Synthesis and Polymerization of Novel Benzoxazine Monomers Containing *p*-Propargyl Ether Groups

Tarek Agag and Tsutomu Takeichi

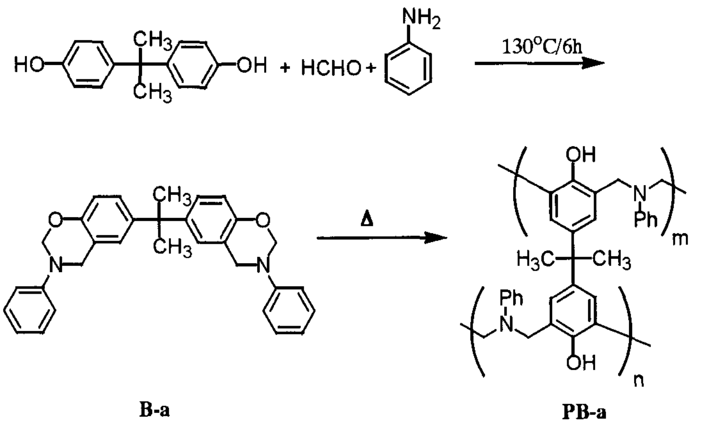
School of Materials Science, Toyohashi University of Technology,
Tempaku-cho, Toyohashi 441-8580, Japan

Abstract: Novel arylpropargyl ether terminated mono- and bifunctional benzoxazine monomers were synthesized. The structure of the novel monomers was confirmed by IR and ^{1}H-NMR. The DSC of arylpropargyl ether-functionalized benzoxazines showed a single exthotherm corresponding the ring opening polymerization of oxazine ring and polymerization of arylpropargyl ether group. The storage modulus of polybenzoxazine based on monofunctional arylpropargyl ether was maintained constant up to higher temperature with Tg at ca. 250°C. For bifunctional polybenzoxazines, the Tg was as high as ca. 300°C. The thermal stability of the novel polybenzoxazines was enhanced greatly with the presence of the arylpropargyl ether as another polymerizable site.

Introduction

Polybenzoxazine has been recently developed and studied as a novel class of phenol resins to overcome the shortcomings of the traditional phenol resins [1]. Besides the advantages of the traditional phenol 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 phenol resins [2].

Scheme 1 shows the preparation and polymerization of typical benzoxazine monomer, **B-a.** The typical polybenzoxazine, **PB-a**, has various advantages as mentioned above. But the shortage in the thermal properties of **PB-a**, e.g. the Tg and 5% wt loss are 150°C and 310°C, respectively, necessitates researches to further enhance the thermal and mechanical properties. One approach for improving the performance of polybenzoxazine is by alloying or blending with fillers or high performance polymers. We have reported some examples of properties improvement of **PB-a** by preparing polybenzoxazine-clay nanocomposites [3,4], by alloying with poly(imide-siloxane)s [5], and by modifying with hydroxyphenyl maleimide [6].



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

In this study, we report another approach for improving the properties of polybenzoxazine by preparing novel benzoxazine monomers containing propargyl ether as a cross-link site. We selected propargyl ether group because it has high temperature resistance and low water absorption as well as polymerizes with any volatiles.

Experimental

1. Preparation of p-nitrophenyl propargyl ether (NPPE)

p-Nitrophenyl propargyl ether (NPPE) was prepared following *Scheme 2* by the reaction between *p*-nitrophenol dissolved in aqueous NaOH and propargyl bromide in presence of tetrabutyl ammonium bromide as phase transferee catalyst. NPPE was obtained as colorless crystals in 92% yield (m.p. 114-115°C).

IR spectra of NPPE: 3240 and 2125 cm^{-1} attributable to the absorption of HC≡ and C≡C respectively. ^{1}H-NMR for NPPE ($CDCl_3$), ppm: δ= 2.6 (t, ≡C–H), 4.8 (d, CH_2), 7.05 (d, H) and 8.3 (d, H),

2. Preparation of p-aminophenyl propargyl ether (APPE)

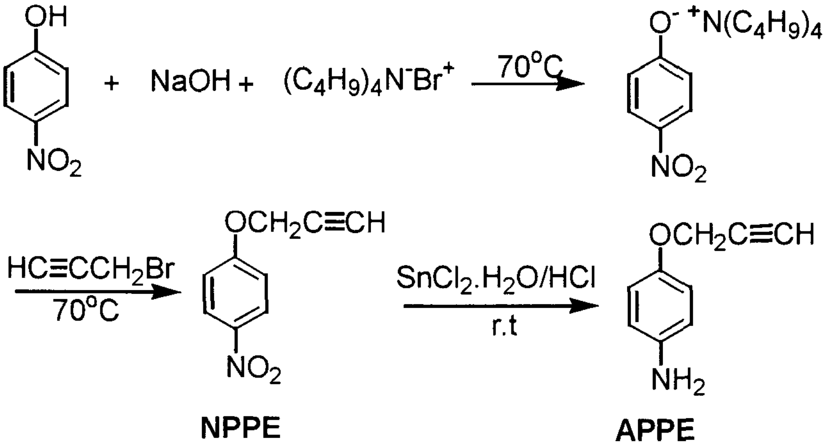
APPE was prepared by the reduction of NPPE in dioxane with stannous chloride dihydrate and conc. HCl. APPE was obtained as colorless crystals in 86% yield (m.p. 49-50°C).

IR spectra of APPE: 3240 and 2125 cm^{-1} attributable to the absorption of HC≡ and C≡C, respectively and at 3400 cm^{-1} due to amino group. ^{1}H-NMR spectra for APPE ($CDCl_3$), ppm: δ= 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).

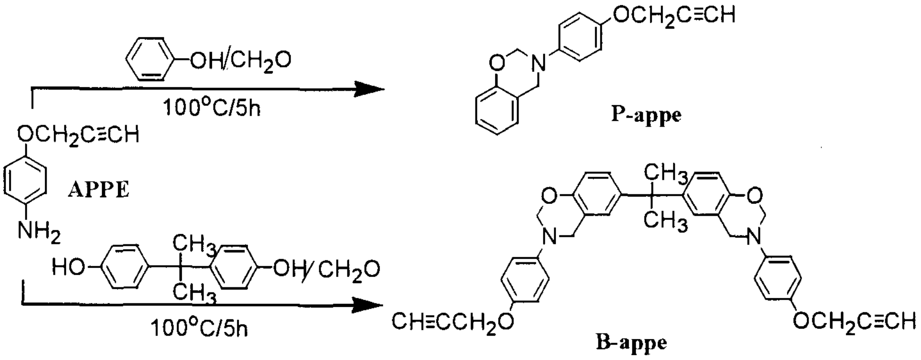
Results and Discussion

1. Preparation of aminophenyl propargyl ether-based monofunctional benzoxazine (P-appe) and bifunctional benzoxazine (B-appe)

For the preparation of P-appe, APPE was reacted with formalin and phenol in dioxane (*Scheme 3)*. P-appe was obtained as a yellow semisolid product in 67% yield. IR spectra of P-appe showed absorptions bands at 3240 and 2125 cm^{-1} attributable to HC≡ and C≡C, respectively, at 952 and 1500 cm^{-1} due to the trisubstituted benzene ring, at 1233 cm^{-1} due to the asymmetric stretching of C-O-C, and at 1327 cm^{-1} due to CH_2 wagging in benzoxazine structure. Also, the ^{1}H-NMR spectra confirmed the structure as follows: ($CDCl_3$), ppm: δ= 2.5 (t, ≡C–H), 4.55 (s, CH_2), 4.6 (d, CH_2), 5.29 (s, CH_2) and 6.75~7.1 (8H, Ar).



Scheme 2. Preparation of NPPE and APPE

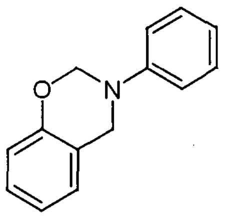


Scheme 3. Preparation of P-appe and B-appe

B-appe was similarly prepared as P-appe from bisphenol A, formalin and APPE. B-appe was obtained as yellow crystals in 64% yield (m.p. 60-62°C). IR spectra of B-appe showed absorptions bands at 3240 and 2125 cm^{-1} attributable to HC≡ and C≡C, respectively, at 952 and 1500 cm^{-1} due to the trisubstituted benzene ring, at 1233 cm^{-1} due to the asymmetric stretching of C-O-C, and at 1327 cm^{-1} due to CH_2 wagging in benzoxazine structure. ^{1}H-NMR spectra confirmed the structure of B-appe as follows: ($CDCl_3$), ppm: δ= 2.05 (s, 6H, $2CH_3$), δ= 2.5 (t, ≡C–H), 4.5 (s, CH_2, oxazine), 4.62 (d, CH_2, propargyl), 5.25 (s, CH_2, oxazine) and 6.6~7.1 (14H, Ar).

2. Cure behavior and polymerization of benzoxazine monomers

The cure behavior of novel monomers, **P-appe** and **B-appe,** was monitored by DSC along with the typical mono and bifunctional benzoxazines, **P-a** (*Fig. 1*) and **B-a**. *Fig. 2* shows the DSC thermogram of P-a and P-appe. The DSC thermogram of P-a showed a cure exotherm with onset at ca. 201°C and max at 230°C. The amount of the exotherm was 62 cal/g. The DSC cure of P-appe also showed an exotherm with onset at 204°C and max at 235°C corresponding to the ring opening polymerization of benzoxazine and polymerization of propargyl ether group with 170 cal/g as an amount exothermic heat which is higher than that of P-a.



P-a

Fig 1. Structure of P-a

The DSC cure of B-a and B-appe is shown in Fig 3. The DSC cure of B-a had an exotherm with onset at ca. 223°C and max at 249°C. In case of B-appe, the exotherm started at ca.177°C with max at 228°C corresponding to both ring opening polymerization of benzoxazine as well as the polymerization of propargyl ether. In addition, the amount of cure exotherm of B-appe (190 cal/g) is higher than that of B-a (80 cal/g). From the results of DSC, it was concluded that the oxazine ring opening polymerization and propargyl polymerization occurred almost the same temperature range.

The monomers were melted at ca. 90°C, and then poured into glass mold or casted as film on a glass plate with thickness in the range of 0.2~0.3 mm. The mold or the cast films were heated under vacuum at 120°C for 2h and then cured at 150°C and 180°C for 1h each, 200°C/2h and 240°C for 1h in an air oven.

IR spectra of the cured product showed that the absorption bands at 952 and 1500 cm^{-1} due to the trisubstituted benzene ring and at 1327 cm^{-1} due to CH_2 wagging completely disappeared. The

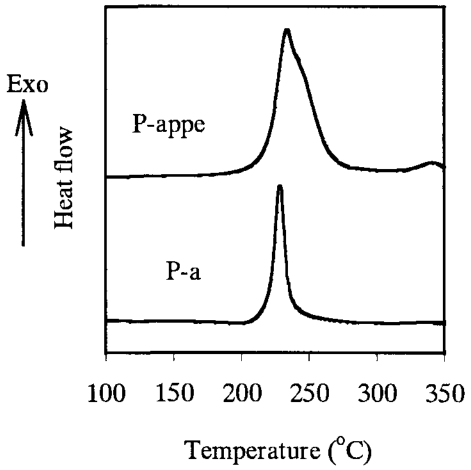


Fig 2. DSC cure of P-a and P-appe

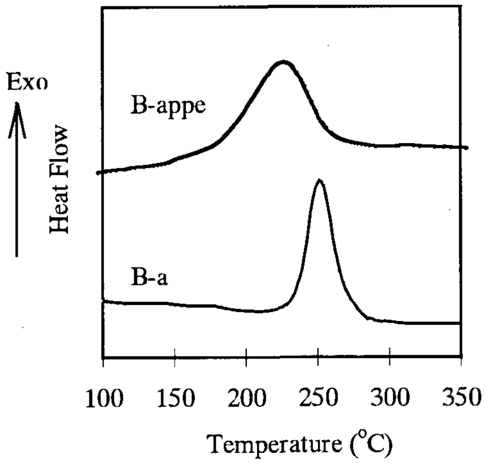


Fig 3. DSC cure of B-a and B-appe

absorption bands at 3272 and 2225 cm^{-1} due to propargyl group also completely disappeared. Whereas a new absorption appeared at 1489 cm^{-1} due to tetrasubstituted benzene ring mode suggesting the ring opening of benzoxazine monomer to afford polybenzoxazine.

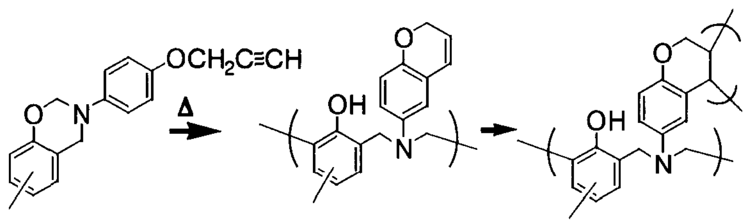
It has been confirmed that phenyl propargyl ether group undergo Claisen type rearrangement to 2H-chromenes (2-H-1-benzopyranes) [7]. The mechanism of the polymerization of propargyl ether shown in *Scheme 4* has been well established [8]. The ring opening of benzoxazine ring and propargyl ether polymerization occurred at the same temperature rage, i.e. simultaneously. Thus, *scheme 4* is shown only to illustrate the polymerization process. IR and DSC suggested that polybenzoxazine-chromene network was formed.

3. Properties of novel polybenzoxazines

i) Dynamic mechanical analyses (DMA)

The DMA of the novel polybenzoxazines are shown in Figs. 4 ~7 along with those of the typical mono- and bifunctional polybenzoxazines without propargyl ether. PP-a, polybenzoxazine derived from P-a, had Tg at ca. 150°C and the storage modulus, E', decreased sharply at ca. 110°C (Figs. 4 and 5). PP-appe, polybenzoxazine derived from P-appe, on the other hand, had Tg at ca. 250°C, and the storage modulus was maintained constant up to higher temperature.

Bifunctional polybenzoxazines, B-appe and B-a, showed the same behavior of the DMA (Figs. 6 and 7). In case of PB-a, polybenzoxazine derived from B-a, the storage modulus started to decrease at ca. 130°C with Tg at ca. 160°C. For PB-appe, polybenzoxazine derived from B-appe, the storage modulus started to decrease at 290°C with Tg at ca. 300°C (Figs. 6 and 7). Thus, the great increase in Tg was confirmed, ca. 100°C for monofunctional and ca. 140°C for bifunctional,



Scheme 4. Polymerization of benzoxazine containing phenylpropargyl ether

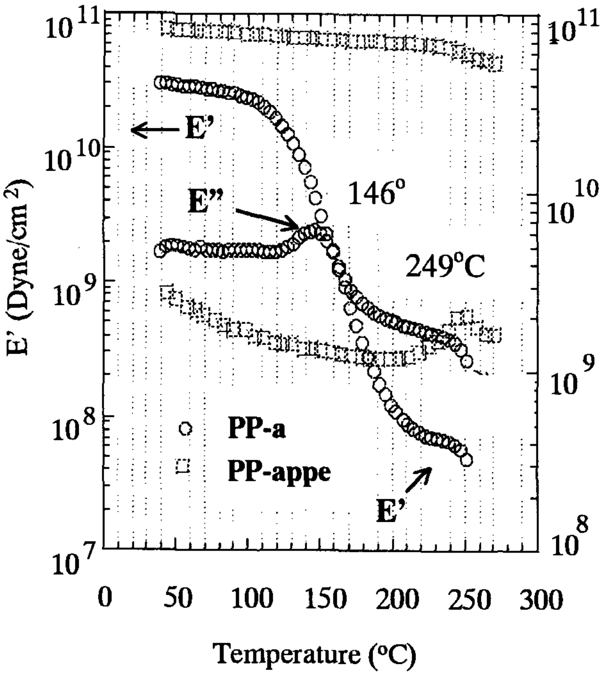


Fig 4.DMA of PP-a and PP-appe

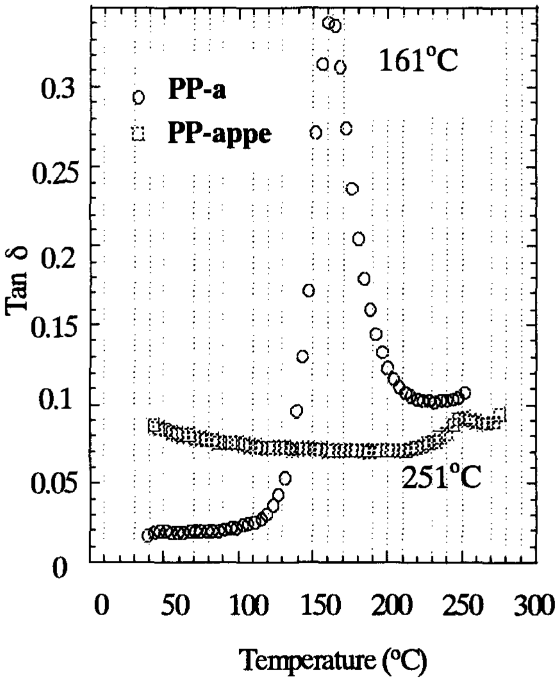


Fig 5. tan δ of PP-a and PP-appe

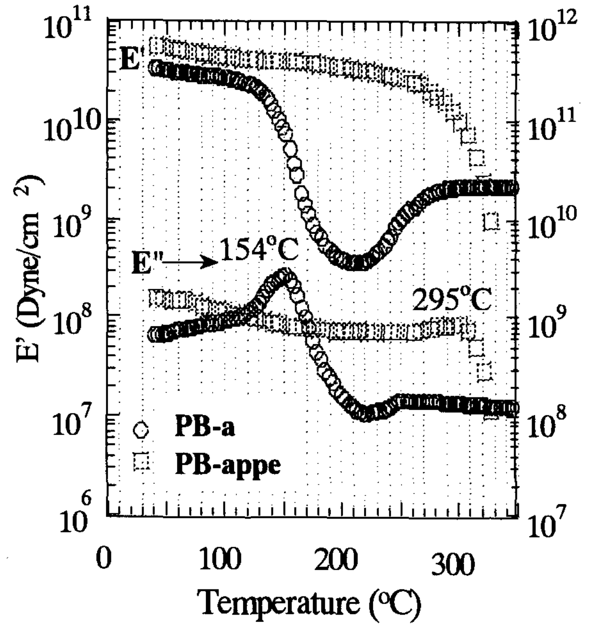


Fig 6. DMA of PB-a and PB-appe

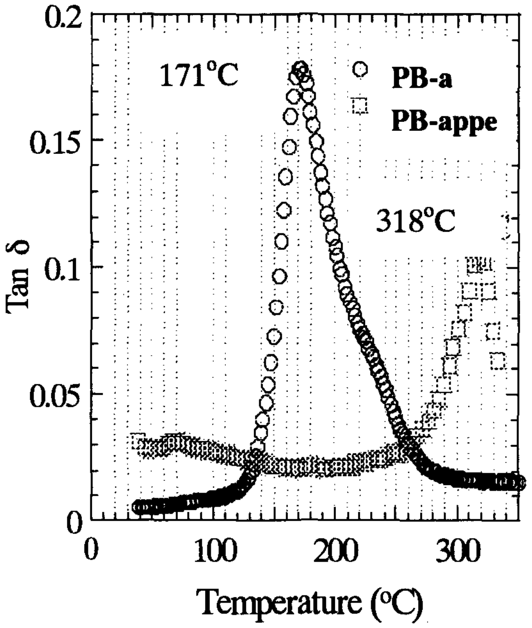


Fig 7. tan δ of PB-a and PB-appe

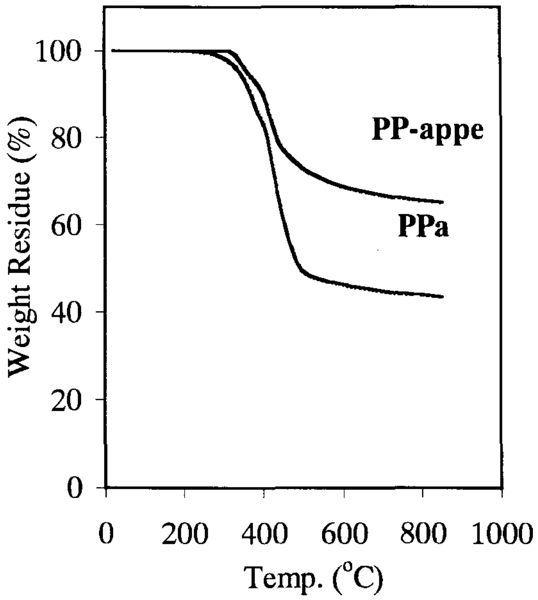


Fig 8. TGA of PP-a and PP-appe

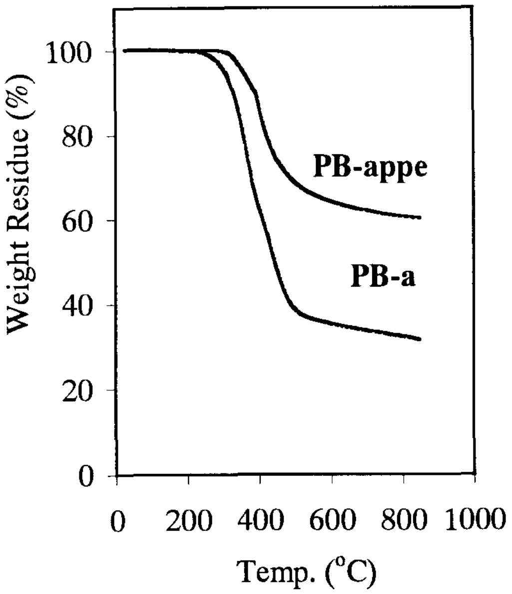


Fig 9. TGA of PB-a and PB-appe

indicating the effect of crosslinking afforded by the introduction of propargyl group.

ii) Thermal stability

Thermal stability of novel polybenzoxazines was investigated by TGA. The TGA degradation profiles of PP-a and PP-appe are shown in Fig. 8, which indicated that the 5 and 10% wt loss temperatures (T_5 and T_{10}) for PP-a are 342 and 369°C. Whereas for PP-appe, T_5 and T_{10} increased to 362 and 400°C. Also, the char yields of PP-a and PP-appe are 44 and 66% respectively. For PB-a, the T_5 and T_{10} are 310 and 327°C respectively (Fig. 9). Whereas for PB-appe, T_5 and T_{10} increased to 352 and 388°C. Also, the char yields for PB-a and PB-appe are 32 and 61%, respectively.

These results reflect the excellent thermal stability of these novel types of polybenzoxazine, which is due to preventing aniline from volatiling as a degradation product by anchoring through incorporation of propargyl ether as another polymerizable group.

References

1. Takeichi, T., Komiya, I., and Takayama, Y. *Kyoka-Purasutikkus* (in Japanese), **43**, 109 (1997)
2. Ning, X. and Ishida, H *J. Polym. Sci., Part A: Polym. Chem.,* **32**, 1121 (1994)
3. Agag, T. and Takeichi, T. *Polymer,* **41**, 7083 (2000)
4. Agag, T., Takeichi, T., Toda, H., and Kobayashi, T. *Int. J. Mater. and Product Tech.* in press
5. Agag, T. and Takeichi, T. *Polym. Prepr. Jpn*; **47**, 2922 (1998)
6. Agag, T. and Takeichi, T. *High Perform Polym.* in press (2001)
7. Reghunadhan Nair, C.P., Bindu, R.L., Krishnan, K. and Ninan, K.N. *Eur. Polym. J.* **35**, 235 (1999)
8. Douglas, W.E. and Overend, A. S. *Eur. Polym. J.* **27**, 1279 (1991)