Thermolysis of Polyphosphazenes. 1. Carbon-13 Nuclear Magnetic Resonance Study of Rearrangement of Poly(bismethoxyphosphazene)

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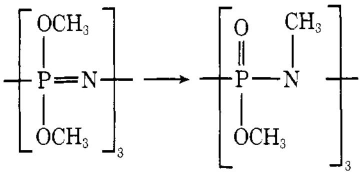
ABSTRACT: It is shown that ^{13}C NMR is a convenient and useful tool for studying thermal rearrangement which involves migration of a methyl group from the methoxy position to the nitrogen in some phosphazenes. It is demonstrated that this rearrangement takes place in poly(bismethoxyphosphazene) as well as in the cyclic tetramer. Data from ^{1}H NMR and IR are also presented, but it is demonstrated that ^{13}C NMR has the decided advantage because the course of the reaction can be followed at elevated temperatures in the bulk polymer.

It has been reported[1-3] that rearrangement of the cyclic trimer, hexakis(methoxy)cyclotriphosphazene (I), to the corresponding trioxycyclotriphosphazane (II) takes place upon distillation at 127 °C and 0.1 mm as shown below:



I II

The cyclic tetramer undergoes a similar rearrangement. Alkyl halides catalyze the reaction, permitting lower temperatures to be used.[3] IR measurements and acid degradation confirmed the rearrangement.[2] The larger ring methoxy derivatives, pentamer, hexamer, and heptamer, also decompose at higher temperatures, but no evidence of the rearrangement has been recorded.[4]

In this paper we report that ^{13}C NMR is a convenient tool for studying this rearrangement which we show also takes place in high molecular weight, solid poly(bismethoxyphosphazene). It is shown that the kinetics of the rearrangement reaction can be easily studied on the solid polymer in the NMR sample tube. This cannot be done with ^{1}H NMR or IR, of course.

Experimental Section

The poly(bismethoxyphosphazene) was prepared by the reaction of poly(dichlorophosphazene) (50 g of polymer in 600 mL of toluene) with sodium methoxide solution (22 g of sodium and 200 g of methanol in 500 mL of THF) at about 75 °C for 6 h. Upon cooling, the polymer was coagulated in hexane and desalted with water. Upon drying in a vacuum oven at 60 °C overnight, an elastomeric polymer was obtained with a glass-transition temperature of −78 °C. The chlorine content of this polymer was less than 0.1%, and the yield of the polymer was about 76% (35 g). From DSV measurements a molecular weight of 220 000 was estimated.

^{13}C NMR measurements were carried out with a JEOL PFT100 Fourier transform NMR spectrometer operating at 25.15 MHz for ^{13}C nuclei in the pulsed (or FT) mode. Spectra were proton decoupled with a heteronuclear white-noise decoupler. Spectra were run at elevated temperatures on the solid polymer[5] placed in 10 mm o.d. NMR tubes sealed with plastic caps. The deuterium external locking system was used for field stabilization. ^{1}H NMR spectra were obtained with a Varian A-60 spectrometer operating at 60 MHz.

Results and Discussion

^{13}C NMR. The spectra in Figure 1 follow the course of the rearrangement reaction in the solid polymer at 130 °C. Spectrum "a" is the "zero time" spectrum. It was actually obtained at 50 °C to ensure that no rearrangement would take place during the finite time (600 s) of the measurement. It is seen that a single methoxy carbon peak is observed at 52.8 ppm with reference to Me_4Si.

Spectrum "b" was taken after 130 min at 130 °C. A weak, broad resonance is barely discernible at 33.6 ppm. This was assumed to be due to the NCH_3 carbon of structure II. Electronic integration shows that this peak accounts for 7.5% of the total CH_3 resonance. Spectrum "c" was obtained after 220 min. The NCH_3 resonance was 20.4% of the total. Spectrum "d" was run after 360 min, and the NCH_3 resonance was 34.7% of the total.

Quartet structure of the two resonance areas in a proton-coupled spectrum confirmed that both peaks are due to methyl carbons. Supporting evidence for the assignment of the peak at 34 ppm to the NCH_3 carbon in structure II is given by somewhat related structures, although satisfactory models are lacking in the literature. For example, the NCH_3 carbon in *N*-methylcyclohexylamine has a chemical shift of 33.5 ppm. Also, the two *N*-methyl carbons in *N,N*-dimethylacetamide have chemical shifts of 34.5 and 37.5 ppm.[6] From these and other examples, it appears that the methyl carbon is relatively isolated by the nitrogen from longer range shielding effects. None of the examples found in the literature had phosphorus attached to the nitrogen, but it is expected that the shielding effect would be roughly the same as having hydrogen attached since they have about the same electronegativity.[7] In fact, methylamine has a ^{13}C shift of 28.3 ppm,[7] which is not too different from the above examples and the polymer peak at 34 ppm.

Several features of these solid polymer spectra should be pointed out. First, the signal-to-noise ratio is quite low because of the relatively inefficient packing of the small chunks of rubber in the NMR tube. This can be overcome by taking many more scans, but since this was a kinetic study, the number of scans was kept small to ensure that the time for a measurement would be short compared to the rate of change in the reaction.

Second, the peaks in these spectra are quite broad, being on the order of 50–100 Hz, and they increase as the reaction proceeds. The line width is related to the segmental chain motions in the polymer such that the broader the line, the slower the chain motions. The line widths of this polymer are an order of magnitude greater than in other elastomers, such as polybutadiene, indicating far less mobility. The P–N backbone is probably responsible for this behavior. The increase in line widths correlates with the observation that the polymer cross-links and stiffens as the reaction proceeds.

Third, in comparing the spectra in Figure 1, it is seen that a shoulder appears on the left side of the OCH_3 peak and increases as the NCH_3 peak increases. This arises from a difference in chemical shift between an OCH_3 carbon which has another OCH_3 neighbor on the same phosphorus atom and one which has a P═O neighbor as in structure II.

Figure 2 shows dilute solution spectra of the same polymer dissolved in $CDCl_3$ with Me_4Si as reference. Spectrum a is the

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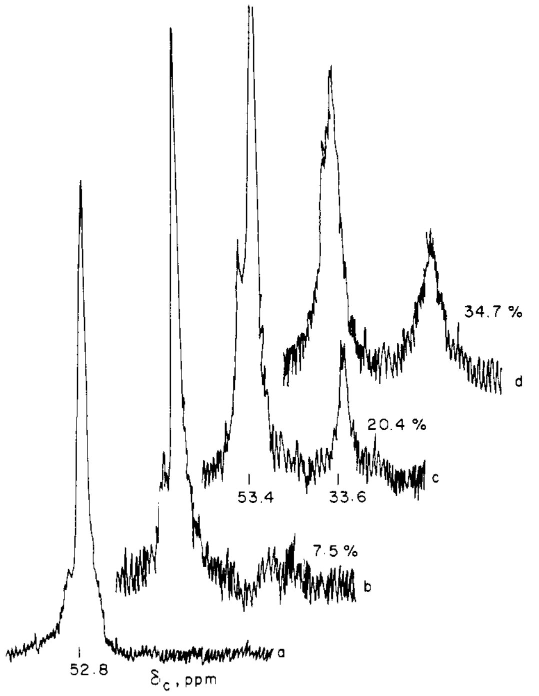

Figure 1. ^1H noise-decoupled ^{13}C NMR bulk spectra of poly(bismethoxyphosphazene) aged at 130 °C. Spectra are offset for clarity. The NCH_3 peak has a T_1 of 0.6 s. 200 scans with 90° pulse, and repetition time of 2.5 s. Chemical shift values are in ppm with reference to Me_4Si. Percent NCH_3 is shown beside the peak at 33.6 ppm: (a) unaged, 50 °C; (b) aged 130 min; (c) aged 220 min; (d) aged 360 min.

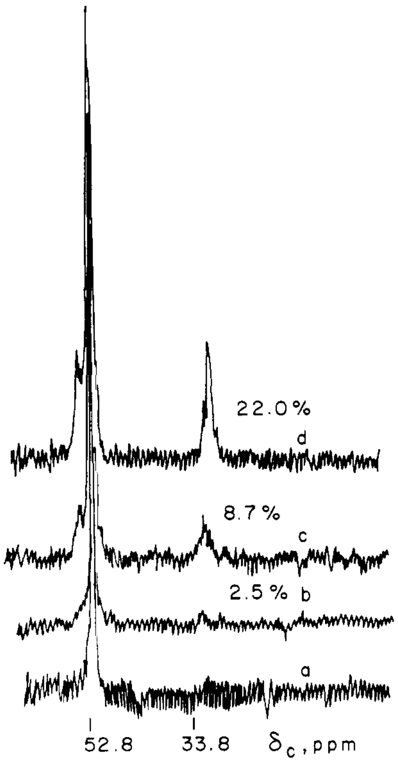

Figure 2. ^1H noise-decoupled ^{13}C NMR spectra of poly(bismethoxyphosphazene) aged at 130 °C and dissolved in $CDCl_3$. The NCH_3 peak has a T_1 of 4 s. Spectra were run at 26 °C with a 45° pulse and a repetition time of 1.5 s. Chemical shift values are in ppm with reference to Me_4Si. Percent NCH_3 is shown above each spectrum: (a) unaged, 3000 scans; (b) aged 1.0 h, 3000 scans; (c) aged 1.5 h, 1400 scans; (d) aged 2.0 h, 2000 scans.

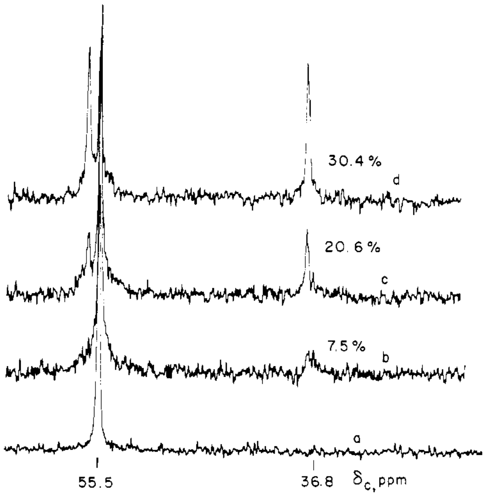

Figure 3. ^1H noise-decoupled ^{13}C NMR spectra of cyclic tetramer, $[NP(OCH_3)_2]_4$, aged in sealed, evacuated NMR tube at 150 °C. The NCH_3 peak has a T_1 of 80 s. Spectra were obtained using a 45° pulse and repetition time of 28 s. Chemical shift values in ppm with reference to Me_4Si. Percent NCH_3 is shown above each spectrum: (a) unaged, 10 scans; (b) aged 3 h, 20 scans; (c) aged 4 h, 20 scans; (d) aged 5 h, 20 scans.

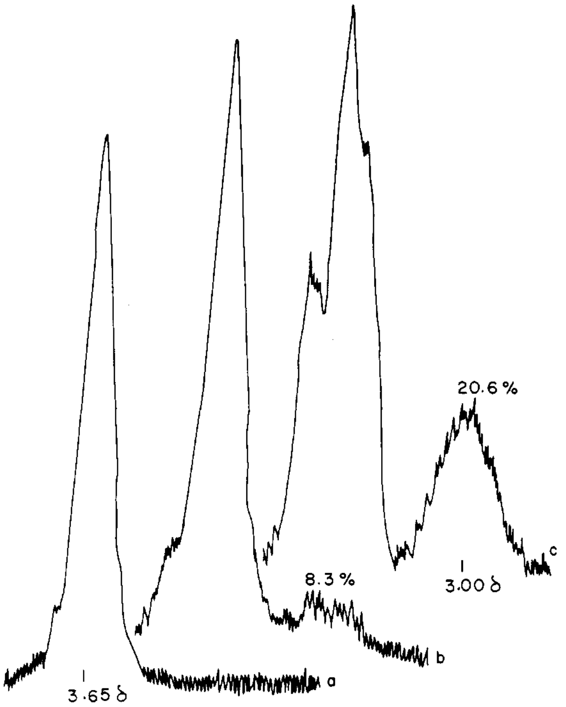

Figure 4. ^1H NMR spectra at 60 MHz of poly(bismethoxyphosphazene) aged at 130 °C and dissolved in $CDCl_3$. Shift values given in δ. Percent NCH_3 is given above peak at δ 3.0: (a) unaged, (b) aged 1.5 h, (c) aged 2.0 h.

polymer before aging and shows a single peak at 52.8 ppm due to OCH_3. Spectrum b results from a sample aged 1.0 h in an oven at 130 °C and exhibits a small peak at 33.8 ppm. Also, a slight shoulder can be seen on the left side of the methoxy peak. Spectrum c was taken after 1.5 h aging at 130 °C. Both the shoulder and the peak at 33.8 ppm due to NCH_3 have increased. Finally, in Spectrum d after aging 2.0 h at 130 °C, the NCH_3 peak is well developed and accounts for 22.0% of the resonance. It is interesting that it has the same structure as the methoxy peak, thus indicating the environment is similar. The shoulder on the downfield (left) side of the methoxy peak

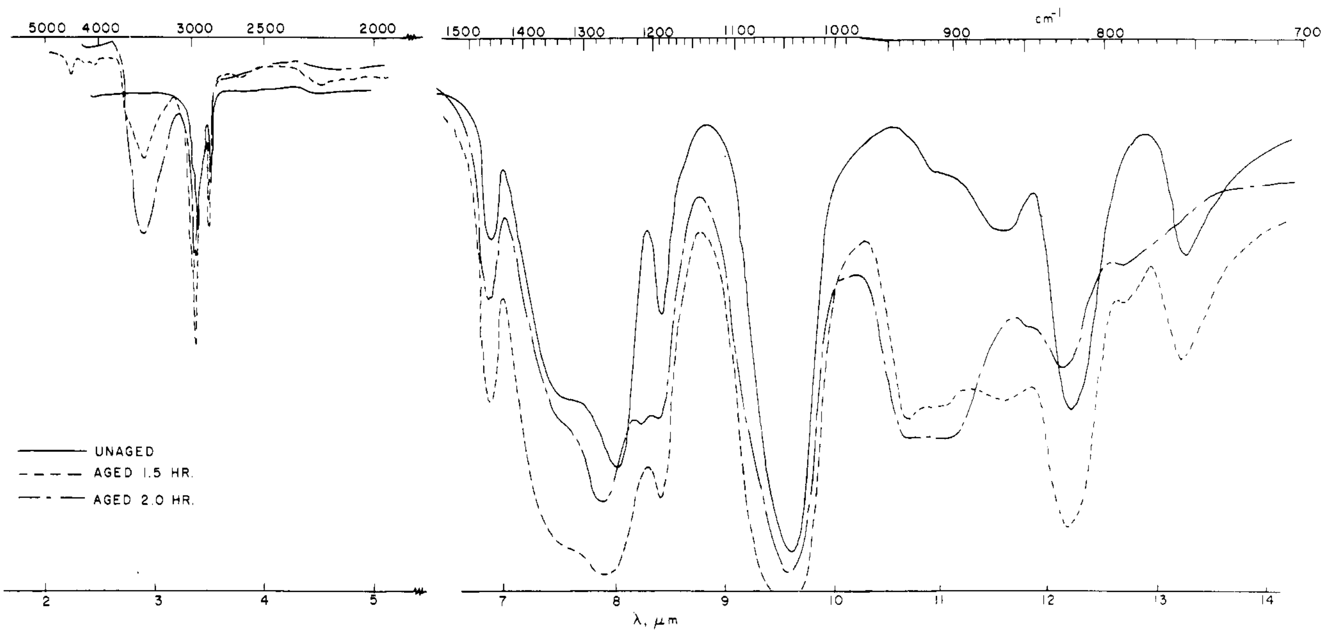

Figure 5. IR spectra of poly(bismethoxyphosphazene) aged at 130 °C. Cast films were used. These are the same samples as described in Figures 2 and 4. Note the break in the spectrum between 5 and 7 μm.

is roughly the same intensity as the NCH_3 peak and must thus be due to the methoxy carbon which remains on the phosphorus after the other has migrated as in structure II. The higher resolution of the solution spectra reveals this feature more clearly than the solid spectra, of course.

The cyclic tetramer, $[NP(OCH_3)_2]_4$, was also studied as a model for the polymer. Although the rate is much lower and higher temperatures are required, it displays a similar behavior as shown in Figure 3. The aging was carried out at 150 °C in a sealed, evacuated NMR tube. Because of the low molecular weight, the peaks are sharper and it is more clearly seen that the downfield methoxy peak has essentially the same intensity as the increasing NCH_3 peak. Expansion of the NCH_3 peak reveals an equal-intensity doublet which indicates the methyl group occupies two slightly different environments. Details of the kinetic study of the tetramer and the polymer will follow in a later publication.

^{1}H NMR. The migration of the methyl group can also be followed by ^{1}H NMR if the samples are first dissolved in a suitable solvent after aging. Figure 4 shows the ^{1}H NMR at 60 MHz of the same samples used in Figure 2. The peaks are quite broad and the noise level is high because of the dilute solution. The single peak at δ 3.65 in spectrum a is due to the methoxy protons. Spectrum b corresponds to Figure 2c in which the polymer was aged at 130 °C for 1.5 h. A broad, weak resonance due to NCH_3 protons at about δ 3 is readily apparent. Also, a shoulder has formed on the downfield side of the methoxy peak as in the ^{13}C spectra. Finally, spectrum c shows the three major peaks after aging 2 h. Electronic integration shows that 20.6% of the methyl groups have migrated from the methoxy to the NCH_3 placement, in good agreement with 22.0% calculated from the ^{13}C spectrum. It is interesting that qualitatively the proton and the ^{13}C spectra look so similar. Quantitatively, the peaks in the ^{13}C spectra are shifted much farther apart and so they are better resolved, especially at the early stages of the reaction.

IR Results. IR spectra were also obtained on the same set of aged samples described in Figures 2 and 4. Significant changes take place in three regions of the IR spectra as illustrated in Figure 5. A band at 3400 cm^{-1} develops and grows larger as the time of aging increases. Since this is in the region of OH and NH, this band could be the result of attack by water and might be only secondarily related to the migration. The samples were aged in air in an oven.

The band at 1250 cm^{-1} shifts to 1270 cm^{-1} after aging 2 h. This is very likely due to a decrease in the P=N-absorption and a corresponding increase in the P=O region at about 1270 cm^{-1}. Also, there is an increase in the band at 1220 cm^{-1}. The strong band at 1040 cm^{-1} is characteristic of P–O–C and decreases drastically upon further aging (not shown).

Probably the most significant changes are observed in the two large bands of about equal intensity which develop at 935 and 900 cm^{-1} upon aging. The former band might arise from the asymmetric P–N–C stretch vibration.[8] If hydrolytic degradation is occurring, as suggested by the band at 3400 cm^{-1}, the band at 900 cm^{-1} could be due to P–O–P asymmetric stretching.

The bands at 820 and 755 cm^{-1} decrease upon aging. The former band is characteristic of $P–O–CH_3$ and the latter is also associated with structure I but its origin is not known. Thus, the band at 820 cm^{-1} could be used to monitor the rearrangement, with appropriate calibration.

Conclusions

It has been shown that thermal rearrangement, involving migration of a methyl group from methoxy to the nitrogen, takes place in poly(bismethoxyphosphazene), as well as in the cyclic tetramer. The course of the reaction in the bulk polymer was followed at elevated temperatures with ^{13}C NMR. It was shown that ^{1}H NMR can be used to follow the reaction if the samples are previously aged and then dissolved in a suitable solvent. Certain bands in IR spectra can also be used, but proper calibration must first be done to quantify the results. ^{13}C NMR offers the advantages that: (1) the reaction is studied in the bulk sample at the temperature of the reaction with immediate results, and (2) no calibration is needed. Complete details of the kinetics of the degradation of this polymer and several similar polyphosphazenes will follow in later publications.

References and Notes

(1) B. Dishon, *J. Am. Chem. Soc.*, **71,** 2251 (1949).
(2) B. W. Fitzsimmons and R. A. Shaw, *Proc. Chem. Soc., London,* 258 (1961).

(3) B. W. Fitzsimmons, C. Hewlett, and R. A. Shaw, *J. Chem. Soc.*, 4459 (1964).

(4) F. Rallo, *Ric. Sci. Chim.*, **8**, 1134 (1965).

(5) T_1 measurements were carried out at the elevated temperatures to determine a proper selection of repetition times and pulse widths for quantitative results. Because of an accompanying reduction in molecular weight, i.e., viscosity, as the thermolysis of the polymer proceeded, T_1 measurements were made in the latter stages of rearrangement when the T_1 values would be the highest. Nuclear Overhauser Enhancement (NOE) measurements were made on the polymer peaks and were within 4% of each other. Consequently, the integral values for the polymer peaks should be quite quantitative. NOE measurements were not made on the cyclic tetramer.

(6) L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra", Wiley, New York, N.Y., 1972, Spectra No. 85 and 275.

(7) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, pp 152 and 160.

(8) N. B. Colthup, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy", Academic Press, New York, N.Y., 1964, p 304.

A New Route for Poly(organophosphazene) Synthesis. Polymerization, Copolymerization, and Ring–Ring Equilibration of Trifluoroethoxy- and Chloro-Substituted Cyclotriphosphazenes[1,2]

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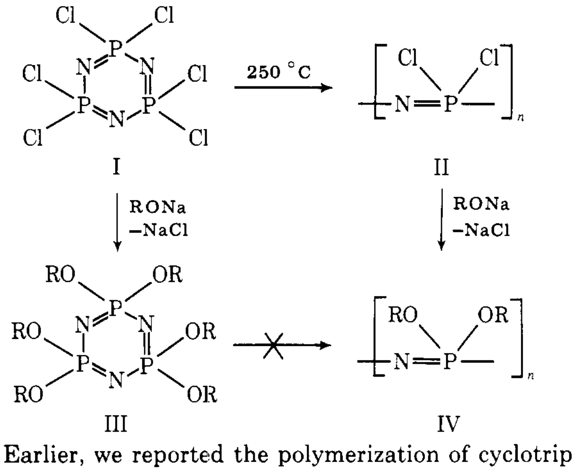
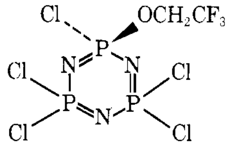
ABSTRACT: The phosphazene cyclic trimer, $[NP(OCH_2CF_3)_2]_3$ (X), copolymerizes with $(NPCl_2)_3$ (I) to yield a new series of elastomers and also undergoes ring-expansion reactions at elevated temperatures. The copolymers were characterized by means of substitution reactions and ^{31}P NMR analysis. The possibility that the polymerization involves a prior ligand exchange was investigated through studies of the thermal behavior of the cyclic phosphazenes, $N_3P_3Cl_5(OCH_2CF_3)$ (V), $N_3P_3Cl_4(OCH_2CF_3)_2$ (trans nongem) (VI), $N_3P_3Cl_3(OCH_2CF_3)_3$ (trans nongem) (VII), $N_3P_3Cl_2(OCH_2CF_3)_4$ (cis nongem) (VIII), and $N_3P_3Cl(OCH_2CF_3)_5$ (IX). All these mixed substituent trimers underwent ring expansion reactions when heated, but only compounds V, VI, and VII yielded linear-type polymers. The gas, CF_3CH_2Cl, was detected as a product from all systems that contained both P–Cl and P–OCH_2CF_3 bonds, with substantial quantities being released at temperatures above 250 °C. This process was apparently connected with the formation of trans-annular-linked cyclic compounds, cross-linked linear chains, or cyclolinear or cyclomatrix-type products. The mechanisms of these reactions are discussed.

Hexachlorocyclotriphosphazene (I) can be polymerized thermally at temperatures above 230 °C to yield the rubbery, hydrolytically labile poly(dichlorophosphazene) (II). Allcock, Kugel, and Valan[3-5] first showed that a broad range of hydrolytically stable and technologically useful polymers can be prepared from II by treatment with nucleophiles such as alkoxides, aryloxides, or amines, and this synthetic route has been widely developed in a number of laboratories.[6-12] The alternative route to the synthesis of poly(organophosphazenes) (IV) via the direct polymerization of hexa(organo)cyclotriphosphazenes (III) has met with little success.



Earlier, we reported the polymerization of cyclotriphosphazenes that contain both phenyl and chloro groups.[13] That work suggested that phosphorus–halogen bonds were necessary before polymerization would occur. Thus, the possibility was foreseen that hexaorgano-substituted cyclotriphosphazenes, such as III, might copolymerize with halogen-containing species, such as I.

To test this hypothesis, copolymerizations were attempted between hexakis(trifluoroethoxy)cyclotriphosphazene (X) and hexachlorocyclotriphosphazene (I). Moreover, compounds V–IX had recently been isolated and characterized in our laboratory,[14] and it was of interest to examine the variation of polymerizability with increasing trifluoroethoxy substitution and the possibility that species, such as V–IX, might be formed as polymerization intermediates when X reacts with I.



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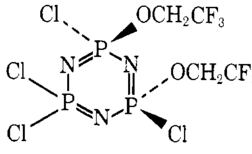

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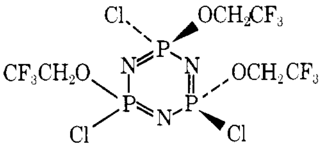

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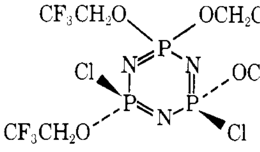

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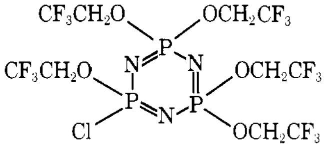

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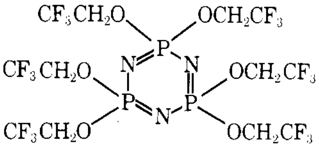

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