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### Phosponitrilic Chloride. XXXII. Homocondensation of 1,1-Diamino-3,3,5,5-tetrakis(2,2,2-trifluoroethoxy)cyclotriphosphazene and Properties of the Products

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**Phosponitrilic Chloride. XXXII.  
Homocondensation of 1,1-Diamino-3,3,5,5-  
tetrakis(2,2,2-trifluoroethoxy)cyclotriphosphazene  
and Properties of the Products**

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**ABSTRACT**

The homocondensation of 1,1-diamino-3,3,5,5-tetrakis(2,2,2-trifluoroethoxy)cyclotriphosphazene and the properties of its products have been studied. When 1,1-diamino-3,3,5,5-tetrakis(2,2,2-trifluoroethoxy)cyclotriphosphazene is heated at 130-190°C in air, ammonia is evolved and hydrazine is not detected. The absence of free radicals due to P<sub>3</sub>N<sub>3</sub> ring cleavage leads to the conclusion that the homocondensation reaction predominates. The reaction products are amorphous solids having molecular weights of about 2400 and soluble in polar organic solvents. The softening points of the products are found to be in the range of 35-46°C. The products are slowly hydrolyzed in boiling water-THF solution, and materials having molecular weights of about 600 are formed.

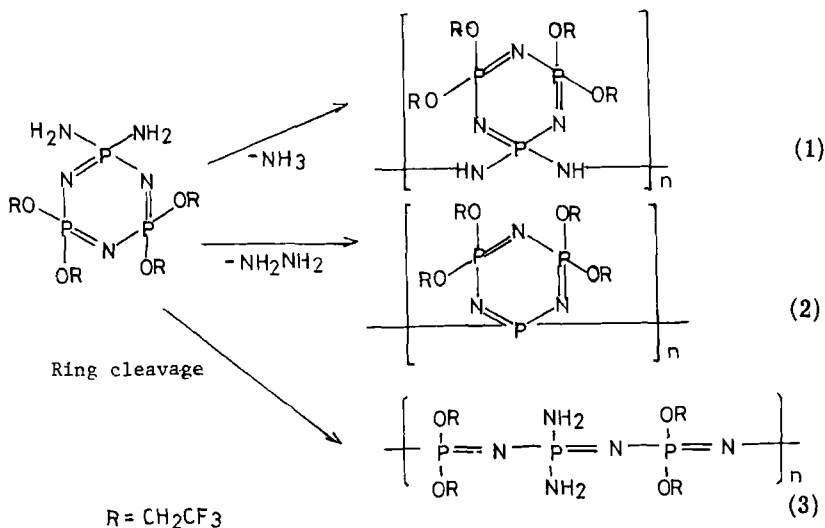
## INTRODUCTION

Linear polydichlorophosphazene, the polymer of linear organophosphazene or cyclomatrix and cyclolinear phosphazene, has been reviewed by Allcock [1].

Lenton [2] has also reported that 1,1-diamino-3,3,5,5-tetrakis(2,2,2-trifluoroethoxy)cyclotriphosphazene undergoes condensation with fluorinated polymethylene  $\alpha,\omega$ -glycols to yield thermally stable elastomeric materials. Homocondensation of 1,1-diamino-3,3,5,5-tetrakis(2,2,2-trifluoroethoxy)cyclotriphosphazene and properties of its products are reported in this paper.

## RESULTS AND DISCUSSION

Heating of 1,1-diamino-3,3,5,5-tetrakis(2,2,2-trifluoroethoxy)-cyclotriphosphazene yields formation of polymers [3-5] following the reactions summarized in Eqs. (1)-(3).



Chemical analysis showed that the product formed by heating in the range  $130-170^\circ\text{C}$  is ammonia and not hydrazine under these experimental conditions. The formation of ammonia may be attributed to the intramolecular or intermolecular condensation reaction of 1,1-diamino-

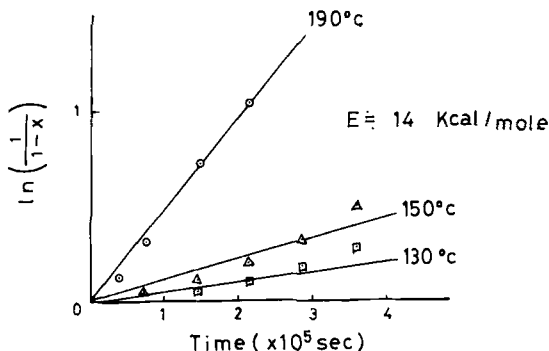


FIG. 1. Relationship between  $\ln[1/(1-x)]$  and time at various temperatures for  $x = 0-0.4$ .

3,3,5,5-tetrakis(2,2,2-trifluoroethoxy)cyclotriphosphazene. Furthermore, the formation of radicals owing to  $P_3N_3$  ring cleavage was not seen by ESR in the range of 2000 to 5000 gauss. Consequently, the deammoniation reaction predominates.

The amount of ammonia formed under various conditions is determined by chemical analysis, and the results are shown in Fig. 1. It is found that the reaction is first order with an apparent activation energy of deammoniation of about 14 kcal/mole.

The resistivity of molten 1,1-diamino-3,3,5,5-tetrakis-(2,2,2-trifluoroethoxy)cyclotriphosphazene was measured during deammoniation (Fig. 2). The resistivity decreases dramatically from 60 to 100° C, then increases, and becomes constant at 160° C. It appears again that the decrease of the resistivity is due to the formation of ammonium ions.

The molecular weight distribution of the products formed at steady state was investigated by high liquid chromatography (HLC) with THF as solvent; the results are shown in Fig. 3. They suggest that the product formed from the polycondensation reaction of 1,1-diamino-3,3,5,5-tetrakis(2,2,2-trifluoroethoxy)cyclotriphosphazene has a rather uniform molecular weight distribution.

The yield and the softening point of the products are listed in Table 1. The products are amorphous solids, soluble in polar organic solvents. Although high yields were obtained, products of high molecular weight or high softening point were not formed under these conditions. However, the products exhibit good adhesion to glass, iron, wood, resins, cloth, metal, and metal oxides.

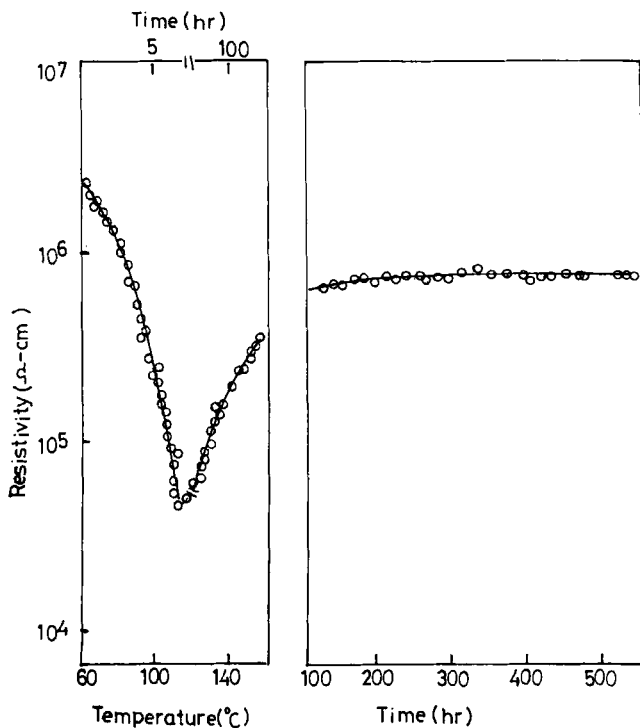


FIG. 2. Variation of resistivity with temperature for condensation of  $N_3P_3(NH_2)_2(OCH_2CF_3)_4$ .

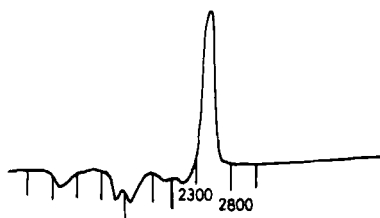


FIG. 3. Molecular weight distribution of the product formed from 1,1-diamino-3,3,5,5-tetrakis(2,2,2-trifluoroethoxy)cyclotriphosphazene by heating at 190°C for 14 days.

TABLE 1. Yield and Molecular Weight of Products Formed from 1,1-Diamino-3,3,5,5-tetrakis(2,2,2-trifluoroethoxy)cyclotriphosphazene (DTP) by Heating

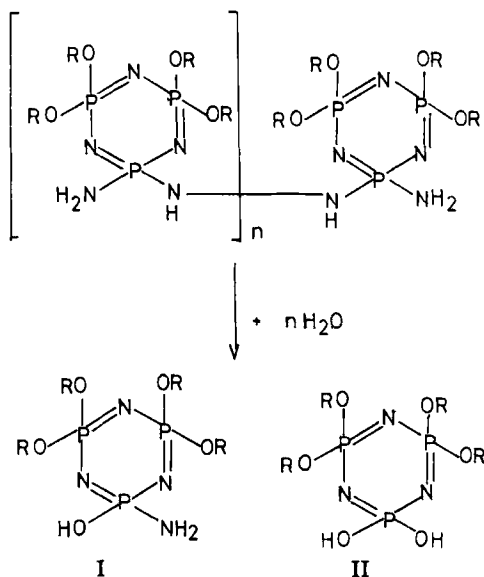
$N_3P_3(NH_2)_2(OCH_2CF_3)_{3/4}$ (g)	Reaction		Amount of $NH_3$ at steady state (mole $NH_3$ / mole DTP)	Yield (g)	Molecular weight	Softening point (°C)	Appearance
	Temp. (°C)	Time (days)					
4.00	130	14	0.4	3.93	2300	41	Pale yellow, amorphous solid, sticky
3.97	150	14	0.5	3.79	2400	44	Pale yellow, amorphous solid, sticky
4.32	190	14	0.6	4.05	800	35	Pale yellow, amorphous solid, sticky

In the infrared spectra of the products, frequencies of  $P=N$ ,  $P-NH-P$ ,  $P_3N_3$  appear in the regions of  $1280-1260\text{ cm}^{-1}$ ,  $1060-840$  or  $630-550\text{ cm}^{-1}$ , and  $890-830\text{ cm}^{-1}$ , respectively. The  $P-NH_2$  frequency in the region of  $3300-3500\text{ cm}^{-1}$  is characterized by a diffuse band, which corresponds to the  $P-NH-P$  bond. The other frequencies are the same as in the spectrum of 1,1-diamino-3,3,5,5-tetrakis(2,2,2-trifluoroethoxy)cyclotriphosphazene.

These results suggest that the polycondensation reaction proceeds as shown in Eq. (1). Consequently, linear cyclophosphazene oligomers are apparently formed under these conditions, since the products have low softening points and are soluble in solvents.

Ultraviolet spectra of the products and the 1,1-diamino-3,3,5,5-tetrakis(2,2,2-trifluoroethoxy)cyclotriphosphazene starting material were measured by use of methanol and ethanol as solvents. The product shows a maximum in the region of  $205\text{ nm}$  ( $\epsilon_{\text{max}} = 49$  in methanol;  $\epsilon_{\text{max}} = 52$  in ethanol); the starting material has a maximum in the region of  $206\text{ nm}$  ( $\epsilon_{\text{max}} = 86$  in methanol).

Upon hydrolysis of the products in a water-THF solution at  $60^\circ\text{C}$  for 48 hr, ortho-, pyro-, and metaphosphorus acids are not formed. Instead, ammonium is detected in solution. It appears likely that hydrolysis occurs at  $NH_2$  groups or  $NH$  linkages in the products. The materials formed from the hydrolysis reaction are oils. Their average



molecular weight by HLG with THF as solvent is about 600, and a reduction of nitrogen content is observed.

However, it is difficult to distinguish the presumed hydrolysis products I and II, where R is  $\text{CH}_2\text{CF}_3$ , since they cannot be separated by chromatography.

### EXPERIMENTAL

Infrared spectra were obtained by use of the KBr-disk technique.

Ultraviolet spectra were recorded on a Hitachi Model-124 spectrometer, methanol and ethanol being used as solvents.

Molecular weights were measured by high liquid chromatography by use of a Shimadzu LC-830 type instrument.

Electron-spin resonance was recorded on a Nippon Denshi-JES-3BX type spectrometer.

Softening points were measured by the method described in previous papers [6, 7].

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