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Synthesis and thermal cure of high molecular weight polybenzoxazine precursors and the properties of the thermosets

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Abstract

High molecular weight polybenzoxazine precursors have been synthesized from aromatic or aliphatic diamine and bisphenol-A with paraformaldehyde. The precursors were obtained as soluble white powder. Molecular weight was estimated from the size exclusion chromatography to be several thousands. The structure of the precursors was confirmed by IR, ^{1}H NMR and elemental analysis, indicating the presence of cyclic benzoxazine structure. The ratio of the ring-closed benzoxazine structure and the ring-opened structure in the high molecular weight precursor was estimated from ^{1}H NMR spectrum and also from the exotherm of DSC, showing that the ratio of the ring-closed benzoxazine structure was 77–98%. The precursor solution was cast on glass plate, giving transparent and self-standing precursor films, which was thermally cured up to 240 °C to give brown transparent polybenzoxazine films. The toughness of the crosslinked polybenzoxazine films from the high molecular weight precursors was greatly enhanced compared with the cured film from the typical low molecular weight monomer. Tensile measurement of the polybenzoxazine films revealed that polybenzoxazine from aromatic diamine exhibited the highest strength and modulus. While, polybenzoxazine from longer aliphatic diamine had higher elongation at break. The viscoelastic analyses showed that the glass transition temperature of the polybenzoxazines derived from the high molecular weight precursors were as high as 238–260 °C. Additionally, these novel polybenzoxazine thermosets showed excellent thermal stability.

Keywords: Polybenzoxazine; High molecular weight; Thermal properties

1. Introduction

The traditional phenolic resins possess excellent characteristics such as high heat resistance and flame retardance, good electric and chemical resistance, low water absorption, and low cost. Therefore, they are widely applied in various fields such as matrix for fiber-reinforced plastics (FRP), structural materials, adhesives, paints and others. The disadvantages of the traditional phenolic resins are their brittleness, the need of catalyst for polymerization, formation of voids because of the volatiles formed during the cure, and large volumetric shrinkage upon cure. Also the volatalization of phenol and formaldehyde into the air during the cure process causes some health concern.

A series of polybenzoxazines obtained by the ring-opening polymerization of cyclic monomers, benzoxazines, has been developing as a novel type of phenolic resin [1]. The monomers are easily prepared from phenols, primary amines and formaldehyde. The wide variations of raw materials, phenols and amines, allow considerable molecular-design flexibility for the cyclic monomers. Polymerization proceeds through the ring-opening of the cyclic monomers only by heat treatment without the need of catalyst and without generating byproducts or volatiles, and thus excellent dimensional stability is obtained. The structure of a typical benzoxazine monomer (B-a) prepared from bisphenol-A, aniline and formaldehyde along with the structure of its polybenzoxazine (PB-a) are shown in Scheme 1.

Polybenzoxazines provide characteristics found in the traditional phenolic resins such as high heat resistance and flame retardance. They also provide characteristics that are not found in the traditional phenolic resins such as excellent dimensional stability, low water absorption and good dielectric properties. Various applications as electronic materials, matrix resin for FRP, and adhesives are expected. However, there are some shortcomings for polybenzoxazines. The cured materials are brittle and a relatively high temperature is needed for the ring-opening polymerization. Also, processing into thin film

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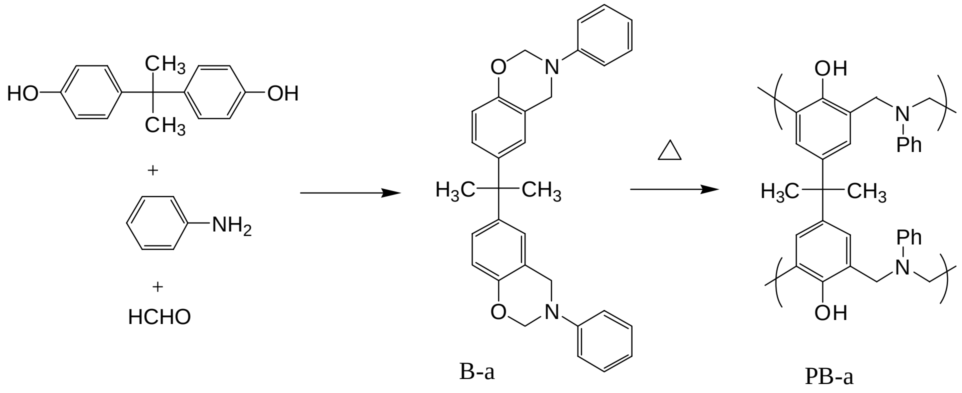


Scheme 1. Structures of B-a and PB-a.

from the typical monomers is difficult because most monomers are powder and the polymers are brittle due to the short molecular weight of the network structure.

Recently, aiming for performance enhancement and lowing the polymerization temperature, various approaches have been examined. One approach is the modification of monomer. Introduction of another crosslinkable functional units is very effective to enhance the thermal properties [2]. As another approach, polymer alloys of polybenzoxazine with high performance polymers or with elastomers resulted in high performance and tough films [3]. Third approach of hybridization with inorganic materials such as layered clay [4] and metal oxide nanoparticles [5] was also successful in obtaining polybenzoxazine with improved properties.

Until now, however, only the low molecular weight cyclic monomers have been studied in detail as precursors of polybenzoxazines. Although Ishida reported in his patent the modification of polyphenol with monofunctional amine to get benzoxazine-functional polymer [6], he did not mention details about the preparation and characterization as well as the properties of the polymer. So far, a high molecular weight polymer containing cyclic benzoxazine structure as a repeating unit in the main chain prepared from the reaction of bisphenols with diamines has not yet been prepared. This is probably due to the belief that the formation of cyclic benzoxazine monomer is usually accompanied with a ring-opening polymerization of the once-formed cyclic monomer, which eventually cause a crosslinking and hence insolubility of the obtained polybenzoxazine precursor. If it is possible to obtain soluble high molecular weight polybenzoxazine precursors, processing into thin films should become very easy, and application into the fields for which the low molecular weight cyclic monomer has not used would realize.

In this study, we report on the preparation of high molecular weight polybenzoxazine precursor from bisphenol-A and aromatic or aliphatic diamine in the presence of formaldehyde. The structure of the obtained precursor was characterized, and the properties of the cured polybenzoxazine films were compared with the typical polybenzoxazine film from typical low molecular weight cyclic monomer.

2. Experimental

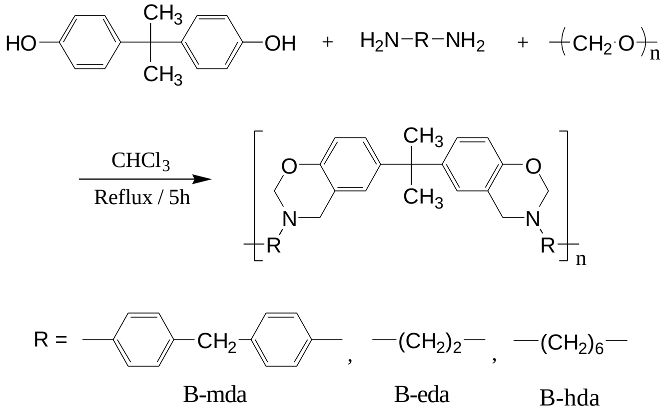
2.1. Materials

Chloroform, 1,4-dioxane, bisphenol-A, formaline, ethylenediamine (eda), and hexamethylenediamine (hda) were used as received from Kishida Chemicals Co., Japan. Paraformaldehyde and methylenedianiline (mda) were used as received from Merck and Aldrich, respectively.

2.2. Syntheses of polybenzoxazine precursors

Polybenzoxazine precursors were prepared by reacting bisphenol-A, diamine, and paraformaldehyde as shown in Scheme 2. The precursors were abbreviated to be B-mda, B-eda and B-hda using the abbreviations of the starting chemicals.

Synthesis of B-hda was performed as follows. To 100 mL of chloroform, hda (40.0 mmol, 4.65 g), bisphenol-A (40.0 mmol, 9.13 g) and paraformaldehyde (172 mmol, 5.15 g) were added and refluxed for 5 h. The reaction mixture was filtered and washed once with 1 N $NaHCO_3$ aqueous solution (200 mL), and dried with anhydrous sodium sulfate for one night. Removal of solvent by evaporation and drying under vacuum afforded B-hda as white powder. The yield was 13.8 g (87%).



Scheme 2. Preperation of polybenzoxazine precursors.

Anal. Calcd for B-hda ($C_{25}H_{32}N_2O_2$): C, 76.53; H, 8.16; N, 7.14. Found: C, 74.94; H, 8.57; N, 7.74.

Syntheses of B-eda and B-mda were performed in the same way, giving precursors as white powder in 77 and 83% yield, respectively.

2.3. Preparation of precursor films and polybenzoxazine films

The precursor (2 g) was dissolved in dioxane (4 g), and the solution was cast on glass plate. The solvent was removed by drying at 50 °C for 5 h, giving yellow transparent precursor films. Heat treatment of the precursor films at 100, 120, 160, 200 and 240 °C for 1 h each gave brown transparent polybenzoxazine films.

2.4. Measurements

IR spectra were obtained with JASCO spectrophotometer model FT/IR-420. ^{1}H NMR spectra were recorded on a Varian Mercury 300 (300 MHz) instrument. Viscosity of the precursor solution was measured using Ubbelohde viscometer at a concentration of 0.5 g dL^{-1} in 1,4-dioxane at 30 °C. Size exclusion chromatography (SEC) was measured with Tosoh instrument with UV-8011 (254 nm) or refractive index detection. THF was used as a carrier solvent at a flow rate of 1.0 mL min^{-1} at 40 °C. Two polystyrene gel columns (Shodex KF806L×2) were used. A calibration curve was made to determine M_n and M_w/M_n values with polystyrene standards. Measurable molecular weight ranges are from 1×10^2 to 2×10^7. Differential scanning calorimetry (DSC) was conducted using Rigaku Thermo Plus 2 DSC8230. Samples (ca. 10 mg) were heated from 30 to 550 °C at a heating rate of 5 °C min^{-1} under nitrogen. Thermogravimetric analysis (TGA) was determined with Rigaku Thermo Plus 2 TG-DTA TG8120. Samples (ca. 10 mg) were heated from 30 to 850 °C at a heating rate of 5 °C min^{-1} under argon. Dynamic viscoelastic measurements were conducted on ORIENTEC automatic dynamic viscoelatomer Rheovibron model DDV-01FP at 35 Hz at a heating rate of 4 °C min^{-1}. Tensile properties were recorded with Imada Seisaku-sho Model SV-3 at a crosshead speed of 0.5 mm min^{-1} using straight films of 25 mm long. Tensile properties of each sample were determined from an average of at least 10 tests.

3. Results and discussion

3.1. Preparation of precursors

The synthesis of precursors is based on the reaction of diamine, bisphenol-A and paraformaldehyde at the molar ratio of 1:1:4. First of all, the reaction conditions were examined for the synthesis of B-eda as an example. When the mixture was heated at 100 °C for 0.5 h without solvent (solvent-less method), insoluble bulky solid was obtained, suggesting the difficulties of applying the solvent-less method. Therefore, solvent method was examined. When the mixture was refluxed for 6 h in chloroform, large amount of gel was formed. Removal of the gel by filtration and drying of the filtrate afforded insoluble materials. But, when the mixture was refluxed in chloroform for 5 h, formation of gel was greatly decreased. The small amount of gel was easily removed by filtration, and the filtrate was washed once with 1 N $NaHCO_3$ solution and dried, affording easily soluble white powder.

Table 1
Properties of polybenzoxazine precursors

	Yield (%)	Viscosity[a] η_{red} (dL g^{-1})	M_w/M_n
B-mda	83	0.07	6733/2232
B-eda	77	0.09	6092/2571
B-hda	87	0.10	8858/2358

[a] 0.5 gdL^{-1} in dioxane at 30 °C.

The reaction condition was thus fixed, in this study, to reflux in chloroform for 5 h. The yield for various precursors was in the range of 77–87% after purification. The molecular weight of the precursors was estimated from viscosity measurement and SEC. The results are summarized in Table 1. The viscosity was in the range of 0.07–0.10 dL g^{-1}, M_w was in the range of 6000–8900 and M_n was 2200–2600, showing that the molecular weight is not so high. But, it should be emphasized that self-standing thin films were easily obtained by casting the precursor solutions.

In the preparation of typical low molecular cyclic monomers, phenolic compounds that were produced by the ring-opening of the once-formed monomer can be completely removed through washing with aqueous alkaline solution. But, in the case of high molecular weight precursors, ring-closed structure and ring-opened structure co-exist randomly in a polymer chain, and it is almost impossible to remove the partially ring-opened structure. But from the practical point of view this is not a problem because both will be involved in the network formation. The ratio of ring-closed and ring-opened structure was estimated from ^{1}H NMR and DSC as described below.

3.2. Structure of the precursors

The structure of the precursors was examined by FT-IR and ^{1}H NMR. IR spectra of the precursors are shown in Fig. 1. The asymmetric stretching of C–O–C (1234 cm^{-1}), the asymmetric stretching of C–N–C (1180–1187 cm^{-1}), CH_2 wagging of oxazine (1325–1328 cm^{-1}) were observed. Additionally, the characteristic absorptions assigned to trisubstituted benzene ring at 1502–1511 cm^{-1} and out of plane bending vibrations of C–H at 937–943 cm^{-1} were observed, indicating that precursors containing benzoxazine structure in the backbone were obtained.

The ^{1}H NMR spectrum was also measured to confirm the structure. The ^{1}H NMR spectrum of B-eda is shown in Fig. 2(a). The characteristic peaks assignable to methylene (O–CH_2–N) and methylene (Ar–CH_2–N) of oxazine ring were observed at 4.86 and 3.97 ppm, respectively. The methyl proton of bisphenol-A and ethylene proton of eda showed peaks at 1.58 and 2.96 ppm, respectively. Here, the ratio of the ring-closed benzoxazine structure and the ring-opened

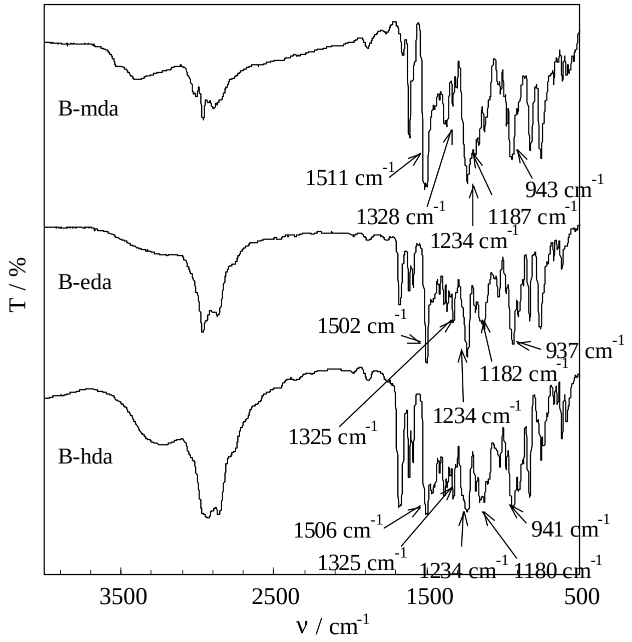


Fig. 1. IR spectra of polybenzoxazine precursors.

structure was calculated from the ^{1}H NMR. The theoretical ratio of the methylene proton of benzoxazine to the ethylene proton of eda for the fully ring-closed structure is 4 to 4. The found ratio was 3.7 to 4.0. Thus, the ratio of the ring-closed structure was calculated to be as high as 93%.

The ^{1}H NMR spectrum of B-hda is shown in Fig. 2(b). The characteristic peaks assignable to methylene (O–CH$_2$–N) and methylene (Ar–CH$_2$–N) of oxazine ring were observed at 4.81 and at 3.92 ppm, respectively. The methyl proton of bisphenol-A appeared at 1.58 and methylene proton of hda were observed at 2.70 and 1.34 ppm, respectively. The ratio of the ring-closed structure in B-hda was calculated to be 87% from the methylene proton of oxazine and terminal methylene proton of hda.

^{1}H NMR spectrum of B-mda is shown in Fig. 2(c). The aromatic protons appeared at 6.60–7.25 ppm. The characteristic peaks assignable to methylene (O–CH$_2$–N) and methylene of oxazine (Ar–CH$_2$–C) was observed at 5.24 and at 4.50 ppm, respectively. Also, the methyl proton of bisphenol-A and methylene proton of mda appeared at 1.52 and 3.79 ppm, respectively, confirming the formation of precursor. The ratio of ring-closed and ring-opened structure of oxazine in B-mda was calculated to be 77:23 from the ratio of the methylene proton of oxazine and methylene proton of mda.

3.3. Ring-opening behavior of precursor

DSC profiles of the precursors are shown in Fig. 3. The exotherm onset corresponding to the ring-opening for the typical low molecular weight monomer, B-a, was observed at 220 °C. The exotherm onset for the precursors, on the other hand, was observed at much lower temperature than that of B-a. It is considered that small amount of phenolic hydroxyl group present in the precursor is working as acid catalyst and shifted the exotherm of the ring-opening to lower temperature. The lowering of exotherm has been observed by the acidic protons such as polyamic acid [3e,h], clay [4], and silica and titania precursors [5].

Here we estimated the ratio of the ring-closed structure from the amount of exotherm by assuming that exotherm of each benzoxazine unit is constant, not depending on the structure. Exotherm of B-a was used as the standard. The ratio of ring-closed structure was calculated based on the theoretical amount of exotherm of precursor in comparison with found amount of exotherm. In the case of B-eda, the observed amount of exotherm was 332 J g^{-1}, which is lower than the theoretical amount of exotherm (339 J g^{-1}). The ratio of the closed structure was thus calculated to be 98%. B-hda and B-mda showed the same tendency, and the ratio of the closed structure was calculated to be 95 and 79%, respectively.

The ratios of ring-closed and ring-opened structure calculated from both ^{1}H NMR spectrum and exotherm of DSC are summarized in Table 2. The ratios from both methods were almost the same, indicating that all precursors contained some ring-opened structure. It was also found that the ratio of the ring-closed benzoxazine structure was reasonably high to be used as polybenzoxazine precursors.

The progress of ring-opening polymerization of the precursors was monitored by DSC and IR. Fig. 4 shows DSC thermogram of B-mda after each cure. The amount of exotherm decreased with the increase of heat treatment temperature. The exotherm completely disappeared after 240 °C cure, showing that ring-opening of oxazine was completed. On the other hand, in the IR spectra shown in Fig. 5, characteristic absorption bands due to the cyclic benzoxazines at 1234 cm^{-1} (asymmetric stretching of C–O–C of oxazine), at 1187 cm^{-1} (asymmetric stretching of C–N–C), at 1328 cm^{-1} (CH$_2$), at 1511 cm^{-1} (stretching of trisubstituted benzene ring) and at 943 cm^{-1} (out of plane bending vibrations of C–H) decreased. By the end of 240 °C cure, also characteristic absorption bands for benzoxazine disappeared, suggesting the completion of the ring-opening polymerization. B-eda and B-hda showed the same ring-opening behavior. Possible structure of the cured polybenzoxazine is depicted in Scheme 3 from the similarity with B-a and PB-a shown in Scheme 1.

3.4. Formation and thermal cure of polybenzoxazine precursor films

The precursors were dissolved in dioxane and cast on glass plate. The solvent was removed by drying at 50 °C for 16 h. The precursor films were colorless and transparent. After heat treatment at 100, 120, 160, 200 and 240 °C for 1 h each, brown transparent polybenzoxazine films were obtained.

The appearances of the cured polybenzoxazine films are shown in Fig. 6. The PB-a film of 100 μm thickness is very brittle, and we could not bend more than as is shown in Fig. 6(a). However, all the polybenzoxazine films from high molecular weight precursors showed remarkably improved toughness. The PB-mda and PB-hda films were very tough, and even the 150 μm thick films are easy to bend as shown in

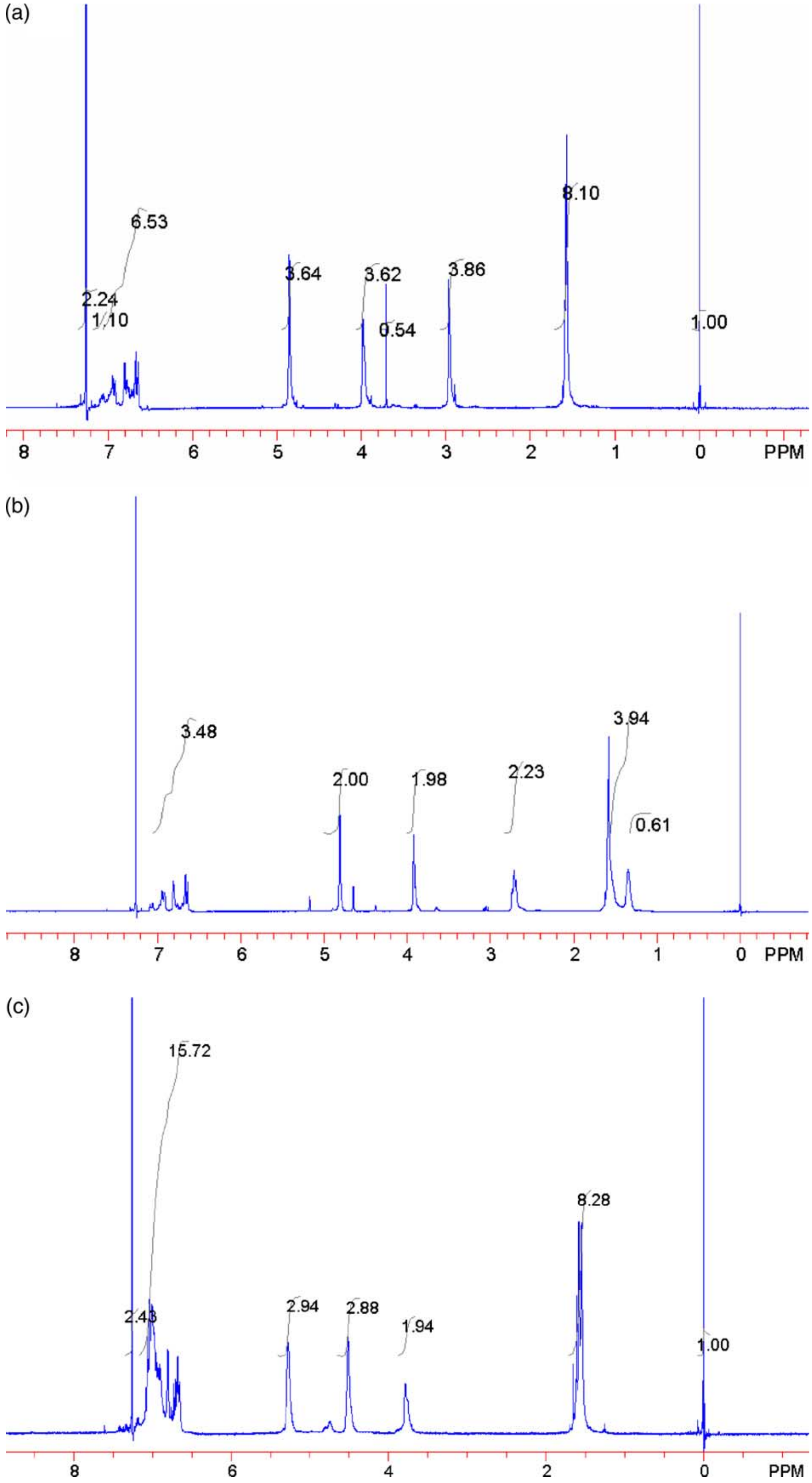


Fig. 2. ^{1}H NMR spectra of polybenzoxazine precursors. B-eda (a), B-hda (b), and B-mda (c).

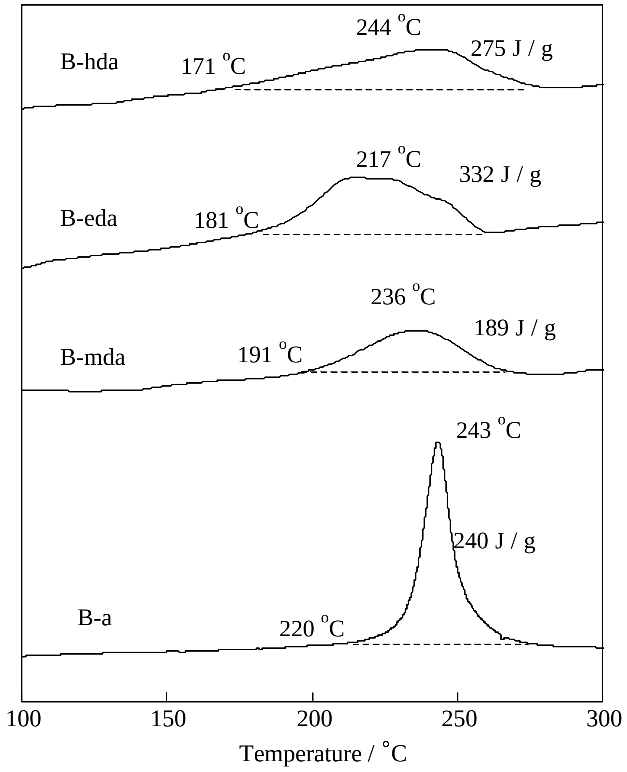


Fig. 3. DSC of polybenzoxazine precursors.

Fig. 6(b) and (d). Although PB-eda film of 200 μm thickness is slightly difficult to bend, 100 μm thick film was tough enough and can be bent without problem as shown in Fig. 6(c).

3.5. Tensile properties of polybenzoxazine films

The tensile properties of the polybenzoxazine films were measured. The stress–strain curves are shown in Fig. 7, and the values of tensile modulus, tensile strength and elongation at break are summarized in Table 3. Typical polybenzoxazine film, PB-a, shows high modulus, but the poor toughness made film easy to break at low elongation. However, tensile strength of polybenzoxazine films from high molecular weight precursors were much higher than that of PB-a, because of the preformed long precursor backbone. PB-mda films have higher modulus than that of PB-a, because PB-mda has high content of rigid aromatics. PB-eda also showed the high modulus because of the rigidity due to the short aliphatic chain. PB-hda with long flexible methylene chain showed higher

Table 2
Ratio of cyclic structure and ring opened structure

	^{1}H NMR Cyclic:open	DSC Cyclic:open
B-a	100:0	100:0
B-mda	77:23	78:21
B-eda	93:4	98:2
B-hda	87:11	95:5

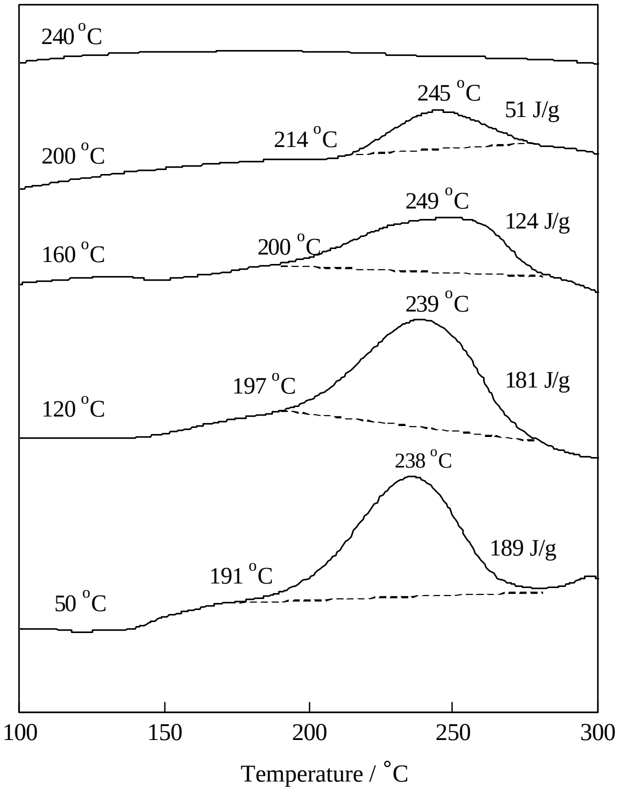


Fig. 4. DSC of B-mda after each cure stage.

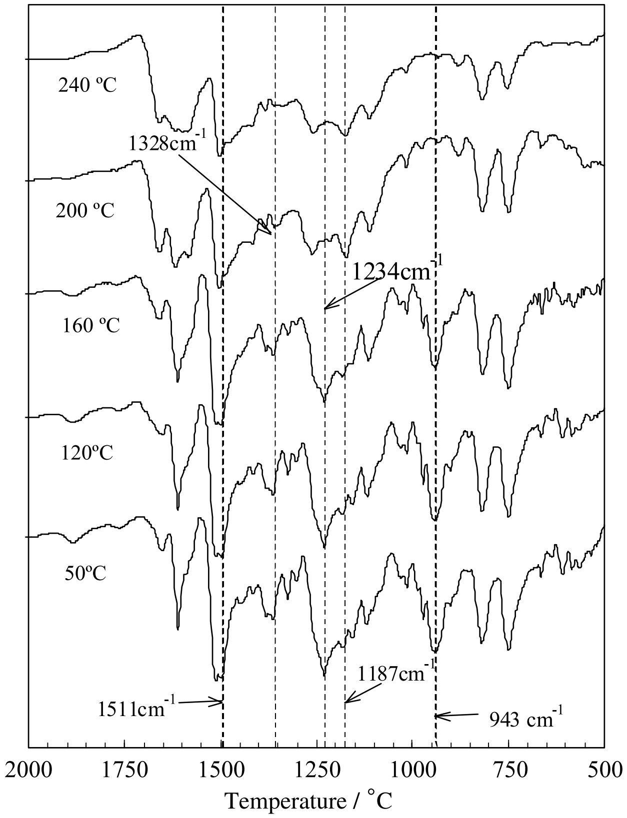
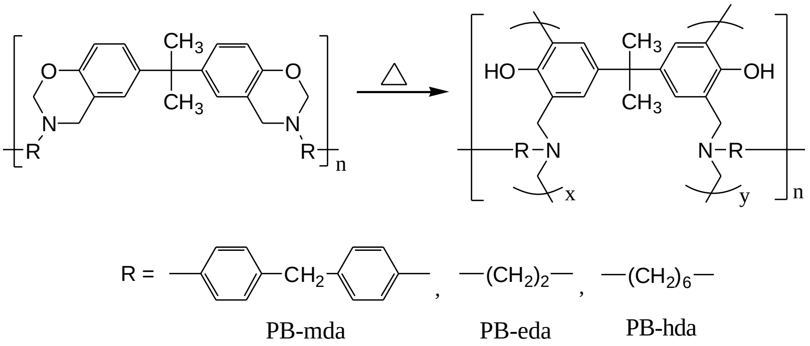


Fig. 5. IR spectra of B-mda after each cure stage.



Scheme 3. Possible structures of polybenzoxazine precursors and the cure resin.

elongation at break and lower tensile modulus compared to PB-eda.

3.6. Viscoelastic analyses of polybenzoxazine films

Viscoelastic analyses of polybenzoxazine films were examined and the results are shown in Fig. 8. The storage modulus at room temperature and T_gs are summarized in Table 4. For the typical polybenzoxazine, PB-a, T_g was found at 153 °C from E''. All the polybenzoxazines from high molecular weight precursors showed much higher T_g values. T_g values for PB-mda, PB-eda and PB-hda were 228, 249 and 247 °C, respectively. The significant increase in T_g indicates the beneficial effect of linear long precursor backbone and high crosslink density, which restricted the movement of the polymer chains. The decrease of storage modulus above glass transition temperature range was also considerably suppressed due to the increased crosslinking density.

3.7. Thermogravimetric analysis of polybenzoxazine

The thermal stability of polybenzoxazine was investigated by TGA, and the results are shown in Fig. 9. The values of 5 and 10% weight loss temperatures and the char yield are

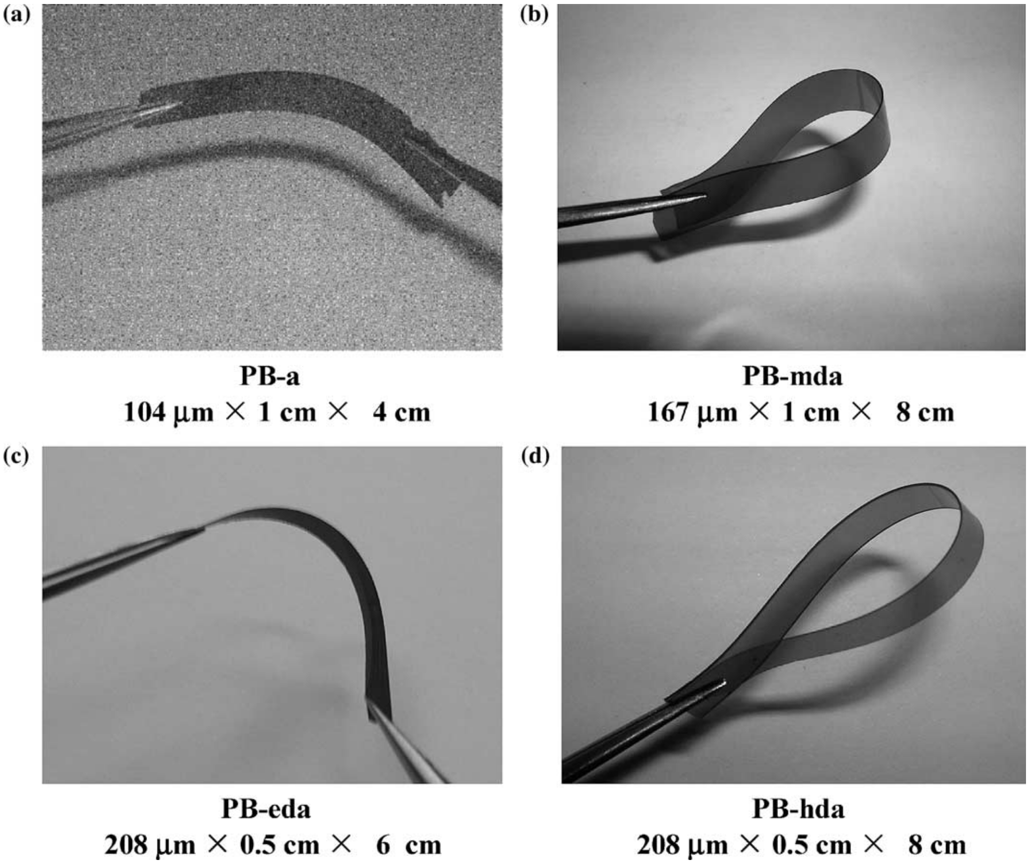

(a) PB-a 104 μm × 1 cm × 4 cm
(b) PB-mda 167 μm × 1 cm × 8 cm
(c) PB-eda 208 μm × 0.5 cm × 6 cm
(d) PB-hda 208 μm × 0.5 cm × 8 cm

Fig. 6. Appearance of polybenzoxazine films.

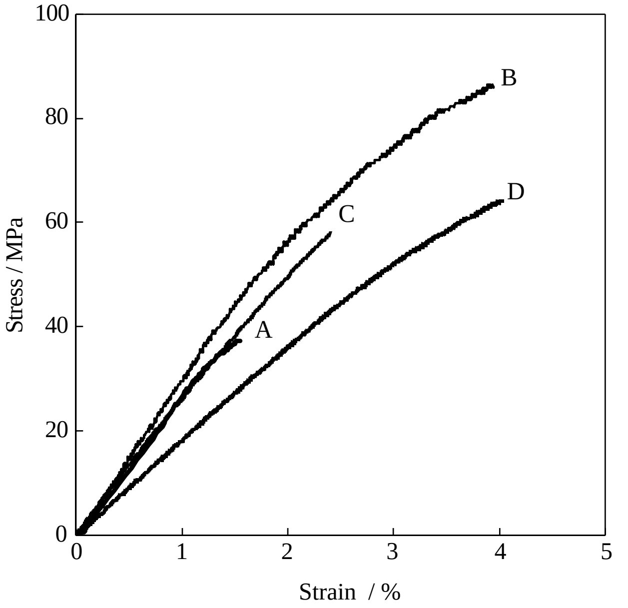


Fig. 7. Tensile properties of polybenzoxazine films. PB-a (A), PB-mda (B), PB-eda (C), and PB-hda (D).

Table 3
Tensile properties of polybenzoxazine films

	E (GPa)	σ_b (MPa)	ε_b (%)
PB-a	3.3	37	1.6
PB-mda	3.5	87	4.1
PB-eda	3.3	58	2.4
PB-hda	2.0	65	4.1

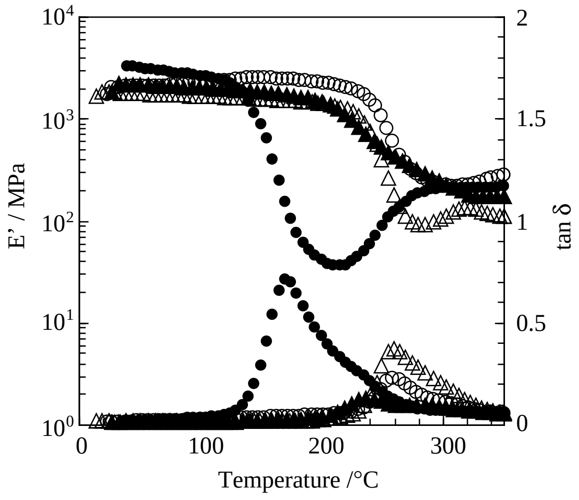


Fig. 8. Viscoelastic analysis of polybenzoxazine films. PB-a (●), PB-mda (▲), PB-eda (○), and PB-hda (△).

summarized in Table 5. PB-eda and PB-hda with low aromatic ring content showed somewhat lower thermal stability because of the high content of thermally labile aliphatic groups. But, the thermal stability of PB-mda was higher than that of PB-a due to the high aromatic content.

Table 4
Viscoelastic analysis of polybenzoxazine films

	E'_{rt} (GPa)	T_g (E'') (°C)	T_g (tan δ) (°C)
PB-a	3.4	153	171
PB-mda	2.4	228	238
PB-eda	2.4	249	259
PB-hda	1.8	247	260

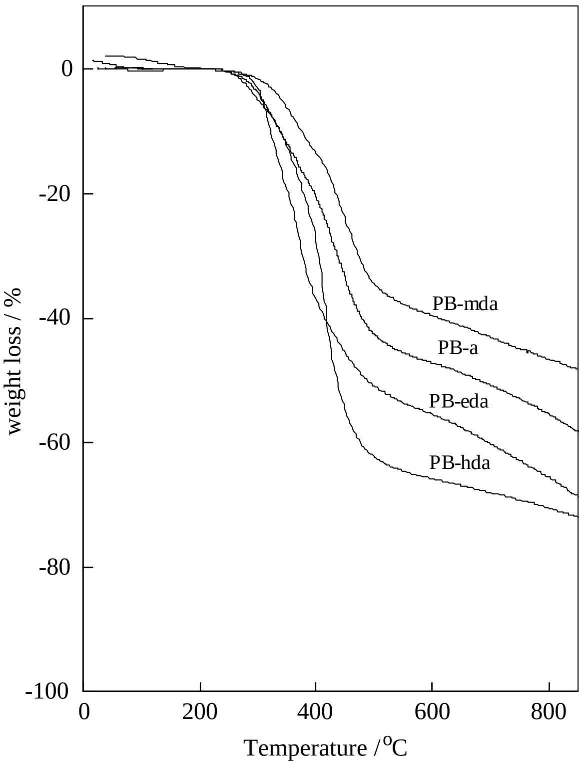


Fig. 9. TGA of polybenzoxazines.

4. Conclusions

High molecular weight polybenzoxazine precursors containing cyclic benzoxazine groups in the backbone were prepared from bisphenol-A, various diamines, and paraformaldehyde. Partially ring-opened structure was observed, but the ratio of the ring-closed structre in the precursor was high enough to be used as polybenzoxazine precursors. Transparent thin precursor films were easily obtained by casting the precursor solution on glass plate. Heat treatment of the precursor films up to 240 °C gave brown transparent polybenzoxazine films. The polybenzoxazine films from

Table 5
Heat resistance of polybenzoxazine films

	$T_{-5\%}$ (°C)	$T_{-10\%}$ (°C)	Char yield (%)[a]
PB-a	308	338	42
PB-mda	341	375	52
PB-eda	282	301	31
PB-hda	301	338	28

[a] At 850 °C.

the high molecular weight precursors exhibited significantly improved toughness than the typical polybenzoxazine, PB-a, due to the long linear backbone and high crosslink density. The T_g values of polybenzoxazines from the high molecular weight precursors were 238–260 °C, much higher than the T_g of the typical PB-a (171 °C). Thermal stability of the polybenzoxazine depended on the aromatic content, and polybenzoxazine from aromatic diamine showed higher thermal stability than that of PB-a.

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