

Novel High Performance Polybenzoxazines Based on Benzoxazine Monomers Containing *p*-Allyl Group

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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. 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 using solvent or solventless method. Fig. 1 shows the structure of the typical monomers P-a and B-a. Polybenzoxazines possess typical characteristics of the traditional phenolic resins such as heat resistance and good flame retardance properties. In addition, they provide unique characteristics like low water absorption and excellent dimensional stability.

Further enhancement on the thermal properties is also strongly expected. Two approaches are considered for performance improvement: (1) by blending with a high performance polymer or inorganic fillers or fibers [2-6], or (2) by preparing specially designed novel monomers [7].

Allylphenol based benzoxazine monomers have been reported [8], but the reported benzoxazine monomers, such as P-*alp* shown in Fig. 2, are not a good candidate for preparing high performance polybenzoxazines due to the absence of activated *ortho* position to the phenolic hydroxyl group rendering them difficult to polymerize through ring-opening, and also the difficulty of the polymerization of allyl phenyl types.

In this study, we report on the preparation of two novel allylamine-based benzoxazines, P-*ala* and B-*ala* with moderate cure condition and the outstanding thermomechanical behavior of the polymers therefrom.

EXPERIMENTAL

Preparation of P-*ala* and B-*ala*. Scheme 1 shows the preparation method for P-*ala* and B-*ala*. P-*ala* was prepared from allylamine (1.000 mol, 57.09 g), phenol (1.000 mol, 94.11 g), and paraformaldehyde (2.00 mol, 60.1 g) by mixing in an ice bath. The mixture was then stirred at 85°C for 2h. The as-synthesized monomer was purified by dissolving in diethyl ether, and washing with aqueous 3N sodium hydroxide, followed by evaporation of ether under vacuum to afford pale yellow liquid (126 g, 0.72 mol, 72%).

B-*ala* was prepared similarly by using bisphenol A instead of phenol for P-*ala*. A colorless crystal with m.p. 55-58°C was obtained in 71% yield.

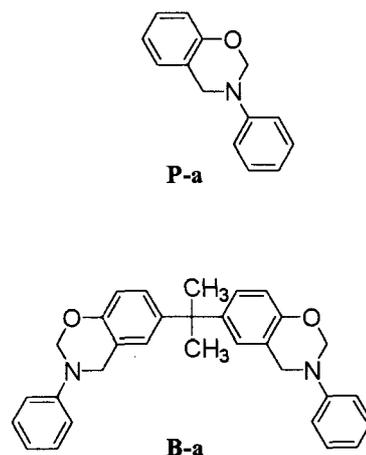


Fig. 1. Structure of the typical

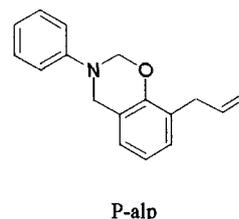


Fig. 2. Structure of P-*alp*

Preparation of P-alp. P-alp was similarly prepared from 2-allylphenol, aniline and paraformaldehyde, affording yellow liquid in 74% yield.

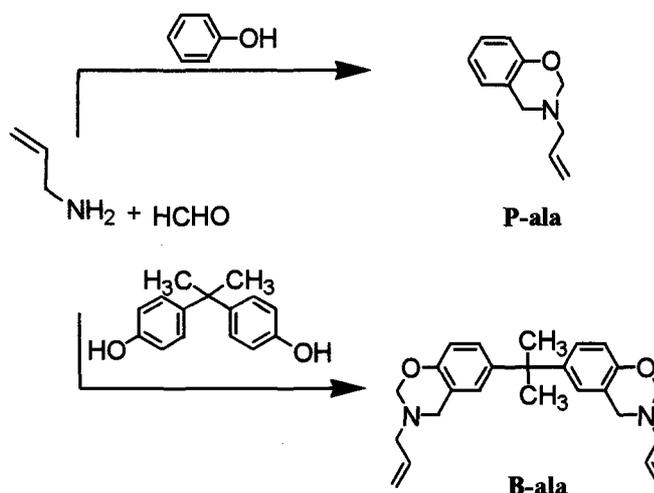
RESULTS AND DISCUSSION

Preparation and curing of the monomers

The chemical structures of both P-ala and B-ala were confirmed by both FT-IR and $^1\text{H-NMR}$. IR spectra showed the characteristic absorptions of benzoxazine structure for both P-ala and B-ala at 1230-1236, 1028-1036, 1327-1340, 920-950 and 1491-1500 cm^{-1} . Characteristic absorption bands assigned to allyl group appeared at 3049 and 1644 cm^{-1} .

The curing behavior of the novel monomers along with the typical benzoxazine monomers was examined by DSC. A sharp exotherm was observed for P-a corresponding to the ring-opening polymerization (Fig. 3). The onset and maximum temperatures of the exotherm were at 202°C and 230°C, respectively. The amount of exotherm for P-a was 62 cal/g. For P-ala, two exotherms were observed; the onset of the first exotherm was at 145°C with exotherm peak at 207°C due to the thermal cure of the allyl group and the onset of the second exotherm at 225°C with exotherm maximum at 260°C due to the ring-opening of the oxazine ring. The total amount of exotherm of P-ala was 84 cal/g. For P-alp, it showed only one exotherm with onset at 241°C and maximum at 263°C. The amount of exotherm was only 20 cal/g (Fig. 3). There was no exotherm for P-alp at lower temperature range corresponding to the thermal cure of the allyl group because of the difficulty of the radical polymerization of the allyl phenyl group due to the stability of the radical by resonance.

The DSC of B-a showed exotherm with onset at ca. 223°C and max at 249°C corresponding to the ring-opening polymerization of benzoxazine (Fig. 4). The amount of exotherm for B-a was 79 cal/g. For the novel B-ala, unsymmetrical broad exotherm was



Scheme 1. Preparation of P-ala and B-ala monomers

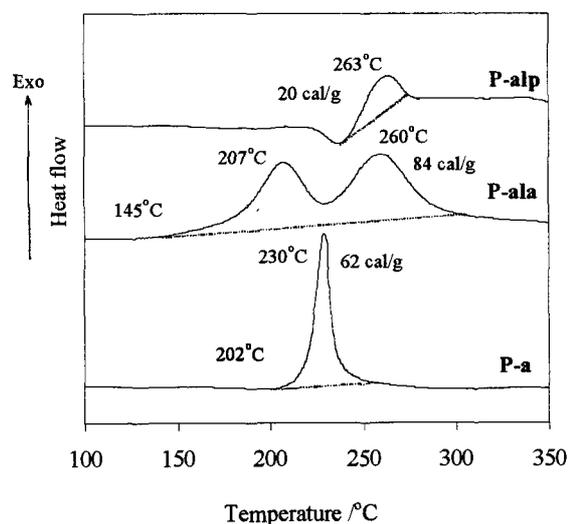


Fig. 3. DSC cure of P-a, P-ala and P-alp

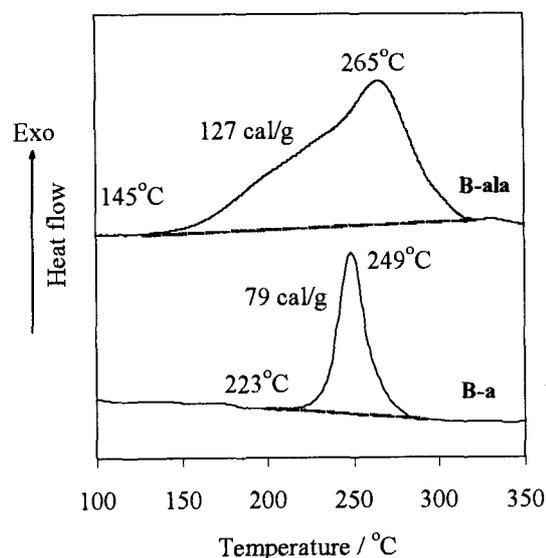


Fig. 4. DSC of B-a and B-ala

observed with onset at 145°C and maximum at 265°C corresponding to both the crosslinking 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.

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 step-wise at 80°C for 5h, 110°C for 3h, and then at 160°C, 180°C and 200°C for 2h each in an air oven. The samples were then postcured at 220°C and 240°C for 1h each in an air-circulating oven. All the cured samples with thickness about 0.4 mm were transparent and having red-brown color.

(b) Viscoelastic analyses of polybenzoxazines

The viscoelastic analyses of the novel monofunctional polybenzoxazine, PP-ala, were examined along with the typical polybenzoxazine, PP-a and PP-alp (Fig. 5). The introduction of allyl group as a crosslinking site into polybenzoxazine increased the rigidity of the polymer by the increase of crosslinking density. As a result, the T_g for PP-ala shifted to as high as 285°C from the maximum of loss modulus. 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 and the storage modulus dropped sharply at ca. 70°C. The poor thermomechanical properties for PP-alp are attributed to the low crosslinking density of the matrix which arises from the difficulty in the polymerization of the monomer.

Polymers derived from bifunctional polybenzoxazines, PB-ala and PB-a, showed similar behavior as shown in Fig. 6. For PB-ala, T_g shifted to as high as 298°C (E'' max), owing to the introduction of allyl group. Accordingly, the storage modulus of PB-ala was maintained up to much higher temperature and started to decrease at 295°C.

These viscoelastic analyses 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 crosslinking afforded by the introduction of allyl group as another crosslinkable site.

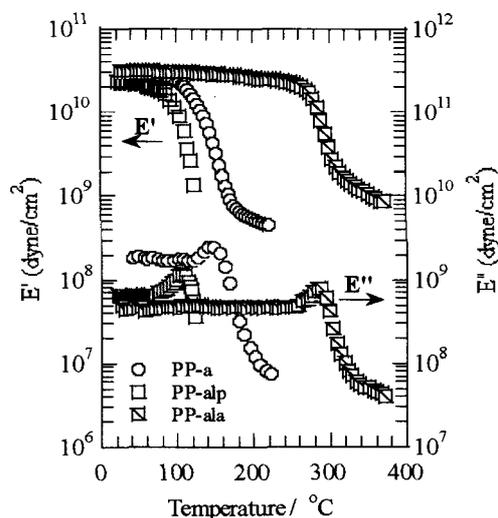


Fig. 5. Viscoelastic analyses of PP-a, PP-alp and PP-ala.

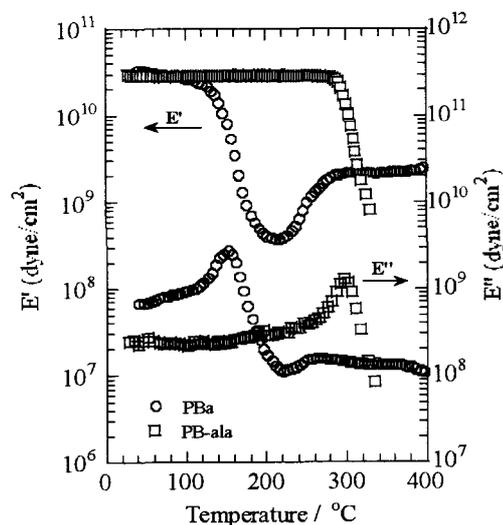


Fig. 6. Viscoelastic analyses of PB-a and PB-ala.

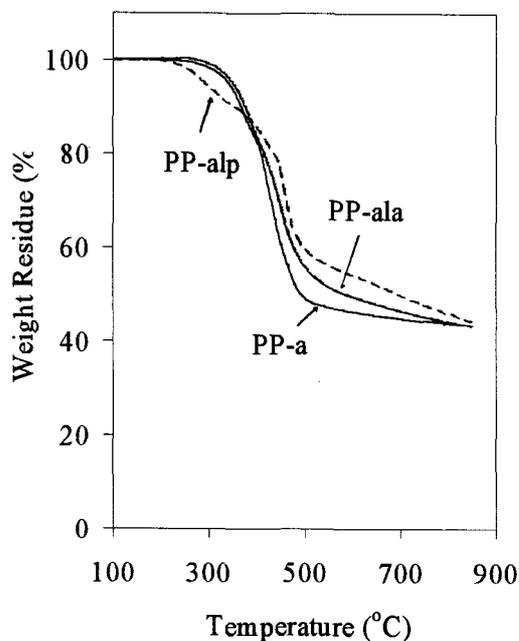


Fig. 7. TGA of PP-a, PP-alp and PP-ala.

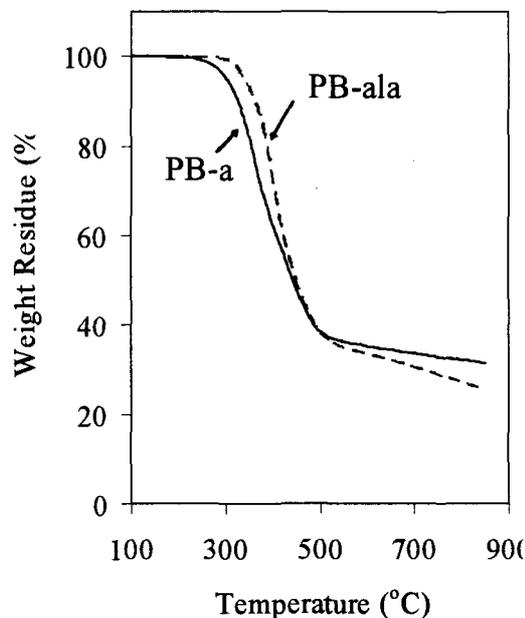


Fig. 8. TGA of PB-a and PB-ala.

(c) Thermal stability of polybenzoxazines

Thermal stability of the novel polybenzoxazines was investigated by TGA. The 5 and 10% weight loss temperatures (T_5 and T_{10}) for PP-a are 342 and 369°C, respectively (Fig. 7). 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.

For typical polybenzoxazine, PB-a, the T_5 and T_{10} are 310 and 327°C, respectively with char yield about 32% (Fig. 8). 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 volatilizing at the initial stages of the degradation due to the crosslinking. The char yield of PB-ala was 28%, which is less than that of PB-a (32%) due to the aliphatic crosslinks resulted from the polymerization of allyl group.

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