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# Polymerization of hexa(phenoxy) cyclotriphosphazene with Friedel–Crafts type catalysts

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The reaction of hexa(phenoxy)cyclotriphosphazene $N_3P_3(OC_6H_5)_6$ with Friedel–Crafts type catalysts in tetrachloroethane solvent or a molten state of $N_3P_3(OC_6H_5)_6$ to prepare polycyclophosphazene having higher molecular weight were formed with $AlCl_3$ and $TeCl_4$ as catalysts. It is assumed that phenoxy groups in $N_3P_3(OC_6H_5)_6$ was condensed with the catalysts without $N_3P_3$ ring cleavage.

## 1. Introduction

Poly(organophosphazenes) can not be prepared from hexa(organo-cyclotriphosphazenes by bulk, solution and radiation polymerization techniques. To prepare poly(organophosphazenes), first $(NPCl_2)_3$ was polymerized by a bulk or solution method, the linear polydichlorophosphazene $(NPCl_2)_n$ extracted with tetrahydrofuran or benzene solvent is then reacted to nucleophilic reagents such as alkoxides, phenoxides or amines. It was found that poly(organophosphazenes) had various uses such as in gas separation membranes [1] and medical materials [2]. On the other hand, the various hexa(organo) cyclotriphosphazenes were synthesized with the reaction between $(NPCl_2)_3$ and a nucleophilic reagent. Recently, Katti [3] reported that poly(organophosphazenes) derived from Friedel–Crafts reaction of hexa(aryloxy)cyclotriphosphazenes with polyhaloalkanes. This report describes the synthesis of polycyclophosphazenes using hexa(phenoxy)-cyclotriphosphazene $N_3P_3(OC_6H_5)_6$ and the well known Friedel–Crafts type catalysts.

## 2. Experimental details

### 2.1. Materials

Hexachlorocycltriphosphazene $(NPCl_2)_3$ was prepared by the method of Saito [4]. Also, hexa(phenoxy)cycltriphosphazene $N_3P_3(OC_6H_5)_6$ was formed by reported procedures [5]. Ten Friedel–Crafts type catalysts were used in this study: $MoCl_5$, $TeCl_4$, $SnCl_4$, $TiCl_4$, $FeCl_3$, $AlCl_3$, $BiCl_3$, $CuCl_2$, $MgCl_2$ and $ZnCl_2$.

### 2.2. Analytical methods

IR spectra of the product were recorded in KBr pellets using a Shimazu IR-450. The molecular weight determination of the products were determined with GPC of Toso 60-B using THF solvent.

### 2.3. Polymerization reaction of hexa(phenoxy)cyclotriphosphazene $N_3P_3(OC_6H_5)_6$ in tetrachloroethane (TCE)

After 1 g of $N_3P_3(OC_6H_5)_6$ was dissolved in 50 ml of TCE, 0.1 g of Friedel–Crafts type catalysts was added to the solution. The reaction mixture was stirred at room temperature and refluxed for 5 h. After the reflux was over, 100 ml of 0.1 N HCl was added to the reaction mixture to decompose the catalysts and the mixture was washed with distilled water several times. The solution dehydrated by anhydrous sodium sulphate was evaporated under vacuum.

### 2.4. Polymerization of a melted hexa(pheoxy)cyclotriphosphazene $N_3P_3(OC_6H_5)_6$

After 1 g of $N_3P_3(OC_6H_5)_6$ was mixed with 0.1 g of Friedel–Crafts type catalysts, the mixture was heated by vigorous stirring at 150° C, 200° C and 270° C for 5 h. After heating was over, 100 ml of 0.1 N HCl and 50 ml of TCE was added to the mixture. The TCE solvent separated was washed with distilled water several times. The TCE solvent dehydrated by anhydrous sodium sulphate was evaporated under vacuum.

## 3. Results and discussion

### 3.1. Molecular weight of the products prepared using tetrachloroethane (TCE)

A typical GPC curve of the product prepared with catalyst $AlCl_3$ is shown in Fig. 1. Also, the molecular

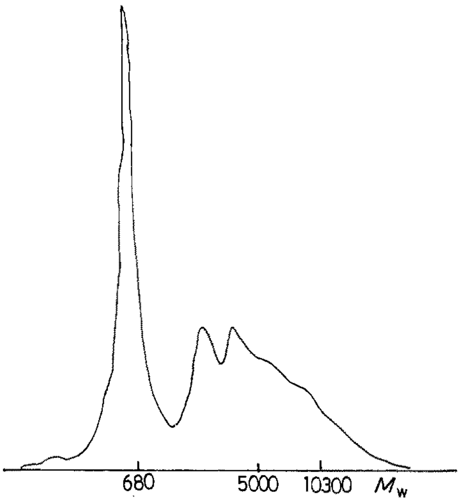

*Figure 1* GPC curve of the product prepared with $AlCl_3$.

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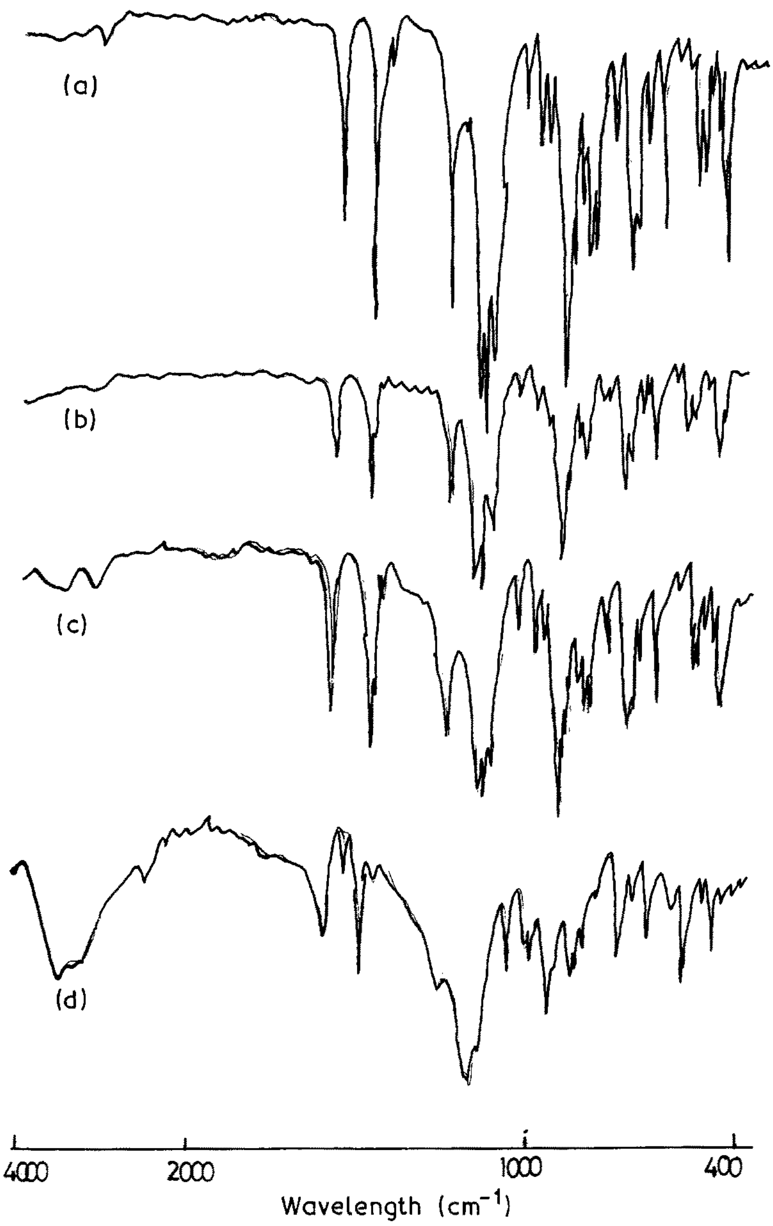

*Figure 2* IR spectra of the product prepared under various conditions (a) $[NP(OC_6H_5)_2]_3$ (b) 150° C, (c) 200° C, (d) 270° C.

weight of other products prepared at room and reflux temperature with various catalysts were determined with GPC, and the weight or number-average molecular weight of the product calculated from GPC curves are summarized in Table I. It is found from Table I that the products prepared with the various Friedel–Crafts type catalysts have higher molecular weights than that of $N_3P_3(OC_6H_5)_6$. In particular, the product having the highest molecular weight is formed with $AlCl_3$ catalyst in this study.

### 3.2. Molecular weight of the products prepared using a molten $N_3P_3(OC_6H_5)_6$

The molecular weight of the products prepared using the various Friedel–Crafts type catalysts are determined with GPC, and the weight and number-average molecular weight calculated with GPC curves are summarized in Table II.

Table II shows that $N_3P_3(OC_6H_5)_6$ which is the starting material is recovered using $TeCl_4$, $SnCl_4$, $BiCl_3$, $MgCl_2$ and $ZnCl_2$. However, a product with higher molecular weight than that of the starting material was obtained with $MoCl_5$, $FeCl_3$, $AlCl_3$ and $CuCl_2$. In particular, the product having the highest molecular weight is formed with $AlCl_3$. Furthermore, the polymerization reaction of $N_3P_3(OC_6H_5)_6$ is carried out using 1.0 g and 3.0 g of $AlCl_3$ as the catalyst. After the reaction is over, the molecular weight of the product prepared under the experimental conditions is determined with GPC and the results are summarized in Table III.

Table III shows that the molecular weight of the product prepared using 1.0 g and 3.0 g of $AlCl_3$ as the catalyst is lower than that of the product formed using 0.1 g of $AlCl_3$.

### 3.3. The polymerization mechanism of $N_3P_3(OC_6H_5)_6$

IR spectra of the products formed with $AlCl_3$ and $N_3P_3(OC_6H_5)_6$ are shown in Fig. 2.

Shaw [6] described that the frequencies of the principal absorption maximum in the IR spectrum of $N_3P_3(OC_6H_5)_6$ were 3100, 1600, 1495, 1260, 1190, 1180, 1070, 1020, 1010, 950, 930, 910, 890, 880, 820, 790, 780, 770, 760, 735 and 690 cm$^{-1}$. The frequency at 1260 cm$^{-1}$ was characteristic of a six-member ring in this case. On the other hand, Allcock [8, 9] described that one striking characteristic of all liner

TABLE I The molecular weight of the product prepared using Friedel–Crafts type catalysts

| Friedel–Crafts type catalysts | Reaction temperature | | | |
|---|---|---|---|---|
| | Refluxing | | Room | |
| | $M_w$ | $M_n$ | $M_w$ | $M_n$ |
| $MoCl_5$ | 1690 | 390 | 884 | 162 |
| $TeCl_4$ | 2427 | 577 | 5425 | 1430 |
| $SnCl_4$ | 2505 | 949 | 2859 | 1140 |
| $TiCl_4$ | 5060 | 178 | 2458 | 1320 |
| $FeCl_3$ | 1503 | 600 | 1128 | 530 |
| $AlCl_3$ | 7310 | 2316 | 3609 | 1361 |
| $BiCl_3$ | 2281 | 1101 | 2583 | 1062 |
| $CuCl_2$ | 1547 | 1276 | 1708 | 649 |
| $MgCl_2$ | 5818 | 2490 | 2048 | 1127 |
| $ZnCl_2$ | 1496 | 757 | 1296 | 657 |

TABLE II The molecular weight of the product under melting point temperature of $N_3P_3(OC_6H_5)_6$

| Friedel–Crafts type catalysts | | The molecular weight of the product | |
|---|---|---|---|
| | | $M_w$ | $M_n$ |
| $MoCl_5$ | 50 h | 1072 | 1072 |
| $TeCl_4$ | 5 | Starting | Starting |
| $SnCl_4$ | | Starting | Starting |
| $FeCl_3$ | | 1107 | 1107 |
| $AlCl_3$ | | 4615 | 4615 |
| $BiCl_3$ | | Starting | Starting |
| $CuCl_2$ | | 1098 | 1085 |
| $MgCl_2$ | | Starting | Starting |
| $ZnCl_2$ | | | |

Starting: $N_3P_3(OC_6H_5)_6$

TABLE III The molecular weight of the product prepared under the various concentration of $AlCl_3$

| $AlCl_3$ (g) | The molecular weight of the product | |
|---|---|---|
| | $M_w$ | $M_n$ |
| 0.1 | 4615 | 4615 |
| 1.0 | 2566 | 1013 |
| 3.0 | 2985 | 1938 |

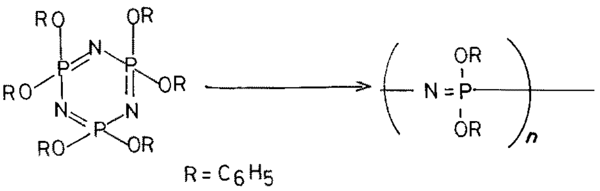

*Figure 3* Scheme I.

phosphazene high polymers were that the ultraviolet and infrared spectra were remarkably similar to those of the corresponding cyclotrimers. Also, the position of the characteristic –P=N– frequencies in the 1200 to 1300 cm$^{-1}$ region suggested that the force constants of the skeltal in the high polymers were comparable to those in cyclic trimers and tetramers. It is found from Fig. 2 that the $N_3P_3$ ring appears in the 1200 to 1150 cm$^{-1}$ region and infrared absorption spectra of the products and $N_3P_3(OC_6H_5)_6$ are not considerably different. On the other hand, Tunnicliff [8, 10] have made the more limited suggestion that absorption of phenyl groups. Whilst Sutherland [11] have noted that absorption at 1600 cm$^{-1}$ was assigned to diphenyl, naphthalenes, phenanthrenes and other compounds. The ratio of absorption intensity which appeared at 1600 and 1585 cm$^{-1}$ is determined using Fig. 2. The results show that the ratio decreases with increasing reaction temperature as follows: 1.38, 25° C: 1.36, 150° C: 1.25, 200° C: 1.09, 270° C. This means that the phenoxy group in $N_3P_3(OC_6H_5)_6$ is condensed with Friedel–Crafts type catalysts such as $AlCl_3$ as shown in scheme I. Also, the polymerization reaction with ring cleavage as shown in scheme II is not proceeded with Friedel–Crafts type catalysts. Furthermore, Tomas [12] described that the yellow-coloured solid was prepared with the reaction between benzene and $FeCl_3$. Also, Kovacic [13] reported that polyphenylene was formed with the reaction between benzene and Friedel–Crafts type catalysts such as $CuCl_2$, $MoCl_5$ and $FeCl_3$. Consequently, the product having molecular weight 4615 prepared with $AlCl_3$ consists of six or seven $N_3P_3$ rings.

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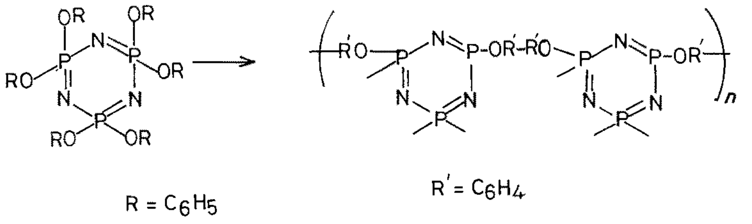

*Figure 4* Scheme II.