

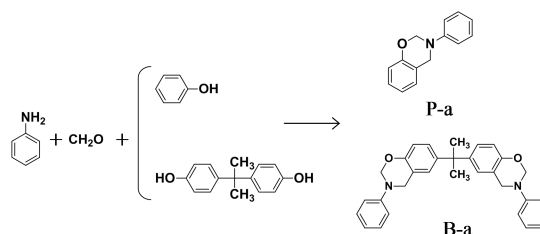
Synthesis of Novel Benzoxazines Having Vinyl Groups and Copolymerization with Vinyl Monomers

Tsutomu Takeichi (竹市 力), Thongpradith SOULIDETH, Takehiro KAWAUCHI (河内岳大)

Department of Environmental and Life Sciences, Toyohashi University of Technology
Tempaku-cho, Toyohashi 441-8580, Japan

1. Introduction

Invention of polybenzoxazines as novel type of phenolic resins has been recognized since over the last decades to recover the disadvantages associated with the conventional phenolic resins. Benzoxazine monomers can be synthesized from the reaction of phenols with formaldehyde and primary amines as shown in **Scheme 1**. Benzoxazine resins possess outstanding properties of the traditional phenolic resins such as excellent heat resistance, flame retardency and low dielectric property. The manner of synthesis provides tremendous molecular design flexibility of the benzoxazine structure. The ring-opening polymerization of benzoxazine through thermal cure process does not need any acid or base catalysts, releasing no byproducts, and excellent dimensional stability is achieved. These remarkable characteristics promoted polybenzoxazines as high performance resins. However, polybenzoxazines have found some disadvantages associated with phenolic resins such as brittle property due to the network structure, high temperature demands (ca. 200 °C) for the ring-opening polymerization and thermal properties is not high enough for high performance applications [1,2].



Scheme 1. Preparation of benzoxazines.

So far, four strategies can be categorized as the promising approaches to overcome the above-mentioned shortcomings of polybenzoxazines: (1) introducing of cross-linkable units into benzoxazine, (2) synthesis of high molecular weight benzoxazines, (3) incorporation of high performance polymers by blending and alloying, and (4) hybridization with inorganic materials.

In this study, novel benzoxazines having vinyl groups, P-4va, B-4va and P-3va, as shown in **Figure**

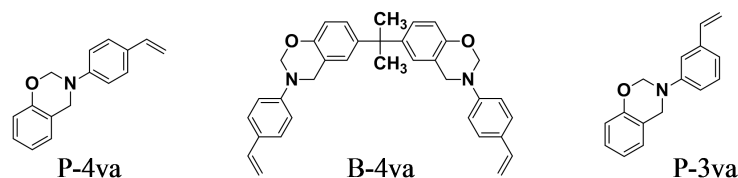


Figure 1. Benzoxazines having vinyl groups.

1, were synthesized, aiming to improve the thermal properties of polybenzoxazines by increasing the cross-link density through the chain polymerization of vinyl groups and the ring-opening polymerization of benzoxazines. Furthermore, the vinyl group-containing benzoxazine was copolymerized with various vinyl monomers, expecting as a novel approach to obtain high performance polybenzoxazine.

2. Results and Discussion

2.1 Syntheses and curing behavior of novel benzoxazines. Benzoxazines having vinyl groups (**Figure 1**) were synthesized from phenol or bisphenol A, 3- or 4-vinylaniline and paraformaldehyde. The chemical structures of the monomers were confirmed by FT-IR and ¹H NMR analyses.

The polymerization behavior of the monomers was monitored by DSC (**Figure 2**). The onsets of exothermic peaks were between 130-210 °C with the exothermic amounts in the range of 49-108 kJ/mol due to the chain polymerization of the vinyl group and the ring-opening polymerization of benzoxazine.

2.2 Preparation and thermal properties of polybenzoxazine films: The 50 wt% solutions were cast on glass substrates. The cast solutions were thermally treated under air oven at 50 °C for 12 h, and further cured at 100, 150, 200 and 240 °C for 1 h each, affording reddish transparent polybenzoxazine films with thickness in the range of 40 - 75 μm.

The thermal cure of the monomers afforded polybenzoxazine films that have glass transition temperature (*T_g*) at 244-250 °C, as shown in **Figure 3**. The 5 % weight loss temperature (*T₅*) of the polybenzoxazines were determined to be 350-358 °C and the char yield at 850 °C was 45-49 %, exhibiting that higher thermal properties were achieved by the introduction of vinyl groups.

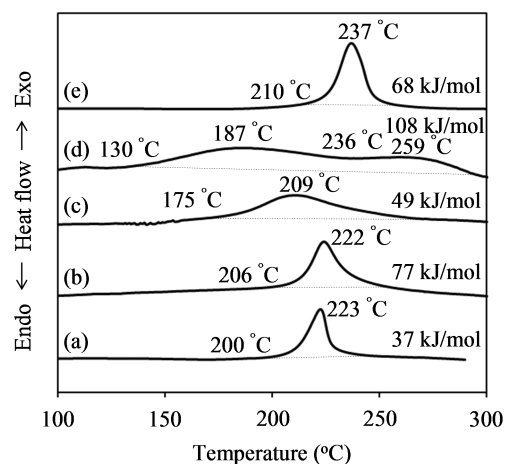


Figure 2. DSC curves of P-a (a), B-a (b),

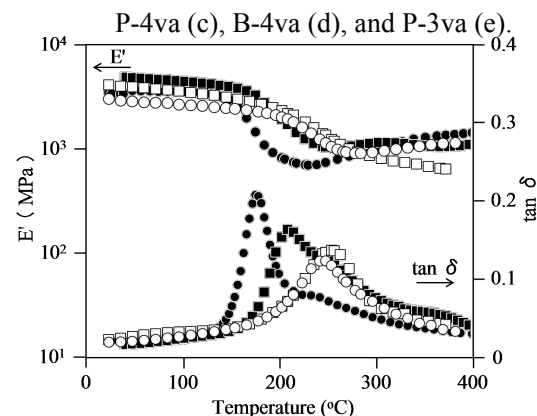
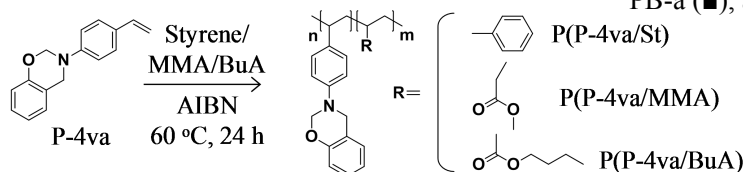


Figure 3. DMA results of PP-a (●), PP-4va (○), PB-a (■), and PB-4va (□).



Scheme 2. Preparation of copolymers.

2.3 Preparation of copolymers. P-4va was copolymerized with various vinyl monomers such as styrene, MMA, or BuA in benzene using AIBN as radical initiator at 60 °C for 24 h (**Scheme 2**). The chemical structures were confirmed by FT-IR and ¹H NMR. The molecular weights were identified by SEC. The *M_w* of P(P-4va/St), P(P-4va/MMA), and P(P-4va/BuA) was 8300, 1900, and 13800, respectively. It was confirmed that the copolymers contain pendent benzoxazine, which can be cured at higher temperature range. The curing behavior of the copolymers was investigated by DSC. The exothermic peaks were found at 229-250 °C, while the exothermic amounts were between 11-37 kJ/mol, corresponding to the ring-opening polymerization of benzoxazine component.

2. 4 Thermal properties of copolymers:

Thermal cure of the copolymer films up to 240 °C gave films having T_g (from $\tan \delta$) at 307 °C for P(P-4va/MMA), and 283 °C for P(P-4va/BuA), against 244 °C of PP-4va by DMA (Figure 4). This higher T_g of the copolymers suggests that reaction of the vinyl group during the polymerization was very effective. The T_5 of the copolymers was found in the range of 339-352 °C with high char yield.

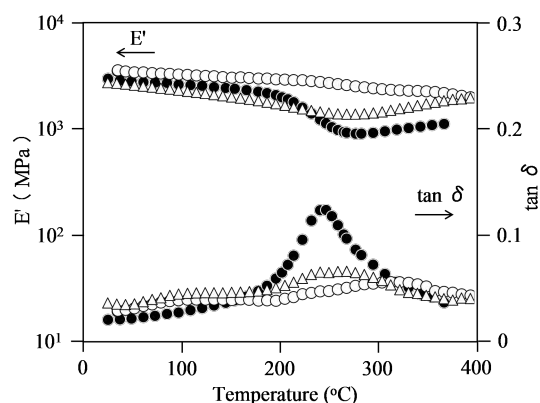


Figure 4. DMA results of PP-4va (●), P(P-4va/MMA) (○), and P(P-4va/BuA) (Δ).

3. Conclusion

Novel benzoxazines having vinyl groups were successfully prepared. The cured polybenzoxazine films exhibited significantly improved thermal properties due to the formation of increased network structures through the chain polymerization of vinyl groups and the ring-opening polymerization of benzoxazines. Furthermore, a series of copolymers having pendent benzoxazine were successfully synthesized through radical copolymerization of P-4va with vinyl monomers. After the ring-opening polymerization of pendant benzoxazines, copolymer with BuA gave significantly improved tough films, and copolymer with PMMA enhanced thermal and mechanical properties of polybenzoxazine.

4. References

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