Synthesis and Characterization of Novel Benzoxazine Monomers Containing Allyl Groups and Their High Performance Thermosets

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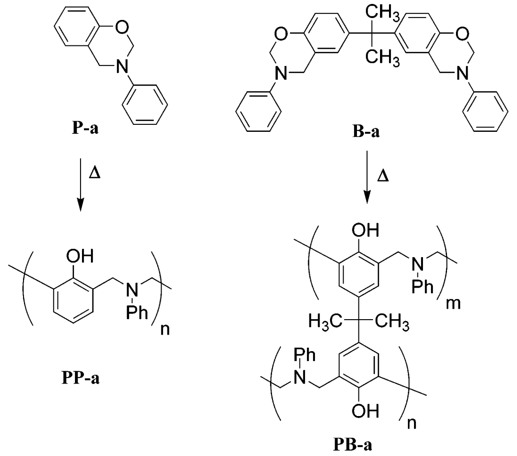
ABSTRACT: Two novel benzoxazine monomers containing allyl groups: 3-allyl-3,4-dihydro-2*H*-1,3-benzoxazine and bis(3-allyl-3,4-dihydro-2*H*-1,3-benzoxazinyl)isopropane have been synthesized from phenol and Bisphenol A with allylamine and formaldehyde. Their DSC exhibit two exotherms at ca. 145 °C and at ca. 220 °C which correspond to allyl and oxazine thermal polymerization, respectively. Both monomers undergo thermal cure with the formation of thermosets having excellent thermomechanical properties. These thermosets exhibit higher T_g (ca. 300 °C), maintain their storage moduli at higher temperature, and have better thermal stability than the corresponding polybenzoxazines without allyl groups.

Introduction

Novel polymeric materials, namely polybenzoxazines,[1] were recently developed as a new type of phenolic resins. They are obtained by the ring-opening polymerization of cyclic monomers by thermal cure. Typical monofunctional and bifunctional benzoxazine monomers, 3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazine (P-a) and bis(3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazinyl)isopropane (B-a), respectively, are shown in Scheme 1 along with the supposed structures of polybenzoxazines. This novel route for phenolic resins has many advantages in compare with the traditional phenolic resin. Benzoxazine monomers can be prepared from inexpensive raw materials including phenols, primary amines and aldehyde. The various raw materials allow considerable molecular-design flexibility for the monomer. The monomers also have long shelf lives and comparatively low viscosities, which are beneficial in processing into desired products. The polymerization proceeds through ring-opening of oxazine rings without using strong acid catalyst and without generating any byproducts. Polybenzoxazines possess typical characteristics of the traditional phenolic resins such as heat resistance, good flame retardance and electronic properties. In addition, they provide unique characteristics like low water absorption and also excellent dimensional stability due to the near-zero volumetric shrinkage upon cure, which cannot be found in the traditional phenolic resins.[2]

The major disadvantages of the typical polybenzoxazines are their brittleness and the high temperature needed for the ring-opening polymerization. Further performance enhancement of polybenzoxazine is also strongly expected. For the performance enhancement, the preparation of copolymers,[3] polymer alloys,[4] fiber-reinforced composites,[5] and clay nanocomposites[6] has become increasingly attractive. For the toughening improvement of polybenzoxazines, the use of liquid rubbers[7] and high performance thermoplastics like poly(imide−siloxane)[4a] has been successfully applied.

Scheme 1. Preparation of PP-a and PB-a as Typical Polybenzoxazines



Another effective approach for the performance enhancement is the preparation of novel high performance polybenzoxazines from benzoxazine monomers containing another polymerizable group such as ethynyl or phenyl ethynyl,[8] nitrile,[9] and propargyl groups.[10] This approach successfully afforded polybenzoxazines with high glass transition temperature (T_g) and improved decomposition temperature in comparison with typical polybenzoxazines.

Allyl-containing monomers have attracted much attention because they are used as reactive diluents of bismaleimides to improve the toughness of the cured resin.[11] We are interested in obtaining polybenzoxazines and their composites with improved thermal and mechanical performance in a wide range of service environment. The main advantage of the allyl group[12] is that it can be easily cured at temperature lower than the ethynyl or propargyl group.

Ishida reported[13] the preparation of an allyl-containing benzoxazine monomer, 3-phenyl-3,4-dihydro-8-allyl-2*H*-1,3-benzoxazine (P-alp), Figure 1, from allylphenol, aniline, and paraformaldehyde. No details were reported, however, on the characterization and properties of P-alp and the polymer therefrom. A similar benzoxazine monomer based on allylphenol was reported for sililation of allyl group to enhance the interface between

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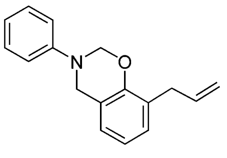


P-alp

Figure 1. Structure of P-alp.

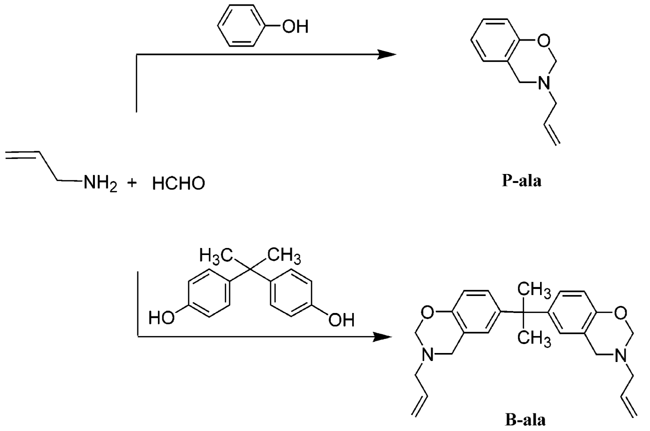
the matrix and glass or carbon fiber in fiber-reinforced polybenzoxazine.[14] Also, Pei et al. reported similar bifunctional allylphenol-derived polybenzoxazine.[15] The reported allylphenol-based benzoxazine monomers, however, do not have activated position ortho to the phenolic hydroxyl group. Thus, the monomers are considered to be difficult to polymerize through ring-opening, and are not a good candidate for preparing high performance polybenzoxazines.

In this paper, the preparation of two novel benzoxazine monomers modified with allyl groups: 3-allyl-3,4-dihydro-2*H*-1,3-benzoxazine (P-ala) and bis(3-allyl-3,4-dihydro-2*H*-1,3-benzoxazinyl)isopropane (B-ala) (Scheme 2) and characterization of their thermosets have been described.

Results and Discussion

1. Preparation of 3-Allyl-3,4-dihydro-2*H*-1,3-benzoxazine (P-ala), bis(3-allyl-3,4-dihydro-2*H*-1,3-benzoxazinyl)isopropane (B-ala), and 3-phenyl-3,4-dihydro-8-allyl-2*H*-1,3-benzoxazine (P-alp). The synthesis of P-ala and B-ala is based on the reaction of either phenol or bisphenol A with allylamine and paraformaldehyde using the solventless method.[13] The yields for both monomers including dimers and oligomers were quantitative, and were about 72–75% after purification by washing with NaOH to remove the partially ring-opened oligomers. P-ala was obtained as a transparent slightly viscous liquid at room temperature. After the purification of P-ala by distillation, it became very low viscous liquid. The nature of P-ala as a liquid resin is a significant advantage in processing and compounding with other polymers, additives and fibers. B-ala, on the other hand, was obtained as yellowish white powder, mp 55–58 °C.

Scheme 2. Preparation of Allylamine-Based Benzoxazine Monomers (P-ala and B-ala)



The chemical structures of both P-ala and B-ala were confirmed by both FT-IR and ^{1}H NMR. IR spectra (Figure 2) showed the characteristic absorptions of benzoxazine structure for both P-ala and B-ala at 1230–1236 cm^{-1} (asymmetric stretching of C–O–C), at 1028–1036 cm^{-1} (symmetric stretching of C–O–C), at 1327–1340 cm^{-1} (CH$_2$ wagging), and at 920–950 and 1491–1500 cm^{-1} (trisubstituted benzene ring of B-ala). Characteristic absorption bands assigned to allyl group appeared at 3084 cm^{-1} (stretching of =C–H) and at 1644 cm^{-1} (stretching of C=C). Additionally, the out of plane bending vibrations of olefinic C–H were observed at 860–864 and 991–997 cm^{-1}, indicating the allyl group.[11c] These absorptions are not present in the IR spectra of B-a and P-a as shown in Figure 2.

The ^{1}H NMR spectrum shown in Figure 3 established the structure of P-ala. The two multiples at 5.25 and 5.95 ppm are typical for the protons of =CH$_2$ and =CH– in allyl group, respectively. The protons of –CH$_2$– of allyl group showed a doublet at 3.39 ppm. The characteristic protons of oxazine ring appeared at 4.02 and 4.87 ppm assigned to –Ar–CH$_2$–N– and –O–CH$_2$–N–, respectively. The aromatic protons appeared as mltiplet at 6.77–7.16 ppm. B-ala showed, similar to P-ala, the characteristic peaks (Figure 4) assignable to allyl at 3.28 (doublet), 5.24 (multiplet), and 5.90 ppm (multiplet). The peaks attributed to oxazine ring appeared at 3.86 (–Ar–CH$_2$–N–) and 4.82 ppm (–O–CH$_2$–N–) as well as the peaks at 1.55 and 6.60–7.05

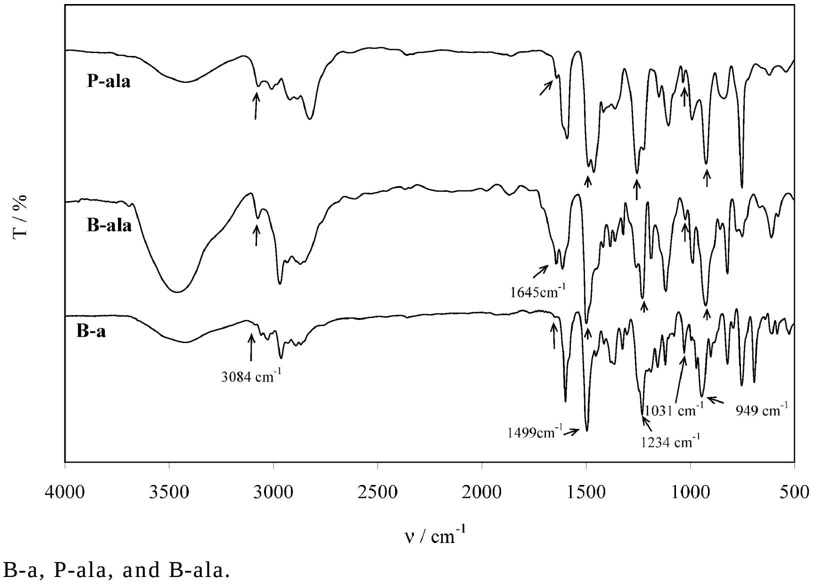


Figure 2. IR spectra of B-a, P-ala, and B-ala.

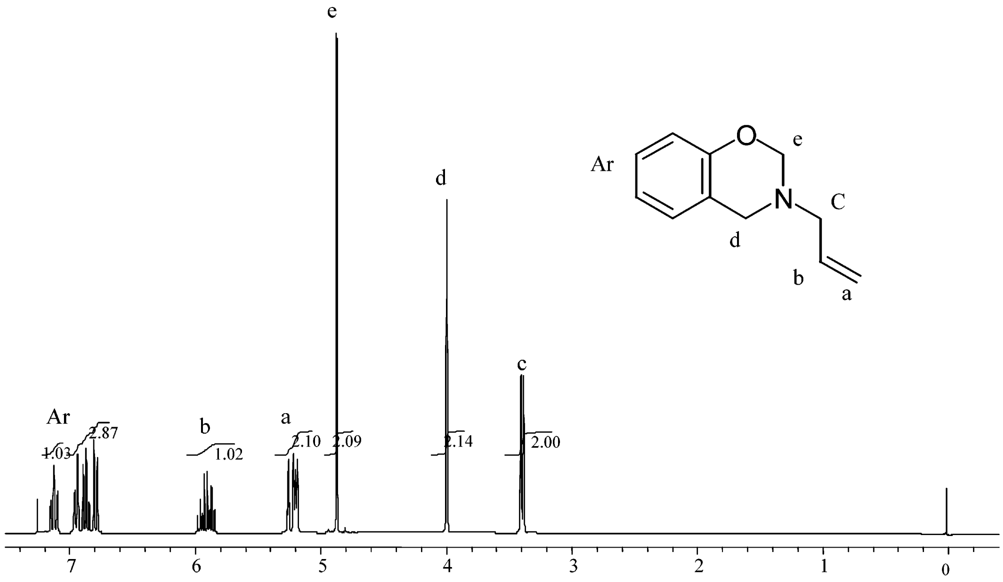


Figure 3. ^{1}H NMR spectrum of P-ala.

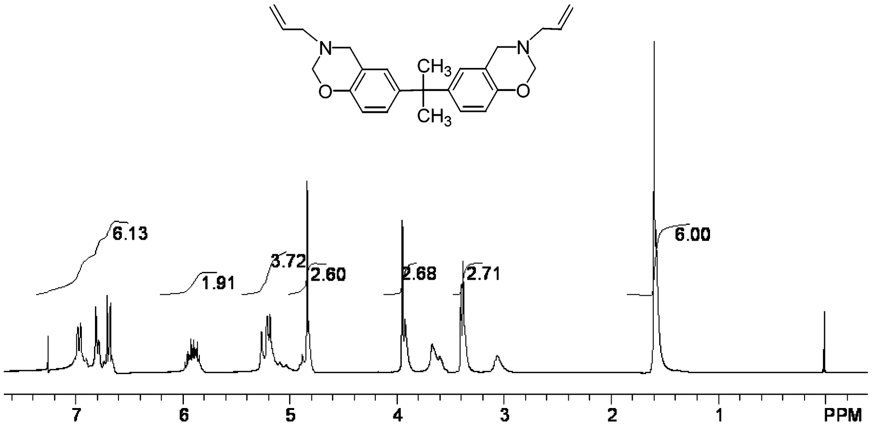


Figure 4. ^{1}H NMR spectrum of B-ala.

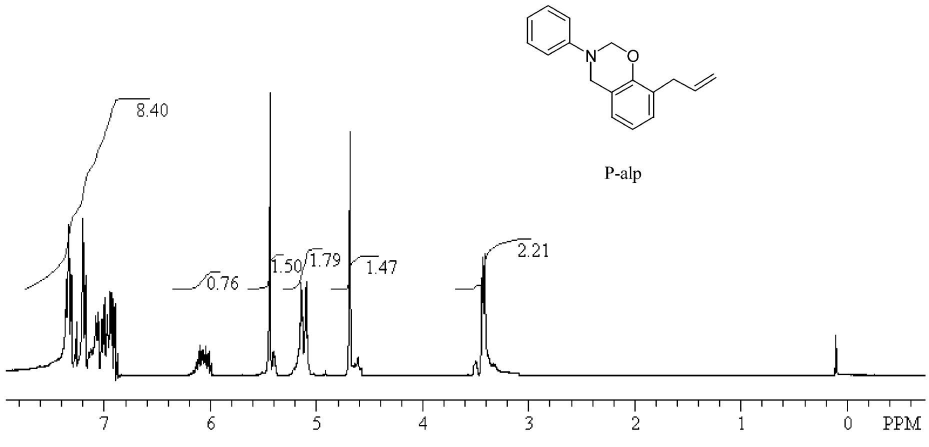


Figure 5. ^{1}H NMR spectrum of P-alp.

ppm assignable to the $C(CH_3)_2$ and aromatic protons. However, there are two peaks at 3.09 and 3.65 ppm which are attributed to the residual ring-opened structures formed during purification with NaOH.[1b,10]

P-alp (Figure 1) was prepared by the reaction of allylphenol, aniline, and paraformaldehyde using the solventless method,[13] followed by purification with aqueous NaOH to remove the partially ring-opened oligomers. The structure of P-alp was confirmed by ^{1}H NMR (Figure 5). The characteristic protons of oxazine ring appeared at 4.65 and 5.43 ppm assigned to $-Ar-CH_2-N-$ and $-O-CH_2-N-$, respectively. The aromatic protons appeared as multiplet at 6.85−7.42 ppm. The $=CH_2$ and $=CH-$ protons in allyl group appeared as multiplet at 5.15 and 6.10 ppm, respectively. The protons of $-CH_2-$ of allyl group appeared as a doublet at 3.4 ppm.

2. Curing Behavior of Allyl-Containing Benzoxazine Monomers. The curing behavior of the novel monomers along with the typical benzoxazine monomers

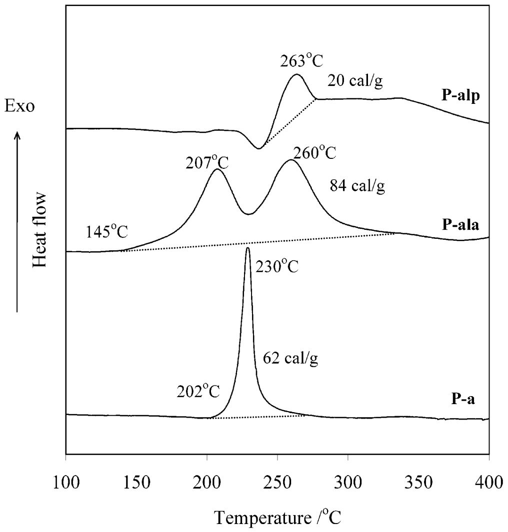


Figure 6. DSC cure of P-a, P-alp, and P-ala.

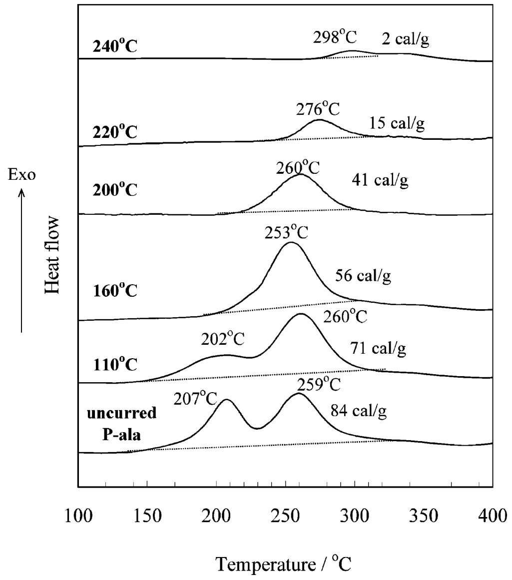


Figure 7. DSC of P-ala after each cure stage.

was examined by DSC. Figure 6 shows the DSC thermogram of the monofunctional benzoxazines, P-a, P-ala, and P-alp. A sharp exotherm was observed for P-a corresponding to the ring-opening polymerization. The onset and maximum temperatures of the exotherm were at 202 and 230 °C, respectively. The amount of exotherm for P-a was 62 cal/g. For P-ala, two exotherms were observed. The onset temperature of the first exotherm was at 145 °C with exotherm peak at 207 °C, and the apparent onset of the second exotherm was at 225 °C with exotherm maximum at 260 °C. The first exotherm is considered to be due to the thermal cure of the allyl group, and the second exotherm to the ring-opening of the oxazine ring. The total amount of exotherm of P-ala was 84 cal/g. DSC after each cure for P-ala was performed as shown in Figure 7. The first exotherm attributable to the cross-linking of allyl groups disappeared by the cure at 200 °C. The amount of the second exotherm decreased with the increase of the heat-treatment temperature, and almost disappeared after the cure at 240 °C.

On the other hand, P-alp had only one exotherm (Figure 6), the onset of which at 241 °C and maximum at 263 °C. The amount of exotherm was 20 cal/g, much smaller than P-ala and P-a. P-alp did not show an exotherm at lower temperature range corresponding to the thermal cure of the allyl group of P-alp. The difficulty of the radical polymerization of the allyl phenyl group is due to the stability of the radical by resonance.[18] In P-alp, the ortho position, the primary reaction site to form phenolic Mannich bridge structure via the ring-opening polymerization, is blocked by allyl group. Therefore, this exotherm at high temperature may be due to the cleavage of the oxazine ring that leads to degradation.[16]

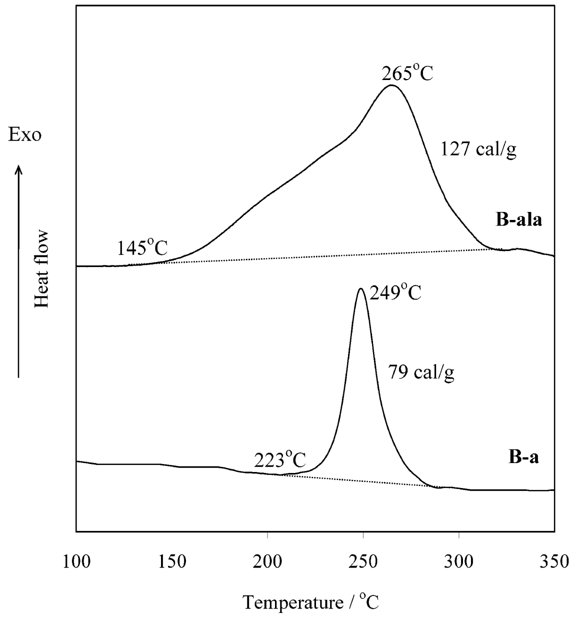


Figure 8. DSC cure of B-a and B-ala.

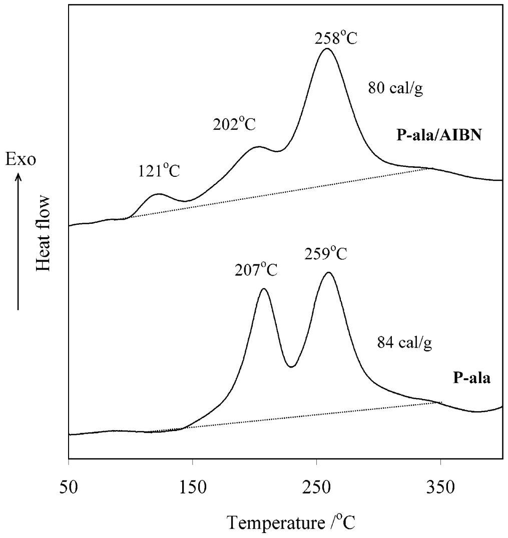


Figure 9. DSC cure of P-ala with and without catalyst.

The DSC of the novel bifunctional allyl-containing benzoxazine, B-ala, was examined with the typical bifunctional benzoxazine, B-a, for comparison. Both B-a and B-ala did not show endotherm corresponding to the melting of crystalline. As shown in Figure 8, B-a showed an exotherm on DSC with onset at ca. 223 °C and max at 249 °C corresponding to the ring-opening polymerization of benzoxazine. The amount of exthotherm for B-a was 79 cal/g. For B-ala, unsymmetrical broad exotherm was observed with the onset at 145 °C and maximum at 265 °C corresponding to both the cross-

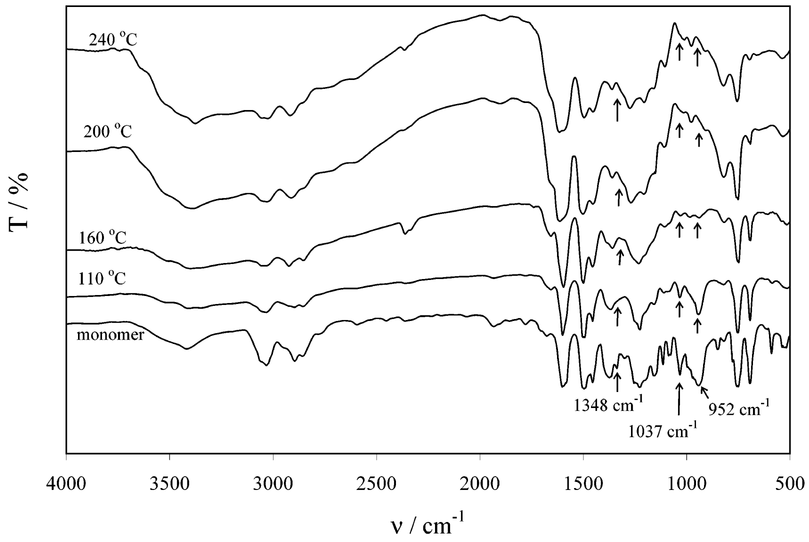


Figure 10. IR spectra of typical P-a after each cure stage.

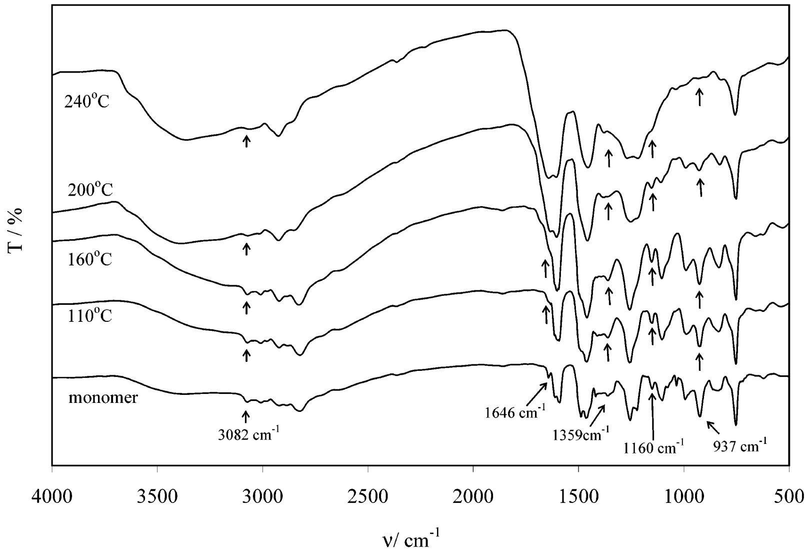


Figure 11. IR spectra of P-ala after each cure stage.

linking of allyl group and the ring-opening polymerization of benzoxazine. The total amount of exotherm was 127 cal/g, which is higher than that of B-a.

Thermal polymerization of *N*-allyl group is known[12] to occur at low temperature. In the case of P-ala, it was considered that the thermal polymerization of allyl group occurred first, followed by the ring-opening polymerization of benzoxazine at relatively higher temperature than P-a. The shift of the ring-opening polymerization to higher temperature range is due to the restricted mobility of P-ala because of the polymerization of allyl group.

To make clear which reaction is occurring at each exotherm, the cure behavior of P-ala was examined by DSC in the presence of radical initiator. Figure 9 shows the DSC of P-ala with and without AIBN as an initiator. DSC showed a new exotherm starting at 92 °C with maximum at 121 °C along with a smaller exotherm cured without catalyst. The decrease of the exotherm at lower temperature range and the appearance of a new exotherm at much lower temperature range show the catalytic effect of the free radial initiator to initiate the addition polymerization of *N*-allyl group. The results confirmed that the exotherm of P-ala at lower temperature range is due to the reaction of the *N*-allyl group.

IR spectra after each cure cycle of P-ala was measured along with that of the typical P-a monomer for comparison. In the IR spectra of P-a (Figure 10), the characteristic absorption bands due to benzoxazine structure at 952 $\mathrm{cm^{-1}}$ (vibrational mode of cyclic C−O−C), at 1037 $\mathrm{cm^{-1}}$ (symmetric stretching of C−O−C), and at 1348 $\mathrm{cm^{-1}}$ (CH_2 wagging) gradually decreased, and disappeared by the end of the 240 °C cure, suggesting the completion of ring-opening of benzoxazine to afford polybenzoxazine. For P-ala, the IR spectra (Figure 11) showed, similar to those for P-a, the disappearance of the absorptions attributed to benzoxazine ring. However, the characteristic absorption band assigned to the unsaturations of the allyl group such as 1646 $\mathrm{cm^{-1}}$ was found to disappeare at much early stage of the cure, confirming that allyl group reacted first, followed by the ring-opening polymerization.

3. Preparation and Properties of the Novel Polybenzoxazines. (a) Preparation of Polybenzoxazines. The solid monomers (P-a, B-a, and B-ala) were processed into films by melting the monomers at 80 °C and casting on glass plates. The liquid monomers, P-ala and P-alp, were processed by casting the monomers over glass plates. The cast films were cured stepwise at 80 °C for 5 h and 110 °C for 3 h, and then

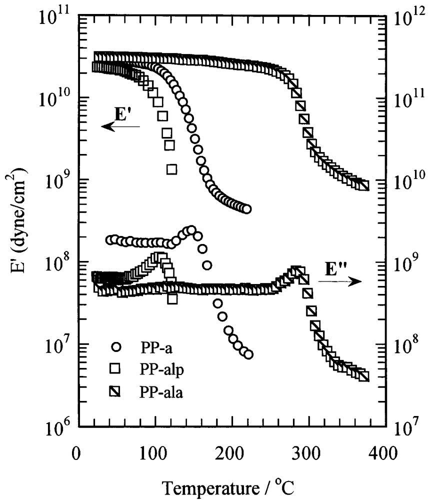


Figure 12. Viscoelastic analyses of PP-a, PP-alp, and PP-ala.

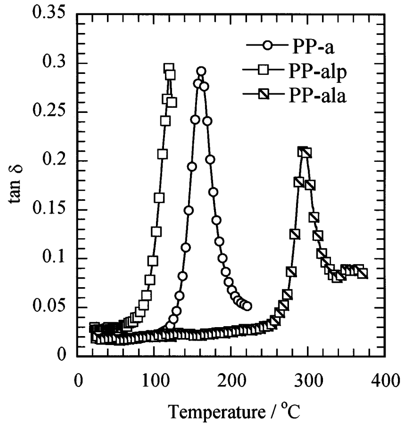


Figure 13. tan δ vs temperature of PP-a and PP-ala.

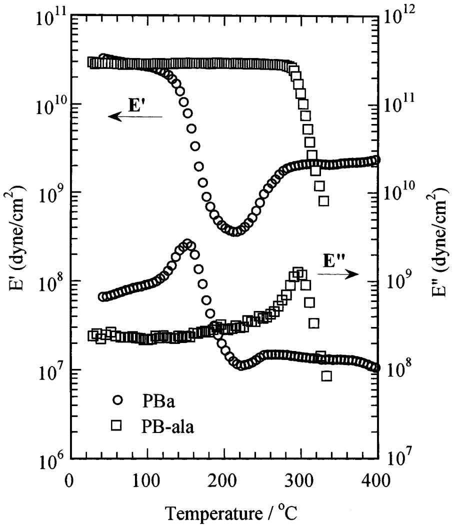


Figure 14. Viscoelastic analyses of PB-a and PB-ala.

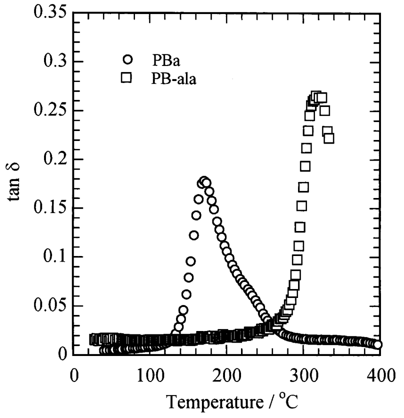


Figure 15. tan δ vs temperature of PB-a and PB-ala.

at 160, 180, and 200 °C for 2 h each in an air oven. The samples were then postcured at 220 and 240 °C for 1 h each in an air-circulating oven. All the cured samples were transparent with dark red color with thickness about 0.4 mm.

(b) Viscoelastic Analyses (DMA) of Polybenzoxazines. The viscoelastic analyses of the novel monofunctional polybenzoxazine, PP-ala, were examined along with the typical polybenzoxazine, PP-a and PP-alp. Figures 12 and 13 show the temperature dependence of the storage modulus, loss modulus and tan δ for the polybenzoxazines. For the typical polybenzoxazine, PP-a, the T_g was 146 °C from the maximum of loss modulus and 161 °C from the maximum of tan δ. The storage modulus, E', decreased sharply at ca. 110 °C. The introduction of allyl group as a cross-linking site into polybenzoxazine increased the rigidity of the polymer by the increase of cross-linking density, and hence the damping was significantly decreased. As a result, the T_g for PP-ala shifted to as high as 285 and 297 °C from the maximum of loss modulus and tan δ, respectively. The storage modulus also was maintained constant up to temperature much higher than that of PP-a. Whereas for PP-alp, the T_g was as low as 107 °C from the maximum of loss modulus, and the storage modulus dropped sharply at ca. 70 °C. The poor thermomechanical properties for PP-alp is attributed to the low cross-linking density of the matrix which arises from the difficulty in the polymerization of the monomer as described above.

Bifunctional polybenzoxazines, PB-ala and PB-a, showed similar behavior as shown in Figures 14 and 15. In the case of the typical polybenzoxazine, PB-a, the storage modulus started to decrease at ca. 130 °C with T_g at 154 and 171 °C from the maximum of the loss modulus and tan δ, respectively. For PB-ala, T_g shifted to as high as 298 and 322 °C from the maximum of loss modulus and tan δ, respectively, owing to the introduction of allyl group. Accordingly, storage modulus for PB-ala was maintained up to much higher temperature and started to decrease at 295 °C.

These viscoelastic analyses thus revealed that a significant increase in T_g was achieved, ca. 150 °C increase for monofunctional and ca. 170 °C increase for bifunctional polybenzoxazine, indicating the beneficial effect of cross-linking afforded by the introduction of allyl group as another cross-linkable site.

(c) Thermal Stability of Polybenzoxazines. Thermal stability of the novel polybenzoxazines was investigated by TGA. The TGA profiles of polybenzoxazines from monofunctional monomers, PP-a, PP-ala, and PP-alp, are shown in Figure 16. The 5 and 10% weight loss temperatures (T_5 and T_{10}) for PP-a are 342 and 369 °C, respectively. For PP-ala, the T_5 and T_{10} were improved slightly to 348 and 374 °C, respectively. Whereas for PP-alp, T_5 and T_{10} were as low as 288 and 356 °C, respectively. The char yield at 800 °C of PP-ala (44%) and PP-alp (45%) was almost the same as PP-a (44%).

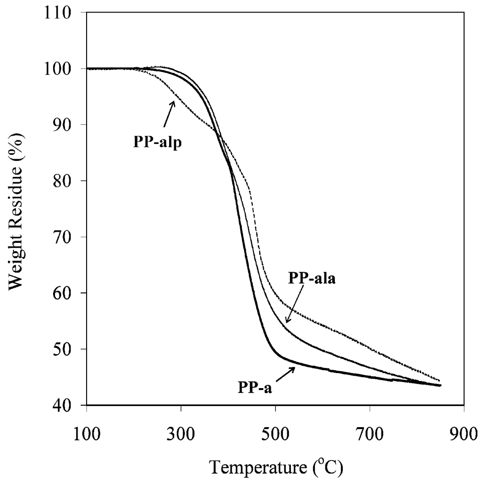


Figure 16. TGA of PP-a, PP-alp, and PP-ala.

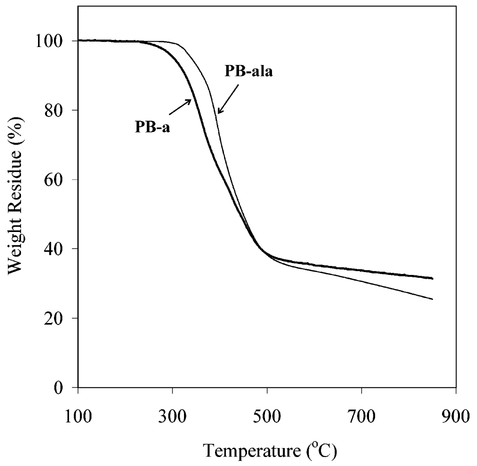


Figure 17. TGA of PB-a and PB-ala.

For typical polybenzoxazine, PB-a, the T_5 and T_{10} are 310 and 327 °C, respectively with char yield about 32% (Figure 17). Whereas for PB-ala, T_5 and T_{10} increased to 343 and 367 °C, respectively. This increase is attributed to the prevention of amines from volatizing at the initial stages of the degradation[17] due to the cross-linking. The char yield of PB-ala was 28%, which is less than that of PB-a (32%) by ca. 4% due to the aliphatic cross-links resulted from the polymerization of allyl group which undergo decomposition at lower temperature.

Conclusion

We introduced allyl group into benzoxazine monomer as another cross-linkable site that work at moderate temperature. The allyl-containing monomers showed the presence of two separate exotherms at different temperature range. The first exotherm started at 145 °C due to the cure of allyl group and the second started at 225 °C due to the ring-opening polymerization of oxazine ring. Polybenzoxazines derived from the novel monomers exhibited significantly improved thermal properties than the typical polybenzoxazines. The T_gs of the polybenzoxazine were as high as ca. 300 °C by the introduction of allyl group. Consequently, the storage modulii of PP-ala and PB-ala were maintained constant up to much higher temperature than those of PP-a and PB-a. The thermal stability of the novel polybenzoxazine was also increased by 20−40 °C from 5% weight loss on TGA owing to the introduction of allyl group.

Experimental Section

Materials. Phenol, allylamine, aniline, bisphenol A, paraformaldehyde, and 2-allylphenol were used as received from Tokyo Kasei, Tokyo, Japan. B-a and P-a were kindly supplied by Shikoku Chemicals Co., Kagawa, Japan, and used as received.

Preparation of P-ala. In a 1 L beaker, allylamine (1.000 mol, 57.09 g) was added to 1.000 mol of phenol (94.11 g), and the clear mixture was stirred for 5 min. This mixture was cooled in an ice bath, then paraformaldehyde (2.00 mol, 60.1 g) was added portionwise over 15 min with stirring in an ice bath. The mixture was kept stirring for 10 min at room temperature to give hazy colorless solution. The temperature was raised gradually up to 85 °C and kept stirring at 85 °C for 2 h. The beaker was allowed to cool to room temperature to afford pale yellow liquid (167 g, 0.95 mol). The as-synthesized monomer was purified by dissolving in 1 L of diethyl ether, and washing three times with 1.5 L of aqueous 3 N sodium hydroxide, and finally two times with 1.5 L of distilled water. The ether solution was dried with anhydrous sodium sulfate, followed by evaporation of ether under vacuum to afford pale yellow liquid (126 g, 0.72 mol, 72%). The monomer was further purified by distillation under reduced pressure, bp 135 °C/(17 mmHg).

Anal. Calcd for P-ala ($C_{11}H_{13}NO$): C, 75.40; H, 7.48; N, 7.99. Found: C, 75.23; H, 7.56; N, 7.93.

Preparation of B-ala. In a 1 L beaker, bisphenol A (0.2700 mol, 61.641 g) was added gradually with stirring to allylamine (0.5400 mol, 30.828 g) at room temperature. A clear transparent mixture was obtained within 30 min by stirring the mixture. The mixture was cooled by ice bath, followed by adding paraformaldehyde (1.0800 mol, 32.508 g) portionwise with stirring for 10 min in an ice bath. The temperature was raised gradually up to 90 °C. The mixture was kept stirring at 90 °C for 2 h. After cooling to room temperature, colorless crystals were obtained as a raw product (99 g, 0.25 mol, 94%). This crude product was purified by dissolving in 1 L of diethyl ether and washing three times with 1.5 L of aqueous 3 N sodium hydroxide, and finally two times with 1 L of distilled water. After evaporation of ether, pale yellowish white crystals were obtained which was dried under vacuum at 40 °C for 24 h to afford 75 g (0.192 mol, 71%) of B-ala with mp 55−58 °C.

Anal. Calcd for B-ala ($C_{25}H_{30}N_2O_2$): C, 76.89; H, 7.74; N, 7.17. Found: C, 75.88; H, 7.53; N, 6.64.

Preparation of P-alp. P-alp was prepared from 2-allylphenol (0.2000 mol, 26.836 g), aniline (0.2000 mol, 18.626 g), and paraformaldehyde (0.4000 mol, 12.04 g) using solventless method at 80 °C for 2 h, according to the reported method.[13] The raw product obtained as viscous yellow liquid (45.0 g, 0.179 mol, 90%) was purified by washing with sodium hydroxide as mentioned above to afford yellow liquid (37.0 g, 0.147 mol, 74%).

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 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.

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References and Notes

(1) (a) Reiss, G.; Schwob, G.; Guth, M.; Roche, M.; Laud, B. In *Advances in Polymer Synthesis*; Culbertson, B. M., McGrath,

J. E., Eds.; Plenum: New York, 1985; 27−49. (b) Ning, X.; Ishida, H. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 1121−1129.

(2) (a) Ishida, H.; Allen, D. J. *J. Polym. Sci., Part B: Polym. Phys.* **1996**, *34*, 1019−1030. (b) Takeichi, T.; Komiya, I.; Takayama, Y. *Kyoka-Purasutikkus* **1997**, *43*, 109−117. (c) Ishida, H.; Low, H. Y. *Macromolecules* **1997**, *30*, 1099−1106. (d) Wang, Y. X.; Ishida, H. *Polymer* **1999**, *40*, 4563−4570. (e) Shen, S. B.; Ishida, H. *J. Polym. Sci., Part B: Polym. Phys.* **1999**, *37*, 3257−3268. (f) Macko, J. A.; Ishida, H. *Polymer* **2001**, *42*, 227−240.

(3) (a) Ishida, H.; Allen, D. *Polymer* **1996**, *37*, 4487−4495. (b) Kimura, H.; Matsumoto, A.; Hasegawa, K.; Ohtsuka, K.; Fukuda, A. *J. Appl. Polym. Sci.* **1998**, *68*, 1903−1910. (c) Takeichi, T.; Guo, Y.; Agag, T. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4165−4176. (d) Takeichi, T.; Guo, Y. *Polym. J.* **2001**, *33*, 437−443.

(4) (a) Takeichi, T.; Agag, T.; Zeidam, R. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2633−2641. (b) Ishida, H.; Lee, Y. *Polymer* **2001**, *42*, 6971−6979. (c) Ishida, H.; Lee, Y. *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 736−749. (d) Takeichi, T.; Kusakabe, Y. *J. Network Polym., Jpn.* **2002**, *23*, 195−202.

(5) (a) Jang, J.; Yang, H. *J. Mater. Sci.* **2000**, *35*, 2297−2303. (b) Jang, J.; Yang, H. *Compos. Sci. Technol.* **2000**, *60*, 457−463.

(6) (a) Agag, T.; Takeichi, T. *Polymer* **2000**, *41*, 7083−7090. (b) Takeichi, T.; Zeidam, R.; Agag, T. *Polymer* **2002**, *43*, 45−53. (c) Agag, T.; Takeichi, T.; Toda, H.; Kobayashi, T. *Int. J. Mater. Product Tech.* **2001**, *2*, 706−711. (d) Agag, T.; Takeichi, T. *High Perform. Polym.* **2002**, *14*, 115−132.

(7) (a) Jang, J.; Seo, D. *J. Appl. Polym. Sci.* **1998**, *67*, 1−10. (b) Agag, T.; Takeichi, T. *High Perform. Polym.* **2001**, *13*, S327−S342.

(8) (a) Kim, H. J.; Brunovska, Z.; Ishida, H. *Polymer* **1999**, *40*, 1815−1822. (b) Kim, H. J.; Brunovska, Z.; Ishida, H. *Polymer* **1999**, *40*, 6565−6573. (c) Kim, H. J.; Brunovska, Z.; Ishida, H. *J. Appl. Polym. Sci.* **1999**, *73*, 857−862.

(9) Brunovska, Z.; Ishida, H. *J. Appl. Polym. Sci.* **1999**, *73*, 2937−2949.

(10) Agag, T.; Takeichi, T. *Macromolecules*, **2001**, *34*, 7257−7263.

(11) (a) Stenzenberger, H. D.; Konig, P. *High Perform. Polym.* **1989**, *1*, 133−144. (b) Liang, G.; Gu, A. *Polym. J.* **1997**, *29*, 553−556. (c) Gouri, C.; Reghunadhan Nair, C. P.; Ramaswamy, R. *High Perform. Polym.* **2000**, *12*, 497−514.

(12) (a) Andre, S.; Guida-Pietrasanta, F.; Rousseau, A.; Boutevin, B.; Caporiccio, G. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2993−3003. (b) Lin, K.-F.; Lin, J.-S.; Cheng, C.-H. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 2469−2478.

(13) Ishida, H. US Patent 5,543,516, 1996.

(14) Ishida, H.; Low, H. Y. *J. Appl. Polym. Sci.* **1998**, *69*, 2558−2567.

(15) Pei, D. J.; Gu, Y.; Cai, X. *Acta Polym. Sin. (Chin.)* **1998**, *5*, 595−598.

(16) Ishida, H.; Sanders, D. P. *Polymer* **2001**, *42*, 3115−3125.

(17) Low, H. Y.; Ishida, H. *Polymer* **1999**, *40*, 4365−4376.

(18) Gu, A.; Liang, G. *Polym.-Plast. Technol. Eng.* **1997**, *36*, 681−694.

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