrystallization from methanol to afford colorless needle crystals (20 g, 77%, m.p. 43–44°C).

Elemental analysis ($C_{18}H_{15}NO$): Calc.; C, 82.73%; H, 5.79%; N, 5.36%. Found; C, 82.33%; H, 5.94%; N, 5.51%. ^{1}H NMR spectra ($CDCl_3$), ppm: δ = 4.95 (s, —CH_2—), 5.54 (s, —CH_2—), 6.95–7.90 (m, Ar, H). IR spectra (KBr, cm^{-1}): 1236 (asym. C—O—C), 1327–1340 (CH_2 wagging).

Preparation of bis(4,5-dihydro-5-phenyl-oxazinyl)naphthalene (15-N-a)

15-N-a was prepared according to the reported method[31] from formaldehyde (37% in water) (400 mmol, 32.432 g), aniline (200 mmol, 18.624 g), and 1,5-dihydroxynaphthalene (100 mmol, 16.005 g). The reddish brown crystalline product was purified by recrystallization from dioxane to afford colorless crystals (29 g, 73%, m.p. 192–193°C).

Elemental analysis of 15-N-a ($C_{26}H_{22}N_2O_2$): Calc.; C, 79.16%; H, 5.62%; N, 7.10%. Found; C, 78.58%; H, 5.72%; N, 7.05%. ^{1}H NMR spectra ($CDCl_3$), ppm: δ = 4.75 (s, —CH_2—), 5.50 (s, —CH_2—) and 6.90–7.75 (m, Ar, H). IR spectra (KBr, cm^{-1}): 954 (C—O—C), 1028–1036 (C—O—C), 1240 (Ar—O—C), 1340 (CH_2 wag. oxazine).

Polymerization of naphthoxazine monomers

1-N-a, 2-N-a, 1-N-ala, and 2-N-ala were dissolved in dioxane and cast over glass plate, followed by evaporation of the solvent at 90°C. The films were gradually cured at 120, 160, 200, and 240°C for 2 h each and then postcured at 260°C for 2 h. 15-N-a and 15-N-ala were dissolved in DMSO and cast over glass plates placed inside a preheated oven at 200°C. Thereafter, the monomers were cured at 240°C for 2 h and postcured at 260°C for 2 h.

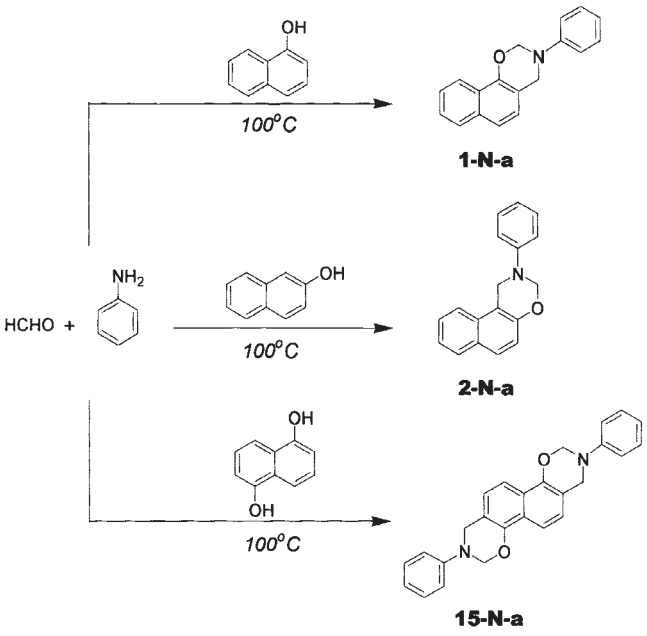
Measurements

IR spectra were obtained with JASCO spectrophotometer model FT/IR-420. NMR spectra were recorded on a Varian Mercury 300 (300 MHz) instrument. Differential scanning calorimetry (DSC) was conducted using Rigaku Thermo Plus 2 DSC8230 at a heating rate of 10°C/min under nitrogen. Thermogravimetric analysis (TGA) was determined with Rigaku Thermo Plus 2 TG-DTA TG8120 at a heating rate of 5°C/min under argon. Dynamic viscoelastic measurements were conducted on Orientec Automatic Dynamic Viscoelastomer Rheovibron model DDV-01FP at 35 Hz at a heating rate of 4°C/min.

RESULTS AND DISCUSSION

Preparation and characterization of naphthoxazine monomers

The synthesis of naphthoxazine monomers is based on the reaction of either 1-naphthol, 2-naphthol, or 1,5-dihrdoxynaphthalene with formalin and allylamine or aniline using dioxane as a solvent. Schemes 1 and 2 show the preparation of naphthoxazine monomers. Table I shows the physical properties of naphthoxazine monomers, including purification method, appearance, and melting points. Generally, the yields of



Scheme 2. Preparation of 1-N-a, 2-N-a, and 15 N-a monomers.

TABLE I
Some Physical Properties of Naphthoxazine Monomers

Monomer	Purification (recrystallization)	Shape	Melting point (°C)
1-N-a	Benzene/hexane	Orange crystals	62–63
1-N-ala	2-Propanol	Colorless crystals	67–68
2-N-a	Methanol	Colorless needles	43–44
2-N-ala	Methanol	Colorless crystals	40–41
15-N-a	Dioxane	Pale brown crystals	196–197
15-N-ala	Dioxane	Pale yellow needles	154–155

the monomers before purification, including oligomers, were quantitative, and the yields were about 70–75% after purification by washing with NaOH and recrystallization to remove the partially ring-opened oligomers. It is noteworthy saying that the recrystallization of monomers could give high purity for monomers, which could not be achieved by washing only with NaOH.[9,10]

The chemical structures of all the monomers were established by FTIR, ^{1}H NMR, and elemental analysis. Figure 1 shows examples of IR spectra of 1-N-ala and 1-N-a. For all monomers, the characteristic absorption bands attributed to oxazine ring appeared at 923–995 cm^{-1} (vib. modes of cyclic C-O-C), 1224–1236 cm^{-1} (asym. str. of Ar—O—C), 1028–1036 cm^{-1} (sym. str. of C—O—C), and 1340–1340 cm^{-1} (CH_2 wag. oxazine). The absorption bands assigned to allyl group appeared at 3082 (str. of ═C—H), 1644 (str. of C═C) and 843 cm^{-1} (out-of-plane bending vibr. of olefinic C—H).[10]

The ^{1}H NMR spectra of benzoxazine monomers were measured, and examples for 2-N-a and 2-N-ala are shown in Figures 2–4. Aniline-based naphthoxazine showed typical two singlet peaks at 4.65 and 5.70, which are due to protons of —Ar—CH_2—N— and —O—CH_2—N— of oxazine ring. Similarly, allyl-containing naphthoxazine monomers showed the same resonances of —Ar—CH_2—N— and —O—CH_2—N— of oxazine at 4.02–4.25 and 4.90–5.01 ppm, respectively. In addition, the NMR spectra of allyl-based monomers showed the resonances of allyl protons as two multiples at 5.25 and 5.95 ppm for the protons of ═CH_2 and ═CH—, respectively, and as a doublet at 3.39 ppm for —CH_2— of allyl group. The aromatic protons appeared as a mltiplet at 6.77–7.16 ppm.

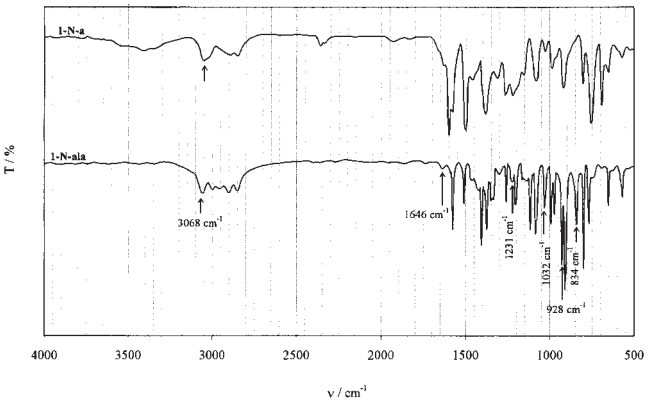


Figure 1 IR spectra of 1-N-ala and 1-N-a.

DSC cure of benzoxazine monomers

The cure behavior of benzoxazine monomers was studied by DSC. Figure 5 shows the DSC traces of 1-N-a and 1-N-ala. The endothermic peaks at 63 and 74°C are attributed to the melting of both 1-N-a and 1-N-ala. For 1-N-a an exotherm was observed corresponding to the ring-opening polymerization with onset at 119°C and maximum at 156°C. The amount of heat of cure is 46 cal/g. For 1-N-ala, however, two exotherms were observed; the onset temperature of the first exotherm was at 162°C with exotherm peak at 180°C and the second unsymmetrical exotherm showed onset at 182°C and exotherm maximum at 191°C. The total amount of heat of cure for 1-N-ala is 68 cal/g, which is higher than that of 1-N-a because it includes both the cure of the allyl group and the ring-opening of the oxazine ring.

DSC for 2-N-a and 2-N-ala are shown in Figure 6. For both 2-N-a and 2-N-ala, sharp endothermic peaks

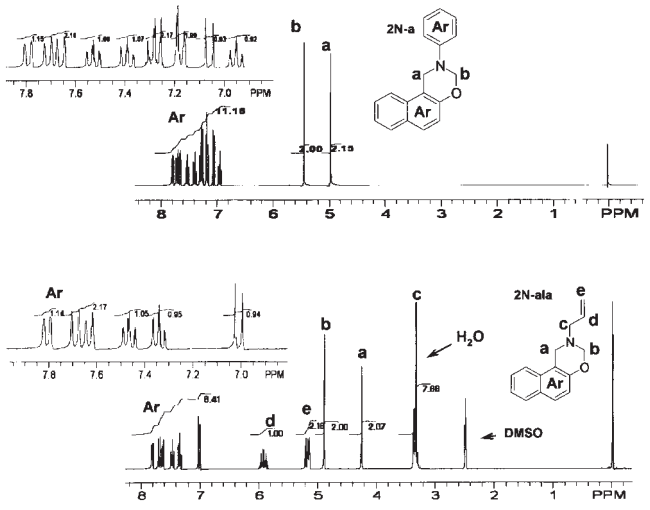


Figure 2 ^{1}H NMR spectrum of 2-N-ala and 2-N-a.

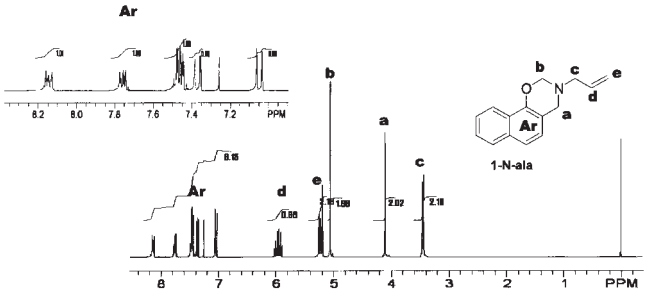


Figure 3 ^{1}H NMR spectrum of 1-N-ala.

due to the melting were observed at 50 and 45°C, respectively. However, neither 2-N-a nor 2-N-ala showed typical cure exothermic peaks similar to 1-N-a and 1-N-ala. In case of 2-N-a, a broad endothermic peak with onset at ~176°C was observed, followed by noised-exothermic peak with onset at 231°C. The amount of the exothermic heat of cure is ~14 cal/g. Similarly, for 2-N-ala, a broad irregular endothermic peak with onset at ~174°C was observed, followed by exothermic peak with onset at 213°C. The amount of exothermic heat of cure is also small as ~25 cal/g. It is noteworthy to mention that evaporation of 2-N-ala was observed at ~170°C when measuring the melting point by a typical melting apparatus. In addition, little residue was found in the sample pan after the DSC scan of 2-N-a and 2-N-ala was up to 500°C. Similar behavior was reported for the difficulty of monomer homopolymerization due to the evaporation.[32] The TGA performed under similar condition as DSC for both 2-N-a and 2-N-ala demonstrated that a sharp weight loss due to the evaporation of monomers started at ~179 and ~150°C, respectively. These observations can explain the abnormal endothermic peaks and the small amount of exthotherm for 2-N-a and 2-N-ala in DSC, which can be attributed to the evaporation of 2-N-a and 2-N-ala. This behavior reflects the difficulty of the polymerization of 2-N-a and 2-N-ala under normal conditions.

Figure 7 shows the DSC traces for the bifunctional naphthoxazine monomers 15-N-a and 15-N-ala. In the DSC trace of 15-N-a, a sharp melt endothermic peak was observed at 202°C because of melting, followed by an exothermic peak with maximum at 216°C corresponding to the ring-opening polymerization of

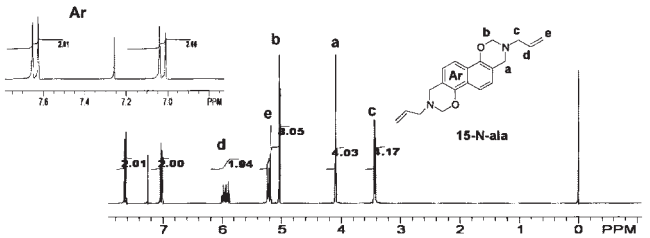


Figure 4 ^{1}H NMR spectrum of 15-N-ala.

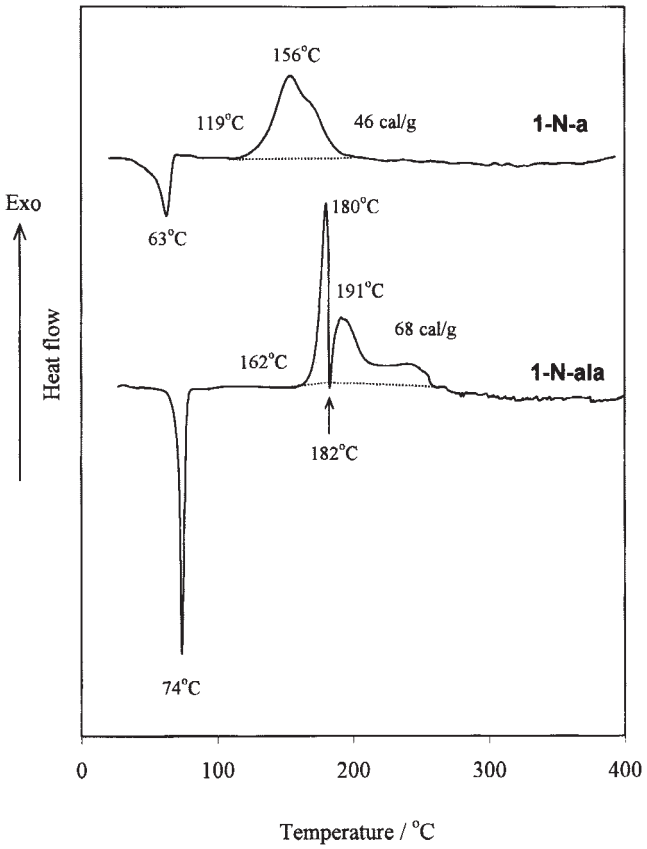


Figure 5 DSC cure of 1-N-ala and 1-N-a.

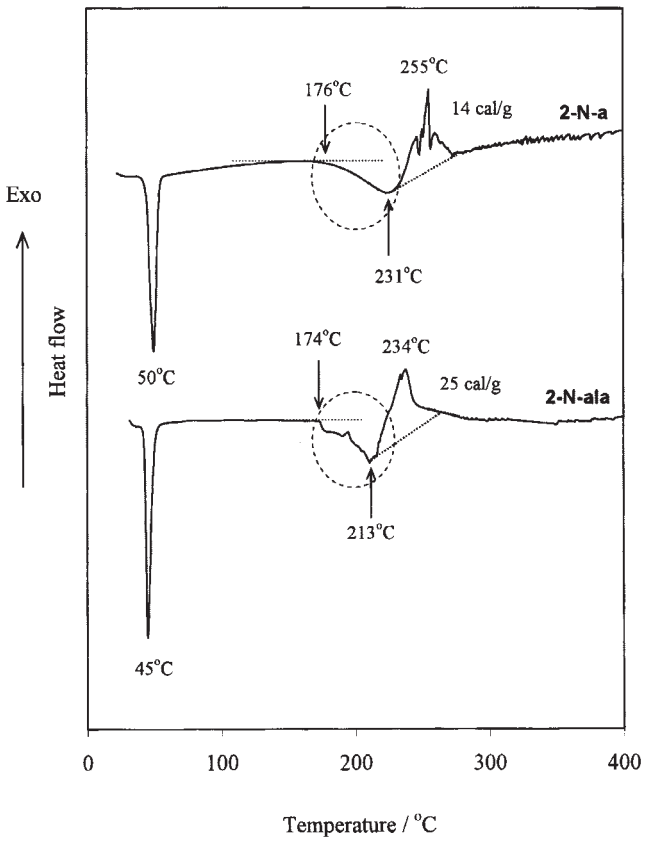


Figure 6 DSC cure of 2-N-ala and 2-N-a.

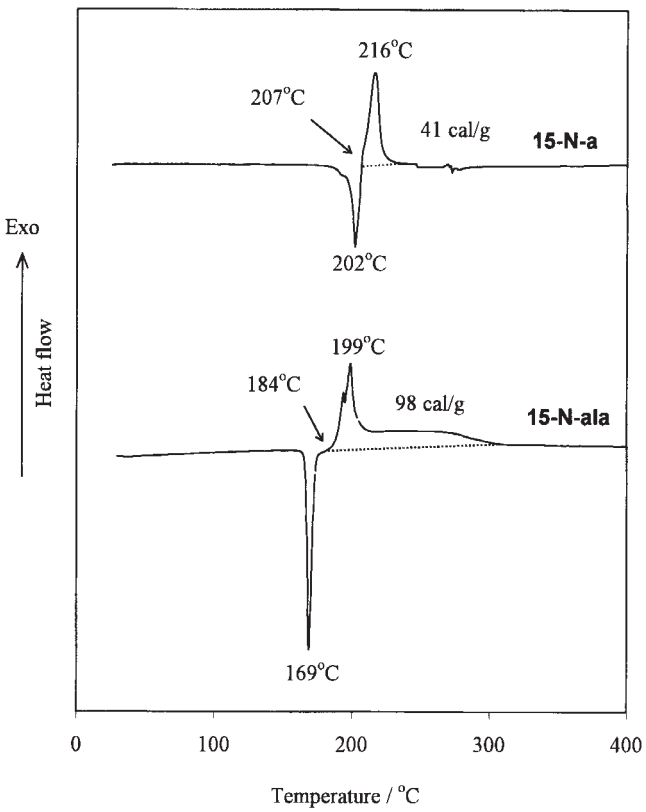


Figure 7 DSC cure of 15-N-ala and 15-N-a.

benzoxazine. The amount of exthotherm for 15-N-a was 41 cal/g. For 15-N-ala, a sharp endotherm was observed at 169°C. Additionally, an unsymmetrical exotherm consisting of sharp exotherm with shoulder was observed; the onset of this exthotherm started at 184°C with maximum at 199°C. The total amount of exotherm was 98 cal/g. This exotherm corresponds to both the crosslinking of allyl group and the ring-opening polymerization of naphthoxazine.

The thermal addition polymerization of N-allyl group is known to occur at relatively low temperatures than that of other end-capping groups like ethynyl, phenylethynyl, propargyl, and maleimide.[33,34] However, the addition polymerization of allyl group occurs at relatively higher temperatures than the typical vinyl monomers. We have previously found that the radical initiators have an effect to initiate the polymerization of N-allyl group.[10] Figure 8 shows the DSC trace of 1-N-ala with and without DCPO as a free radical initiator. DSC trace of 1-N-ala in the presence of DCPO indicated that the onset of the first exotherm due to the polymerization of allyl group decreased by ~25°C than those in the absence of DCPO. The shift of the exotherm to lower temperature range supports the contention that the free radial initiator has an effect to initiate the addition polymerization of N-allyl group. The results also confirmed that the first exotherm is due to the cure of allyl group and the second one is attributed to cure of oxazine ring.

Polymerization of polybenzoxazines

Low melting monomers such as 1-N-a, 2-N-a, 1-N-ala, and 2-N-ala were cast from their solution in dioxane, followed by evaporation of the solvent at 90°C. The samples were cured step-wise at 120°C for 3 h and then at 160, 200, and 240°C for 2 h each, and postcured at 260°C for 2 h in an air oven. High melting monomers such as 15-N-a and 15-N- ala were cast from dimethylsulfuoxide solution over glass plates that were preheated at 200°C. This condition allows the material to be kept in a melted film form after evaporation of the solvent at this high temperature. The monomers were postcured at 240 and 260°C, respectively. IR spectra of 1-N-ala (Fig. 9) indicated that the characteristic absorption bands attributed to oxazine structure at 928, 1032, 1230, and 1347 cm^{-1} gradually decreased after each cure and disappeared after 240°C cure. The absorption bands that are assigned to allyl group at 1644 and 843 cm^{-1} disappeared as well.

The DSC cure of 1-N-ala after each cure cycle (Fig. 10) indicated that the amount of exotherm attributed to the cure of ally gradually decreased and disappeared by the end of 200°C cure. However, the second exotherm attributed to ring opening of naphthoxazine disappeared after the cure at 240°C. The proposed structure for thermoset obtained by the thermal polymerization of allyl-contain-

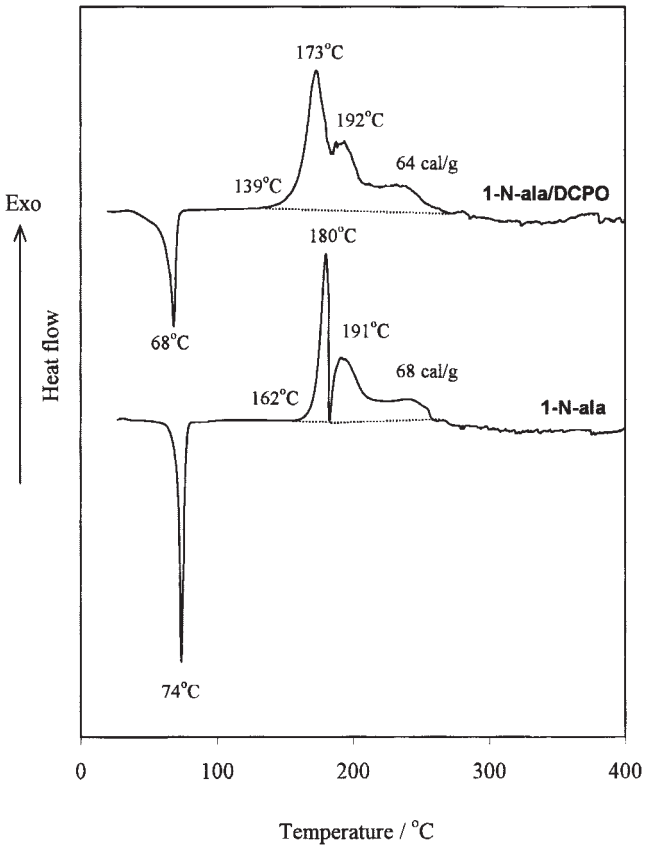


Figure 8 DSC cure of 1-N-ala with and without DCPO as catalyst.

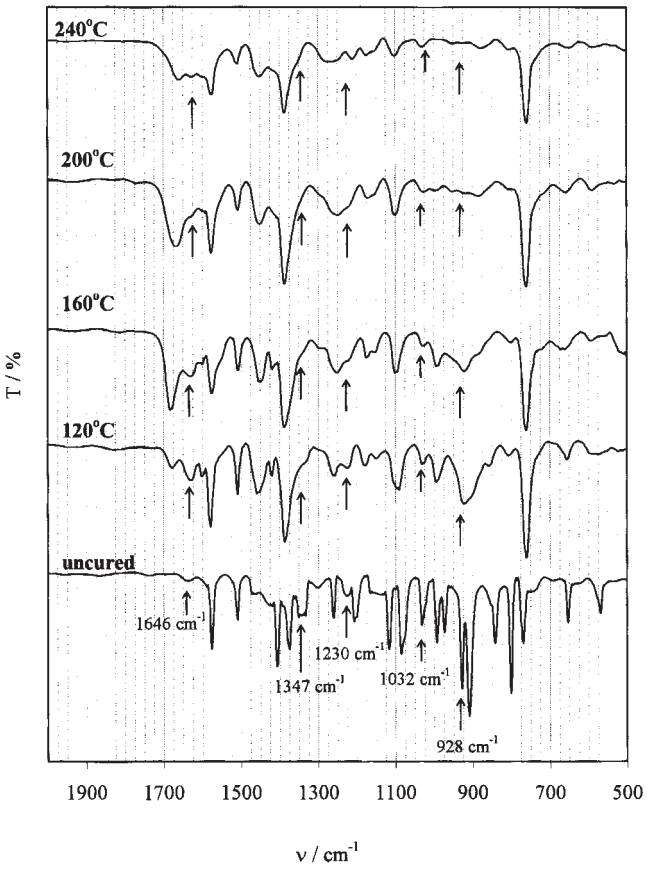


Figure 9 IR spectra of 1-N-ala after each cure stage.

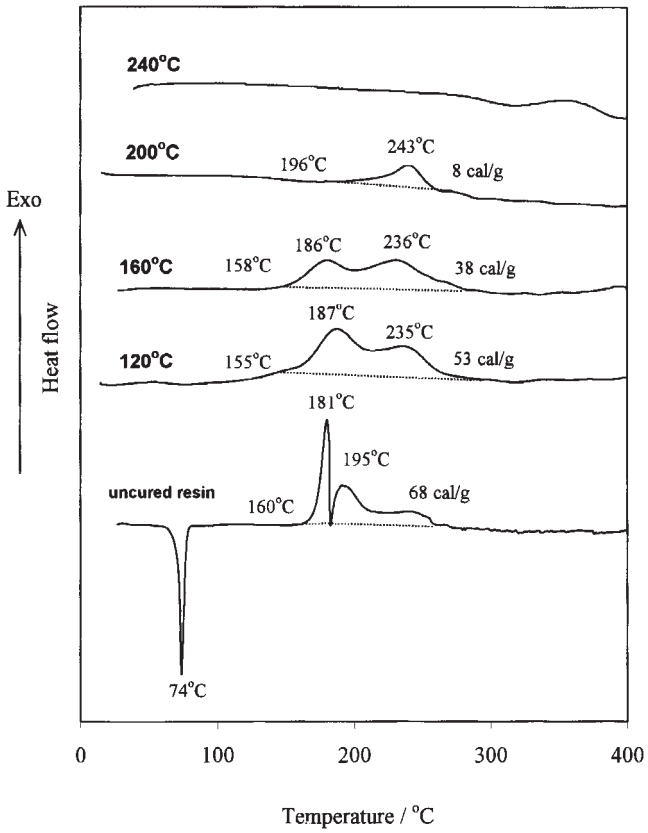


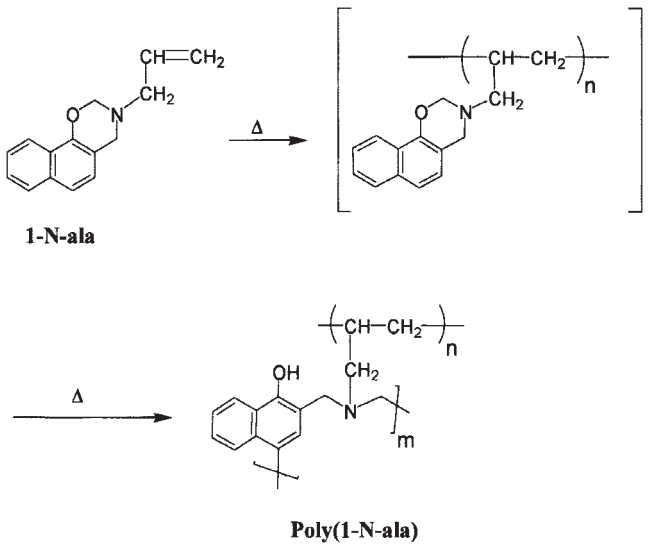
Figure 10 DSC cure of 1-N-ala after each cure stage.

ing naphthoxazines is shown in Scheme 3. The polymerization of the monomers proceeded by two different polymerization pathway, the first by the addition polymerization of allyl group and the other by the ring opening polymerization of the oxazine ring.

Dynamic mechanical analysis of naphthoxazines-based thermosets

The viscoelastic properties of poly(1-N-a), poly(15-N-a), and poly(15-N-ala) were examined by dynamic mechanical analyses. Figures 11 and 12 show the temperature dependence of the storage modulus, loss modulus, and tan δ for the naphthoxazine-based thermoset. The viscoelastic analysis for poly(1-N-a) showed that the storage modulus (E') gradually started to drop at 164°C, with T_g at 186 and 198°C from the maximum of loss modulus (E'') and tan δ, respectively. For the typical polybenzoxazine prepared from phenol, E' decreased sharply at ~110°C, with T_g at 146 and 161°C from the maximum of E'' and tan δ, respectively.[10] These results support the contention that the inclusion of naphthalene moieties into polymer structure enhance the thermomechanical stability to higher temperature. For poly(15-N-a) film cured at 260°C, the storage modulus started to gradually decrease at ~179°C, with T_g at 237 and 259°C from the maximum of E'' and tan δ, respectively.[10] Shen and Ishida reported that a higher T_g of 305°C for poly(15-N-a) could be obtained by curing in autoclave under pressure (1.33 MPa).[31]

The introduction of allyl group as a crosslinking site into naphthoxazine is expected to increase the crosslinking density and hence the rigidity of the ther-



Scheme 3. Proposed structure of polynaphthoxazine derived from 1-N-ala monomer.

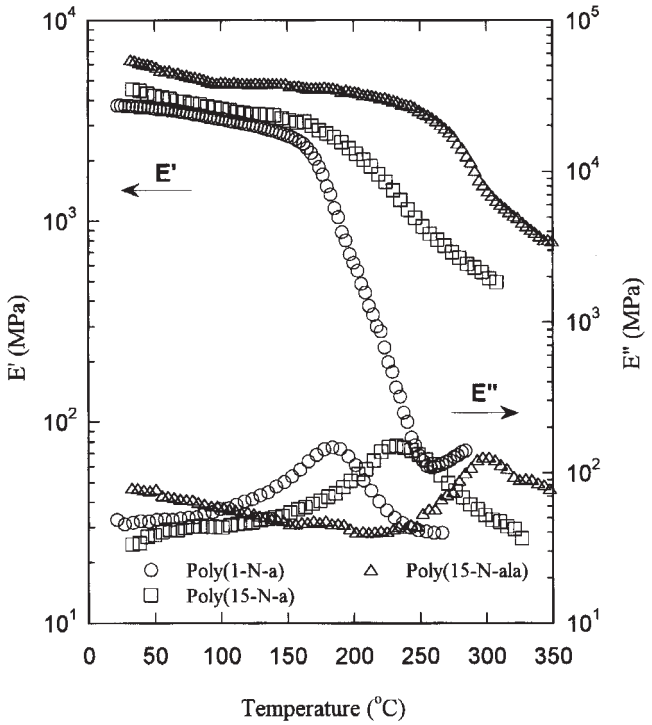


Figure 11 Viscoelastic properties of poly(1-N-a), poly(15-N-a), and poly(15-N-ala).

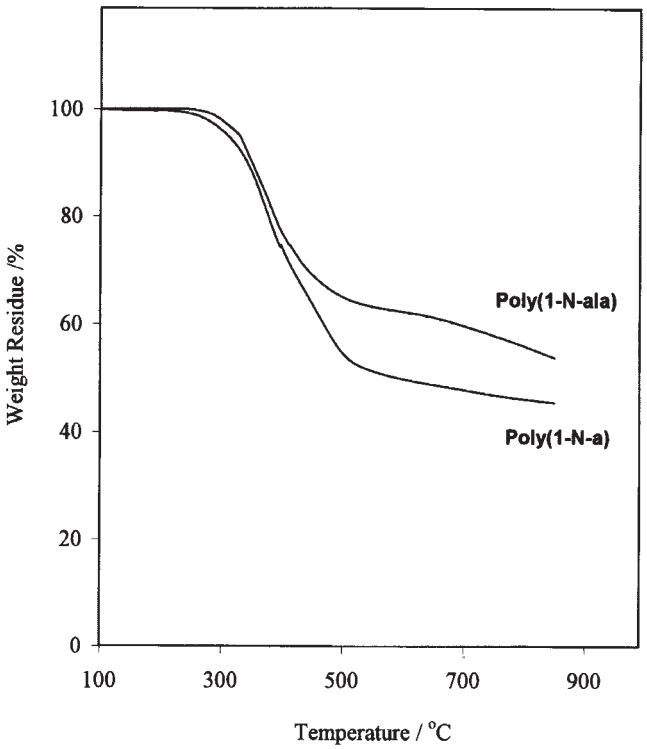


Figure 13 TGA of poly(1-N-ala) and poly(1-N-a).

moset therefrom. The DMA analysis of poly(15-N-ala) as an example was studied. The storage modulus of poly(15-N-ala) was maintained constant up to 275°C, which is higher by ~100°C than that of poly(15-N-a). The T_g of poly(15-N-ala) shifted to as high as 303 and 316°C from the maximum of E'' and tan δ, respectively. These results suggest that the presence of allyl group into naphthoxazine had significant beneficial effect on the viscoelastic properties of thermoset therefrom.

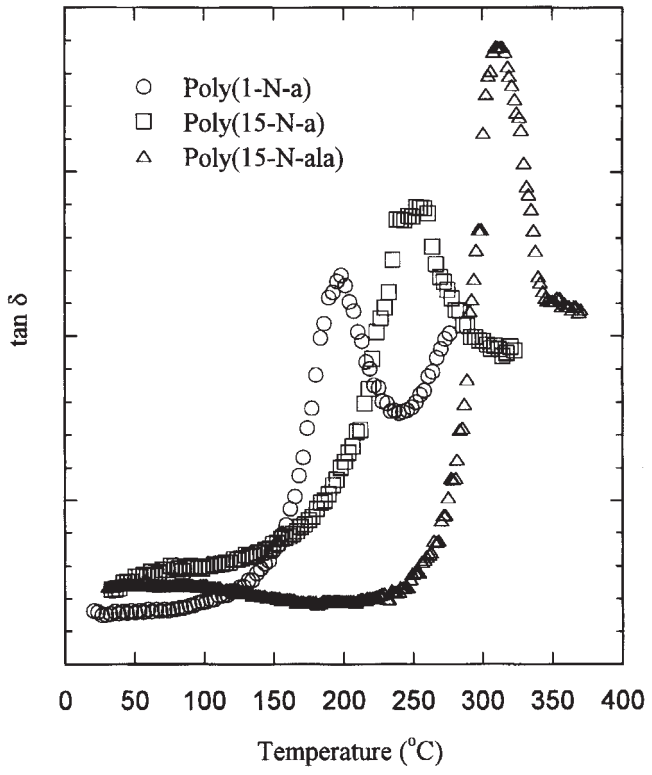


Figure 12 Tan δ and temperature relationship of poly(1-N-a), poly(15-N-a), and poly(15-N-ala).

Thermal stability of naphthoxazines-based thermosets

Thermal stability of the cured naphthoxazines was investigated by TGA traces. The TGA for poly(1-N-a) and poly(1-N-ala) are shown in Figure 13 as example. Other data are summarized in Table II. The results indicate the

TABLE II
Thermal Properties of Polynaphthoxazines

Polymer	5% DT (°C)	10% DT (°C)	Char Yield[a] (%)
Poly(1-N-a)	310	341	46
Poly(1-N-ala)	328	350	56
Poly(2-N-a)	216	236	20
Poly(2-N-ala)	292	318	30
Poly(15-N-a)	326	350	64
Poly(15-N-ala)	340	365	60
Poly(P-ala)[b]	348	374	44
Poly(B-ala)[b]	343	367	28

DT, decomposition temperature
[a] Char yield at 800°C.
[b] Reference no. 10.

higher thermal stability of the allyl-based resin in comparison with the aniline-based resin. The shortage of the thermal stability of aniline-based is attributed to the decomposition of the Mannish bridges leading to volatilization of aniline derivatives, resulting in low char yield. For allyl-containing naphthoxazine, the allyl group is incorporated into another network with higher thermal stability, leading to prevention of amine derivatives from volatizing at the initial stages of the degradation due to the crosslinking.

Generally, as shown in Table II, the thermal stability of thermosets derived from allyl- based naphthoxazines is higher than that of the reported allyl-based benzoxazines.[10] For example, the use of 1-naphthol instead of phenol increased the char yield by ~12%, reflecting the enhanced thermal stability obtained by the incorporation of naphthalene structure.

CONCLUSIONS

A series of novel allylamine-based and aniline-based naphthoxazine were synthesized based on 1-naphthol, 2-naphthol, and 1,5-dihdroxynaphthalene. DSC cure of the allyl-containing monomers showed two exotherms at different temperature range, due to the cure of allyl group and the ring-opening polymerization of oxazine ring. The thermal polymerization of the allyl-based naphthoxazines gave novel thermoset resin comprising of polynaphthoxazine and allyl-polymerized networks. The resins obtained from allyl-containing naphthoxazine showed higher T_g and better thermal properties than the polymers derived from aniline-based naphthoxazines. The presence of a suitable reactive group into naphthoxazines leads to increase the reactivity of naphthoxazines towards other monomers or polymers, which is going to widen the fields of applications of naphthoxazines.

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