

# Novel Method for Preparation of Poly(benzoxazinone-imide)

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Poly(amide acid) containing pendant ethoxycarbonyl groups was prepared as a precursor of poly(benzoxazinone-imide). DSC of poly(amide acid) showed two broad endotherms, one at 153°C due to imidization and the other at 359°C due to benzoxazinone ring formation. Poly(amide-imide) was prepared by the thermal treatment of poly(amide acid) at 300°C/1h, and then was cured further at 350°C/2h to convert into poly(benzoxazinone-imide) by dealcoholization. The storage modulus of poly(benzoxazinone-imide) was almost constant up to 400°C and no T<sub>g</sub> was detected below 400°C. A remarkable increase in the tensile modulus occurred in compare with poly(amide-imide). The poly(benzoxazinone-imide) showed higher hydrolytic stability than Kapton type polyimide. Thermogravimetric analysis indicated that poly(benzoxazinone-imide) has very good thermal stability.

**Key words:** Poly(benzoxazinone-imide), Tensile property, Thermal stability.

## Introduction

Polymers containing heterocyclic rings in the main chain are becoming increasingly important technologically because of the attractive combination of thermal and mechanical properties conferred by the presence of heterocyclic units. Aromatic polyimides are one of the most important engineering materials because of their outstanding thermal and mechanical properties as well as oxidative stability [1]. Thus, polyimides have been used in various applications [2].

On the other hand, polybenzoxazinone is a class of heterocyclic polymers of considerable promise due to its high thermal resistance and particularly highly resistance to hydrolytic degradation against strong acid or alkali [3-6]. A series of polybenzoxazinones containing imide ring, amide and ester linkage have been

recently synthesized as new thermostable polymers [7-9]. The reported methods for preparation of poly(benzoxazinone-imide), however, have some drawbacks like the long pathway and the solubility problems of the precursors [9]. In this study, we prepared poly(amide-imide) with ester groups *ortho* to the amide linkage as a precursor of novel type of poly(benzoxazinone-imide).

## Experimental

### 1. Preparation of 4,4'-diamino-6-ethoxy carbonyl benzanilide (AECB)

4,4'-Dinitro-6-ethoxycarbonyl benzanilide which was prepared according to the reported method [10] was reduced by 5% Pd/C and ammonium formate in DMF. AECB was obtained as pale yellow fine needles after recrystallization from propanol. The overall yield was 82% with m.p. 156-157°C.

## 2. Preparation of poly(benzoxazinone-imide)

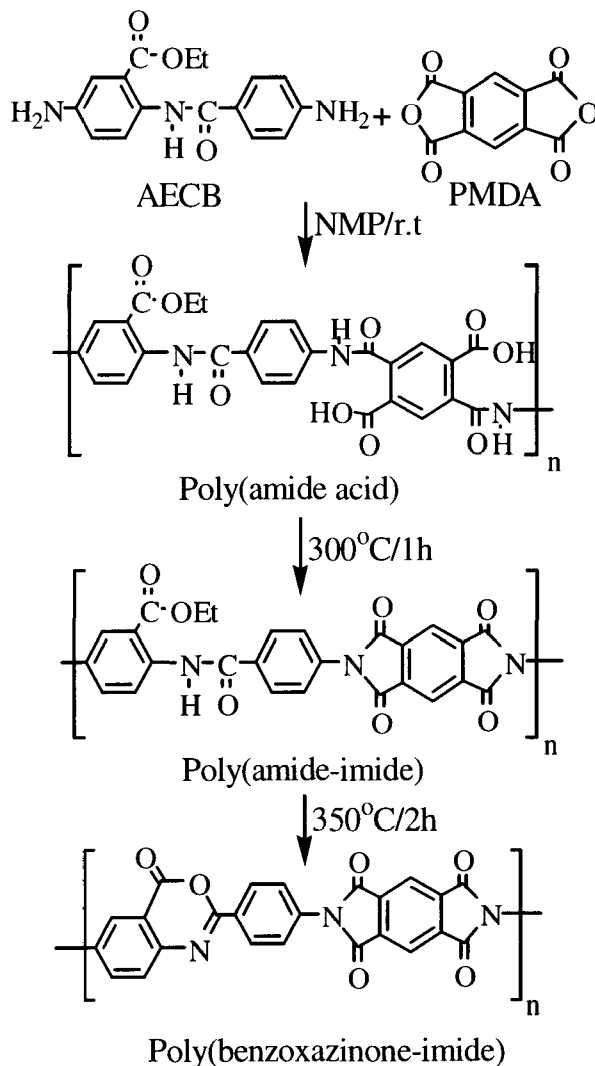
Poly(amide acid) has been prepared by reacting a mixture of AECB and PMDA in NMP. The yellow viscous solution was cast on glass plate, dried (70°C/5h) and imidized as fixed on glass plate by heat treatment at 150°C, 200°C, 250°C, and 300°C for 1h each to get yellow transparent film of poly(amide-imide). Poly(amide-imide) film was further cured at 350°C for 2h in air to get transparent poly(benzoxazine-imide) film of pale wine color.

### Results and Discussion

#### 1. Preparation of the poly(benzoxazinone-imide)

The preparation of poly(benzoxazinone-imide) is shown in Scheme 1. AECB was reacted with PMDA to prepare poly(amide acid) containing pendant ester groups with relatively high viscosity ( $\eta_{red} = 1.28$  dL/g in NMP at 30°C).

The imidization of poly(amide acid) was monitored by IR after each cure stage. The peaks at 1780 and 1720  $\text{cm}^{-1}$  attributable to the imide linkage increased after each stage of curing at 150°C, 200°C, 250°C, and 300°C for 1h suggesting the formation of poly(amide-imide) containing pendant ester groups in *ortho* position to the amide linkage. Poly(amide-imide) film was cured further at 350°C for cyclization by dealcoholization from the amide linkage and the *ortho* ester group to form poly(benzoxazinone-imide) as shown in Scheme 1. After 350°C/2h cure stage, new absorptions appeared at 1750  $\text{cm}^{-1}$  and at 1050  $\text{cm}^{-1}$  due to the carbonyl and ether of lactone in benzoxazinone ring. At the same time, the absorption at 1680  $\text{cm}^{-1}$  due to carbonyl of amide functionality almost



Scheme 1. Preparation of poly(benzoxazinone-imide)

disappeared.

DSC was measured to monitor the curing of the poly(amide acid). Fig. 1a shows the DSC of the poly(amide acid) after drying at 70°C for 5h. As shown in this figure, there are two broad endotherms, the first started at 122°C with maximum at 153°C due to imidization. The second endotherm started at 274°C with maximum at 359°C due to cyclization to form benzoxazinone ring. Both of the two endotherms are in accord with the weight loss in the TGA of poly(amide acid) as shown in Fig. 2a. Fig. 1b showed

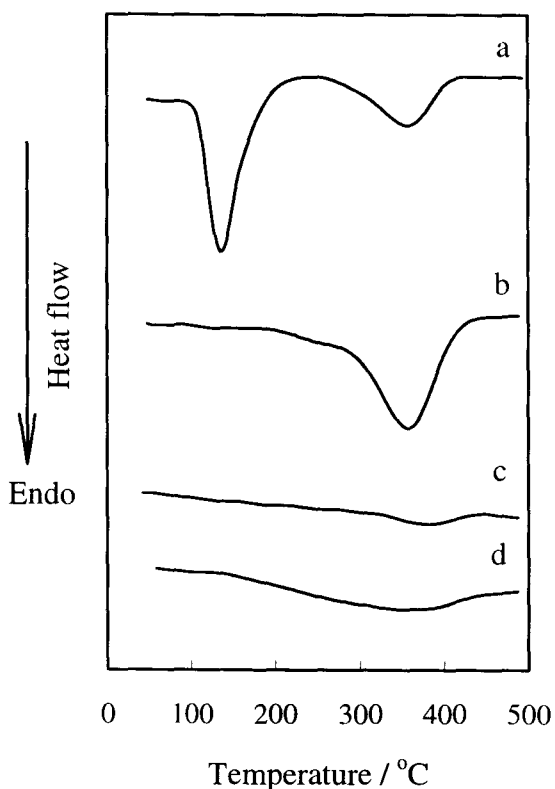


Fig.1. DSC of poly(amide acid) after different thermal treatment. a; 70°C/5h, b; 300°C/1h, c; 350°C/1h, and d; 350°C/2h.

the DSC thermogram of the film after 300°C/1h cycle which showed the disappearance of the first endotherm due to imidization. The endotherm due to dealcoholization, however, is still present after 300°C cure cycle. DSC and TGA suggested that the 300°C/1h cure cycle was enough to achieve complete imidization and formation of poly(amide-imide). In case of the film cured at 350°C for 1h (Fig. 1c), there was still a small endotherm. This endotherm was completely disappeared by the 350°C/2h cure cycle (Fig. 1d) due to the completion of dealcoholization and cyclization. The DSC after the 350°C/2h cure cycle was also in accord with TGA decomposition after curing at 350°C/2h. Fig. 2c shows the finishing of the dealcoholization after the last cure cycle which indicates cyclization was achieved to

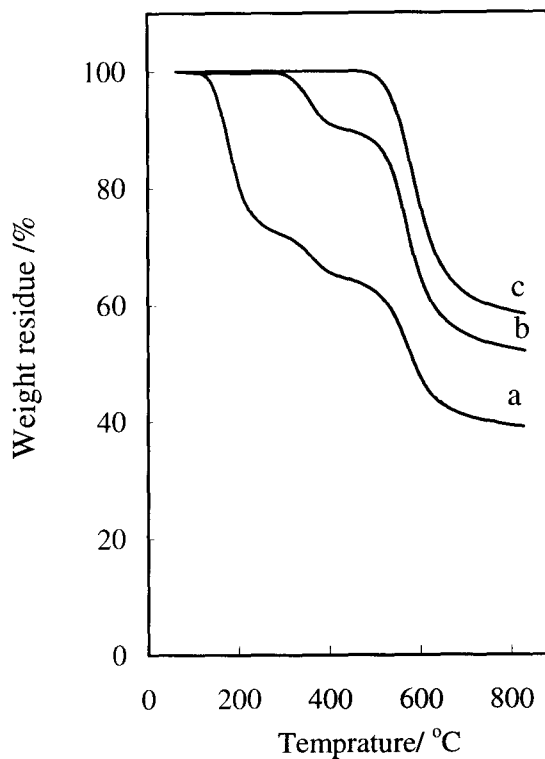


Fig.2. TGA of poly(amide acid) after different thermal treatment. a; 70°C/5h, b; 300°C/1h, and c; 350°C/2h under argon.

form poly(benzoxazinone-imide).

## 2. Properties of the poly(benzoxazinone-imide)

The dynamic mechanical properties were recorded for the poly(amide-imide) film prepared by the thermal treatment of poly(amide acid) at 300°C/1h and poly(benzoxazinone-imide) film prepared by further heating of the poly(amide-imide) film at 350°C/2h. The storage modulus of the poly(amide-imide) film (Fig. 3a) dropped at ca. 260°C and started to increase again at 350°C. In case of poly(benzoxazinone-imide) film (Fig. 3b), little drop was observed on the modulus up to 400°C. This behavior reflects that the film became stiffer due to the increase of the rigidity of the chain after cyclization and benzoxazinone ring formation.

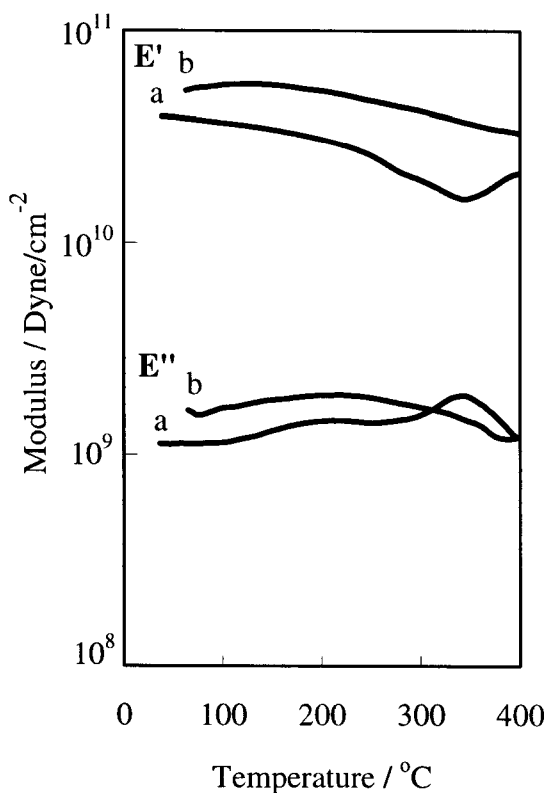


Fig.3. Viscoelastic analyses of a; poly(amide-imide) and b; poly(benzoxazinone-imide)

Tensile properties of poly(amide-imide) and poly(benzoxazinone-imide) were measured. The tensile modulus of the poly(amide-imide) film which was thermally treated at 300°C/1h was ca. 3.6 GPa. The tensile modulus increased to be ca. 7.1 GPa after postcuring at 350°C/2h. The tensile strength increased slightly, but the elongation at break decreased. This behavior occurred due to the formation of benzoxazinone ring in addition to imide ring which led the chain to be a rigid rod.

The hydrolytic stability of poly(benzoxazinone-imide) and Kapton type polyimide was studied by immersing in 10% NaOH solution. It was found that the increase in the weight of the polyimide film was much faster than of poly(benzoxazinone-imide) due to the hydrolysis of the imide ring.

The increase in the weight is due to the formation of sodium salt of poly(amide-acid). This behavior reflects the higher hydrolytic stability of the poly(benzoxazinone-imide) in compare with polyimide due to the presence of the highly hydrolytically stable oxazinone ring.

TGA measurement of poly(benzoxazinone-imide) in argon atmosphere shows that the 5% weight loss temperature was at 535°C which reflects the good thermal stability of this material. This poly(benzoxazinone-imide) is more thermally stable than the reported aromatic poly(benzoxazinone-imide)s which contain methylene bridge in the diamine used [8,9].

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