

Thermolysis of Poly[bis(trifluoroethoxy)phosphazene]¹

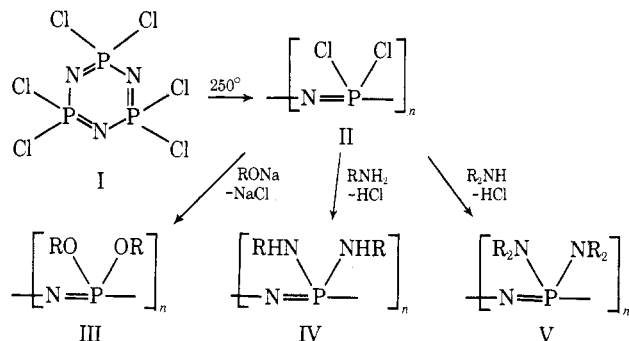
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ABSTRACT: Poly[bis(trifluoroethoxy)phosphazene], $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$, depolymerizes at temperatures above 150° to yield the cyclic trimer, tetramer, pentamer, higher oligomers, and medium molecular weight polymers. The reactions were studied by the use of gel permeation chromatography, mass spectrometry, and solution viscosity. At temperatures near 400°, depolymerization of some polymer samples was accompanied by the elimination of small amounts of gaseous ClCH_2CF_3 . This constitutes a diagnostic test for the presence of residual P-Cl bonds in the polymer. The depolymerization was also studied in the presence of acidic and basic reagents and in solution: acids accelerate the depolymerization. The reaction mechanisms are discussed. The thermal behavior of $[\text{NP}(\text{OCH}_2\text{CF}_2\text{CF}_2\text{H})_2]_n$ is also described.

In earlier papers we described various routes to the synthesis of poly(organophosphazenes).²⁻⁶ These syntheses utilized a prior thermal polymerization of hexachlorocyclotriphosphazene (I) to high molecular weight poly(dichlorophosphazene) (II), followed by nucleophilic replacement of the chlorine atoms in II by alkoxy, aryloxy, or amino groups to yield polymers of structure III, IV, or V (see Scheme I). Mixed substituent polymers have also been prepared,⁵⁻⁹ and the range of polymers now accessible in this system is very large. The developments in this area have recently been summarized.^{10,11}

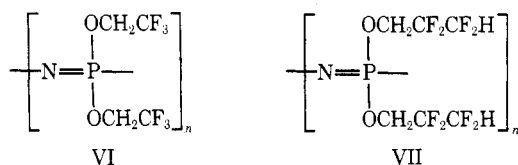
Scheme I



The poly(organophosphazenes) are low-temperature elastomers or flexible, film-forming thermoplastics, depending on the nature of the substituent groups. The chain lengths often exceed 15,000 repeating units. Many of these polymers show impressive hydrolytic and general chemical stability, and specific polymers show unusual low-temperature flexibility, solvent resistance, water repellency, and oxidative stability. A number of derivatives are under development for technological purposes.

However, early work with poly(alkoxy- and aryloxyphosphazenes) demonstrated the tendency of some derivatives to undergo molecular weight decreases when heated at temperatures above 150°. ^{2,3,12} This present work was undertaken to establish the nature of the thermal breakdown process and to determine which factors destabilized the system.

In this paper we report the results of a study of the thermal behavior of poly[bis(trifluoroethoxy)phosphazene] (VI), together with comparisons with the behavior of poly-



[bis(tetrafluoropropoxy)phosphazene] (VII) and a brief

comment on poly(dichlorophosphazene) (II). A later paper will deal with the thermolysis of poly(diphenoxyphosphazene). In the present work, product analysis experiments were conducted, together with gel permeation chromatography, mass spectrometry, and solution viscosity studies for the reactions of the solid or molten polymers. Solution reactions were also performed. Although thermogravimetric analysis data were also obtained, these curves provided virtually no useful information about the thermolysis reactions since the weight losses at specific temperatures merely reflected the boiling points of species formed at lower temperatures.

Experimental Section

Materials. Hexachlorocyclotriphosphazene (I) was obtained from El Monte Chemical Corp., Pasadena, Calif. The commercial trimer-tetramer mixture was purified by vacuum sublimation at 60°, two recrystallizations from hexane, and two final vacuum sublimations. Trifluoroethanol (Halocarbon Products) and tetrafluoropropanol (Pfaltz and Bauer) were used as received. Vapor phase chromatography was used to establish the absence of water in these reagents. Solvents, such as benzene or tetrahydrofuran (Fisher Reagent grade), were dried before use by boiling at reflux over calcium hydride, followed by distillation from the same reagent.

Synthesis of $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ (VI). The procedure used was an improved modification of the one described previously.³ Purified hexachlorocyclotriphosphazene (I) (200 g, 0.57 mol) was degassed by a melt-freeze technique on a vacuum line and was sealed within an evacuated glass tube. The tube was placed in a thermoregulated oven at 250° for 24 hr, during which time polymerization to poly(dichlorophosphazene) (II) took place. The polymer-trimer mixture was transferred to a vacuum sublimator and part of the residual trimer was removed by sublimation at 50-60°/1 × 10⁻² mm for 4 hr. The poly(dichlorophosphazene) residue weighed 194 g. A 97-g portion of this was then dissolved in dry benzene (1200 ml) prior to substitution.

A solution of sodium trifluoroethoxide was prepared by the addition of sodium (59 g) to 2,2,2-trifluoroethanol (250 g, 2.5 mol) in dry tetrahydrofuran (1200 ml). The reaction mixture was filtered through glass wool and was added dropwise to the stirred solution of poly(dichlorophosphazene). The reaction was exothermic and the mixture was heated to maintain boiling of the solvent for 20 hr. At the conclusion of the reaction the mixture was cooled and acidified with dilute hydrochloric acid, and benzene was added to coagulate the polymer. After isolation of the polymer by filtration, it was washed with a large excess of water and was then purified by reprecipitation from tetrahydrofuran into water to remove salts and from tetrahydrofuran into benzene to remove oligomers and low polymers. The polymer was then exhaustively dried under vacuum (yield, 134 g, 66%). In two successive syntheses, the chlorine analyses were slightly different as indicated in the following data. *Anal.* Calcd for $\text{C}_4\text{H}_4\text{F}_6\text{NO}_2\text{P}$: C, 19.75; H, 1.65; Cl, 0; F, 47.0; N, 5.76; P, 12.75. Found (synthesis 1): C, 19.53; H, 1.77; Cl, 0.44; F, 46.87; N, 5.51; P, 12.55. Found (synthesis 2): C, 19.74; H, 1.68; Cl, 0.11. Although the products from both syntheses 1 and 2 were thermolyzed, unless specifically mentioned to the contrary, the work reported here was carried out

with product 2, which had the lowest residual chlorine content.¹³ The number-average molecular weight and solution viscosity data for the polymer from synthesis 2 are reported in a later section.

Synthesis of $[\text{NP}(\text{OCH}_2\text{CF}_2\text{CF}_2\text{H})_2]_n$ (VII). The reaction procedure was essentially the same as for the preparation described above. The reaction mixture was prepared from poly(dichlorophosphazene) (256 g), dry tetrahydrofuran (9 l.), and the alkoxide prepared from 2,2,3,3-tetrafluoropropanol (732 g, 2.88 mol) and excess sodium in tetrahydrofuran (1500 ml). The mixture was stirred and boiled at reflux for 3 days, and 6 l. of tetrahydrofuran were removed by distillation. The polymer was purified by precipitation from tetrahydrofuran into petroleum ether, and twice from acetone into water. The yield of the adhesive, vacuum-dried polymer was 146.4 g (22%). *Anal.* Calcd for $\text{C}_6\text{H}_8\text{F}_8\text{N}_2\text{O}_2\text{P}$: C, 23.4; H, 1.95; Cl, 0; F, 49.5; N, 4.56; P, 10.10. Found: C, 23.49; H, 2.12; Cl, 0.42; F, 49.75; N, 4.41; P, 10.20. A Beilstein test for chlorine was negative.

Poly(dichlorophosphazene) for Direct Depolymerization. The poly(dichlorophosphazene) used for direct depolymerization experiments was prepared and purified as described previously. However, the absence of residual oligomers was ensured by two successive precipitations from benzene into *n*-heptane followed by vacuum drying at 25°. No sublimate was isolated from a sample of this material after heating in a vacuum sublimator at 50° (0.5 mm) for 14 days.

Equipment and Technique. A Hewlett-Packard Model 5750 unit was used for vapor phase chromatography. Mass spectra were obtained with an A.E.I. MS 902 instrument. Solution viscosities were measured in acetone solution at 30° with the use of Cannon-Ubbelohde dilution viscometers. Microanalyses were by Schwartzkopf Microanalytical Laboratories.

Gel permeation chromatography was effected with the use of a Waters Associates ALC/GPC 501 instrument fitted with a refractive index detector. The columns consisted of a total of 8 ft of Corning porous glass beads arranged in 2-ft lengths of 75-, 175-, 700-, and 2000-Å pore size segments. The solvent used was acetone (Baker), with an elution rate of 2 ml/min. The sample injection volume was 2 ml of a 0.5% solution, and the instrument sensitivity range was $\times 1$. Calibration of the system to polystyrene standards was accomplished with the use of chloroform as a solvent.¹⁴ In a typical experiment, high molecular weight polyphosphazenes (estimated $\bar{M}_n = 1 \times 10^6$ to 5×10^6) were eluted in about 23 min (46 ml), whereas the lowest cyclic oligomers and other low molecular weight species appeared after about 45 min (90 ml). It should be noted that the absence of uniform trends in the height of this low molecular weight peak (Figure 1) is a consequence of the fact that the cyclic trimer and tetramer show a negative refractive index relative to acetone, whereas higher oligomers and other species present show positive peaks. The superimposition of these peaks leads to the apparently anomalous peak pattern shown.

Depolymerization Procedure Using Sealed Tubes. Poly[bis(trifluoroethoxy)phosphazene] (2 g) was cut into small pieces and placed in constricted glass tubes. Each tube was evacuated and sealed while attached to a vacuum line. The volume within each sealed tube was ~ 5 ml. Gaseous additives were introduced *via* the vacuum line. Three methods were employed for heating of the tubes. For reactions carried out at temperatures below 300° for 30 hr or less, the sealed tubes were placed in a thermoregulated Freas Model 104 oven. Temperature regulation was within $\pm 0.5^\circ$. For long-term reactions within the same temperature range, the tubes were suspended above the surface of boiling organic liquids. Reactions carried out at 300° or above were effected by suspension of the tubes below the surface of a Techne type SBL fluidized sand bath. At the completion of each reaction, the tubes were cooled and opened, and samples of the reaction mixture were analyzed.

Sublimation Depolymerizations. A few depolymerizations were carried out by heating of the polymer in a vacuum sublimator at $\sim 100^\circ$ (1×10^{-2} mm). The slow removal of cyclic oligomers under these circumstances constituted a nonequilibrium depolymerization process.

Flow-Tube Depolymerizations. This constituted a second nonequilibrium method of depolymerization. The polymer sample (~ 1 g) was placed in a porcelain boat which was itself located inside a glass tube within a Lindberg type 55035A tube furnace. The sample was heated to 400° as a flow of helium gas (37 cm³/min) passed over the sample. The volatile thermolysis products were swept out of the heated region and were condensed in a trap

cooled at -196° . These volatile products were then analyzed by mass spectrometry and vapor phase chromatography.

Solution Depolymerizations. One per cent solutions of the polymer in acetone, tetrahydrofuran, methyl ethyl ketone, ethyl acetate, and cyclohexanone were boiled at reflux (56.2, 67, 79.6, 77, and 156°, respectively) for various times. After completion of each reaction, the solvents were removed at reduced pressure and the residue was analyzed by the methods discussed above.

γ Irradiation. Polymer film samples (~ 1 g) were sealed in evacuated glass tubes and were irradiated by exposure to a ⁶⁰Co source at a dose rate of 9×10^5 rads/hr in the reactor at The Pennsylvania State University. The sample temperature was 30° during irradiation.

Results and Discussion

Reaction Products, Low Molecular Weight. Three types of reactions were performed for each polymer to determine (1) products formed in a gas flow tube (see Experimental Section), (2) products formed under nonequilibrium vacuum sublimation conditions, and (3) products formed within evacuated sealed tubes.

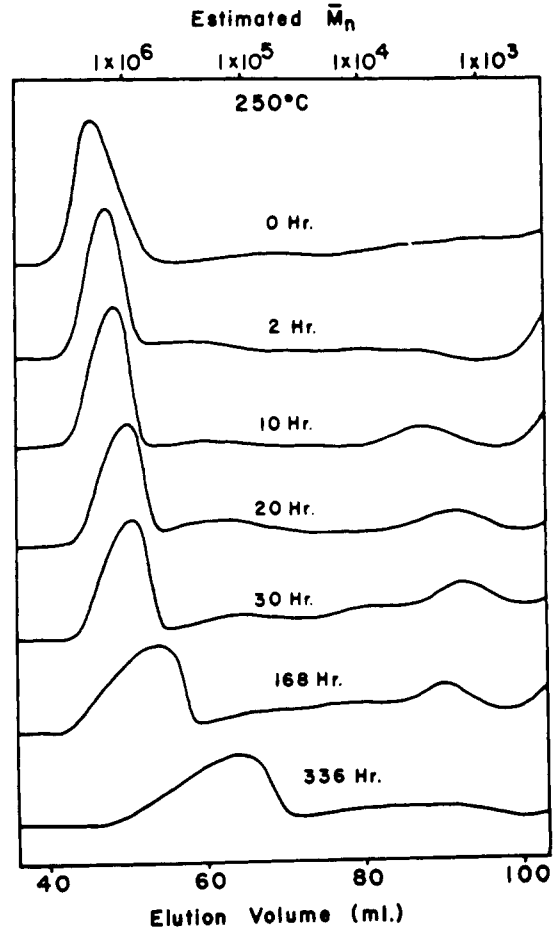
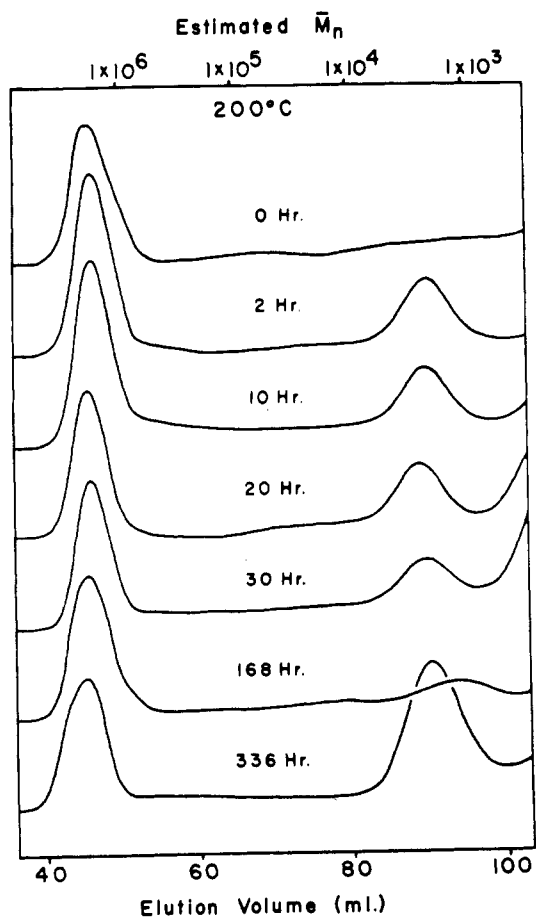
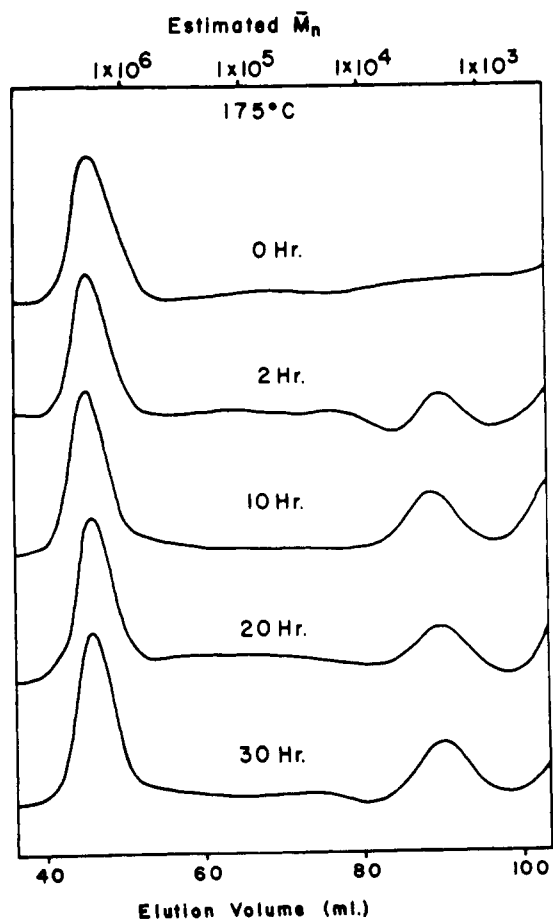
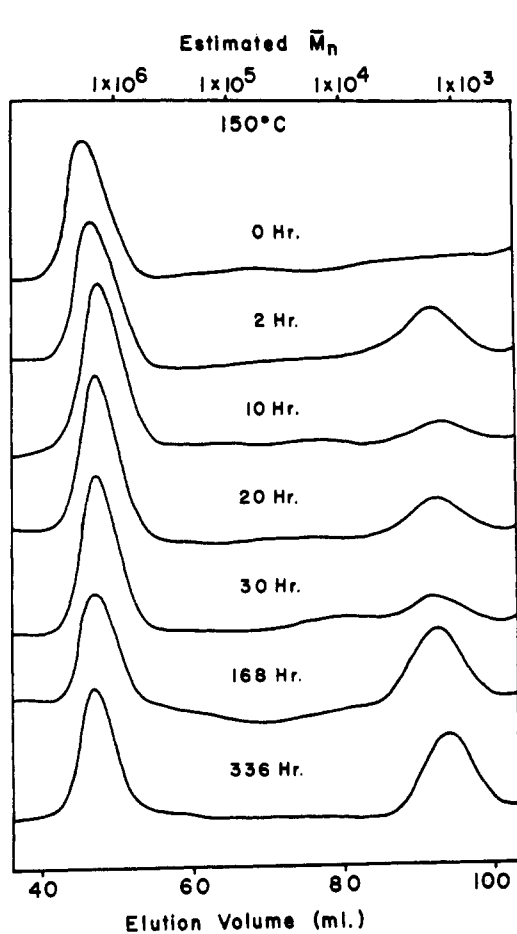
For poly[bis(trifluoroethoxy)phosphazene] (VI) in a helium flow system at 400°, the principal reaction products were 1,1,1-trifluoro-2-chloroethane, the cyclic trimeric through hexameric trifluoroethoxyphosphazenes, $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_{3-6}$, higher cyclic oligomers, and a non-volatile, pyrolyzed residue ($<10\%$). The latter product showed a much higher phosphorus and nitrogen content by microanalysis than did the polymeric and oligomeric phosphazenes.¹⁵

The gaseous product, $\text{CF}_3\text{CH}_2\text{Cl}$, was identified from its infrared and mass spectra. In the latter identification the parent peak was observed together with the chlorine isotope peaks and fragmentation peaks at 120, 118, 83, and 69 amu. It is especially significant that this product was detected even when the chlorine content of the polymer was only 0.11%. Thus, pyrolysis of the polymer to $\text{CF}_3\text{CH}_2\text{Cl}$ at temperatures above 250° constitutes a sensitive technique for the detection of residual chlorine in the polymer.

However, the principal reaction product from the flow tube pyrolysis was an oily, liquid distillate. The constituents of this mixture were identified by infrared, vapor phase chromatographic, and mass spectral techniques as low molecular weight cyclic homologs of the polymer. In the mass spectral identification, a continuous series of cyclic species extended upward from the trimer. Although species up to the hexamer were positively identified, the spectrum continued beyond the highest mass limit of the instrument. The cyclic trimer and tetramer predominated in the mixture. Thus, it appeared that pyrolysis at 400° yields a continuous spectrum of cyclic oligomeric homologs. Similar oligomeric products were identified when $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ was heated at $\sim 150^\circ$ in a vacuum sublimator. The sublimate consisted of $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_{3-5}$ cyclic species.

The same pattern was repeated when $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ was heated at temperatures between 150 and 300° in evacuated sealed tubes. Again the oligomers of formula $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_{3-5}$ were definitely identified, but the experimental evidence indicated that the series extended to $n = 10$ and probably beyond. At 300°, the tetramer, $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_4$, appeared to be the preferred product. It should be noted that sealed tubes containing the polymer exploded after they had been heated at 300° for more than 24–30 hr or when heated at higher temperatures for shorter times. These explosions were attributed to the pressure buildup resulting mainly from the formation of $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_3$ and $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_4$.

Poly[bis(tetrafluoropropoxy)phosphazene] (VII) behaved similarly when heated. At temperatures between 260 and



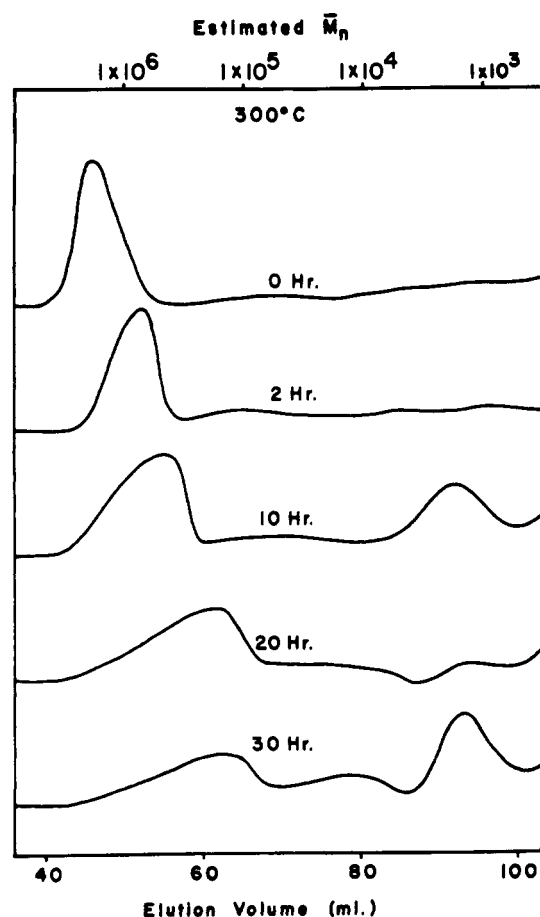
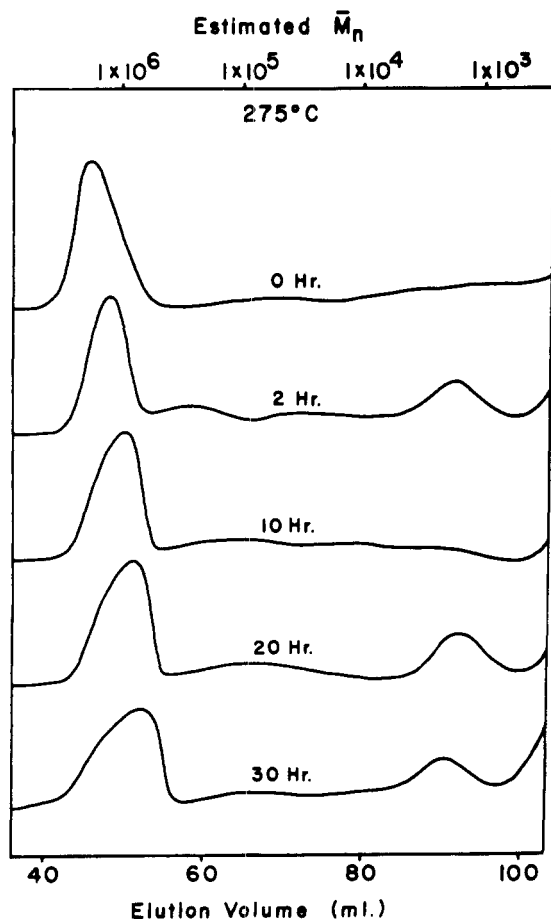


Figure 1. Gel permeation chromatography curves for samples of $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ heated in evacuated sealed tubes at various temperatures.

400° in a helium flow system, the cyclic species, $[\text{NP}(\text{OCH}_2\text{CF}_2\text{CF}_2\text{H})_2]_{3-20}$ were formed, together with $\text{HCF}_2\text{CF}_2\text{CH}_2\text{Cl}$. The latter product was identified by mass spectrometry (parent peak, chlorine isotopes, and fragments at 152 and 150 amu).

Reaction Products, High Molecular Weight. When the polymers were heated in evacuated sealed tubes the formation of low molecular weight oligomers was accompanied by a general decrease in the molecular weight of the high polymers. In fact, the overall thermal reaction leads to the formation of a broad range of both low and high molecular weight species which have the same basic formula, $[\text{NP}(\text{OR})_2]_n$. The molecular weight changes in the higher molecular weight region were followed by solution viscosity and gel permeation chromatography techniques.

Thermolysis of $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ in the Bulk Phase. The following discussion is divided into (1) an analysis of the effect of reaction time at a given temperature, (2) the effect of temperature at a uniform time, and (3) the effect of various additions on the thermolysis reaction.

Figure 1 illustrates the molecular weight changes which occurred when $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ was heated in sealed evacuated tubes for various times at 150, 175, 200, 250, 275, and 300°, as measured by gel permeation chromatography. In these curves, high polymer (estimated $\bar{M}_n \approx 2 \times 10^6$) appeared at an elution volume of ~46 ml, near the exclusion limit of the columns, and low molecular weight cyclic oligomers were eluted at ~90 ml ($\bar{M}_n \approx 2 \times 10^3$). At 150° a slow decrease occurred in the intrinsic viscosity values over a period of 336 hr, although the most rapid fall-off (from 2.2 to 1.6 dl per g) took place during the first

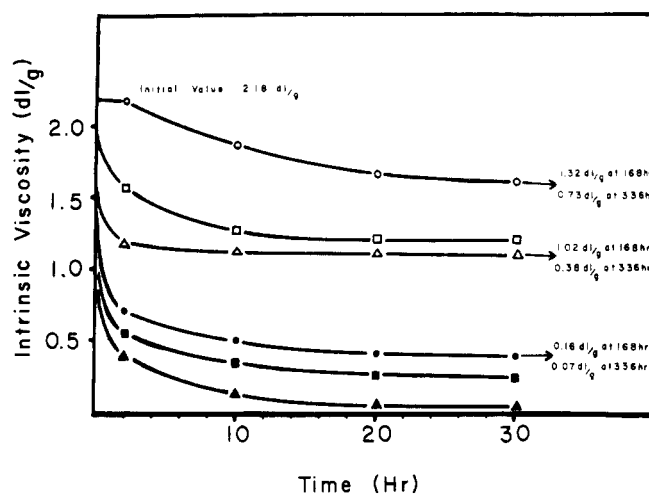


Figure 2. Variation of intrinsic viscosity with time for samples of $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ heated in evacuated sealed tubes: (○) 150°, (□) 175°, (Δ) 200°, (●) 250°, (■) 275°, (▲) 300°.

30 hr (Figure 2). These molecular weight decreases were only marginally discernible from the GPC curves.

As the temperature was raised to 300° the initial fall-off in intrinsic viscosity occurred more rapidly, although in each case the molecular weight decrease reached a point beyond which the intrinsic viscosity declined little with time (Figure 2). This rapid initial molecular weight decrease was hardly detectable in the GPC spectra obtained from the 175 and 200° runs, and this suggests that these initial changes affect only the highest molecular weight

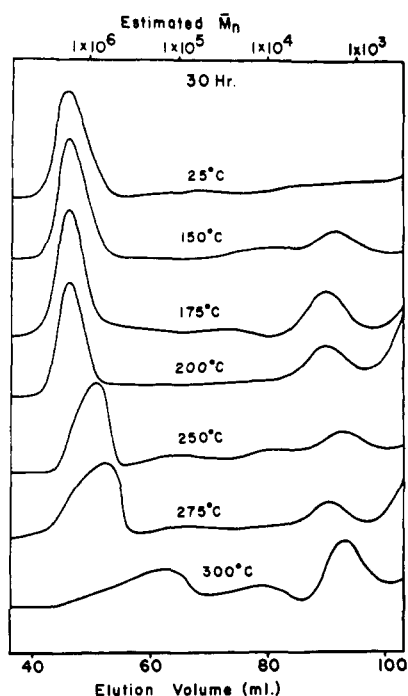


Figure 3. Changes in the gel permeation chromatography curves of $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ after heating of the polymer for 30 hr at different temperatures.

species.¹⁶ The oligomers formed by depolymerization were also evident from the GPC spectra.

At 250° and above, marked changes occurred in the GPC spectra (Figure 1). For the 250° runs, the GPC spectra showed a steady movement of the center of the distribution curve from $\bar{M}_n \approx 2 \times 10^6$ to $\bar{M}_n \approx 2 \times 10^5$ over a period of 336 hr. This was accompanied by a broadening of the curve. Similar effects were noted on an accelerated time scale for the 275° runs. The most dramatic effect was seen for the 300° runs, which exhibited a marked molecular weight decrease within 2 hr, and almost total depolymerization within 30 hr. Long-term reactions at 300° or short-term reactions at higher temperatures were precluded by explosion of the tubes due to the internal vapor pressure of the depolymerization products. Thus, it was apparent that heating of the polymer, especially above 250° causes a redistribution of molecular weights which progressively favors the medium and low molecular weight species.

These molecular changes were accompanied by changes in the bulk properties of the polymer. Heating at temperatures of 200° or below did not appreciably change the appearance or manipulative properties of the polymer, even after 336 hr. However, at 250° and higher, marked changes took place in the physical properties of the polymers, and the products were dark oils when cooled to room temperature. It is noteworthy that the most dramatic changes take place above the crystalline melting point of the polymer (247°) and the significance of this will be discussed later. Microanalysis of the products formed after 30 hr at 150–250° showed an identical composition to that of the starting material. Supplementary information about the depolymerization process is provided by Figures 3 and 4, which show the effect of temperature changes for a given reaction time (30 and 336 hr).

The effect of various additives on the thermolysis is shown in Figure 5. Ammonia, potassium hydroxide, sodium carbonate, aluminum chloride (~2 wt %), and nitrogen gas (>760 mm) had no accelerating influence on the

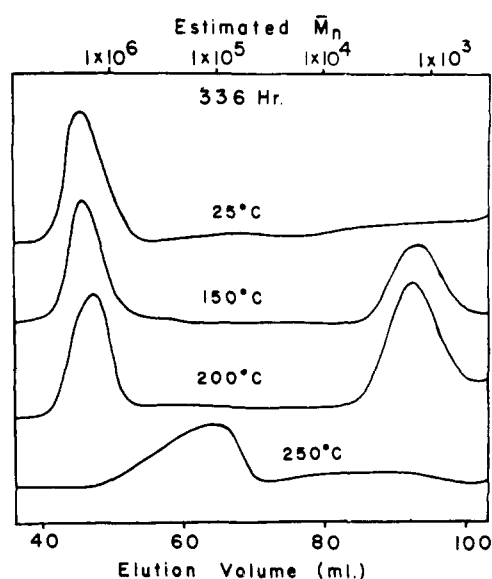


Figure 4. Effect of temperature on the gel permeation chromatography curves of $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ after heating of the polymer for 336 hr.

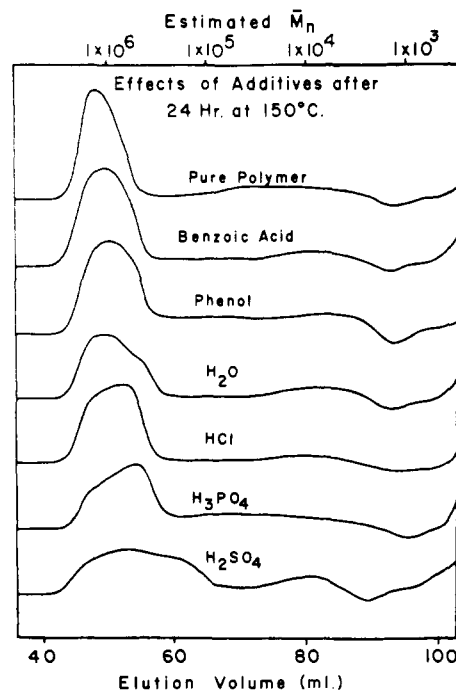


Figure 5. Gel permeation chromatograms for $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ after heating of the polymer for 24 hr at 150° in the presence of additives (~2 wt %).

depolymerization. Pressure changes had no discernible effect on the reaction. However, the addition of acids or water did accelerate the reaction. The following order of catalytic effect was found: phenol \approx benzoic acid < H_2O < HCl < H_3PO_4 \ll H_2SO_4 . Sulfuric acid especially (2%) brought about a rapid depolymerization of the polymer to a yellow oil after only 24 hr at 200°. The reaction products consisted mainly of the cyclic trimer and higher cyclic oligomers. The implications of this catalysis are discussed in a later section.

Thermolysis of $[\text{NP}(\text{OCH}_2\text{CF}_2\text{CF}_2\text{H})_2]_n$ in the Bulk Phase. Poly[bis(tetrafluoropropoxy)phosphazene] (VII) depolymerized more readily than the trifluoroethoxy derivative. At 150° appreciable depolymerization of VII occurred within 30 hr and at 250° an almost complete con-

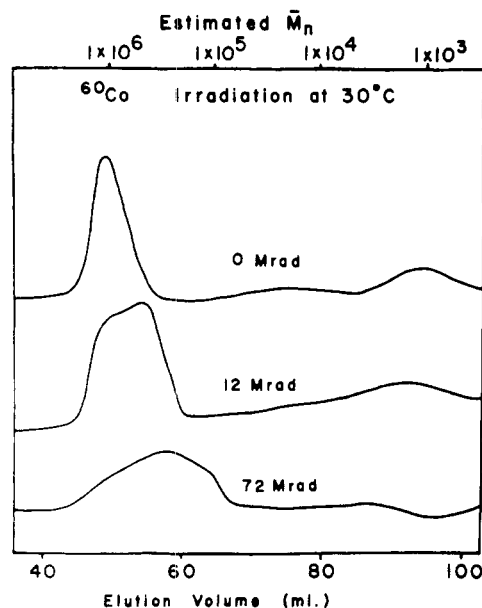


Figure 6. Gel permeation chromatograms of $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ following γ irradiation. The 72-Mrad curve represents the polymer remaining after removal of the cross-linked portion.

version to cyclic oligomers had taken place within 20 hr. The solution viscosity data were also consistent with a rapid thermal depolymerization process at temperatures above 150° .

γ Irradiation. Poly[bis(trifluoroethoxy)phosphazene] (VI) was subjected to γ irradiation from a ^{60}Co source at 30° . After irradiation with a total dose of ~ 12 Mrads, the polymer was no longer flexible. A GPC spectrum showed that appreciable broadening of the molecular weight distribution had occurred (Figure 6). Irradiation with a total dose of ~ 72 Mrads embrittled the sample even more and caused cross-linking of 50% of the polymer. The uncross-linked fraction showed a very broad molecular weight distribution. Poly[bis(tetrafluoropropoxy)phosphazene] also depolymerized during γ irradiation.

Stability in Solution. Solutions of $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ in acetone, tetrahydrofuran, and methyl ethyl ketone, ethyl acetate, and cyclohexanone (1 wt % concentration) were boiled at reflux for 2 weeks. No change in intrinsic viscosity was detected for the acetone, tetrahydrofuran, or ethyl acetate solutions, but the intrinsic viscosity of the methyl ethyl ketone solution fell from 2.1 to 0.55 dl per g. Similarly, the product from the cyclohexanone solution was extensively depolymerized ($\mu = 0.24$ dl/g). The changes in the GPC curves were indicated in Figure 7. The fact that this polymer can depolymerize in solution at the relatively low temperature of 79.6° suggests that, unless special precautions are taken, some depolymerization will occur during the synthesis of poly(alkoxyphosphazenes). However, the nature of the solvent clearly affects the depolymerization behavior.

Depolymerization of Poly(dichlorophosphazene). The depolymerization of $(\text{NPCl}_2)_n$ cannot be studied as readily as the thermolyses of poly(organophosphazenes). Gel permeation chromatography and solution viscosity work are difficult to perform in a reproducible manner because of the tendency shown by $(\text{NPCl}_2)_n$ to cross-link in solution. Samples of reprecipitated polymer turn black and cross-link when heated in evacuated sealed tubes at 300° . However, some information has been obtained by the use of the sublimation-type depolymerization techniques and a helium flow tube apparatus, coupled with mass spectrometry, and vapor phase chromatography. The results of

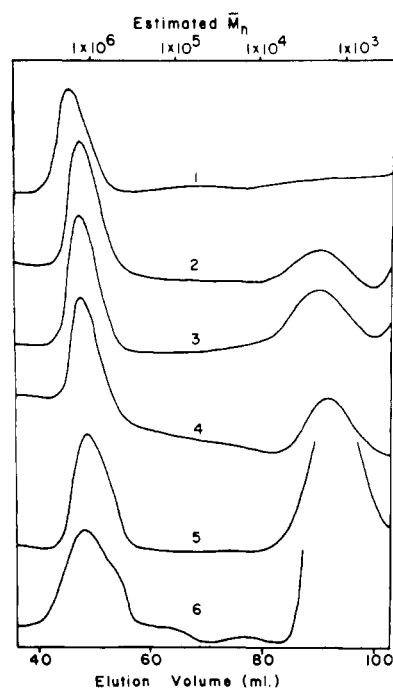
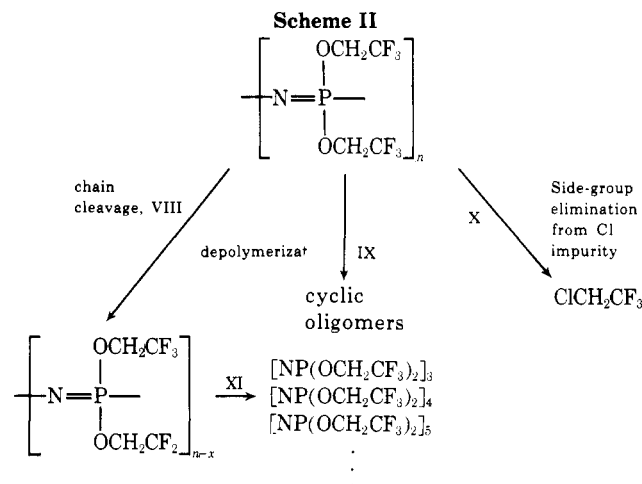


Figure 7. Gel permeation chromatograms obtained following 2-weeks refluxing of 1% solutions of $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ in the following solutions: 1, no solvent, 25° ; 2, acetone at 56° ; 3, tetrahydrofuran at 67° ; 4, ethyl acetate at 77° ; 5, methyl ethyl ketone at 79° ; 6, cyclohexanone at 155° .

sublimation experiments show that the heating of the oligomer-free $(\text{NPCl}_2)_n$ at 260° yielded a sublimate which contained cyclic oligomers of formula, $(\text{NPCl}_2)_{3-7}$. Similarly, in the flow tube experiments at 400° , the cyclic oligomers, $(\text{NPCl}_2)_{3-9}$ distilled from the polymer. Mass spectral data obtained suggested that the hexamer, $(\text{NPCl}_2)_6$, was the predominant product under these reaction conditions. It should be noted that these depolymerizations were performed under nonequilibrium type conditions, and that polymerization of the trimer in the same temperature range apparently yields no higher cyclic oligomers.

Reaction Mechanism. Four basic reactions are proposed for the thermolysis of $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ and $[\text{NP}(\text{OCH}_2\text{CF}_3\text{CF}_2\text{H})_2]_n$. These are depicted as reactions VIII-XI (Scheme II).

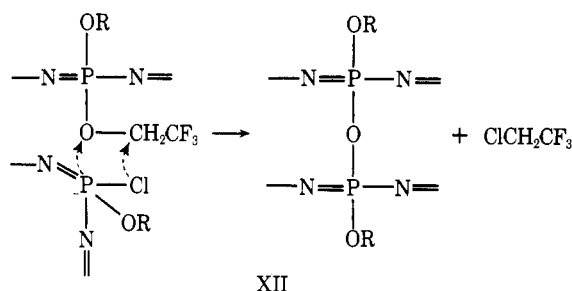


First, the chain cleavage process (VIII) is considered to be responsible for the initial, sharp molecular weight decline which is obvious from the solution viscosity data (Figure 2). It is believed that such a cleavage could occur at "weak" points along the chain. Possible cleavage sites

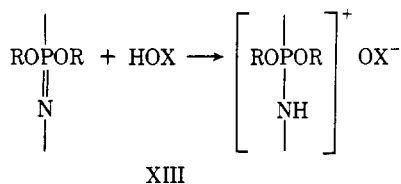
could be P-OH side groups, P(O)-NH units, chain branch points, or residual P-Cl units. The evidence at present available suggests that such chain-breaking processes could, in a carefully synthesized polymer, lead to cleavage of a chain into perhaps 2 to 10 smaller linear fragments. The larger the number of weak links per chain, the more precipitous is likely to be the initial rapid molecular weight decline.

A second, and probably concurrent, process is believed to be a slower "unzipping" type of reaction to yield cyclic trimer, tetramer, pentamer, etc. At present it is not clear if such a cyclization process can occur from the original polymer molecules (mechanism IX) or if it only initiated from the terminal units of linear fragments (mechanism XI). Either of these processes could account for the appearance of cyclic oligomers at temperatures in the 150–300° range. It is presumed that this reaction is equilibrium controlled, with a higher concentration of oligomers being formed (in a closed system) at high temperatures. It also seems likely that the relative concentrations of cyclic oligomers formed will depend on the ease with which a chain end can "bite back" on the middle units to generate a 6-, 8-, 10-, etc. membered ring.

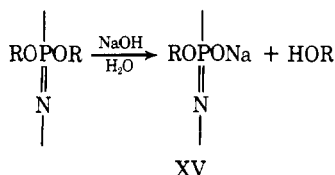
The ligand elimination process (reaction X) is clearly dependent on the degree of halogen replacement in the polymer. It is not known if such an elimination mechanism provides an initiation site for chain cleavage or for cyclization-depolymerization. Elimination of ClCH_2CF_3 (XII) between repeating units would generate a cross-link.



The role of acids in the acceleration of depolymerization can be understood if it is assumed that protonation of a chain nitrogen atom can occur in the presence of strong acid. Protonation could conceivably weaken a chain bond sufficiently to constitute a site for cleavage, while the presence of the cationic charge could open a pathway to a backbiting attack elsewhere on the same chain.



It appears to be significant that bases do not function as depolymerization accelerators in this system. Cleavage of fluoroalkoxy groups from phosphorus by base is a well-established reaction¹⁷⁻²⁰ (XV). It must be assumed that the



presence of a P-ONa unit in the polymer is not a destabilizing influence, presumably because a rearrangement of such species to a phosphazane is not possible.

Two other points are of particular interest with respect

to this depolymerization. First, the depolymerization process is markedly accelerated in the bulk phase above the melting point of $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$. This reinforces the view that a more complex mechanism is involved than a simple random cleavage of chains followed by cyclization. In the melt or in solution, more extensive opportunities exist for the active chain end to "back bite" on the same chain in order to liberate cyclic species. The fact that depolymerization occurs in dilute solution reinforces the view that an intramolecular rather than intermolecular mechanism is operative.

The second point is concerned with the driving force for depolymerization. From an entropic point of view, rings are favored at high temperatures relative to chains, irrespective of the nature of the backbone or side group.²¹ However, an additional factor involves the enthalpy of cyclization. The geometry of the phosphazene repeating unit is such that the substituent groups incur less intramolecular steric hindrance in a cyclic trimeric ring than in a linear chain.^{10,11,21} Thus, the presence of bulky substituent groups should favor the formation of cyclic oligomers from linear polymer molecules if the temperature is sufficiently high to permit the mechanism of equilibration to operate. It is believed that this interpretation may explain why the tetrafluoropropoxy-substituted polymer is apparently more prone to depolymerization than the trifluoroethoxy derivative, and why depolymerization in the bulk phase takes place at an observable rate only above 150°.

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References and Notes

- (1) This paper is Part XIX in a series on phosphorus-nitrogen compounds.
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- (13) The amount of residual chlorine present in these polymers is a function of the time and temperature used for the substitution reaction. Excessive reaction temperatures can lead to depolymerization. Insufficient reaction time or too low a temperature can lead to partial substitution. It should also be noted that incorrect information about the degree of substitution can be deduced from the chlorine analysis alone if the polymer has previously been subjected to hydrolytic conditions.
- (14) The slope of the calibration line ($\log \bar{M}_n$ /elution volume in ml) was -0.0774 as derived from 10 polystyrene standards with \bar{M}_n values in the range of 1950 to 1,990,000. An elution volume of 62 ml corresponded to an \bar{M}_n value of 159,000 for polystyrene. A sample of $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ which showed a GPC peak elution time of 46 ml in acetone was found to have an \bar{M}_n value of at least 250,000 from osmotic pressure measurements in acetone. These data and molecular weight data obtained for related polymers^{8,9} were used as a basis for a correlation of GPC elution volume with approximate \bar{M}_n .
- (15) Anal. for the pyrolyzed residue was N, 8.92; F, 14.52; P, 24.88. Analyses for the volatilized oligomeric reaction products corresponded closely to the theoretical values reported for $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ in the Experimental Section.
- (16) It should also be noted that because GPC elution curves are logarithmic, changes in the highest molecular weight regions are less noticeable than those in the lower molecular weight region. Furthermore, porous glass GPC columns show sharp exclusion limits.
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