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Synthesis of Inorganic-Organic Oligomers Including Cyclotriphosphazenes and the Adhesive Properties of the Products

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ABSTRACT

The reaction of diaminotetraalkoxy- and aryloxycyclotriphosphazene with toluendiisocyanate (TDI) was investigated in various solvents. It was found that benzene or electron negative groups such as the trifluoroethoxy group ($-\text{OCH}_2\text{CF}_3$) were the most suitable solvents for the growing of molecules having an N_3P_3 ring. The adhesive property of the products to a hard polyvinyl chloride laminate was studied by bonding strength measurements. The product formed from the reaction of diaminotetramethoxycyclotriphosphazene with TDI had the strongest adhesive strength even though it had the low molecular weight.

INTRODUCTION

Linear polydichlorophosphazene $(\text{NPCl}_2)_n$ was prepared from dichlorocyclotriphosphazene $(\text{NPCl}_2)_3$ by radiation or heat treatment in the presence of various catalyzers with or without solvents. However, the polymer as prepared was unstable toward moisture or water and had an activity for nucleophilic agents such as amines, alcohols, and

phenols. Firestone Rubber Co. PNF 100 and PNF 200 elastomers were formed by the substitution reaction of polyorganophosphazenes with fluoroalcohols. Also, the other polyorganophosphazenes can be used in such biomedical fields as antitumor agents, artificial heart pumps, replacement of blood vessels, artificial skin, and models for biological polymers such as proteins. Allcock [1] reported the preparation of polyorganophosphazenes by a new method using dichloro- or difluorocyclotriphosphazene and organocyclotriphosphazenes such as mono- or diphenylcyclotriphosphazenes. Furthermore, polycyclo-linear- or polycyclomatrixphosphazenes have attracted much interest in the field of phosphazene polymers chemistry. This paper describes the reaction of diaminotetraalkoxy- and phenoxy cyclotriphosphazene with toluendiisocyanate (TDI) and the adhesive property of the products.

EXPERIMENTAL

Preparation of $(\text{NPCl}_2)_3$ and $\text{N}_3\text{P}_3(\text{NH}_2)_2\text{R}_4$

$(\text{NPCl}_2)_3$. Hexachlorocyclotriphosphazene $(\text{NPCl}_2)_3$ was prepared from the reaction with phosphorus pentachloride (PCl_5) and ammonium chloride (HN_4Cl) by the method of Kajiwara [2]. The melting point of the pure trimer was about 112°C .

$\text{N}_3\text{P}_3(\text{NH}_2)_2\text{R}_4$. Diaminotetrachlorocyclotriphosphazene ($\text{N}_3\text{P}_3(\text{NH}_2)_2\text{Cl}_4$), diaminotetrafluoroethoxycyclotriphosphazene ($\text{N}_3\text{P}_3(\text{NH}_2)_2(\text{OCH}_2\text{CF}_3)_4$ (I)), diaminotetraphenoxy cyclotriphosphazene ($\text{N}_3\text{P}_3(\text{NH}_2)_2(\text{OPh})_4$), diaminotetraanylinocyclotriphosphazene ($\text{N}_3\text{P}_3(\text{NH}_2)_2(\text{NHPh})_4$), and diaminotetrakis methylaminocyclotriphosphazene ($\text{N}_3\text{P}_3(\text{NH}_2)_2(\text{NMe}_2)_4$) were prepared by the method of Feistal [3], Lenton [4], McBee [5], Bode [6], and Keat [7], respectively. Also, diaminotetraalkoxy- and phenoxy cyclotriphosphazenes ($\text{R} = \text{OMe}$, OEt , OPr^n , OPr^i , OBu^n , SC_6H_5 , $\text{OC}_6\text{H}_4\text{Cl-p}$, $\text{OC}_6\text{H}_4\text{O-o}$, $\text{OC}_6\text{H}_4\text{C}_6\text{H}_4\text{O-o}$) were prepared by the reaction of diaminotetrachlorocyclotriphosphazene with alkoxides or phenoxides using THF as the solvent.

The Reaction of Diaminotetraalkoxy- or Aryloxy-cyclotriphosphazenes with TDI

The reaction of diaminotetraalkoxy- or phenoxy cyclotriphosphazenes with TDI was carried out in various solvents such as benzene with stirring for 24 h. The mole ratio of the phosphazene compounds to TDI was 1:1. When the reaction was over, the reaction mixture was filtered. The residue was washed with benzene, and the filtrate was evaporated under vacuum.

Analysis of the Products and Application of the Products as Adhesive Agents to Hard Laminated Polyvinyl Chloride

The molecular weight of the products was determined by gel permeation chromatography using THF as the solvent and a Shimazu LC-830 type instrument. $^1\text{H-NMR}$ and IR spectra were recorded on a Nippon Denshi Model-100 type spectrometer and a Shimazu Model-450 type spectrometer ($4000\text{-}200\text{ cm}^{-1}$), respectively.

Adhesive agents were made by dissolving the products in DMF to make a 30% solution. Then 0.5 g of the solution was coated between two laminated polyvinyl chloride sheets and they were pressed together under a load of 500 g for 48 h. The size of the hard polyvinyl chloride laminate used was $25 \times 15 \times 3\text{ mm}$, and the adhesive test was carried out on a JIS-K 6850. Test pieces were examined with a tensile tester.

RESULTS AND DISCUSSION

Effect of Solvents and the Reaction Temperature

The reaction of (I) and TDI was carried out in various solvents under refluxing for 24 h. The molecular weights of the purified products were determined and the distribution curve is shown in Fig. 1.

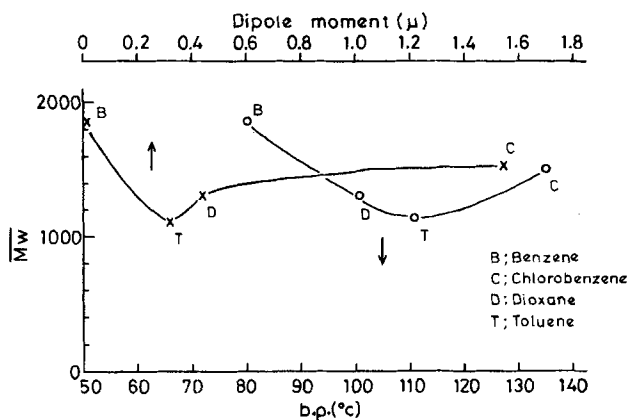


FIG. 1. The relation between molecular weight (\overline{M}_w) of products, boiling point, and dipole moments of solvents.

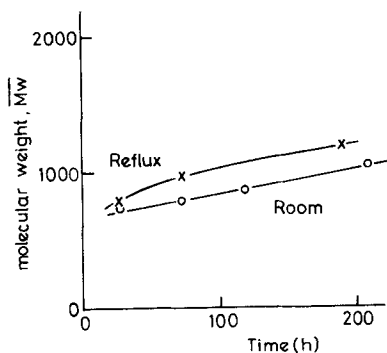


FIG. 2. The relation between molecular weight and reaction time for $N_3P_3(NH_2)_2(OCH_2CF_3)_4$ -TDI in benzene.

It was found that benzene is a suitable solvent for the preparation of high molecular weight products.

The relation between molecular weight and the reaction temperature or time was investigated using benzene as the solvent. The results are shown in Fig. 2.

Figure 2 shows that the molecular weight of the products increase with rising temperature and longer reaction periods. To determine the effects of pendant groups on the products, the other diamino-organocyclotriphosphazene compounds were allowed to react with TDI by refluxing for 24 h using benzene as the solvent.

The molecular weight of the products as measured are summarized in Table 1.

It was found that the product having the highest molecular weight had been prepared from the reaction of TDI with compounds consisting of electron-attracting groups such as trifluoroethoxy.

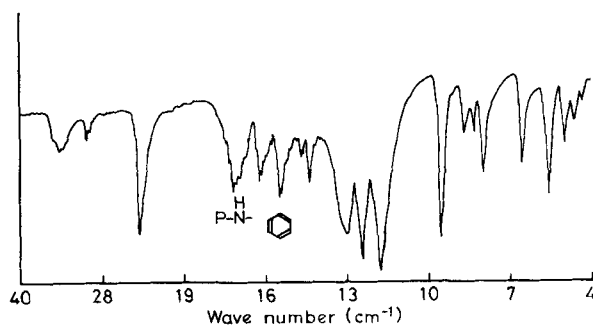
Because of the reaction of $P(NH_2)_2$ with $-NCO$ groups, the product could have such bonds as $HNP-NH$ and $NH-C(O)NH$. In order to investigate the bonding, the IR absorption spectrum of the product obtained from the reaction of (I) with TDI was recorded using the KBr disk technique, and the result is shown in Fig. 3.

Derkach [8] described the N-H stretching of compounds of the type $-PNHC(O)R$ as occurring in the rather low range of 3160 to 3040 cm^{-1} and appeared adjacent to the $C=O$ group stretching. The band occurring at 1600 cm^{-1} in Fig. 3 is assigned to $-PNHC(O)NH$.

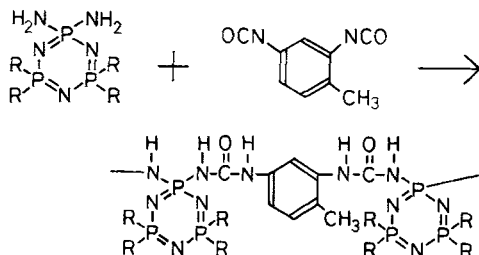
The H-NMR of the product was measured in $CDCl_3$ using TMS. Two peaks appeared at 3.339 and 1.796 ppm. They can be assigned to $-NH$. The proton $-NH$ disappears with D_2O . Also, $-NH_2$ in diaminotetrafluoroethoxycyclotriphosphazene (I) appears at 1.80 ppm. It is assumed that a peak appearing at 1.796 ppm belongs to $-PNH$ and the one at 3.339 ppm to $-CNH$. The ratio of $-PNH$ to $-CNH$ is about 1:1. $-C_6H_4$ and $-CH_3$ appear at 7.275 and 4.286 ppm, respectively.

TABLE 1. Molecular Weight of Products Obtained from the Reaction of $N_3P_3(NH_2)_2(R)_4$ with TDI in Benzene for 24 h

$N_3P_3(NH_2)_2(R)_4$ with R =	\overline{M}_w	\overline{M}_n	$\overline{M}_w/\overline{M}_n$
OMe	532	224	2.38
OEt	479	379	1.21
OCH ₂ CF ₃	1,825	326	5.60
OPr ⁿ	964	371	2.60
OPr ⁱ	1,209	1,180	1.02
OBu ⁿ	964	371	2.60
OC ₆ H ₅	774	614	1.26
SC ₆ H ₅	548	331	1.66
p-OC ₆ H ₄ Cl	935	786	1.19
o-OC ₆ H ₄ O	808	539	1.50
o-OC ₆ H ₄ ·C ₆ H ₄ O	405	255	1.59
NMe ₂	676	371	1.82

FIG. 3. Infrared spectra of the product formed from the reaction of $N_3P_3(NH_2)_2(OCH_2CF_3)_4$ and TDI.

The ratio of CH_2 to C_6H_4 is about 1:1. Consequently, the structure of the product is assumed to be as follows:



Bonding strength was measured after the products prepared from the reaction of the various phosphazenes compounds with TDI were coated on polyvinyl chloride laminates, and the results are summarized in Table 2.

The product prepared from the reaction of diaminotetramethoxycyclotriphosphazene with TDI give the highest bonding strength compared to other products. Also, interfacial or cohesive failure was

TABLE 2. Bonding Strength and Failure of Molded Laminate

$(\text{OCN})_2\text{C}_6\text{H}_3\text{CH}_3$ + $\text{N}_3\text{P}_3(\text{NH}_2)_2(\text{R})_4$, with R =	Bonding strength (kg/cm^2)	Failure (I = interfacial failure, C = cohesive failure)
OCH_2CF_3	1.12	I
OC_6H_5	0.16	I
SC_6H_5	4.48	C
<i>o</i> - $\text{OC}_6\text{H}_4\text{O}$	0.32	C
<i>o</i> - $\text{OC}_6\text{H}_4\text{C}_6\text{H}_4\text{O}$	0.16	I
<i>p</i> - $\text{ClC}_6\text{H}_4\text{O}$	0.16	I
OMe	24.96	C
OEt	0.16	I
OPr^i	0.16	I
OPr^n	10.91	C
OBu^n	0.16	I
NMe_2	0.16	I

observed but there is no correlation between the failure or the molecular weight distribution and bonding strength. It is difficult to explain why the product prepared from diaminotetramethoxycyclotriphosphazene and TDI gives the highest bonding strength.

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