# Thermal Degradation Chemistry of Poly(diphenoxyphosphazene)

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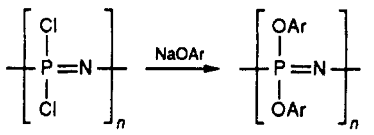
ABSTRACT: The thermal degradation of poly(diphenoxyphosphazene) has been reexamined with emphasis on the roles of P–Cl and P–OH weak links. The polymers studied had residual chlorine contents of <0.05%, 2.4%, and 9.9%. Thermal degradations were performed either in a dynamic mode on the direct insertion probe of a mass spectrometer or under isothermal conditions in sealed ampules at temperatures up to 440 °C. Several model compounds (products observed from the dynamic degradation of the polymers) were also subjected to isothermal degradation in order to better distinguish between primary and secondary products. The primary degradation products included chlorine-containing cyclic trimer and tetramer species, which were themselves too unstable to be observed in isothermal degradation studies. Triphenyl phosphate was formed as a secondary product from the degradation of the cyclic oligomers rather than as a primary product from polymer chain ends, as had been previously suggested. Hydrolysis of P–Cl weak links was obtained only with difficulty, requiring steam treatment. Steam hydrolysis reduced the thermal stability of polymers with high initial P–Cl contents.

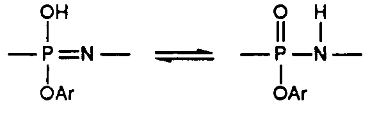
## Introduction

(Aryloxy)phosphazene polymers[1–4] are made by the reaction of the hydrolytically unstable chloropolymer with aryl oxides, as in eq 1.

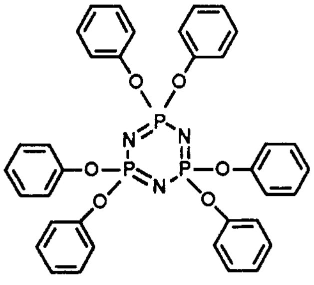


$$\left[\begin{array}{c}\mathrm{Cl}\\ |\\ -\mathrm{P}{=}\mathrm{N}-\\ |\\ \mathrm{Cl}\end{array}\right]_n \xrightarrow{\mathrm{NaOAr}} \left[\begin{array}{c}\mathrm{OAr}\\ |\\ -\mathrm{P}{=}\mathrm{N}-\\ |\\ \mathrm{OAr}\end{array}\right]_n \tag{1}$$

These polymers are film-forming thermoplastics that have excellent physical properties and flame resistance. Furthermore, they do not give off harmful toxic degradation products at high temperatures, in contrast to halogen-containing flame-retardant polymers or additives. Unfortunately, the thermal stability of these polymers is adversely affected by the presence of residual P–Cl weak-link sites[5,6] in the chain due to incomplete substitution during synthesis. Allcock et al.[5] have proposed that the actual weak links are P–OH groups, which are assumed to weaken the chain through protonation of the nitrogen in the tautomeric equilibrium shown in eq 2.



$$\begin{array}{c}\mathrm{OH}\\ |\\ -\mathrm{P}{=}\mathrm{N}-\\ |\\ \mathrm{OAr}\end{array} \rightleftharpoons \begin{array}{c}\mathrm{O}\quad\mathrm{H}\\ \|\quad |\\ -\mathrm{P}-\mathrm{N}-\\ |\\ \mathrm{OAr}\end{array} \tag{2}$$



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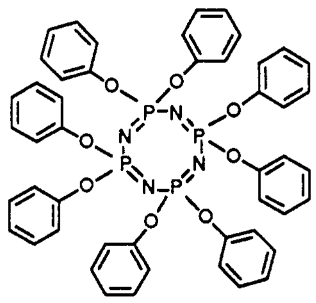

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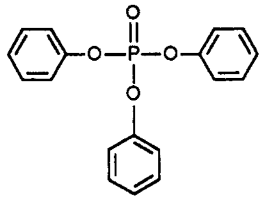

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Allcock and co-workers[5] studied the thermal degradation of the prototypical (aryloxy)phosphazene, poly(diphenoxyphosphazene) (PDPP), using two different procedures. Polymer samples with residual chlorine contents of <0.40% and 2.31% were examined. Depolymerization was monitored by using gel permeation chromatography and solution viscosity measurements. Mass spectrometry and gas chromatography were the primary tools for chemical identification of low molecular weight degradation products. The first procedure used 1-g samples, which were degraded in a flow tube at 400 °C. The volatiles were collected in a cold trap at cryogenic temperatures. The volatile species identified in those experiments were, for the most part, the phenoxy cyclic trimer (structure 1), tetramer (structure 2), and pentamer. Traces of chlorobenzene, phenol, and triphenyl phosphate (structure 3) were also observed. A black, insoluble residue formed in the flow tube. The second procedure involved isothermal degradation in sealed tubes at temperatures up to 300 °C. The experiment produced phenoxy cyclic oligomers, phenol, and triphenyl phosphate as the nonpolymeric products. The chlorobenzene observed in the flow tube experiment was attributed to a cross-linking mechanism proposed to be operative at high temperature. Triphenyl phosphate was assumed to arise from the cleavage of polymer end units, and the formation of phenol was proposed to result from interaction of $POC_6H_5$ with P–OH weak links. The latter sites were assumed to originate from the hydrolysis of P–Cl weak links and were suspected to control the initiation of depolymerization at temperatures below 250 °C.

The present investigation differs from the previous study[5] in several important ways. Our investigation has emphasized the chemical aspects of the degradation process and has further elucidated the role of weak links through studies of polymers intentionally prepared with appreciable weak-link contents. By rapidly heating small samples of polymer on the direct insertion probe of a mass spectrometer (dynamic degradation), we have identified thermally unstable products that were not previously observed. Also, by independently studying the thermal

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degradation of cyclic oligomers[7]—the first products of polymer degradation—we have clarified the significance of several low molecular weight species previously observed. These results also allow us to reach several conclusions about the thermal depolymerization mechanism.

## Experimental Section

**Materials.** Hexachlorotriphosphazene, $[NPCl_2]_3$ (Aldrich Chemical Co.), was purified by vacuum sublimation at 56 °C. Phenol (99.99%), 1,4-dioxane (99.99%), triphenyl phosphate (99.9%), *n*-heptane, and acetone were used as received. Tetrahydrofuran (THF) and benzene were purified by distillation over sodium metal and benzophenone prior to use.

**Polymerization of $[NPCl_2]_3$.** The preparation of linear poly(dichlorophosphazene) was based on the procedure of Fieldhouse and Graves.[8] Linear poly(dichlorophosphazene) was prepared from hexachlorocyclotriphosphazene using $BCl_3$ as a catalyst. Polymerization tubes (Pyrex glass, ca. 150 mm long, 32 mm o.d., 24 mm i.d.) were annealed for 12 h at 560 °C, heated at 90 °C under vacuum for 24 h, cooled under an argon purge, and then evacuated. In a typical polymerization, a tube was filled with $[NPCl_2]_3$ (30.0 g, 0.0863 mol) in a drybox, attached to a vacuum line, and degassed by the freeze–thaw technique. $BCl_3$ (1:15 molar ratio $BCl_3$ to chlorotrimer) was condensed into the tube at liquid-nitrogen temperature. The tube was sealed under vacuum and placed in a rocker assembly in an oven. After the tube was heated at 180 °C for ca. 18 h, a hairline crack was produced in the side of the tube by scoring with a glass file and placing a molten glass rod on the score (thermal shock); the tube was immediately transferred to a nitrogen atmosphere in a glovebox and broken open. Any unreacted hexachlorocyclotriphosphazene was removed from the linear poly(dichlorophosphazene) by vacuum sublimation at 56 °C.

**Synthesis of PDPP-0.0.** The preparation of PDPP is based on the procedure of Allcock and co-workers.[5] Linear poly(dichlorophosphazene) (12.5 g) was dissolved in 1,4-dioxane (250 mL). The polymer solution was added dropwise (ca. 30 min) to a stirred solution of 4 equiv of sodium phenoxide, prepared from sodium metal and phenol in 1,4-dioxane (1000 mL). After all the linear poly(dichlorophosphazene) solution was added, the reaction temperature was increased, and the solution was refluxed for 4 days. The solution was then cooled to room temperature, concentrated to ca. 500 mL, and poured into distilled water (1500 mL). The polymer precipitating from this solution was collected by filtration, dissolved in a minimal amount of benzene, and poured into methanol (1000 mL). Two further precipitations were made from benzene into *n*-heptane. The polymer was then dissolved in a minimal amount of benzene and freeze-dried to minimize any solvent effects in the subsequent degradation studies. This polymer contained <0.05% Cl and was designated PDPP-0.0. The yield of PDPP-0.0 was 12.4 g (50% yield).

**Synthesis of PDPP-2.4 and PDPP-9.9.** Poly(diphenoxyphosphazene) samples containing large concentrations of residual chlorine were prepared by a modification of the method described above for the fully substituted polymer. Limiting amounts of sodium phenoxide were used. The substitution reactions were carried out for shorter periods of time and at lower temperatures. Neutron activation analysis and solution-state $^{31}P$ NMR spectroscopy were used to determine the residual chlorine concentrations in the PDPP samples. These methods gave identical results, as was reported previously in a determination of residual chlorine in alkoxyphosphazene polymers.[9] Two such preparations were the focus of this work. The chlorine concentrations in these preparations correspond to one $[N{=}PCl(OPh)]$ unit for every six $[N{=}P(OPh)_2]$ units (2.4% residual chlorine, designated PDPP-2.4) and one $[N{=}PCl(OPh)]$ unit for every $[N{=}P(OPh)_2]$ unit (9.9% residual chlorine, designated PDPP-9.9), assuming random distribution of chlorine atoms within the polymer molecules.

**Synthesis of Cyclic Oligomers.** Compound 1 (phenoxy cyclic trimer) was prepared by the procedure of Karthikeyan and Krishnamurthy.[10] The observed melting point was 114 °C (lit. mp 115–115.5 °C). Compound 2 (phenoxy cyclic tetramer) was prepared by an analogous procedure (mp 81 °C, lit. mp 85–86 °C). Mass spectral characterization of these two compounds is reported elsewhere.[7] The effects of residual chlorine on the thermal degradation of cyclic trimer derivatives were addressed through the synthesis of a mixture of chlorine-containing cyclic trimer compounds, which was prepared with sodium phenoxide as the limiting reagent. This mixture (an oil) consisted of phenoxy cyclic trimer (3.6 mol %) and phenoxy cyclic trimer compounds with one (68.3 mol %), two (21.6 mol %), and three (6.5 mol %) residual chlorine atoms per ring, respectively.

**Analytical Characterization Methods.** Solution-state $^{31}P$ NMR spectra were recorded at room temperature on a Varian XL-200 NMR spectrometer operating at a field strength of 4.7 T or on a Varian XL-400 NMR spectrometer operating at a field strength of 9.4 T. Proton decoupling was used for all spectra. Tetrahydrofuran was used as the solvent, and deuterioacetone was used as the lock solvent.

Solid-state $^{31}P$ NMR spectra were recorded at room temperature on a Chemagnetics M-100S NMR spectrometer operating at a magnetic field strength of 2.35 T. Spectra were obtained by using single-pulse excitation and magic-angle spinning (MAS), or cross-polarization and MAS (CP/MAS). High-power proton decoupling was used for all experiments. All $^{31}P$ chemical shifts are reported with respect to external 85% $H_3PO_4$; more positive shifts represent deshielding.

Mass spectral analyses of isothermally degraded samples were performed on a VG Analytical 70-S mass spectrometer using electron impact ionization at 70 eV. Samples were introduced by direct insertion probe and heated at a rate of approximately 30 °C/min, starting at ambient temperature and ending at ca. 480 °C. Full mass spectra of volatile materials were acquired as the materials evolved directly into the ion source region. Compounds were identified by their molecular ions, doubly charged molecular ions, structurally significant fragment ions, and (when possible) comparison with mass spectra of authentic samples.

**Dynamic Degradation.** Samples for dynamic degradation were prepared by loading several milligrams of sample into a glass capillary tube and were degraded in the mass spectrometer as described above.

**Isothermal Degradation.** Degradation tubes (Pyrex glass, ca. 76 mm long, 32 mm o.d., 24 mm i.d.) were filled with 0.3–0.5-g samples of model compounds, PDPP-0.0, PDPP-2.4, or PDPP-9.9, sealed under vacuum, and heated isothermally for 2 h in an oven at one of several temperatures between 160 and 440 °C. After heat treatment, the tubes were cracked by thermal shock, transferred to a nitrogen atmosphere in a drybox, and broken open. Approximately 10 mg of the degraded sample was placed in a capillary tube, sealed, and analyzed by using mass spectrometry, essentially as described above. The rest of the degraded sample was characterized nondestructively by using solid-state $^{31}P$ NMR spectroscopy. The sample was then dissolved in dry THF, and a solution-state $^{31}P$ NMR spectrum was obtained. Any matter that was insoluble in THF was isolated and dissolved in $D_2O$ for solution-state $^{31}P$ NMR spectroscopy. Any residue that was insoluble in both THF and $D_2O$ was dried by evacuation and characterized by using solid-state $^{31}P$ NMR spectroscopy.

**Steam Degradation.** Samples of PDPP-0.0, PDPP-2.4, and PDPP-9.9 (0.3 g) were degraded in the presence of steam. Each degradation tube was filled with a polymer sample, and distilled water (50 $\mu$L) was added to the tube by syringe. The tubes were attached to a vacuum line, cooled to liquid-nitrogen temperature, evacuated, and sealed. Samples were subsequently degraded by using the previously described isothermal degradation procedure and characterized by using the sample analysis protocol described above.

## Results and Discussion

Figure 1 shows the 162-MHz solution-state $^{31}P$ NMR spectra of the three polymer samples. In the absence of weak links, the polymer has a single resonance at a chemical shift of ca. −19 ppm. The spectrum of PDPP-2.4 also shows a well-resolved triplet at −16.5 ppm, which is assigned to P–Cl weak links. The spectrum of PDPP-2.4 also shows a poorly resolved multiplet on the high-field shoulder of

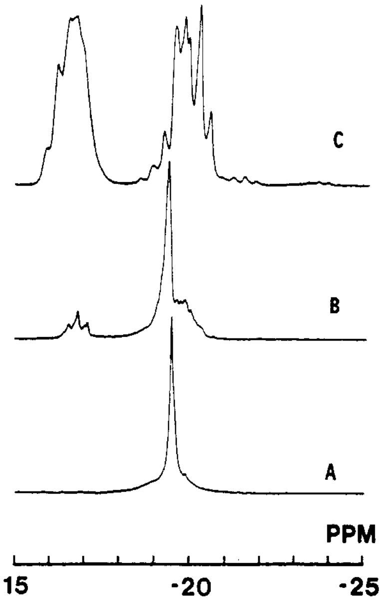


**Figure 1.** $^{31}P$ NMR spectra of the three poly(diphenoxyphosphazene) (PDPP) polymer samples. The residual chlorine contents of these polymers were (A) <0.05%, (B) 2.4%, and (C) 9.9%.

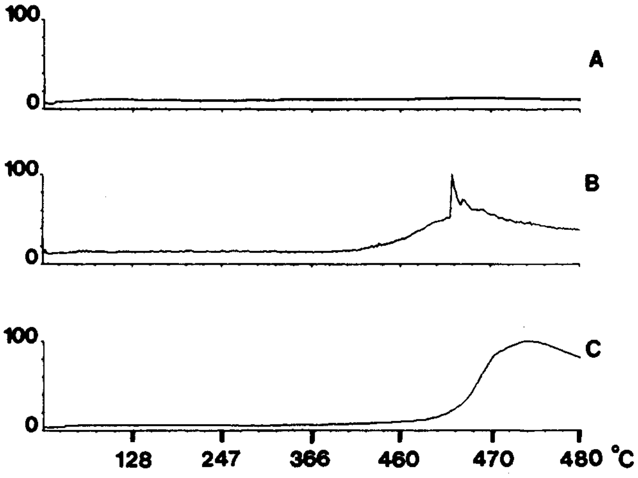


**Figure 2.** Mass spectrometric total ion current traces from the dynamic thermal degradation experiments on the three polymers: (A) PDPP-0.0; (B) PDPP-2.4; (C) PDPP-9.9. The indicated probe temperature was calibrated by using a set of standards.

the main polymer peak, which is assigned to $P(OC_6H_5)_2$ groups adjacent to P–Cl weak links. The $^{31}P$ NMR spectrum of PDPP-9.9 clearly reflects the very high chlorine content of this polymer—one PCl(OPh) group for every $P(OPh)_2$ group. We cannot rule out the possibility that this polymer contains some $PCl_2$ groups, as the chemical shift of poly(dichlorophosphazene) (−17 ppm) suggests that $PCl_2$ groups might have very similar chemical shifts to those of PCl(OPh) groups. Solution-state $^{31}P$ NMR spectra of the three polymer samples (not shown) showed no evidence of phenoxy cyclic trimer or tetramer.

**Dynamic Degradation of PDPP Samples.** The profound effects that P–Cl weak links have on the thermal stability of PDPP can be appreciated by inspecting the dynamic degradation data in Figure 2, where the total ion current (TIC) from the detector of the mass spectrometer is shown as a function of the direct insertion probe temperature. Very little volatile material evolved from PDPP-0.0 (Figure 2a) up to a probe temperature of 480 °C. In contrast, large amounts of volatile degradation products were evolved from PDPP-2.4 and PDPP-9.9 under identical conditions. The probe temperature in this experiment overstates the thermal stability of the polymer because of the rapid heating rate, short measurement time, and the fact that low molecular weight degradation products must distill out of the sample before they are observed. The dynamic degradation experiment does, however, provide important mechanistic information about the depolymerization chemistry that is not available with other degradation protocols.

Mass spectra obtained during the course of the dynamic degradations revealed that traces of phenol and phenoxy cyclic trimer were evolved from PDPP-0.0, not a surprising result in view of the earlier work by Allcock and coworkers.[5] However, we also observed traces of monochlorophenoxy cyclic trimer, which was not reported in their study.

PDPP-2.4 and PDPP-9.9 degraded extensively to volatile products under dynamic degradation in the mass spectrometer, reflecting the high concentrations of weak links in these materials. Mass spectra obtained during this experiment on PDPP-2.4 revealed not only phenoxy cyclic trimer **1** and tetramer **2** but also monochloropentaphenoxy cyclic trimer, monochloroheptaphenoxy cyclic tetramer, and dichlorohexaphenoxy cyclic tetramer (probably a mixture of isomers). PDPP-9.9 evolved dichlorotetraphenoxy cyclic trimer(s), trichloropentaphenoxy cyclic tetramer(s), and HCl, as well as those products that were observed from PDPP-2.4. The relative ion intensities due to various cyclic oligomers were roughly in accord with random statistical distributions of P–Cl weak links in the polymers. For example, mono- and dichlorophenoxy cyclic trimers and tetramers were the dominant molecular ions in spectra of the volatile products evolved during the dynamic degradation of PDPP-9.9.

The above results have several implications for the thermal degradation chemistry of PDPP. It is necessary to reconcile the observation of chlorine-containing cyclic oligomers with the absence of such species in either the previous study or our own isothermal degradation experiments described below. In the flow tube experiment of the previous study, 1 g of polymer sample was heated at 400 °C in a stream of helium, and volatile products were collected downstream in a cold trap. In contrast, the dynamic degradations employed ca. 5 mg of material, which was rapidly heated to evolve volatiles into the vacuum of the mass spectrometer ion source region. A reasonable hypothesis for the discrepancy between these results is that the chlorine-containing phenoxy cyclic oligomers are less thermally stable than the phenoxy cyclic trimer **1** or tetramer **2**. Secondary thermal reactions in the polymer matrix due to slow mass transport in a 1-g sample and/or gas-phase reactions in the hot carrier stream might then be expected to mask the identities of the first-formed products. Significantly, Ballistreri and co-workers[11] also observed monochloro cyclic trimer and tetramer when poly(di-$\beta$-naphthoxyphosphazene) was degraded in a mass spectrometer by a direct probe method similar to ours. The thermal instability of chlorine-containing phenoxy cyclic trimers will be demonstrated below.

In their earlier study, Allcock and co-workers[5] observed traces of chlorobenzene when a 1-g sample of PDPP was degraded in a flow tube and the volatile products were cryogenically trapped. They concluded that the observation of chlorobenzene was a sensitive test for residual P–Cl groups in the polymer. In our study, where PDPP was intentionally prepared with large concentrations of residual chlorine, no chlorobenzene was observed under either dynamic degradation or isothermal degradation

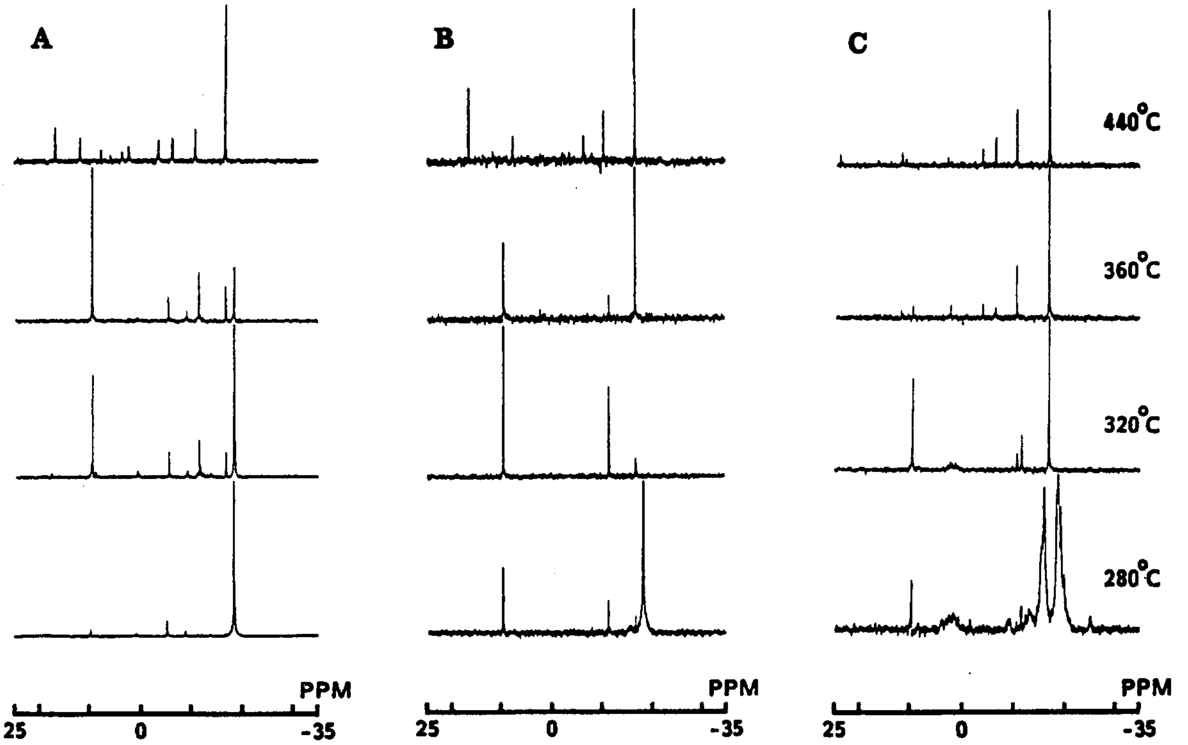


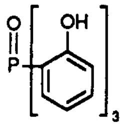
**Figure 3.** 81-MHz solution-state $^{31}P$ NMR spectra of the THF-soluble fractions obtained after isothermal degradation of the three polymers at the temperatures indicated: (A) PDPP-0.0; (B) PDPP-2.4; (C) PDPP-9.9.

conditions. These results can be reconciled if chlorobenzene is assumed to form in trace quantities as a product of the degradation of chlorine-substituted oligomers.

It has also been suggested that P–Cl sites in PDPP can readily be hydrolyzed to P–OH groups, or their tautomeric phosphazene moiety, and that these are the most important weak links. No evidence of volatile species incorporating such hydrolyzed sites could be found in the mass spectra obtained during dynamic degradation of our samples. The results of our study suggest that P–Cl weak links are themselves able to destabilize the polymer. Chlorine-containing phenoxy cyclic trimer molecules are presumably formed by the same cyclization–depolymerization process that forms the phenoxy cyclic trimer 1.

**Isothermal Degradation of Model Compounds.** In order to elucidate any reaction mechanism, it is important to distinguish primary products from secondary products. The results of the above dynamic degradation study indicate that the primary volatile products of PDPP thermal degradation are phenoxy cyclic trimer 1, tetramer 2, and their chlorine-containing derivatives (in concentrations reflecting the chlorine content of the original polymer). The primary products can reasonably be expected to undergo secondary decomposition reactions in sealed tubes or if mass transport through the polymer matrix is slow. In order to distinguish primary products from secondary products, samples of the phenoxy cyclic trimer and tetramer and a mixture of chlorine-containing phenoxy cyclic trimers were each subjected to the same isothermal degradation and chemical characterization procedures used for study of the polymers.

A pure sample of phenoxy cyclic trimer 1 was unreactive at temperatures below 400 °C, whereupon it formed some phenoxy cyclic tetramer 2 through a known equilibrium reaction. It also formed a trace of triphenyl phosphate (3), which was previously observed in degradation studies of PDPP and attributed to polymer chain ends. Degradation of the phenoxy cyclic trimer at 440 °C produced an 80% yield of an insoluble, resinous mass. $^{31}P$ NMR analysis of the THF-soluble portion of that sample revealed triphenyl phosphate to be the dominant phosphorus-containing product. Mass spectral analysis of the trimer sample degraded at 440 °C revealed spectral details consistent with the volatile components being triphenyl phosphate, diphenylamine, phenylamine, phenoxy cyclic trimer, and phenoxy cyclic tetramer, listed in order of importance. Following isothermal degradation at 440 °C, each of the model compounds or polymers yielded small $^{31}P$ NMR signals from three or more of the compounds 4–12.



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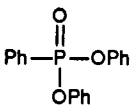
$\mathrm{Ph{-}\underset{\underset{OPh}{|}}{\overset{\overset{O}{\|}}{P}}{-}OPh}$

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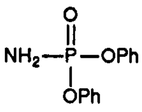
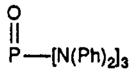
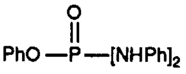

$\mathrm{NH_2{-}\underset{\underset{OPh}{|}}{\overset{\overset{O}{\|}}{P}}{-}OPh}$

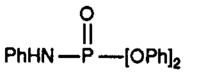
6


$\mathrm{\overset{\overset{O}{\|}}{P}{-}[N(Ph)_2]_3}$

7


$\mathrm{PhO{-}\overset{\overset{O}{\|}}{P}{-}[NHPh]_2}$

8


$\mathrm{PhHN{-}\overset{\overset{O}{\|}}{P}{-}[OPh]_2}$

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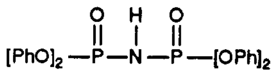
$\mathrm{[PhO]_2{-}\overset{\overset{O}{\|}}{P}{-}\overset{\overset{H}{|}}{N}{-}\overset{\overset{O}{\|}}{P}{-}[OPh]_2}$

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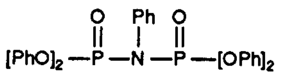
$\mathrm{[PhO]_2{-}\overset{\overset{O}{\|}}{P}{-}\overset{\overset{Ph}{|}}{N}{-}\overset{\overset{O}{\|}}{P}{-}[OPh]_2}$

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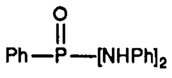

$\mathrm{Ph{-}\overset{\overset{O}{\|}}{P}{-}[NHPh]_2}$

12

These compounds evidently form through pathways similar to those that produce the phenylamines and triphenyl phosphate. $^{31}P$ chemical shift assignments for all of the low molecular weight species observed in this investigation are summarized in Table I.

The results of the isothermal degradation of phenoxy cyclic tetramer were identical with those for phenoxy cyclic trimer, except that the phenoxy cyclic trimer began forming at 280 °C (presumably reflecting its greater

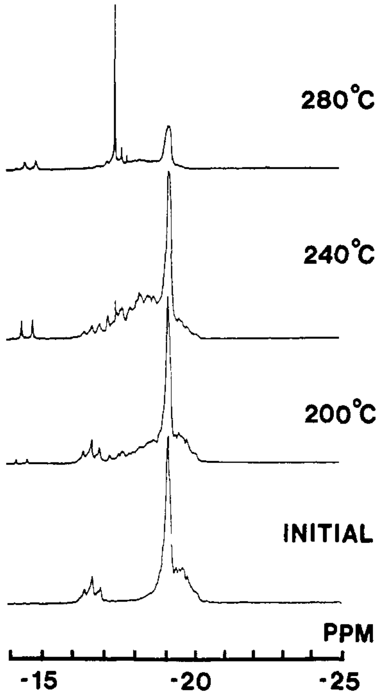


**Figure 4.** 162-MHz solution-state $^{31}P$ NMR spectra of samples of PDPP-2.4 after steam hydrolysis at the temperatures indicated.

**Table I**
**$^{31}P$ NMR Chemical Shifts of Degradation Products**

| compd | chemical shift, ppm | compd | chemical shift, ppm |
|---|---|---|---|
| 1 | 9.0 | 7 | 1.7 |
| 2 | -12.5 | 8 | -2.3 |
| 3 | -17.5 | 9 | -7.1 |
| 4 | 16.0 | 10 | -11.2 |
| 5 | 11.8 | 11 | -11.6 |
| 6 | 2.2 | 12 | 8.4 |

stability) and that decomposition to an insoluble resin, triphenyl phosphate, phenylamine, and other products was essentially complete by 400 °C.

The mixture of chlorine-containing phenoxy cyclic trimer compounds showed qualitatively similar isothermal degradation behavior. Decomposition of the chlorine-containing species began by 280 °C and was essentially complete at 320 °C. The main soluble and/or volatile products included triphenyl phosphate, phenylamine, and diphenylamine. HCl was also observed. The chlorine-containing phenoxy cyclic trimer compounds are obviously less stable than fully substituted phenoxy cyclic trimer, suggesting that the weak-link effect is an intrinsic chemical property of residual P–Cl groups in phenoxyphosphazene compounds.

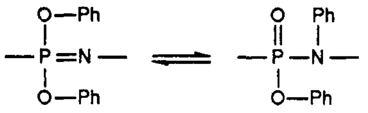
From the above model compound studies we conclude that the chlorine-containing phenoxy cyclic oligomers observed in the dynamic degradation experiments are too unstable to be readily observed with isothermal or "static" degradation protocols. All of the compounds studied decompose to form an insoluble resinous mass and significant quantities of phenylamines, triphenyl phosphate, and related compounds. Traces of phenol were also seen in some experiments. Since we did not observe triphenyl phosphate in the dynamic degradation experiments, we conclude that it forms as a secondary product from the degradation of either the cyclic species or this resinous solid and not from the chain ends of polymers, as has been previously suggested.

**Isothermal Degradation of PDPP-0.0, PDPP-2.4, and PDPP-9.9.** Solution-state $^{31}P$ NMR spectra of the isothermally degraded polymer samples are compared in Figure 3. Chemical shift assignments are reported in Table I.

Polymer PDPP-0.0 had undergone substantial degradation after 2 h at 320 °C and was essentially gone from an identical sample, which was degraded at 360 °C. PDPP-0.0 produced large quantities of phenoxy cyclic trimer and tetramer during isothermal degradation. Approximately 80% of the sample was an insoluble, resinous mass following degradation at temperatures of 400 °C or above. Isothermal heating at temperatures greater than 360 °C also produced large quantities of triphenyl phosphate and other compounds in Table I. Mass spectral analyses of PDPP-0.0 samples after degradation at 400 and 440 °C showed that the volatile components included triphenyl phosphate and diphenylamine.

Inspecting the $^{31}P$ NMR spectra of isothermally degraded samples of PDPP-2.4 and PDPP-9.9 in Figure 3, one notes that the destabilizing effect of chlorine is apparent. Both polymers were totally destroyed after 2 h at 320 °C. Chlorine-containing phenoxy cyclic trimer and tetramer molecules were not observed in the isothermal degradation experiments, consistent with their low thermal stability. Mass spectral analysis of the products from the isothermal degradation of PDPP-2.4 and PDPP-9.9 showed that the volatile components included phenol, phenylamine, diphenylamine, triphenyl phosphate, and HCl.

None of the spectra in Figure 3 show any features that can easily be interpreted in terms of the phenyl migration process shown in eq 3. An analogous reaction is known



$$-\underset{\displaystyle O-Ph}{\overset{\displaystyle O-Ph}{P}}=N- \rightleftharpoons -\underset{\displaystyle O-Ph}{\overset{\displaystyle \overset{\displaystyle O}{\|}}{P}}-\overset{\displaystyle Ph}{N}- \qquad (3)$$

for the methoxy polymer,[12,13] but it is not thought to occur for PDPP. The observation of phenylamines in this study suggests that phenyl migration does occur at some point in the thermal degradation chemistry, but we suspect that it occurs during or after the formation of the resinous mass rather than as the initial step.

Solid-state $^{31}P$ NMR spectra (not shown) of the resinous masses obtained after thermal degradation of the polymers and model compounds revealed a broad, featureless line—a result consistent with a highly cross-linked material.

**Steam Degradation of PDPP Samples.** Phosphazene polymers in end-use environments will likely be exposed to water. Given the ease with which the chloropolymer hydrolyzes, it is appropriate to consider the role of water in the thermal degradation chemistry of PDPP samples containing P–Cl weak links. Allcock and Walsh[14] have shown that PDPP itself is very difficult to hydrolyze at low temperatures. Residual P–Cl groups would presumably be easier to hydrolyze. An attempt was made to hydrolyze all three polymer samples by refluxing for 48 h in dioxane solutions containing 10% water. No obvious changes were observed in solution-state $^{31}P$ NMR spectra of the polymers so treated. PDPP-2.4 did undergo hydrolytic cross-linking, however, when a higher temperature was applied during the vacuum distillation of the wet solvent.

In order to assess the hydrolytic stability of PDPP samples at elevated temperatures and the effect that P–OH weak-link sites have on the thermal degradation of PDPP, polymer samples were subjected to isothermal degradation between 160 and 360 °C in the presence of small quantities of water. Isothermal degradation experiments were performed in which 50 μL of water was added to each sample.

Degradation in the presence of steam had little effect on the temperature stability of PDPP-0.0, and the stability of PDPP-2.4 was only slightly reduced. The stability of PDPP-9.9, on the other hand, was reduced by nearly 100 °C.

Solution-state $^{31}P$ NMR spectra of PDPP-2.4 samples steam-degraded at 200–280 °C (Figure 4) show features that we can interpret as evidence for the hydrolysis of P–Cl weak links. These spectra show a decrease in the triplet due to P–Cl groups (−16.5 ppm) with a corresponding increase in a broad resonance from −17.5 to −19 ppm as the degradation temperature is increased. It is reasonable to associate this spectral feature with either P–OH or P=O weak links formed from the hydrolysis of P–Cl groups and their adjacent $P(OPh)_2$ groups.

## Conclusions

Isothermal and dynamic degradation studies have probed the role of P–Cl and P–OH weak links in the thermal degradation chemistry of PDPP. Model compound studies gave insight into the thermal degradation of cyclic species formed during polymer degradation, allowing primary and secondary products to be distinguished.

P–Cl weak links lower the thermal stability of PDPP. P–Cl groups can be incorporated into cyclic trimer and tetramer compounds formed during cyclization depolymerization. The presence of chlorine-containing cyclic oligomers in the products evolved during dynamic degradation of PDPP in the mass spectrometer is a sensitive test for the presence of P–Cl weak links. Chlorine-containing oligomers are less stable than the phenoxy cyclic trimer and tetramer and are not, therefore, observed in isothermal degradation experiments. Triphenyl phosphate is formed in appreciable quantities when cyclic oligomers are isothermally degraded. This compound is not primarily derived from polymer chain ends, as was previously thought.

Significant hydrolysis of the P–Cl weak links in PDPP is achieved only with difficulty, i.e., steam hydrolysis conditions, but P–OH weak links, once formed, appreciably reduce the thermal stability of the polymer.

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## References and Notes

(1) Allcock, H. R. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 147.
(2) Allcock, H. R. *Chem. Eng. News* **1985**, *63*, 22.
(3) Allcock, H. R.; Kugel, R. L.; Valan, K. J. *Inorg. Chem.* **1966**, *5*, 1709.
(4) Singler, R. E.; Schneider, N. S.; Hagnauer, G. L. *Polym. Eng. Sci.* **1975**, *15*, 323.
(5) Allcock, H. R.; Moore, G. Y.; Cook, W. J. *Macromolecules* **1974**, *7*, 571.
(6) Peddada, S. V.; Magill, J. H. *Macromolecules* **1983**, *16*, 1258.
(7) Sharp, T. R.; Maynard, S. J.; Haw, J. F. *Org. Mass Spectrom.* **1990**, *25*, 631.
(8) Fieldhouse, J. W.; Graves, D. F. In *Phosphorus Chemistry: Proceedings of the 1981 International Conference*; Quin, L. D., Verkade, J. C., Eds.; ACS Symposium Series 171; American Chemical Society: Washington, DC, 1982; p 315.
(9) Crosby, R. C.; Haw, J. F. *Macromolecules* **1987**, *20*, 2324.
(10) Karthikeyan, S.; Krishnamurthy, S. S. *Z. Anorg. Allg. Chem.* **1984**, *513*, 231.
(11) Ballistreri, A.; Foti, S.; Montaudo, G.; Lora, S.; Perzin, G. *Macromol. Chem.* **1981**, *182*, 1319.
(12) Mochel, V. D.; Cheng, T. C. *Macromolecules* **1978**, *11*, 176.
(13) Cheng, T. C.; Mochel, V. D.; Adams, H. E.; Longo, T. F. *Macromolecules* **1980**, *13*, 158.
(14) Allcock, H. R.; Walsh, E. J. *J. Am. Chem. Soc.* **1972**, *94*, 4538.

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