Novel Benzoxazine Monomers Containing *p*-Phenyl Propargyl Ether: Polymerization of Monomers and Properties of Polybenzoxazines

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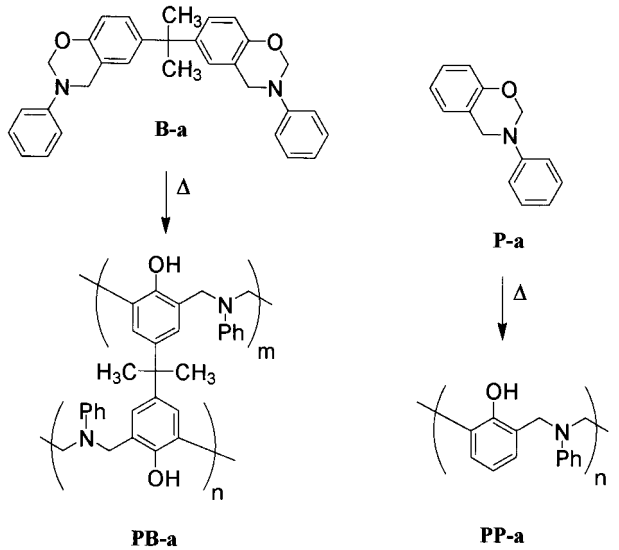
ABSTRACT: Novel benzoxazine monomers containing arylpropargyl ether were prepared, and highly thermally stable polybenzoxazines were obtained by the thermal cure of the monomers. One monomer is a monofunctional benzoxazine, 4-propargyloxyphenyl- 3,4-dihydro-2***H***-1,3-benzoxazine (P-appe), and the other is a bifunctional benzoxazine, bis(4-propargyloxyphenyl-3,4-dihydro-2***H***-1,3-benzoxazinyl)isopropane (B-appe). The chemical structures of these novel monomers were confirmed by IR and ^{1}H NMR. The cure behavior of the monomers, P-appe and B-appe, and the properties of the resulting polymers were studied in comparison with 4-phenyl-3,4-dihydro-2***H***-1,3-benzoxazine (P-a) and bis(4-phenyl-3,4-dihydro-2***H***-1,3-benzoxazinyl)isopropane (B-a) as typical benzoxazine monomers without propargyl groups. DSC cure of both P-appe and B-appe showed a single exotherm corresponding to the ring-opening polymerization of oxazine ring and cross-linking of arylpropargyl ether group at almost the same temperature range as P-a and B-a. The T_g values of polybenzoxazines derived from propargyl-containing monomers, PP-appe and PB-appe, were higher by ca. 100 and 140 °C than those of typical polybenzoxazines without propargyl groups, PP-a and PB-a, respectively. The storage moduli of PP-appe and PB-appe were maintained constant up to higher temperature for ca. 100 °C than that of PP-a and PB-a. The higher thermal stability of the novel polybenzoxazines, PP-appe and PB-appe, than that of the typical polybenzoxazines, PP-a and PB-a, was proved from thermogravimetric analyses.

Introduction

Polybenzoxazine, as a recently developed phenolic resin, has many fascinating characteristics such as outstanding performance, low cost, and acceptable processing characteristics by the conventional techniques that are being used industrially.[1] In addition to the advantages of the traditional phenolic resins, such as heat resistance, good electronic properties, and flame retardance, polybenzoxazines also provide unique characteristics like low water absorption, relatively low dielectric constant, dimensional stability, and near-zero shrinkage upon cure, which overcome the shortcomings of the traditional phenolic resins.[2] Benzoxazine monomers can be easily prepared from inexpensive raw materials like phenols, formaldehyde, and primary amines. Accordingly, they have a tremendous flexibility in molecular design for monomers and consequently a versatile performance for polymers. Furthermore, they can be polymerized without using strong acid or basic catalysts and without producing byproducts through the heterocyclic ring opening, affording polybenzoxazines. Consequently, polybenzoxazines are promising to be a novel type of phenolic resins.

Two typical examples for benzoxazine monomers and polybenzoxazines therefrom are shown in Scheme 1**,** for monofunctional one, P-a, and bifunctional one, B−a. It is hard to obtain high molecular weight linear polybenzoxazine from monofunctional benzoxazine by thermal curing.[3] Therefore, polybenzoxazine derived from bifunctional monomer is typically used. The glass transition temperature and degradation temperature of the typical polybenzoxazine, PB-a, are ca. 150 and ca. 310 °C, respectively.[4] Further enhancement in thermal properties is expected for applications in harsh conditions. Two approaches are considered for performance improvement: (1) by blending with a high-performance polymer or filler and fiber or (2) by preparing specially designed novel monomers. As for the first approach, many studies have been reported on polybenzoxazine-based alloys or copolymers taking advantage of the reactive phenolic groups in polybenzoxazine. The examples are blend with epoxy resin,[5] traditional phenolic resin,[6] polyurethane,[7] poly(ϵ-caprolactone),[8] poly(imide−siloxane),[9] and carbon fibers.[10] Hydroxyphenyl maleimide-modified polybenzoxazine was also reported.[11] We have also reported a successful approach to enhance the thermal properties by incorporating clay nanolayers into

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



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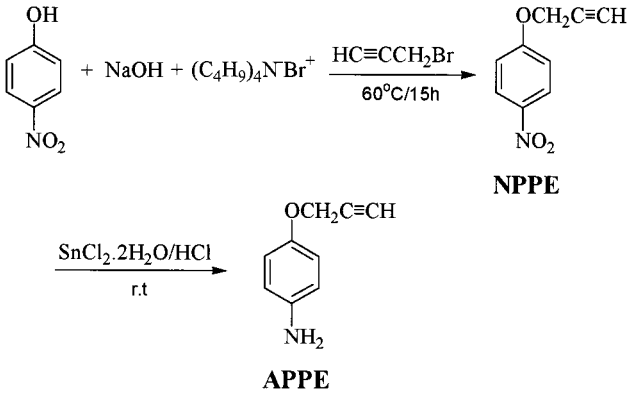
Scheme 2. Preparation of Aminophenyl Propargyl Ether (APPE)



a polybenzoxazine matrix.[4,12] As for the second approach, a series of naphthoxazines were prepared affording polybenzoxazines of high mechanical and good thermal properties.[13]

The study on the thermal decomposition of polybenzoxazines revealed that polybenzoxazines decomposed by volatilizing aniline fragments during thermal degradation.[14] Therefore, the introduction of a cross-linkable site into aniline should be effective to enhance thermal stability of polybenzoxazines. Ishida et al. introduced ethynyl[15] and nitrile[16] groups into the benzoxazine structure, which afforded polybenzoxazines with improved decomposition temperature, char yield, and T_g.

Propargyl ether group, as a thermally reactive endcapping agent, has attracted much attention because monomers containing this group can be synthesized in high yield with low cost, in contrast to ethynyl-containing monomers which need multistep preparation procedure in low yield and high price.[17] Recently, thermosetting compounds incorporating a propargyl ether end group have been reported showing high-temperature resistance and low water absorption.[18] In the current study, we prepared novel benzoxazine monomers containing a propargyl ether group as the cross-linkable functional group to anchor aniline from volatilizing. As a result, we obtained novel polybenzoxazines with attractive thermal properties.

Results and Discussion

Preparation of *p*-Aminophenyl Propargyl Ether (APPE). An aniline derivative that contains a propargyl group, APPE, was prepared according to the pathway shown in Scheme 2, which is different than the reported method.[18c] First, *p*-nitrophenyl propargyl ether (NPPE) was prepared by the reaction between *p*-nitrophenol dissolved in aqueous NaOH and propargyl bromide in the presence of phase transfer catalyst.[19] NPPE was obtained as colorless crystals in 92% yield with mp 114−115 °C. NPPE was reduced with stannous chloride dihydrate in concentrated HCl. The crude product was purified either by distillation (bp 95 °C at 10 mmHg) or by sublimation to afford APPE as a colorless crystal in 86% yield with mp 49−50 °C.

IR spectra of both NPPE and APPE were identical to the reported spectra.[18c,20] The characteristic absorptions were observed at 3240 and 2125 cm^{-1} attributed to the stretching mode of HC≡ and C≡C, respectively. Absorptions are also observed at 1500 and 3400 cm^{-1} due to nitro and amino groups, respectively. The chemical structures of NPPE and APPE were also confirmed by ^1H NMR spectra, which showed a triplet attributed to ≡C−H in NPPE and APPE at $\delta = 2.60$ and 2.18 ppm, respectively. The spectra of APPE also showed a broad peak at 3.2−3.6 ppm for NH_2.

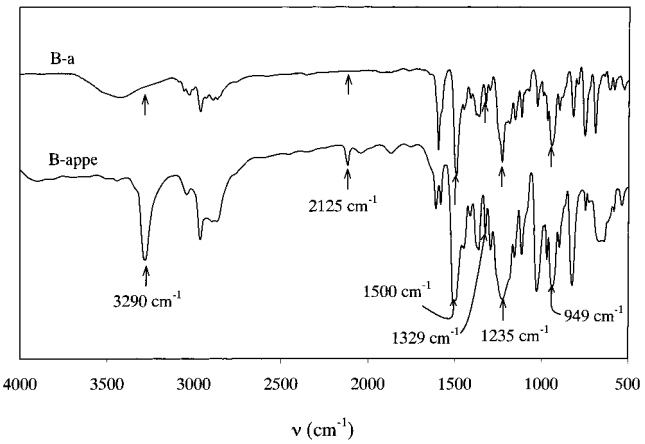


Figure 1. IR spectra of B-a and B-appe.

Preparation of Propargyl Ether-Based Monofunctional Benzoxazine (P-appe) and Bifunctional Benzoxazine (B-appe). P-appe and B-appe were prepared according to Scheme 3. For the preparation of P-appe, APPE was reacted with formalin and phenol in dioxane. The crude product was dissolved in ether and washed with aqueous sodium hydroxide to remove any phenolic oligomers. Thereafter, ether was evaporated to afford P-appe as a yellow viscous product in 67% yield. Similarly, B-appe was prepared from APPE, formalin, and bisphenol A. B-appe was obtained as yellow crystals (mp 61−63 °C) in 64% yield.

The chemical structures of both P-appe and B-appe were confirmed by both FT-IR and ^1H NMR. Figure 1 shows the IR spectra of B-appe along with the typical B-a. The characteristic absorptions of benzoxazine structure appeared on both B-a and B-appe at 1235 cm^{-1} due to the asymmetric stretching of C−O−C, at 1329 cm^{-1} due to CH_2 wagging, and at 949 and 1500 cm^{-1} due to the trisubstituted benzene ring. Characteristic bands for B-appe assigned to HC≡ and C≡C appeared at 3290 and 2125 cm^{-1}, respectively. The ^1H NMR spectrum of P-appe (Figure 2) showed a triplet at 2.49 ppm and a doublet at 4.61 ppm which are assigned to ≡C−H and CH_2 (propargyl), respectively. The ^1H NMR spectrum of B-appe also showed the same peaks assignable to ≡C−H and CH_2 of propargyl at 2.48 ppm (triplet) and 4.62 ppm (doublet), respectively. The molecular structures of both P-appe and B-appe were also supported by the elemental analyses, which indicated a small difference between the theoretical and experimental values. This may be due to the possibility of oxazine ring opening by alkaline solution during the purification stage.[21]

Curing Behavior and Polymerization of the Novel Benzoxazine Monomers. The curing behavior of the novel monomers was examined by DSC. Figure 3 shows the DSC profiles for the monofunctional benzoxazines with and without propargyl group, P-appe and P−a, respectively. Conventional monomer without propargyl group, P−a, showed an exotherm with onset at ca. 201 °C and a maximum at 230 °C due to the ring-opening polymerization of benzoxazine. The amount of exthotherm was 62 cal/g. Novel monomer with propargyl group, P-appe, showed an exotherm starting at 191 °C

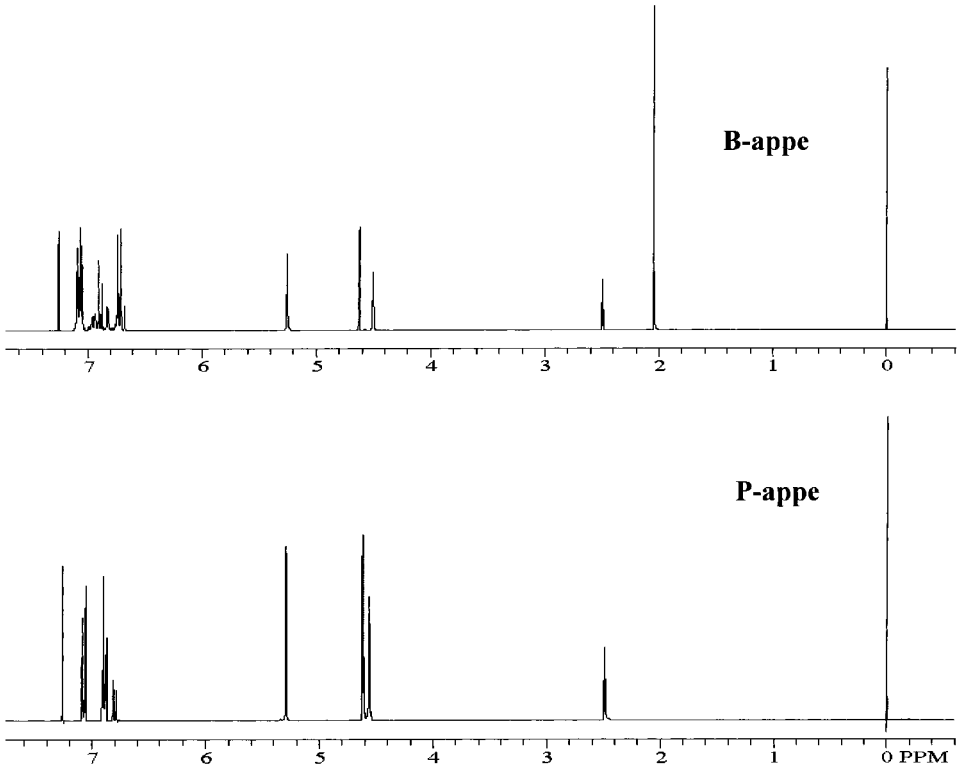
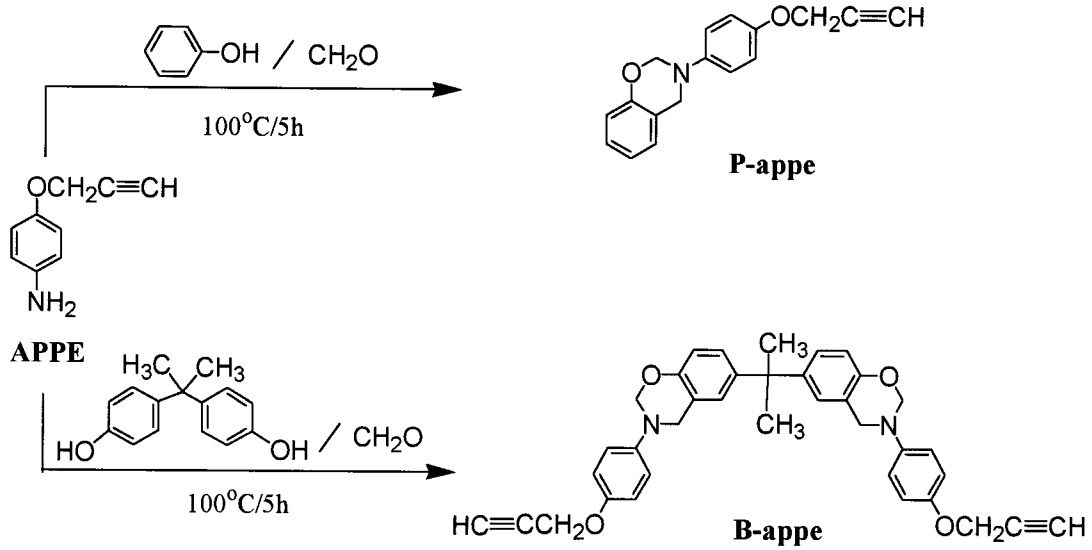


Figure 2. ^{1}H NMR spectra of P-appe and B-appe.

Scheme 3. Preparation of Benzoxazine-Based Phenyl Propargyl Ether (P-appe and B-appe)



with a maximum at 235 °C. The amount of exotherm of P-appe was 170 cal/g and was much larger than that of P−a. This shows that the ring-opening polymerization and cross-linking of propargyl group take place within the same temperature range. Another exotherm starting at ca. 325 °C with maximum at 341 °C was found only in the DSC thermogram of P-appe, which is attributed to the degradation of the cross-link structure.

Figure 4 shows the DSC profiles for the bifunctional benzoxazines with and without propargyl group, B-appe and B-a, respectively. B-a showed an exotherm on DSC with onset at ca. 223 °C and a maximum at 249 °C corresponding to the ring-opening polymerization of benzoxazine. The amount of exthotherm for B-a was 79 cal/g. For B-appe, the exotherm started at ca. 191 °C with a maximum at 241 °C corresponding to both the ring-opening polymerization of benzoxazine and the cross-linking of propargyl ether. The amount of exotherm of B-appe was 190 cal/g and was much higher than that of B-a. Another exotherm was also found in B-appe starting at ca. 330 °C, which is attributed to the degradation of the cross-linked polybenzoxazine.

Figure 5 shows the DSC profiles of B-appe after each cure cycle. The amount of exotherm corresponding to the ring opening of oxazine ring and cross-linking of propargyl group decreased after each cure cycle and disappeared completely after 240 °C/1 h cure, suggesting the completion of curing after 240 °C cure.

The monomers were processed into mold or into film form by melting the monomers at 90 °C and pouring into a glass mold or by casting as a film on a glass plate with thickness in the range 0.2−0.3 mm. The mold or

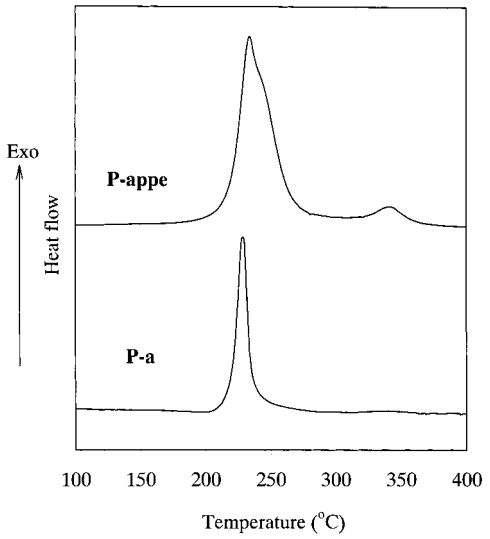


Figure 3. DSC profile of P-a and P-appe.

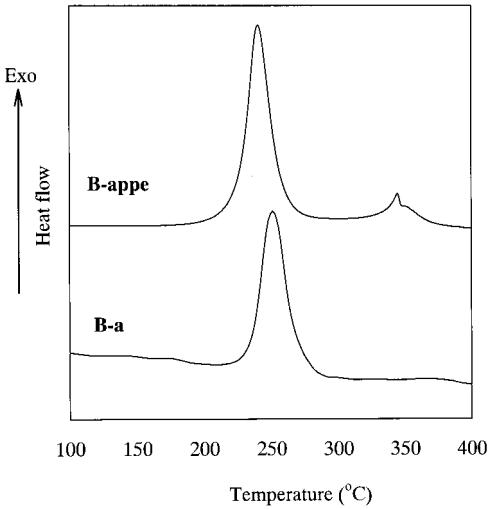


Figure 4. DSC profile of B-a and B-appe.

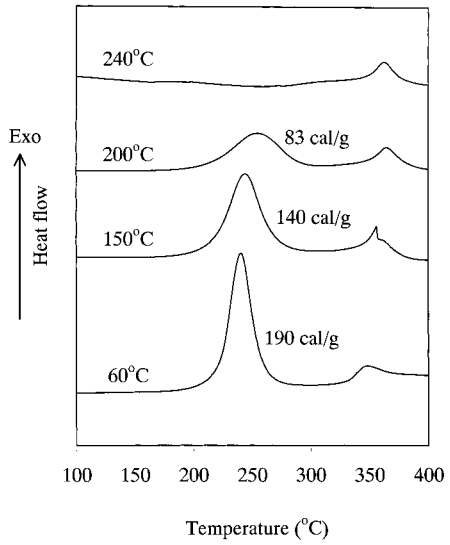


Figure 5. DSC profile of B-appe after each cure stage.

the cast films were heated under vacuum at 120 °C for 2 h and then cured at 150 and 180 °C for 1 h each, 200 °C for 2 h, and 240 °C for 1 h in an air-circulating oven. The cured samples of both PP-appe and PB-appe are transparent with a deep wine color.

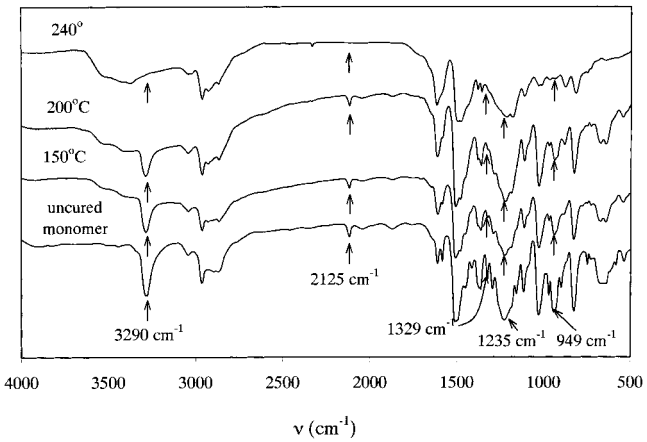
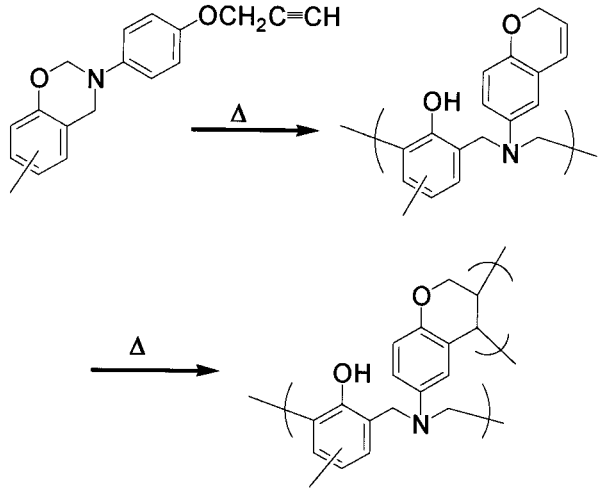


Figure 6. IR spectra of B-appe after each cure stage.

Scheme 4. Polymerization Mechanism of Benzoxazine-Based Propargyl Ether



The IR spectrum of B-appe after each cure cycle was recorded (Figure 6). We see clearly the disappearance of the characteristic absorption bands at 3290 and 2125 cm^{-1} due to the propargyl group. In addition, the characteristic absorption bands at 949 cm^{-1} disappeared, and the absorption at 1500 cm^{-1} due to the trisubstituted benzene ring and at 1329 cm^{-1} due to CH_2 wagging decreased. Instead, a new absorption appeared at 1489 cm^{-1} due to the tetrasubstituted benzene ring mode, suggesting the ring opening of benzoxazine to afford polybenzoxazine, whereas the absorptions at 1031 and 1235 cm^{-1} assigned to symmetric and asymmetric stretching of C−O−C did not disappear completely, similar to the typical PBa spectra due to the presence of the same absorption in the resultant chromene ring.

Aryl propargyl ether is known to undergo Claisen type rearrangement to 2***H***-chromenes (2***H***-1-benzopyranes) with thermal treatment and was then subsequently polymerized without any volatiles.[17b,18a] The mechanism of the polymerization of propargyl ether, Scheme 4, has been well established.[19] The ring opening of the benzoxazine ring and propargyl ether polymerization were found to occur in the same temperature range, i.e., simultaneously as described above in DSC analyses. Thus, Scheme 4 only illustrates the polymerization process.

Properties of the Novel Polybenzoxazines. ***(a) Dynamic Mechanical Analyses (DMA) of Polybenzoxazines.*** The DMA of the novel polybenzoxazines are

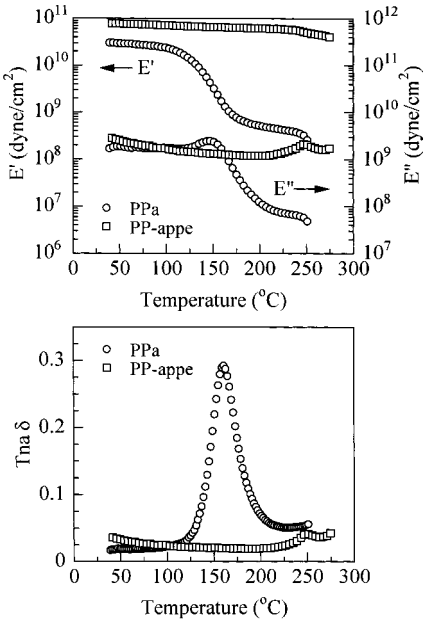


Figure 7. Viscoelastic analyses of PP-a and PP-appe.

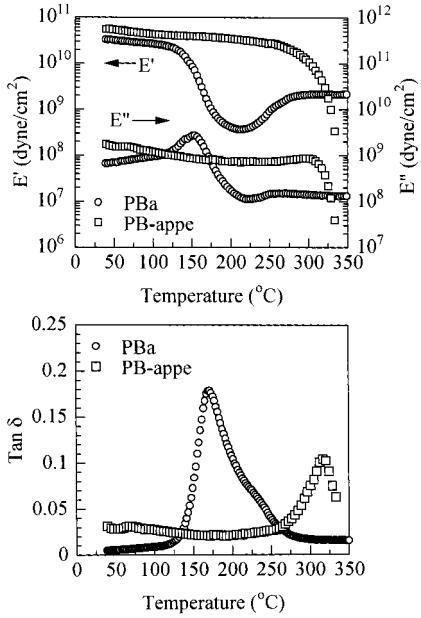


Figure 8. Viscoelastic analyses of PB-a and PB-appe.

shown in Figure 7 along with those of the typical polybenzoxazines without propargyl ether. The DMA results confirmed that the properties of polybenzoxazines are significantly improved by the incorporation of propargyl group. Figure 7 shows the temperature dependence of the storage and loss modulus for novel polybenzoxazine, PP-appe, along with PP-a. The introduction of the propargyl group as a cross-link site into polybenzoxazine increased the rigidity of the polymer by the increase of cross-link density, and hence the damping significantly decreased. As a result, the T_g shifted to relatively higher temperature. For PP-a, the T_g was 146 °C from the maximum of loss modulus and 161 °C from the maximum of tan δ peak, and the storage modulus, $\boldsymbol{E'}$, decreased sharply at ca. 110 °C, whereas the T_g for PP-appe was observed at 249 and 251 °C from the maximum of loss modulus and tan δ peak, respectively. Also, the storage modulus was maintained constant up to temperature higher than that of PP-a.

Bifunctional polybenzoxazines, B-appe and B-a, showed similar behavior of the DMA (Figure 8). In the case of PB-a, the storage modulus started to decrease at ca. 130 °C with T_g at 154 °C from the maximum of the loss modulus and 171 °C from the maximum of the tan δ peak. For PB-appe, the storage modulus started to decrease at 290 °C with T_g at 295 and 318 °C from the maximum of loss modulus and the maximum of tan δ peak, respectively. Care has to be taken in the interpretation of DMA because α-transition actually overlaps the onset of the decomposition. Anyway, the significant increase in T_g was confirmed, ca. 100 °C for monofunctional and ca. 140 °C for bifunctional, indicating the beneficial effect of cross-linking afforded by the introduction of propargyl group.

(b) Thermal Stability of Polybenzoxazines. Thermal stability of the novel polybenzoxazines was investigated by TGA. The TGA profiles of PP-a and PP-appe are shown in Figure 9, which indicated that the 5 and 10% weight loss temperatures ($\boldsymbol{T}_5$ and $\boldsymbol{T}_{10}$) for PP-a are 342 and 369 °C, whereas for PP-appe, $\boldsymbol{T}_5$ and $\boldsymbol{T}_{10}$ increased to 362 and 400 °C. Also, the char yield of PP-appe was 66% and much higher than PP-a (44%). A similar degradation profile was observed for polybenzoxazines obtained from bifunctional monomers. For typical polybenzoxazine, PB-a, the $\boldsymbol{T}_5$ and $\boldsymbol{T}_{10}$ are 310 and 327 °C, respectively (Figure 10), whereas for PB-appe, $\boldsymbol{T}_5$ and $\boldsymbol{T}_{10}$ increased to 352 and 388 °C. Also, the char yield of PB-appe was 61% and much higher than that of PB-a (32%). The increase in char yield suggests the reduction of polymer flammability.[22]

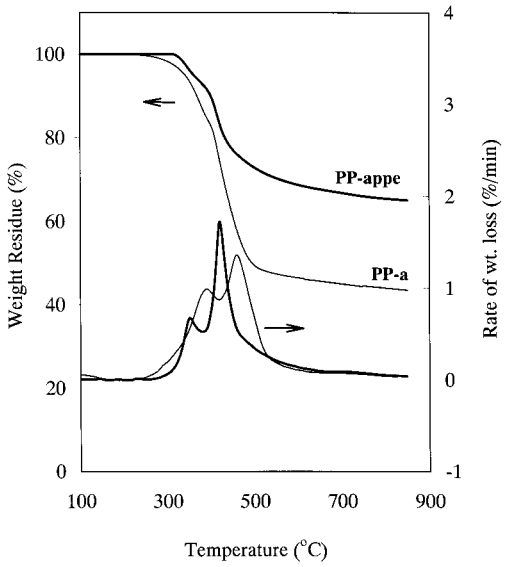


Figure 9. TGA of PP-a and PP-appe.

Another noticeable feature is that the degradation of both PP-appe and PB-appe occurred through two steps, as clearly observed from the derivatives of the weight loss in Figures 9 and 10. The typical polybenzoxazines, PP-a and PB-a, also appear to degrade through two or more steps. From the comparison of PP-a and PP-appe, we see that the amount of the weight loss in the first stage for PP-appe (9.8%) is smaller than that for PP-a (20.2%). The same result was obtained for the weight loss in the first stage of the bifunctional polybenzoxazines, PB-a (43.3%) and PB-appe (10.6%). These TGA results reflect the excellent thermal stability of the novel types of polybenzoxazine, which was realized by preventing aniline derivatives from volatilizing as a deg-

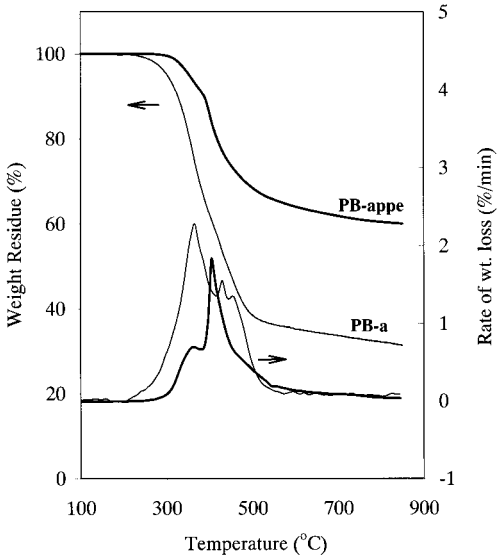


Figure 10. TGA of PB-a and PB-appe.

radation product by anchoring the aniline component through cross-linking by the propargyl ether groups.

Conclusion

We have successfully prepared novel benzoxazine monomers containing a propargyl ether group as the cross-link site. Ring-opening polymerization of oxazine ring and cross-linking of propargyl ether group occurred at almost the same temperature range, with the exotherm maximum on DSC at 230 °C for monofunctional and 249 °C for bifunctional monomer. Polybenzoxazines derived from the novel monomers exhibited significantly improved thermal properties than the typical polybenzoxazines. The T_g of the novel polybenzoxazines increased by ca. 100−140 °C than the typical polybenzoxazines. The storage moduli of PP-appe and PB-appe were maintained constant up to temperature higher by ca. 100 °C than those of PP-a and PB-a. The onset of the decomposition by 5% weight loss was increased by ca. 20−40 °C than the typical polybenzoxazines. The char yield of the novel polymers increased by ca. 22−29% more than the typical polybenzoxazines, suggesting the superior thermal stability of the novel polybenzoxazine.

Experimental Section

Materials. *p*-Nitrophenol, propargyl bromide, formalin (37%), tetrabutylammonium bromide, and tin(II) chloride monohydrate were used as received from Tokyo Kasei. Bis(3-phenyl-3,4-dihydro-2***H***-1,3-benzoxazinyl)isopropane (B-a) and 3-phenyl-3,4-dihydro-2***H***-1,3-benzoxazine (P-a) were kindly supplied by Shikoku Chemicals Co. and used as received.

Preparation of NPPE. In a 1 L flask, 400 mmol (55.65 g) of *p*-nitrophenol was dissolved in 500 mL of 0.8 N NaOH. The mixture was heated at 60 °C until a clear solution was formed. To this solution 40 mmol (12.89 g) of tetrabutylammonium bromide was added as a phase transfer catalyst. A solution of propargyl bromide (420 mmol, 49.96 g) in 200 mL of toluene was added portionwise to the solution. The mixture was kept stirring at 60 °C for 24 h. The mixture was cooled to afford a yellowish white precipitate, which was collected by filtration. In addition, the toluene layer was separated and washed repeatedly with water. Evaporating toluene afforded pale yellow white crystals. The crude product was dissolved in dioxane (ca. 300 mL) and poured into ca. 500 mL of water, then filtered, and finally washed repeatedly with 2 L of water until a white powder was obtained. The product was further purified by sublimation affording 63 g (92%) of NPPE as white crystals (mp 114−115 °C).

^{1}H NMR for NPPE ($CDCl_3$), ppm: $\delta = 2.58$ (t, ≡C−H), 4.79 (d, CH_2), 7.05 (d, H) and 8.30 (d, H).

Preparation of APPE. To a 2 L beaker equipped with a magnetic stirrer was added NPPE (31.9 g, 180 mmol) in 700 mL of dioxane. A cooled solution of stannous chloride dihydrate (203 g, 900 mmol) in concentrated HCl (500 mL) was added portionwise into the colorless solution of NPPE with keeping the temperature at ca. 10 °C by ice bath. After finishing the addition, the temperature was raised to room temperature. The mixture was stirred at room temperature for 2 days. The solution became more yellow in color. After neutralizing with aqueous sodium hydroxide, the solution was extracted with dichloromethane, and the organic layer was dried over anhydrous sodium sulfate. Evaporation of dichloromethane gave a yellowish brown viscous product. The crude product was purified by distillation under reduced pressure (bp 95 °C, 10 mmHg) to afford a colorless and highly viscous liquid, which crystallized into white platelet crystals after a while in the flask (mp 49−50 °C). Yield of APPE was 23 g (87%).

^{1}H NMR spectra for APPE ($CDCl_3$), ppm: $\delta = 2.18$ (t, ≡C−H), 3.2−3.6 (broad, NH_2), 4.5 (d, CH_2), 6.4−6.7 (d, d, 4Ar, H).

Preparation of Monofunctional Benzoxazine (P-appe). In a 500 mL flask, 200 mmol (16.23 g) of formalin (37%) in 100 mL of dioxane was cooled by ice bath. To this solution, APPE (100 mmol, 14.71 g) in 100 mL of dioxane was added portionwise. The solution was kept stirring for 30 min below 5 °C. Thereafter, a solution of phenol (100 mmol, 9.41 g) in 100 mL of dioxane was added. The solution was refluxed at 110 °C for 4 h. Removal of the solvent in a rotary evaporator at 50 °C gave a viscous residue (25.5 g) that was dissolved in 200 mL of ether and washed several times with 3 N sodium hydroxide solution and finally with distilled water. Then, the ether solution was dried with anhydrous sodium sulfate, followed by evaporation of ether under vacuum to afford pale yellow viscous fluid (19 g, 67%).

Elemental analysis of P-appe: Calcd for $C_{17}H_{15}NO_2$: C, 76.96%; H, 5.70%; N, 5.28%. Found: C, 75.85%; H, 5.71%; N, 4.90%.

^{1}H NMR ($CDCl_3$), ppm: $\delta = 2.49$ (t, ≡C−H), 4.55 (s, CH_2, oxazine), 4.61 (d, CH_2, propargyl), 5.29 (s, CH_2, oxazine) and 6.75−7.1 (8H, Ar).

Preparation of Bifunctional Benzoxazine (B-appe). Similar to the preparation of P-appe, B-appe was prepared from 200 mmol (16.23 g) of formalin (37%), APPE (100 mmol, 14.71 g), and bisphenol A (50 mmol, 11.41 g) in 300 mL of dioxane. The raw product (23 g) was purified by washing with 3 N sodium hydroxide solution to afford pale yellow crystals (17 g, 64%) with mp 61−63 °C.

Elemental analysis of B-appe: Calcd for $C_{37}H_{34}N_2O_4$: C, 77.87%; H, 6.01%; N, 4.91%. Found: C, 76.29%; H, 5.86%; N, 4.62%.

^{1}H NMR ($CDCl_3$), ppm: $\delta = 2.05$ (s, 6H, $2CH_3$), $\delta = 2.48$ (t, ≡C−H), 4.50 (s, CH_2, oxazine), 4.62 (d, CH_2, propargyl), 5.25 (s, CH_2, oxazine), and 6.6−7.1 (14H, Ar).

Measurements. IR spectra were obtained with JASCO spectrophotometer model FT/IR-420. Differential scanning calorimetry was conducted using Rigaku Thermo Plus 2 DSC8230 at a heating rate of 10 °C/min under nitrogen. NMR spectra were recorded on a Varian Mercury 300 (300 MHz) instrument. 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.

References and Notes

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