The Thermal Breakdown of Poly(diphenoxyphosphazene)[1,2]

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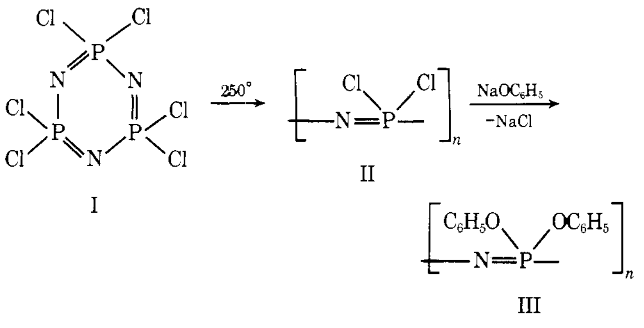
ABSTRACT: Poly(diphenoxyphosphazene), $[NP(OC_6H_5)_2]_n$, was subjected to thermal degradation studies over the temperature range of 100–400°, and the reaction products were analyzed by gel permeation chromatography, solution viscosity, and mass spectrometry. A general lowering of the molecular weight with increasing temperature was observed at temperatures above 100°. An initial sharp decrease in molecular weight was ascribed to chain cleavage at weak points along the backbone, and the formation of cyclic oligomers appeared to result from a subsequent cyclization–depolymerization process. The mechanism whereby chlorobenzene is formed as a trace fragmentation species is discussed. Depolymerizations in solution at temperatures between 30 and 161° were also studied.

Some of the reasons for the growing interest in poly(organophosphazenes) have been discussed previously.[2-9] Many of these polymers show unusual low temperature flexibility, solvent resistance, or useful surface properties. The molecular weights, dilute solution properties, and thermal transition characteristics of a number of poly(aryloxyphosphazenes) have recently been described.[10] However, the thermal behavior of these polymers has been the subject of some discussion. Thermogravimetric analysis curves for several poly(organophosphazenes) show a weight loss only at temperatures above 300°.[11-14] However, the thermogravimetric analysis method, while useful for preliminary evaluation, nevertheless overestimates the thermal stability of polyphosphazenes because the weight loss reflects the boiling points of oligomers formed by equilibration at lower temperatures, rather than the stability of the polymer itself. For this reason we have undertaken a more detailed investigation of the thermolysis reactions of poly(organophosphazenes). The thermal behavior of poly[bis(trifluoroethoxy)phosphazene], $[NP(OCH_2CF_3)_2]_n$, and poly[bis(tetrafluoropropoxy)phosphazene], $[NP(OCH_2CF_2CF_2H)_2]_n$, were reported in an earlier paper.[2] Here we describe the thermolysis of high molecular weight poly(diphenoxyphosphazene)(III). This polymer is a crystalline, film-forming thermoplastic, prepared from hexachlorocyclotriphosphazene (I) by a modification of the method described by us previously.[5,6]



Experimental Section

Materials. Hexachlorocyclotriphosphazene (I) (El Monte Chemical Co.) was purified by vacuum sublimation at 50° (1×10^{-2} mm) to yield material with a melting range of 110.5–113.0°. Phenol (J. T. Baker Chemical Co., U.S.P.) was purified by distillation to yield a fraction with bp 178.5–180.0° (760 mm). 1,4-Dioxane (Baker Reagent grade) was purified by distillation from potassium hydroxide, followed by distillation from sodium immediately before use. The tetrahydrofuran (Fisher Reagent grade) was used as received for solution viscosity or gel permeation chromatography work but was dried by distillation from calcium hydride when used in the synthesis procedure.

Poly(diphenoxyphosphazene). Hexachlorocyclotriphosphazene (I) (180 g, 0.52 mol) was sealed in an evacuated glass tube and was allowed to polymerize at 250° for 19 hr. The mixture of unchanged trimer (I) and poly(dichlorophosphazene) (II) was then subjected to vacuum sublimation at 50° (0.01 mm) for 16 hr to remove the trimer. The yield of II was 107 g (59.4%). The poly(dichlorophosphazene) was dissolved in 1,4-dioxane (2000 ml) and to this solution was added slowly a solution of sodium phenoxide, prepared from phenol (310 g, 3.3 mol) and sodium (81 g, 3.5 g-atom) in dioxane (2000 ml). This constituted the use of a 15% excess of sodium phenoxide. The reaction mixture was first stirred at reflux for 48 hr and then cooled to 25° and filtered to remove the precipitate of sodium chloride, before addition of a further 1.1 mol of sodium phenoxide solution, followed by continued stirring at reflux for 24 hr. This two-step reagent addition sequence was designed to ensure the maximum replacement of chlorine by phenoxy.

The reaction mixture was cooled to 25° and the substituted polymer was precipitated by dropwise addition of the mixture into water. The precipitate was subsequently redissolved in tetrahydrofuran and precipitated into water a total of three times and precipitated twice from tetrahydrofuran into acetone. It was then vacuum dried to yield 40 g (19%) of polymer. *Anal.* Calcd for $C_{12}H_{10}O_2NP$: C, 62.34; H, 4.33; N, 6.06; P, 13.42. Found: C, 62.09; H, 4.45; N, 6.35; P, 13.64; Cl, <0.40. By contrast, samples of III prepared in benzene–xylene mixtures without the two-step reagent addition yielded polymers which contained 2.31% of residual chlorine. The depolymerization experiments reported in this paper are for the polymer which showed the lower chlorine content. Significantly, the polymer with the higher chlorine content had a higher viscosity average molecular weight (3.6 dl/g, compared to 2.0 dl/g), which indicates that the more forcing conditions required to remove the last few per cent of chlorine resulted in some depolymerization.

Viscosity Measurements. Solution viscosity data were obtained with the use of a Cannon-Ubbelohde dilution viscometer (size 75) at 30°. Solutions were prepared in tetrahydrofuran at concentrations of 1.0, 0.5, and 0.33 g/100 ml.

Gel Permeation Chromatography (gpc). Gel permeation chromatography measurements were made with the use of a Waters Associates ALC/GPC 501 instrument. The columns consisted of four ⅜ in. × 2 ft stainless steel columns which contained 75, 175, 700, and 2000 Å pore size Corning controlled pore glass beads. Tetrahydrofuran was employed as a solvent at a flow rate of 2.0 ml/min, with samples injected at a concentration of 0.1 wt vol %. A refractive index detector was used. Approximate calibration of the columns was accomplished by means of narrow molecular weight polystyrene standards obtained from Waters Associates, together with the use of $\bar{M}_n$ and viscosity data for other phosphazenes.[10,13,16]

Thermolysis Techniques. The techniques used were the same as those described in an earlier paper.[2] Specifically, polymer samples were pyrolyzed at 400° in a helium flow tube apparatus and the volatilized products were analyzed by mass spectrometry. In addition, polymer samples were heated in evacuated sealed tubes and the products were then analyzed by microanalysis and by mass spectrometry. Samples contained in the evacuated sealed tubes were heated at 100, 125, 150, 200, 250, and 300° for 2, 10, 20, 30, 168, and 336 hr. The long term reactions at temperatures up to 250° were performed with the sealed tubes suspended in the vapor of boiling water, ethylene glycol monomethyl ether, anisole, *m*-cresol, or diethylene glycol. For reaction times up to 30 hr, the tubes were heated in a thermoregulated oven at temperatures up to 250°.

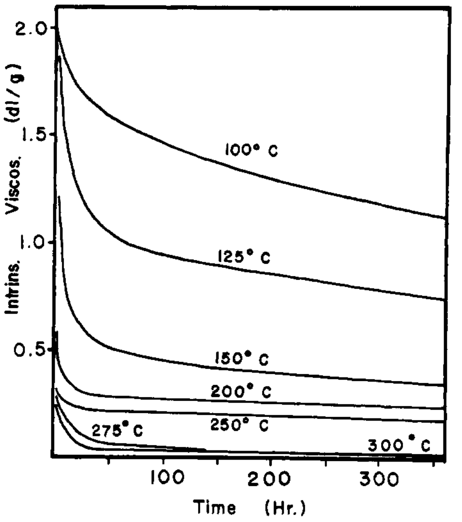


Figure 1. Diagram showing the effects of heating time and temperature on the intrinsic viscosity of $[NP(OC_6H_5)_2]_n$.

The 300° runs were carried out with the tubes suspended beneath the surface of a heated, fluidized sand bath.

Solution Depolymerizations. One per cent solutions of the polymer in tetrahydrofuran, benzene, chlorobenzene, or diglyme (bp 67, 79, 132, and 161°, respectively) were heated at reflux for periods of up to 2 weeks. The solvents were then removed by vacuum evaporation and the residues were analyzed by gpc and solution viscosity techniques.

γ **Irradiation.** Samples of the polymer (~1 g) were sealed in evacuated glass tubes and were exposed to a ^{60}Co source at a dose rate of 9×10^5 rads/hr at 30°.

Results and Discussion

Poly(diphenoxyphosphazene) depolymerizes when heated to yield a broad range of cyclic oligomers and medium molecular weight polymers. Smaller amounts of fragmentation products are also formed. In the following discussion the low molecular weight products will be considered first and the polymeric products will then be described.

Low Molecular Weight Thermolysis Products. At 400° in a helium flow tube system, poly(diphenoxyphosphazene) decomposed to yield a number of volatile products. These included traces of chlorobenzene, phenol, and triphenylphosphate together with a range of cyclic oligomeric phosphazenes of formula, $[NP(OC_6H_5)_2]_{3-5}$. These compounds were unambiguously identified by mass spectrometry. Control experiments confirmed that these compounds were not present in the polymer before pyrolysis. The nonvolatile residue left after pyrolysis was a black, insoluble material.

The cyclic tetramer, $[NP(OC_6H_4)_2]_4$, was the predominant cyclic oligomer detected. The cyclic oligomeric series appeared to extend beyond the pentamer, although the higher oligomers had molecular weights beyond the limits of detection of the mass spectrometer. However, the fragments from these higher oligomers were visible in the mass spectra. The cyclic oligomeric products together comprised at least 99 wt % of the volatile components from the thermolysis.

As might be expected, thermolysis of polymer samples which contained higher residues of unsubstituted chlorine resulted in an increase in the amount of chlorobenzene liberated. Thus, the release of this product at 400° can be used as a sensitive test for the presence of residual chlorine.

At lower temperatures (200–300°), thermolysis of $[NP(OC_6H_5)_2]_n$ in evacuated sealed tubes also yielded low molecular weight products. These species were shown by mass spectrometry to include a mixture of cyclic oligomers, together with traces of phenol and triphenylphosphate. The principal component of the cyclic oligomeric mixture again was the tetramer, $[NP(OC_6H_5)_2]_4$, which predominated over the trimer, $[NP(OC_6H_5)_2]_3$, in a ratio of approximately 3:1.

Polymeric Reaction Products. When poly(diphenoxyphosphazene)was heated at temperatures from 100 to 300° in evacuated sealed tubes, lower molecular weight polymers as well as cyclic oligomers are formed. The overall result of this process is to generate a broad spectrum of oligomers and polymers all of which have the formula $[NP(OC_6H_5)_2]_n$. In addition to these high temperature thermolyses, γ irradiation catalyzed reactions and depolymerizations in solution were also examined. In each case, the changes in the weight average molecular weight and molecular weight distribution were followed by solution viscosity and gel permeation chromatography techniques. Each of these three types of depolymerizations will be considered in turn.

Thermal Depolymerization of $[NP(OC_6H_5)_2]_n$ in the Bulk Phase. The influence of heating time and temperature on the viscosity average molecular weight is illustrated by the intrinsic viscosity data shown in Figure 1. Two points are of particular interest. First, the data illustrate that thermally induced chain cleavage can take place even at 100°. Above 150° the depolymerization was especially rapid, and at 250° the intrinsic viscosity fell from 2.0 dl/g to 0.3 dl/g in less than 4 hr. Second, at temperatures above 100°, a precipitous decrease in chain length occurred initially, which was then followed by a more gradual molecular weight decrease.

The manner in which the molecular weight distribution changed with temperature and heating time is shown by the gel permeation chromatography (gpc) curves in Figure 2. Even at 100°, the molecular weight distribution slowly changed over a period of 2 weeks to progressively favor the lower polymers. At 125° the depolymerization process was evident after 10 hr and after 2 hr at 150°. At 200° the center of the distribution peak had moved from $\bar{M}_n \approx 1 \times 10^6$ to $\bar{M}_n \approx 1 \times 10^5$ during 2 hr. At 250° the value fell to $\bar{M}_n \approx 7 \times 10^4$ during the first 2 hr. At temperatures between 275 and 300° the depolymerization process was so rapid that virtually no high polymer remained after 2 hr of reaction.

The gpc curves shown in Figure 2 illustrate that the oligomer peak ($\bar{M}_n \approx 1 \times 10^3$) grew in size as the high polymer peaks declined, and that cyclic oligomers constituted the principal components of the reaction mixture after the polymer had been heated at 300° for only 10 hr.

A further insight into this process is provided by a comparison of the effects of increased temperature at constant thermolysis time, as shown by the gpc curves in Figure 3. These illustrate the rapid decline in molecular weight that occurs above 150°. Coincidentally, the melting temperature of the polymer is near 160°.

The appearance and manipulative properties of the polymer did not change during 2 weeks heating at 100 or 125°. Some discoloration occurred at 150°, but at 250° depolymerization was accompanied by rapid liquifaction of the polymer, and solidification did not occur when the samples were cooled to 25°. Thus, 150° appears to represent a maximum useful operating temperature for applications of this particular polymer. However, it should be recognized that crosslinking or the introduction of thermolysis inhibitors might raise the useful operating temperature to 200° or perhaps even to 300°.

γ **Irradiation.** γ irradiation of bulk samples for from 1 to 7 days at 30° at a dose rate of 9×10^5 rads/hr resulted in an almost complete conversion of the polymer to a cross-

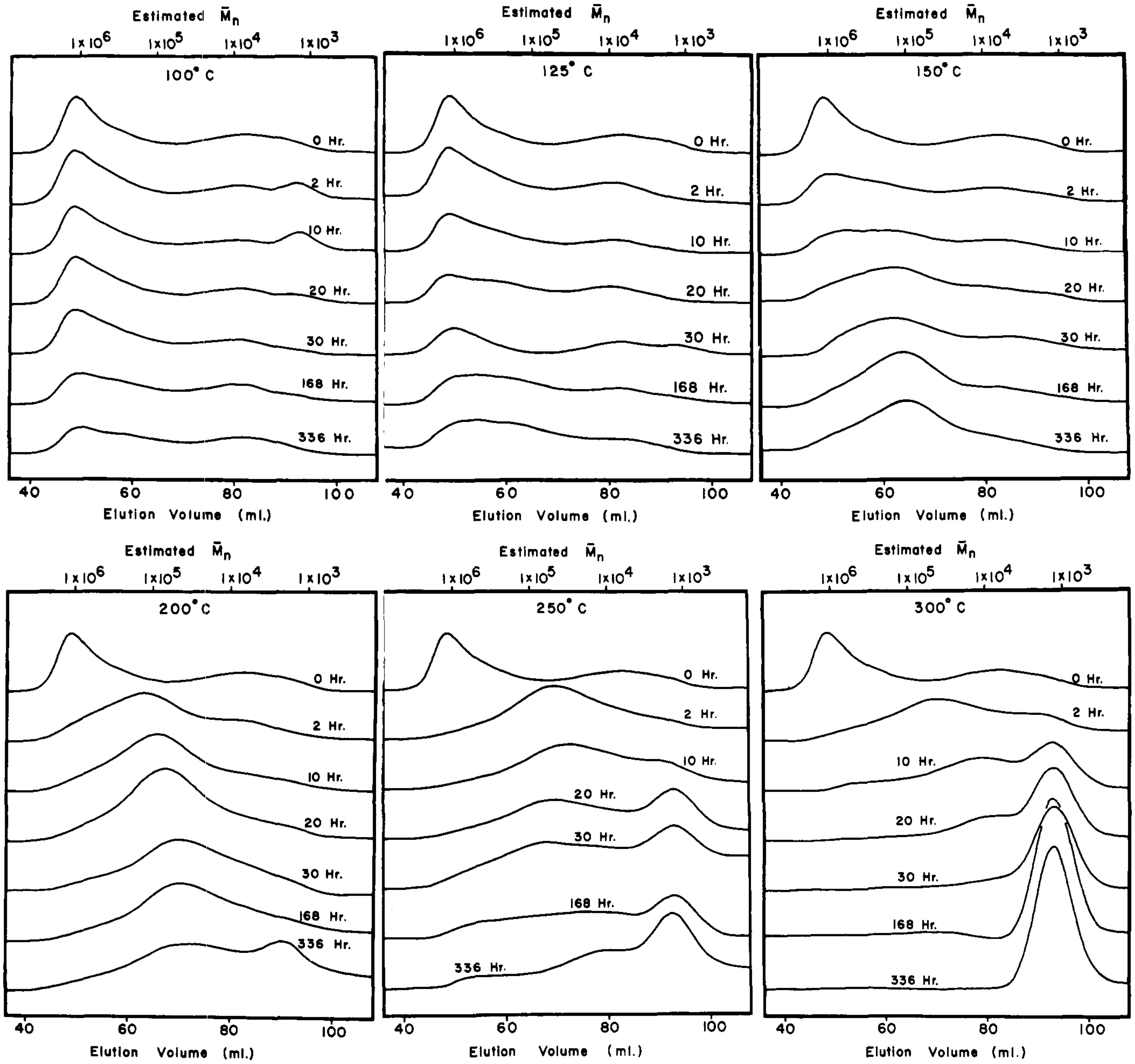


Figure 2. Gel permeation chromatograms showing the effects of temperature and heating time on the molecular weight distribution of $[NP(OC_6H_5)_2]_n$.

linked modification. After 12 hr at the same dose rate a thin film showed identical manipulative properties to the starting material but it was not insoluble in the usual solvents. Crosslinking could also be induced by ultraviolet irradiation of thin films.

Depolymerization in Solution. Table I illustrates the changes in intrinsic viscosity that accompanied the heating of solutions. of poly(diphenoxyphosphazene)in tetrahydrofuran, benzene, chlorobenzene, or diglyme. Marked molecular weight decreases were evident even in boiling tetrahydrofuran at 67°, or in benzene at 79°. Thus, serious depolymerization effects are to be anticipated if the phenoxylation of poly(dichlorophosphazene) is allowed to continue for excessive reaction times at temperatures above 100° (see Experimental Section). Acceleration of the depolymerization in solution was observed when sulfuric acid or water were introduced. The gpc curves for the products of these solution reactions are given in Figure 4.

The Reaction Mechanism. Hexaphenoxycyclotriphosphazene, $[NP(OC_6H_5)_2]_3$, does not polymerize when heated at temperatures up to 350°, whereas, as shown in this paper, poly(diphenoxyphosphazene), $[NP(OC_6H_5)_2]_n$, will depolymerize to cyclic species when heated. This result strongly suggests that depolymerization occurs in response to thermodynamic factors since the *mechanism* for equilibration is clearly operative even at ambient temperatures in solution and above 100° in the bulk phase. This thermodynamic driving force for depolymerization appears to result from intramolecular steric hindrance in the polymer that is essentially absent in the cyclic oligomers.[3,4,17] Molecular models show that poly(diphenoxyphosphazene) is especially subject to intramolecular crowding compared to related phosphazene polymers. Indeed, $[NP(OC_6H_5)_2]_n$ is more prone to depolymerization than is poly[bis(trifluoroethoxy)phosphazene].[2]

In view of these facts it seems probable that poly(diphenoxyphosphazene) is stable at ambient temperatures mainly because the rate of depolymerization is infinitely slow in

Table I
Changes in Intrinsic Viscosity Following the Heating of Solutions of $[NP(OC_6H_5)_2]_n$^{a}

Solvent	Time, days	μ, dl/g	Solvent	Time, days	μ, dl/g
THF^b (30°)	0	2.00	Benzene + benzoyl peroxide (0.2%) (79°)		
	7	1.74			
THF (67°)	2	1.48		7	1.56
THF + H_2SO_4 (0.06 *M*) (67°)	2	0.79	Chlorobenzene (132°)	2	0.68
				7	0.57
THF (67°)	14	0.31		14	0.51
Benzene (79°)	2	1.66	Diglyme (161°)	2	0.14
	7	1.58		7	0.12
Benzene + H_2O (1%) (79°)	7	1.22		14	0.12

^{a} The concentration was 1 wt %. ^{b} Tetrahydrofuran.

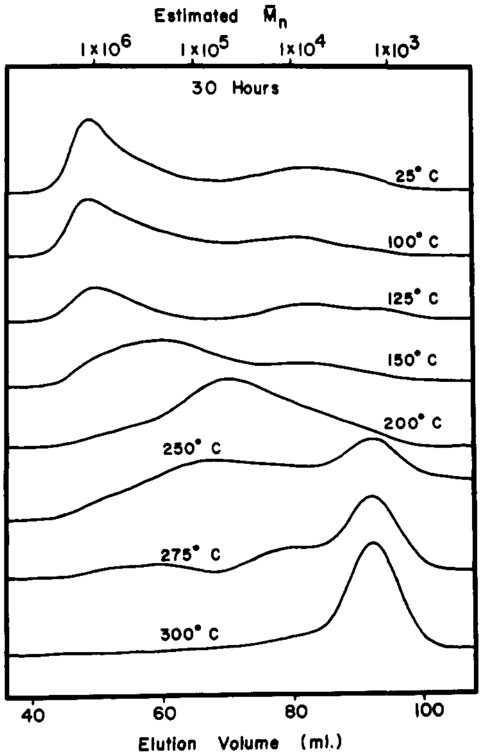


Figure 3. Gel permeation chromatograms showing the effects of increased temperature at constant thermolysis time (30 hr) for the depolymerization of $[NP(OC_6H_5)_2]_n$.

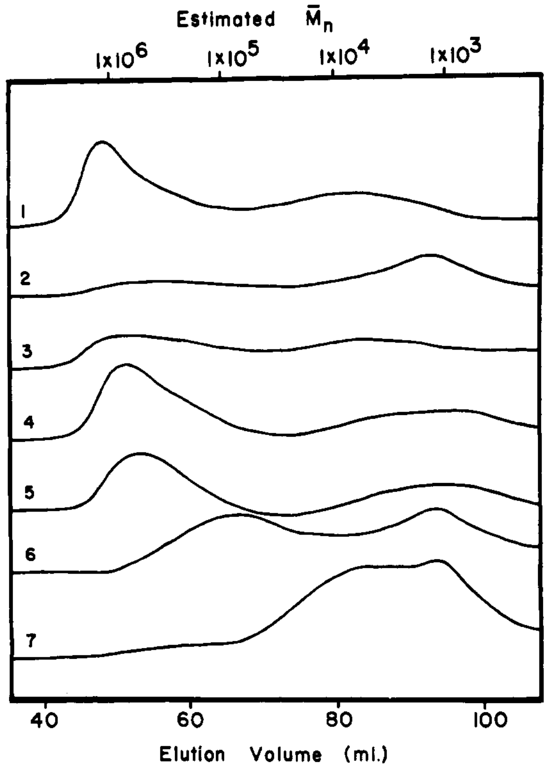
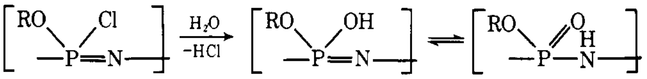


Figure 4. Gel permeation chromatograms showing the effects of heating of 1 wt % solutions of $[NP(OC_6H_5)_2]_n$: (1) no solvent, 25°; (2) in tetrahydrofuran (THF) for 336 hr at 67°; (3) in 0.06 *M* H_2SO_4 in THF for 48 hr at 67°; (4) in benzene for 168 hr at 79°; (5) in 1% water in benzene for 168 hr at 79°; (6) in chlorobenzene for 336 hr at 132°; (7) in diglyme for 336 hr at 161°.

the bulk phase. At higher temperatures (or in solution in tetrahydrofuran at 30°) the depolymerization mechanism becomes accessible. Enhancement of the thermal stability of the polymer clearly requires a blocking of this mechanism.

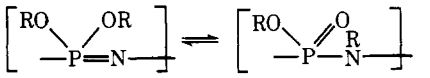
Two items of information provide clues about the mechanism. First, acids accelerate the depolymerization. Second, the presence of substantial amounts of residual chlorine atoms (2.3%) resulted in an accelerated depolymerization. A similar sequence of reactions to those described in this paper was also performed with a poly(diphenoxyphosphazene) that contains 2.3% of unreacted chlorine. This polymer underwent a more precipitous percentage intrinsic viscosity decline than the polymer discussed here. Thus, residual chlorine atoms may provide sites for the initiation of depolymerization.

A second contributing factor may be protonation of chain nitrogen atoms to provide sites for skeletal cleavage and subsequent cyclization–depolymerization. Protonation could occur in the presence of acids or by rearrangement of trace amounts of P–OH units formed by the prior hydrolysis of residual phosphorus–chlorine bonds. Thus, hydrolysis of P–Cl bonds may introduce sites for chain cleavage.



IV

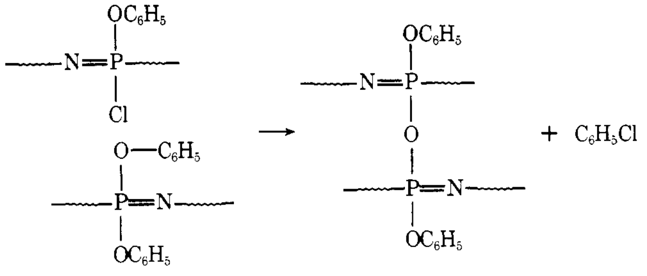
Aryl group migration from oxygen to nitrogen to yield V is conceivable but less likely. Evidence for alkyl rearrangements has been reported for alkoxycyclotri- and tetraphosphazenes, but the migration of phenyl or trifluoroethyl units was not observed.[18] The presence of phosphazane units (IV or V) would constitute weak links along the chain.



V

Hydrolytic chain cleavage could occur readily at these sites and thermal cleavage at elevated temperatures is also likely. It is possible that the initial precipitous molecular weight decline observed results from a chain cleavage process such as this.

The elimination of chlorobenzene can occur by an intra- or intermolecular interaction between residual P–Cl and



VI

P–O–C_6H_5 units (VI). Phenol could be formed by the interaction of P–OH units with P–O–C_6H_5 groupings. Traces of triphenylphosphate could presumably arise from the cleavage of polymer end units. Thus, the depolymerization mechanism is complex. High thermal stability appears to require the absence of P–Cl or P–OH units along the chain and the absence of acids in the polymer matrix. Presumably, the presence of crosslinks would also interfere with the depolymerization process.

Finally, some indirect evidence exists that the depolymerization may take place in two steps: first by a cleavage of chains at weak points (Cl, OH, NH, or branch points), followed by a second process which involves a cyclization depolymerization initiated from the ends of the linear fragments. A comparison of the intrinsic viscosity curves shown in Figure 1 with the gpc curves shown in Figure 2 suggests that the initial rapid decrease in intrinsic viscosity coincides with a rather sharp transposition of the main gpc peak from $\bar{M}_n \approx 1.7 \times 10^6$ to $\bar{M}_n \approx 6.5 \times 10^4$. (This is especially evident in the gpc curves obtained for the depolymerizations carried out at 150–250°.) This behavior is consistent with a fragmentation of the initial polymer molecules into, on the average, 20 to 30 fragments. Subsequently, the low molecular weight cyclic oligomers ($\bar{M}_n \approx 1 \times 10^3$) make their appearance in the gpc curves. If this mechanism is correct, approximately one initial chain cleavage site should be present for every 300 repeating units (or one for every 100 trimer molecules originally converted to $(NPCl_2)_n$). However, microanalysis of the poly(diphenoxyphosphazene) indicated that the residual chlorine content of the polymer was approximately eight times higher than this (one chlorine atom per 39 repeating units). Thus, the suspicion exists that below 250° the depolymerization process is initiated mainly by OH or NH units or at branch points along the chain. Presumably, the destabilizing influence of chlorine becomes important mainly at the higher temperatures (300–400°) where chlorobenzene elimination occurs.

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References and Notes

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Poly(phenyl-*as*-triazines) and Poly(phenylquinoxalines). New and Cross-Linked Polymers[1]

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ABSTRACT: Several new, high molecular weight, soluble poly(phenyl-*as*-triazines) (PPT) and poly(phenylquinoxalines) (PPQ) were prepared where various substituents were placed in the para position of the pendant phenyl group attached to the heterocyclic ring. The effect which these substituents had upon the properties (*e.g.*, T_g) of the polymer was determined. Preliminary work was performed where reactive groups were introduced within the polymer which could undergo a latent cross-linking reaction without the evolution of volatiles to reduce the thermoplasticity of these polymers at elevated temperatures. The T_g of several PPT and PPQ containing cyano or cyanato groups increased significantly or could not be detected after exposure to 400°. The cyano and cyanato groups apparently undergo trimerization to form *sym*-triazine cross-links. A cyano-containing PPQ provided tensile shear strengths on the Ti adherend at *RT* of 3500 psi, at 316°, of 1500 psi which increased to 2100 psi after a postcure at 371° for 1 hr.

Poly(phenyl-*as*-triazines) (PPT) and poly(phenylquinoxalines) (PPQ) are high performance heterocyclic polymers which are potentially useful in functional and structural applications. These two families of polymers are very similar in their method of preparation, processability, and overall properties except for the difference in use temperature. The PPT exhibit long term (*e.g.*, >1000 hr) performance at temperatures as high as 260°, whereas the PPQ