

# PREPARATION AND PROPERTIES OF POLYIMIDES CONTAINING CROSSLINK SITE IN THE MAIN CHAIN

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## ABSTRACT

Various polyimides containing crosslink sites in the backbone were prepared and characterized. As crosslink sites, internal acetylene units that are linked *meta* and *para* to the aromatic units, *m-intA* and *p-intA*, respectively, were utilized. Crosslinking affords high glass transition temperature ( $T_g$ ) and thus excellent physical properties even at high temperatures. The use of *p-intA* in combination with appropriate acid dianhydrides gave polyimides that have excellent physical properties, especially by drawing the films uniaxially.

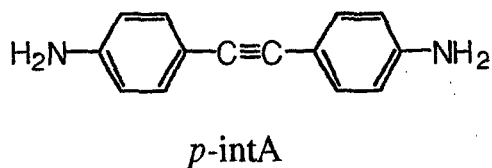
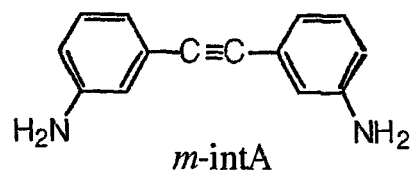
## INTRODUCTION

Polyimide is one of the most thermally stable polymers and has been used in many applications. The insoluble and infusible nature of the initial polyimide was improved by several approaches, which in turn made those processable polyimides less thermally stable and less solvent resistant. One prospect approach to solve this problem is the introduction of crosslink site into the polyimide backbone or as a pendent group, thus making it possible to cure at or after processing.

We have been studying crosslinking behavior of internal acetylene units that are linked *meta* to the aromatic units (*m-intA*). The *m-intA* units were introduced into the backbone of oligoimide [1-4], polyimide [5-7], and oligoamide [8], and it was shown that the acetylene units crosslinked to give polyimides and polyamides having high performance at high temperature due to the increase of  $T_g$ . Solvent resistance also increased. It is to be noted that the crosslink density is easily controlled by changing the ratio of introduced internal acetylene monomer, thus enabling the control of thermal and physical properties. The reactive polyimides and oligoimides were also used for the preparation of polyimide/polyimide molecular composite films, which were proved to have excellent thermal and physical properties [9-11]. Laminate processing became possible by utilizing the reactive polyimide.

As an extension of our work on the crosslinking behavior of the *meta*-linked acetylene units, we were also interested in the crosslinking behavior of *para*-linked acetylene units (*p-intA*). Inoue and Imai reported on the polyimide and polyamide incorporating the internal acetylene units linked *para* to the aromatic rings [12]. They compared thermal stability of the acetylene-containing polymers with the stilbene-containing polymers and the bibenzyl-containing polymers. But the crosslinking behavior and physical properties of the polymers have scarcely been studied.

We were interested in the polyimide having *p*-intA from the point of examining the crosslinking behavior of the acetylene units. It is considered that *p*-intA reacts to crosslink as was *m*-intA in the polyimide backbone. The difference in the chemical structure should affect the temperature necessary for crosslinking. We were also interested in the *para*-linked acetylene units from the point of physical properties of the polyimide films, since the *para*-linked acetylene unit is rod-like. By reacting with an appropriate acid dianhydride, we can expect higher modulus for the polyimide films that contain *para*-linked acetylene units than those that contain *meta*-linked acetylene units. Here, we compare the crosslinking behavior of the *p*-intA and *m*-intA introduced into the backbone of polyimide, and also thermal and physical properties of the polyimide films.



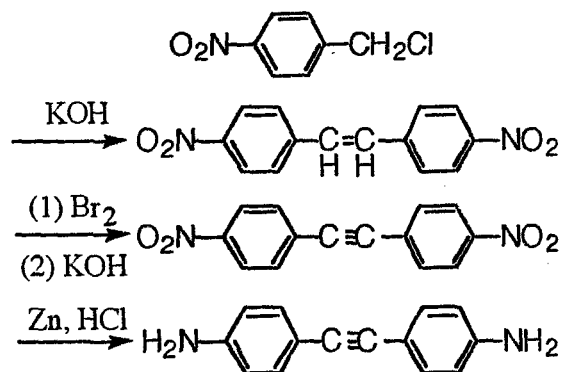
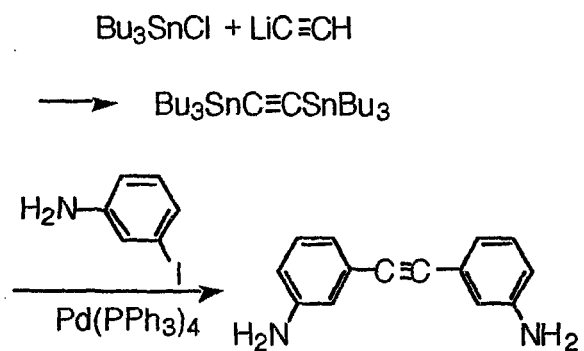
## EXPERIMENTAL

### 1. Preparation of *m*-intA

Internal acetylene units that are linked *meta* to the aromatic units were prepared according to the reported method [2] as shown in Scheme 1.

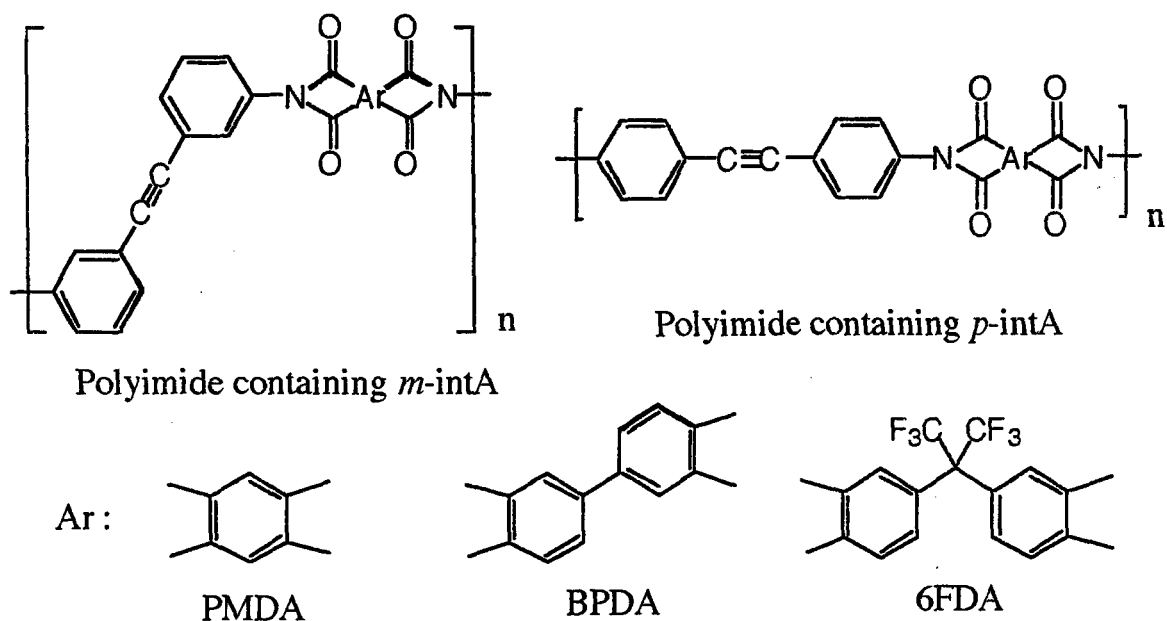
### 2. Preparation of *p*-intA

Internal acetylene units that are linked *para* to the aromatic units were prepared according to the reported method [12] as shown in Scheme 2.



### 3. Preparation of polyimide

Several kinds of polyimides containing *p*-intA were prepared by the reaction of equimolar amount of acid dianhydride with *p*-intA in NMP, to give moderately to highly viscous poly(amide acid) solutions. These poly(amide acid) solutions were cast on glass plates and thermally treated to give polyimide films. As acid dianhydride, 6FDA, BPDA, and PMDA were employed. Polyimides containing *m*-intA were prepared similarly. To evaluate the effect of crosslinking of the acetylene units on the thermal and physical properties of polyimides, a series of polyimides were prepared using PDA instead of *p*-intA.



## RESULTS AND DISCUSSION

### 1. Crosslinking behavior of polyimide containing *p*-intA [13,14]

At first, the crosslinking behavior of acetylene monomers were studied by DSC. The *m*-intA showed broad exotherm soon after the melting point at around 120°C. The amount of the exotherm was calculated to be 58.5 cal/g. The *p*-intA showed exotherm starting at much higher temperature at around 250°C because of the higher melting temperature. The amount was slightly smaller than that of *m*-intA.

In the case of 6FDA/*m*-intA, onset of the exotherm appeared at around 320°C and amount of the exotherm was c.a. 10 cal/g. After higher heat treatment at 350°C, onset of the exotherm shifted to higher temperature and amount of the exotherm became smaller. After 400°C treatment, exotherm was not appreciable. In the case of 6FDA/*p*-intA, exotherm was found to appear at 330°C, almost the same temperature range as the *meta*-counterpart. The amount of the exotherm was 3 - 4 cal/g, less than half of the *meta*-counterpart.

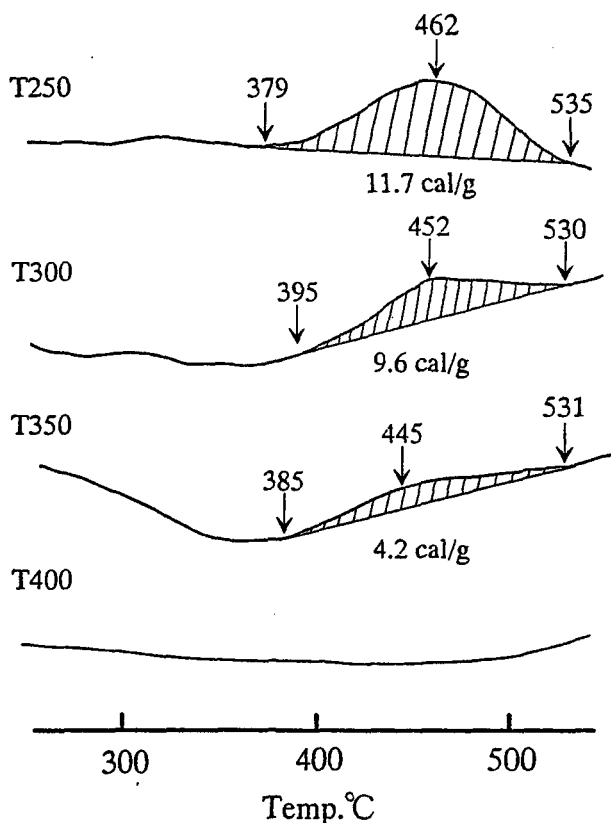


Fig. 1 DSC of BPDA / *p*-intA

In the case of BPDA/*m*-intA, onset of the exotherm appeared at 340°C and amount of the exotherm was 27 cal/g. After higher heat treatment, onset of the exotherm shifted to higher temperature and amount of the exotherm became smaller. In the case of rod-like BPDA/*p*-intA, onset of the exotherm appeared at c.a. 390°C, about 50°C higher than the *meta*-counterpart as shown in Fig. 1. The amount of the exotherm is about 10 cal/g, less than half of the *meta*-counterpart. In the case of rigid-rod PMDA/*p*-intA, the exotherm started at c.a. 390°C (about 50°C higher than PMDA/*m*-intA), and the amount of the exotherm was considerably small.

These DSC measurements show that *p*-intA units crosslink at somewhat higher temperature range than the *meta* counterpart. The crosslink density of polyimide having *p*-intA is considered smaller than the polyimide having *m*-intA from the amount of exotherm. These observations can be explained from the steric hindrance of acetylene units. The *m*-intA is rather exposed, and another *m*-intA can be easily approach the site. But, *p*-intA is protected in the rod-like chain, and reaction with another *p*-intA in the rod must be difficult.

## 2. Viscoelastic properties of polyimide containing *p*-intA

The crosslinking behavior can also be followed from viscoelastic analyses. In the case of linear polyimide such as 6FDA/ODA, modulus drops considerably at around T<sub>g</sub>. In the case of 6FDA/*m*-intA treated at 400°C, T<sub>g</sub> was found at 380°C, much higher than that of 6FDA/ODA, and modulus was maintained to higher temperature, showing clearly the effect of crosslinking.

In the case of 6FDA/*p*-intA treated at 250°C, T<sub>g</sub> was found at 330°C and modulus lowered at around T<sub>g</sub>. The polyimide film treated at 400°C did not show T<sub>g</sub> below 400°C, and modulus was maintained to higher temperature. Thus it was confirmed that introduction of *p*-intA, instead of *m*-intA, afforded higher T<sub>g</sub>.

In the case of BPDA/*m*-intA, uncrosslinked polyimide film treated at 300°C showed T<sub>g</sub> at 282°C and modulus dropped considerably at around T<sub>g</sub>. With higher heat treatment, T<sub>g</sub> shifted to higher temperature. For the crosslinked polyimide treated at 400°C, T<sub>g</sub> was observed at 362°C.

In the case of BPDA/*p*-intA, uncrosslinked polyimide film treated at 250°C showed T<sub>g</sub> at 290°C. With the crosslinked polyimide films treated at 400°C, as shown in Fig. 2, T<sub>g</sub> increased

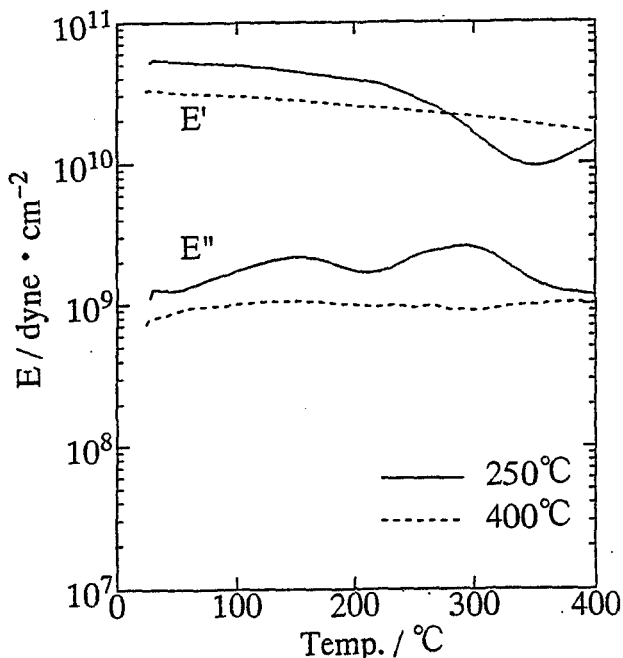


Fig. 2 Viscoelastic analyses of BPDA / *p*-intA