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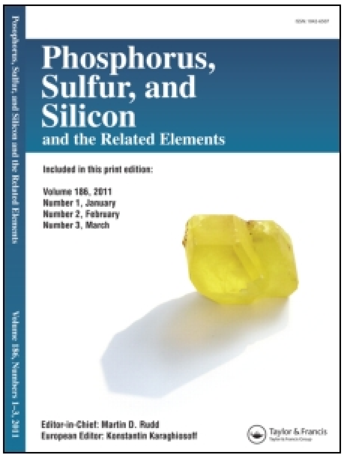

## Phosphorus, Sulfur, and Silicon and the Related Elements

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# A Study of Synthesis and Thermal Properties of Cyclotriphosphazene-Containing Polyimides

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# A STUDY OF SYNTHESIS AND THERMAL PROPERTIES OF CYCLOTRIPHOSPHAZENE-CONTAINING POLYIMIDES

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Abstract New novel fire- and heat-resistant cyclotriphosphazene-containing polyimides were prepared from polymerization of bis(*p*-aminophenoxy)tetra(phenoxy) cyclotriphosphazene with 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and 3,3',4,4'-diphenylsulfonetetracarboxylic dianhydried (DSDA). The imidization of the polyamic acids and the thermal stabilities of the polyimides were evaluated by FTIR, differential scanning calorimetry(DSC), and thermogravimetric analysis(TGA). These polyimides, in which the cyclic triphosphazene structure is preserved, showed good thermal stability and fire-resistance.

## INTRODUCTION

Organocyclotriphosphazene materials are known to exhibit good thermal stability. The presence of phosphorus and nitrogen atoms in the backbone as well as the ether linkages in the form of phenoxy groups introduced in the cyclotriphosphazene as side groups have resulted in the development of a new class of hybrid inorganic-organic phosphazene polymers, such as polyurethanes[1], polyamides[2], polysulfones[3], maleimide resins[4-7], and epoxy resins[8] etc.. These studies have shown that incorporation of a substituted cyclotriphosphazene ring into the polymer backbone has signficantly improved heat- and fire-resistance. Therefore, it is expected that incorporation of substituted cyclotriphosphazene ring into polyimide backbone can give the merits of cyclotriphosphazene and polyimide. In this study, the reactive bis(*p*-aminophenoxy)tetra(phenoxy)cyclotriphosphazene was synthesized as a precursor for incorporating the cyclotriphosphazene ring onto the traditional organic polyimide. The preparation and the properties of the phosphazene-containing polyimides prepared are discussed in this report.

## EXPERIMENT

### Synthesis of bis(*p*-nitrophenoxy)tetra(phenoxy)cyclotriphosphazene, (3), and bis(*p*-aminophenoxy)tetra(phenoxy)cyclotriphosphazene, (4):

(3) and (4) were synthesized following the procedures reported before[2].

### Preparation of polyamic acids:

Diamine(4) was reacted with equimolar amount of dianhydride a and b separately in DMAc at ambient temperature under $N_2$ to give the polyamic acids 5a and 5b respectively.

### Imidization of polyamic acids:

The polyamic acid 5a in THF was cast on a glass plate and dried at room temperature overnight under vaccum. It was then heated in oven at 100℃ for 1h, 200℃ for 1h, and 250℃ for 1h to convert to the corresponding polyimide 6a. 5b were imidized in an analogous procedure to obtain 6b.

## RESULTS AND DISCUSSION

### Synthesis and characterization of polyimides:

The bis(*p*-aminophenoxy)tetra(phenoxy)cyclotriphosphazene (4) was synthesized according to the procedure outlined in Scheme I. As shown in Scheme II, compound (4) was reacted with BTDA and DSDA separately to give the polyamic acids 5a and 5b. The corresponding polyimides 6a and 6b were then obtained by the imidization of 5a and 5b respectively.

Fig.1 shows the FTIR spectra of polyamic acid 5a and that of polyimide 6a. It is seen that the cyclotriphosphazene is intact in both polymers. The four typical characteristic imide bands at 1780cm$^{-1}$ (C=O, imide), 1726cm$^{-1}$ (C=O,phenyl), 1370cm$^{-1}$ (C-N-C, imide), and 721cm$^{-1}$ (C-N-C, out-of-plane bending) were found for the polyimide. In order to find a proper temperature for the imidization, the band at 1370cm$^{-1}$ was followed with temperature variation using 949cm$^{-1}$ (P-O-C) as the reference band. It was found that for 30 minutes heating, the absorbance at 1370cm$^{-1}$ is increased with increasing temperature and reaches a steady absorbance at about 200℃ as indicated by the plot of absorbance ratio vs. temperature in Fig.2. This suggests that although the imidization occurs initiially at 100℃, polymer 5a can be imidized as effectively as at 250℃. Furthermore, the DSC thermogram of 5a shows an endothermic peak between 100℃ and 150℃ indicating the melting process occured. Therefore, it is believed that the imidization took place concurrently with melting process between 100℃ and 200℃. In order to make sure the imidization was complete, heating at 100℃ for 1h, at 200℃ for 1h, and 250℃ for 1h were conducted for converting polyamic acid 5a in the form of film to the polyimide 6a. Similar results were obtained for polyamic acid 5b and the corresponding polyimide 6b.

## Thermal properties of the polyimides

The glass transition temperatures (Tg) of the polyimides measured by DSC are only 140℃-160℃. It reveals that the polyimides can be processable at relatively low temperature. The thermal stabilities of the polyimides 6a, and 6b were investigated by dynamic TGA(Fig.3). As listed in Table I, the temperature of 5% weight loss is at 400℃-410℃, and the temperature at which major thermal decomposition occurs in $N_2$ is at 410℃-450 ℃. This suggests that the synthesized polymers are thermally stable. In addition, the high char yield feature gives these polyimides good potential for use in fire-resistant application.

TABLE I. The thermal analysis data of the polyimide prepared.

| polymer | Tg (℃) | $T_{5\%}$ (℃) | $T_{max}$ (℃) | char yield at 600℃(%) |
|---|---|---|---|---|
| **6a** | 160.0 | 410.9 | 445.8 | 78.5 |
| **6b** | 142.4 | 402.8 | 413.5 | 74.0 |

## ACKNOWLEDGMENTS

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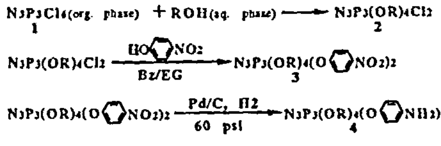
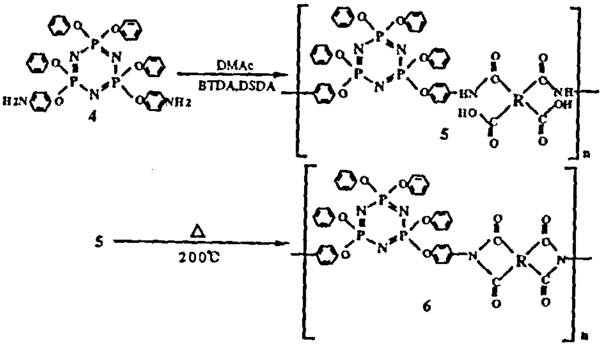


Scheme I



Scheme II

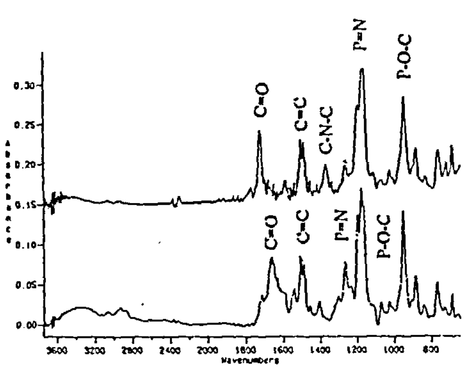


Fig.1 The FTIR spectra of polyamic acid 5a and polyimide 6a in the rang of 700-3600cm$^{-1}$

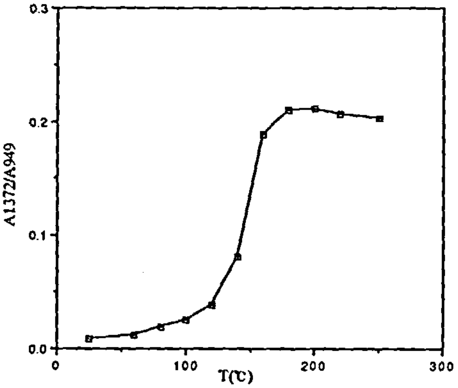


Fig.2 Dependence of the absorbance ratio at 1372cm$^{-1}$ peak on different temperature during the course of imidization

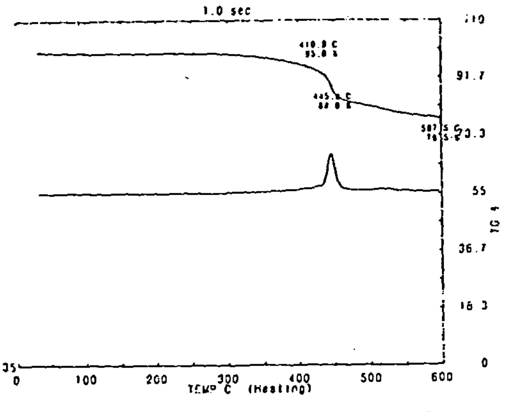


Fig.3 TGA thermogram of the polyamic acid 6a.