Photolysis of Poly(alkoxy- and aryloxyphosphazenes), $[NP(OR)_2]_n$[1,2]

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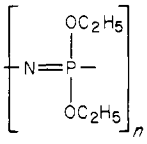
ABSTRACT: The poly(organophosphazenes), $[NP(OC_2H_5)_2]_n$, $[NP(OCH_2CF_3)_2]_n$, $[NP(OC_2H_5)_{0.4}(OCH_2CF_3)_{1.6}]_n$, and $[NP(OC_6H_5)_2]_n$, as films have been subjected to ultraviolet irradiation under vacuum, and the behavior of these polymers has been compared with that of the crystalline cyclic tetrameric model compounds, $[NP(OC_2H_5)_2]_4$, $[NP(OCH_2CF_3)_2]_4$, $[NP(OC_6H_5)_2]_4$, $(NPCl_2)_4$, and $[NP(N(CH_3)_2)_2]_4$. As a class, the polymeric and cyclic phosphazenes were moderately resistant to radiation damage. The general sensitivity to radiation-induced reactions increased in the order $[NP(OCH_2CF_3)_2]_n < [NP(OC_6H_5)_2]_n < [NP(OC_2H_5)_{0.4}(OCH_2CF_3)_{1.6}]_n < [NP(OC_2H_5)_2]_n$. However, extensive cleavage of the phosphorus–nitrogen skeleton was not detected. Photolytic cleavage of the C–O bond was the primary reaction, and this resulted in the formation of volatile alkanes and arenes together with cross-linking and discoloration after extended irradiation. Residual P–Cl bonds in the high polymers provided a facile photodecomposition pathway. Secondary photooxidation processes that yielded carbon dioxide were observed for the polymers (but not for the cyclic model systems), and these were attributed to the presence of traces of dissolved molecular oxygen. Photodecomposition pathways are suggested that account for the products.

An acute need exists for the synthesis of elastomeric and film-forming macromolecules that exhibit prolonged stability to ultraviolet radiation either in contact with atmospheric oxygen or in a space environment. A primary theoretical requirement for such polymers is transparency to ultraviolet radiation. However, it is known that hydrocarbon polymers, such as polyethylene or polypropylene, which do not themselves absorb radiation in the near ultraviolet region, are, nevertheless, susceptible to cross-linking, chain scission, and discoloration when exposed to light in this wavelength range. Traces of solvents or other impurities, the presence of oxygen or additives, the degree of crystallinity, and the type of radiation all affect the response of a polymer to light or ionizing radiation.[3-9]

Poly(organophosphazenes) constitute a new class of polymers that, in theory, offer a number of potential advantages for resistance to ultraviolet-induced degradation. First, a number of earlier reports[10-13] indicated that cyclic oligomeric halogenophosphazenes, such as $(NPCl_2)_{3\text{ and }4}$ and $(NPF_2)_{3\text{ and }4}$, show virtually no spectral absorption in the 2400–6500-Å range. Moreover, those absorptions that were detected (at wavelengths below 2400 Å) were ascribed to excitation of halogen lone-pair electrons rather than to transitions involving the skeletal electrons.[12] Second, it can be reasoned that the free-radical induced skeletal cleavage reactions that are characteristic of carbon-backbone polymers might not occur in macromolecules that possess an inorganic phosphorus–nitrogen skeleton. Third, the ease with which different side groups can be attached to the phosphazene skeleton provides facile opportunities for an investigation of the role played by different side groups.

In this paper we report the results of a fundamental study of the behavior of four poly(organophosphazenes) (I–IV) when irradiated with near-ultraviolet light of wavelength 2537 Å. All four polymers are flexible elastomers (I and III) or flexible microcrystalline materials (II and IV) that can be formed readily into thin films by solution-casting techniques.[14] The glass transition temperatures are below room temperature.[15,16] The behavior of these polymers was compared with that of the five cyclic tetrameric model compounds of general structure V, where $R = OC_2H_5$, OCH_2CF_3, OC_6H_5, Cl, and $N(CH_3)_2$. The model compound comparisons were made with highly purified crystalline compounds from which traces of chromophoric impurities could be unambiguously excluded and for which the absence of structural nonuniformities (branch points, end units, etc.) could be guaranteed.



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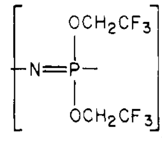

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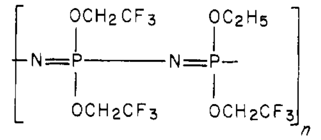

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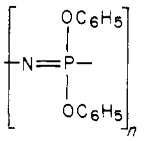

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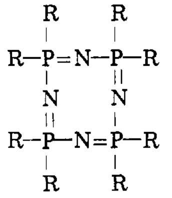

V

Experimental Section

Materials. Hexachlorocyclotriphosphazene, $(NPCl_2)_3$, was obtained from El Monte Chemical Corp., Pasadena, Calif. The commercial trimer–tetramer mixture was purified first by vacuum sublimation at 60 °C, then by recrystallization from heptane, followed by another vacuum sublimation. Octaethoxycyclotetraphosphazene was prepared by the method of Fitzsimmons and Shaw[17] and was purified by several vacuum sublimations to give a white, crystalline solid, mp 46 °C. Octakis(dimethylamino)cyclotetraphosphazene,[18] $[NP(NMe_2)_2]_4$, mp 237 °C dec, was prepared from $(NPCl_2)_4$ and dimethylamine. Poly(diphenoxyphosphazene), $[NP(OC_6H_5)_2]_n$, was synthesized by the method reported previously,[16] with purification effected by three precipitations from tetrahydrofuran into water and two reprecipitations from tetrahydrofuran into acetone. The polymer was cast as a thin film and was subjected to prolonged storage in vacuum to remove traces of residual solvent or precipitant. Trifluoroethanol (Halocarbon Products) was dried over 4 Å

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molecular sieves. Ethanol (Fisher) was distilled over calcium hydride and collected over 4 Å molecular sieves before use. Sodium spheres (MC/B) were cleaned with trifluoroethanol or ethanol before use. Solvents, such as benzene, tetrahydrofuran, or dioxane (Fisher) were dried before use by boiling at reflux over lithium aluminum hydride, followed by distillation from the same reagent. Spectrograde toluene was obtained from Aldrich. Phenol from Fisher was used as received.

Octakis(trifluoroethoxy)cyclotetraphosphazene, $[NP(OCH_2CF_3)_2]_4$. This compound was prepared from octachlorocyclotetraphosphazene (80 g, 0.17 mol) and trifluoroethanol (350 mL, 4.83 mol) in the presence of pyridine (400 mL) by a scale-up of the procedure described previously.[19] The purification procedure involved a removal of pyridine hydrochloride by treatment with diethyl ether and filtration, followed by recovery of $[NP(OCH_2CF_3)_2]_4$ by evaporation of the ether. Final purification was accomplished by several vacuum sublimations at 105 °C (0.1 torr) to yield white crystals, mp 67–69 °C.

Octaphenoxycyclotetraphosphazene, $[NP(OC_6H_5)_2]_4$. This compound was prepared as described previously[20] from octachlorocyclotetraphosphazene (60 g, 0.13 mol) and sodium phenoxide in dioxane (1 L). The sodium phenoxide was prepared from solid phenol (126 g, 1.34 mol) and sodium pellets (30 g, 1.30 mol). Purification was effected by recrystallization from benzene–petroleum mixtures, followed by sublimation several times at 180 °C (0.1 torr) to yield a white, crystalline solid, mp 85–86 °C.

Poly(dichlorophosphazene), $(NPCl_2)_n$. A typical polymerization of $(NPCl_2)_3$ to $(NPCl_2)_n$ involves the sublimation of hexachlorocyclotriphosphazene at 60 °C, recrystallization from heptane, and a second sublimation.[16] Hexachlorocyclotriphosphazene was sealed in an evacuated glass tube and was allowed to polymerize at 250 °C for 19 h (or until the contents became viscous). The mixture of unchanged trimer and poly(dichlorophosphazene) was then heated in a vacuum sublimator at 50 °C (0.5 mm) for 16 h to remove the unchanged trimer.

Poly[bis(trifluoroethoxy)phosphazene], $[NP(OCH_2CF_3)_2]_n$. The synthetic procedure reported previously[16] was employed, with the exception that the nucleophilic reagent (CF_3CH_2ONa) was used in the absence of excess free trifluoroethanol. The polymer was purified by several precipitations from acetone into water and by precipitation from acetone into benzene. Trapped solvent was removed from the polymer by storage under vacuum at 50 °C for 24 h followed by prolonged storage under vacuum at 25 °C.

Poly(diethoxyphosphazene), $[NP(OC_2H_5)_2]_n$. A solution of poly(dichlorophosphazene) (180 g, 1.57 mol) in benzene (1800 mL) was added over a 3–5-h period to a stirred solution of sodium ethoxide, prepared from sodium (109 g, 4.74 mol) and ethanol (1600 mL), in a nitrogen atmosphere. The reaction was allowed to proceed at 25 °C for 5 days. The mixture was then neutralized with dilute (5%) hydrochloric acid and the resultant aqueous layer was removed. The remaining benzene solution was washed again with water and was dried with magnesium sulfate. The viscous solution was filtered to remove the magnesium sulfate and was precipitated into *n*-heptane. The polymer (150 g) was then allowed to dry in air before being redissolved in tetrahydrofuran for precipitation into water, followed by a final precipitation from tetrahydrofuran into excess heptane to eliminate any remaining linear or cyclic low molecular weight oligomers. The polymer was then heated at 40–50 °C for 12 h in vacuum to remove traces of residual solvent and was stored thereafter in vacuum at 25 °C until subjected to ultraviolet irradiation. The physical characteristics of this polymer matched those of samples prepared previously.[16]

Poly[(ethoxy)(trifluoroethoxy)phosphazene]. A 5-L three-necked flask was charged with toluene (300 mL) which had been dried over 4 Å molecular sieves for 2 days. Sodium (43 g, 1.87 mol) was cleaned in ether (300 mL) containing ethanol (2 mL) followed by several washings with anhydrous ether. It was then added to the reaction flask. The flask was flushed with dry nitrogen for 0.5 h and a nitrogen bubbler was fitted to maintain the nitrogen atmosphere throughout the remainder of the reaction. The contents of the flask were heated to reflux with vigorous mechanical stirring until the sodium became molten, at which time the heating was terminated and the contents were allowed to cool to room temperature to produce a fine sodium sand. Tetrahydrofuran (600 mL) was added, followed by a dropwise addition of ethanol (74.5 mL, 1.27 mol) at 25 °C, and this was followed by a dropwise addition of trifluoroethanol (91.7 mL, 1.26 mol). After the addition was complete, the contents were allowed to stir for 24 h and were then boiled at reflux until all the sodium had been consumed and a clear solution of the ethoxides remained. Poly(dichlorophosphazene) (98 g, 0.85 mol) in benzene (1800 mL) was added dropwise to the alkoxide solution over 4 h. After the addition of the polymer, the contents were allowed to stir at 25 °C for 3 days, followed by a heating to 57 °C with stirring for an additional 24 h. The reaction mixture was neutralized with 6% hydrochloric acid, and the product was collected using suction filtration. The material was washed with large quantities of water and then dried in vacuo for 3 days. Several precipitations from acetone into water removed the residual sodium chloride, and this was followed by several precipitations from acetone into benzene. Residual solvent was removed by storage at 50 °C under vacuum for 24 h and subsequent storage at 25 °C under vacuum, yield 128 g. The polymer was a white, very tough elastomer. It showed a lower degree of crystallinity than the trifluoroethoxy homopolymer. Anal. Calcd for $[NP(OCH_2CH_3)_{0.4}(OCH_2CF_3)_{1.6}]_n$: C, 21.71; H, 2.37; N, 6.33; P, 13.91; F, 41.21; Cl, 0. Found: C, 21.46, H, 2.35; N, 6.36; P, 13.23; F, 43.44; Cl, 0.34.

Polymer Characterization. Solution viscosity data were obtained with the use of a Cannon-Ubbelohde dilution viscometer (size 75) at 30 °C. Solutions were prepared in tetrahydrofuran at concentrations of 0.65, 0.50, 0.33, 0.25 g/100 mL. Gel permeation chromatography (GPC) measurements were made with the use of a Waters Associates ALC/GPC 501 instrument. The columns consisted of two 1 by 61 cm stainless steel columns with linear 10^5 styragel packing. Tetrahydrofuran was employed as a solvent at a flow rate of 1.7 mL/min, with samples injected at a concentration of 0.3 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. The physical properties of the polymers were monitored by torsional braid analysis with the use of a modified Chemical Instruments Corporation Unit.

Ultraviolet Irradiation Apparatus. The irradiation cells were fabricated from quartz flasks (125-mL volume) connected to Teflon stopcocks that opened to a vacuum line or to an AEI MS-902 high resolution mass spectrometer. Before being placed in the cell, the polymers were heated in vacuo at 60 °C (where appropriate) for 36 h to remove residual traces of trapped solvent. The polymer film (0.2-mm thick) or precipitated bulk samples were then inserted into the cells, and the cells were evacuated to 10^{-5} torr. The cyclic tetrameric phosphazenes were subjected to melt–freeze–pump cycles (when appropriate) to remove the last traces of oxygen or solvent. The compounds were then allowed to solidify as crystalline layers on the walls of the cells. Before irradiation, the atmosphere within each cell was monitored by mass spectrometry.

The cells were placed in the center of a metal cylinder (30-cm diameter × 36-cm high), the inside wall of which was lined with 12 "Rayonet" RPR 2537 Å low pressure mercury arc lamps. Each cell was irradiated for periods of up to 3 weeks in the unfiltered radiation. The light intensity in the center of the enclosure, as measured by ferrioxalate actinometry, was 2.57×10^{-6} einsteins/min. The temperature in the apparatus did not exceed 45 °C, as monitored by a thermocouple attached to an aluminum plate suspended in the center of the cylinder. Following irradiation, each cell was reconnected to the mass spectrometer for analysis of the volatile photolysis products. The identification of the products was carried out by comparisons with standard fragmentation spectra for the components isolated, by analysis of isotopic peaks, and fragmentation patterns where applicable or, when possible ambiguities were seen to exist, by analysis using high-resolution mass spectrometry.

Results and Discussion

Ultraviolet Spectra. The ultraviolet absorptions at 2537 Å of the compounds used in this work are listed in Table I. The polymers, $[NP(OC_2H_5)_2]_n$, $[NP(OC_2H_5)_{0.4}(OCH_2CF_3)_{1.6}]_n$, and $[NP(OCH_2CF_3)_2]_n$, either

Table I
Ultraviolet Absorption of Selected Phosphazenes at 2537 Å

sample	solvent	ε
$[NP(OCH_2CF_3)_2]_n$	film[b]	~10[a]
$[NP(OCH_2CF_3)_2]_4$	methanol	<10[a]
$[NP(OCH_2CH_3)_2]_n$	film[b]	~10[a]
$[NP(OCH_2CH_3)_2]_4$	methanol	<10
$[NP(OC_6H_5)_2]_n$	film[b]	<10[a]
$[NP(OC_6H_5)_2]_4$	ethyl acetate	2400
$[NP(OCH_2CF_3)_{0.4}(OCH_2CH_3)_{1.6}]_n$	film[b]	~10
$[NPCl_2]_4$	methanol	<10[a]
$[NP(N(CH_3)_2)_2]_4$	cyclohexane	2200

[a] Absorption increasing with decreasing wavelength.
[b] Absolute extinction coefficients were not obtained for films.

do not absorb at all or absorb only weakly ($\epsilon < 10$) in the 6500–2400-Å region of the spectrum. However, as expected, the phenoxy-substituted polymer, $[NP(OC_6H_5)_2]_n$, showed an appreciable absorption ($\epsilon \approx 10^3$). In general, the spectral characteristics of the cyclic tetramers were similar to those of the high polymers.

General Photolytic Behavior. All four poly(organophosphazenes) underwent low-yield photochemical reactions during irradiation under vacuum with 2537-Å ultraviolet radiation for periods of up to 1 week. The extent of reaction generally increased in the order $[NP(OCH_2CF_3)_2]_n$ < $[NP(OC_6H_5)_2]_n$ < $[NP(OCH_2CH_3)_{0.4}(OCH_2CF_3)_{1.6}]_n$ < $[NP(OC_2H_5)_2]_n$, although, as will be discussed, these changes were only partly a consequence of changes in the organic substituent groups. The reactions were apparent from the discoloration, changes in physical properties, the formation of volatile decomposition products, and, in some cases, the formation of cross-linked products. However, the extent of the radiation damage was not sufficient to be detectable by electronic or conventional transmission infrared spectral absorption, NMR analysis, or vapor phase chromatography of the volatile products. Instead, the photolytic reactions were monitored by the direct introduction of the volatile products into a mass spectrometer. Table II shows the volatile products detected in this manner together with estimates of their relative concentrations. The behavior of specific phosphazenes on photolysis is described in the following sections.

$[NP(OCH_2CF_3)_2]_{n\text{ and }4}$. The high polymer, $[NP(OCH_2CF_3)_2]_n$, yielded carbon dioxide as the major volatile photolytic product, together with 1,1,1-trifluoroethane, trifluoromethane, the cyclic $[NP(OCH_2CF_3)_2]_3$, and the cyclic *gem*-1,1-$N_3P_3Cl_2(OCH_2CF_3)_4$.[21] After irradiation, the relative molecular weight (as determined by gel permeation chromatography) was unchanged (6×10^6), but the slight increase in intrinsic viscosity from 2.4 to 2.5 dL/g suggested a small amount of interchain coupling. By contrast, the cyclic tetramer, $[NP(OCH_2CF_3)_2]_4$, irradiated as a thin crystalline layer, yielded only 1,1,1-trifluoroethane and a trace of trifluoromethane.

These results indicate that the formation of carbon dioxide from the polymer can be attributed to the presence of dissolved oxygen. Trapped oxygen can be rigorously excluded from the cyclic tetramer by melt–freeze–pump techniques, but it is notoriously difficult to remove dissolved gases from polymer films.

The formation of 1,1,1-trifluoroethane and trifluoromethane in both the polymeric and cyclic tetrameric systems suggests a photolytic carbon–oxygen bond cleavage process to yield a trifluoroethyl radical. Such a radical could undergo carbon–carbon bond cleavage and subsequent hydrogen abstraction to yield trifluoromethane. It is significant that no trifluoroethanol was detected among the volatile products, and this indicated that the phosphorus–oxygen bonds are much more stable to scission than are the carbon–oxygen bonds in this system.

The formation of the cyclic trimers, $[NP(OCH_2CF_3)_2]_3$ and $N_3P_3Cl_2(OCH_2CF_3)_4$, from the high polymer is of considerable interest. It has been shown earlier[22] that cyclic oligomers are formed during the *thermal* degradation of $[NP(OCH_2CF_3)_2]_n$. Moreover, the isolation of a *chlorine*-containing cyclic trimer (albeit in very low concentrations) from a polymer that had been shown by microanalysis to contain less than 0.1% chlorine illustrates the potential value of photolysis as a sensitive test for the presence of residual halogen.

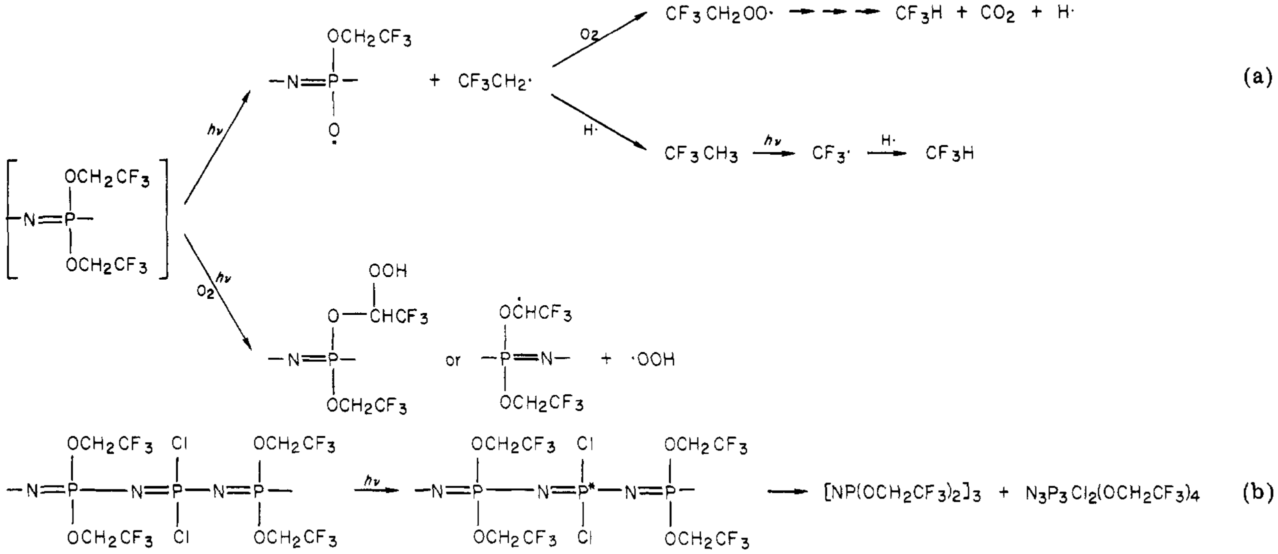
The overall reaction pathways for the photolysis of $[NP(OCH_2CF_3)_2]_n$ are shown in Scheme I. Reaction sequence (a) provides a plausible explanation for the formation of fluorocarbon fragmentation products, for the generation of carbon dioxide in the presence of oxygen, via a series of degradation reactions, and for interchain linkage. In this sequence, it is assumed that H· radicals are ab-

Table II
Volatile Products from Irradiation at 2537 Å of Selected Phosphazenes and Polyethylenes in the Solid State under Vacuum[a]

sample	irradiation time, h	initial cell pressure, mm Hg	major products	estimated[b] ratios of volatile products
$[NP(OC_6H_5)_2]_4$	167	1×10^{-5}	C_6H_6, $(C_6H_5)_2$	c
$[NP(OC_6H_5)_2]_n$	167	3×10^{-5}	CO_2, C_6H_6 $(C_6H_5)_2$, C_6H_5OH	10:1[c]
$[NP(OCH_2CF_3)_2]_4$	167	2×10^{-5}	CH_3CF_3, CF_3H[e]	
$[NP(OCH_2CF_3)_2]_n$	167	2×10^{-5}	CO_2, CH_3CF_3, CF_3H, $[NP(OCH_2CF_3)_2]_3$,[d] $N_3P_3(OCH_2CF_3)_4Cl_2$[d]	31:1:1
$[NP(OCH_2CH_3)_2]_4$	167	1×10^{-5}	$CH_3CH_2CH_2CH_3$[e]	
$[NP(OCH_2CH_3)_2]_n$	167	1×10^{-5}	CO_2, $CH_3CH_2CH_2CH_3$, CH_3CH_2Cl, CH_3CH_3	11:5:4:1
$[NP(OCH_2CH_3)_{0.4}(OCH_2CF_3)_{1.6}]_n$	648	5×10^{-5}	CO_2, CF_3CH_3, CF_3H	10:2:1
$[NPCl_2]_4$	194	1×10^{-5}	PCl_3	
$[NP(N(CH_3)_2)_2]_4$	194	4×10^{-5}	H_2	
$(-CH_2-)_n$	194	1×10^{-5}	H_2, CH_4, CO_2, H_2O	11:4:3:1

[a] It was not possible from mass spectrometric data to determine the absolute concentrations of photolysis products in each irradiated sample, primarily because of inherent nonquantitative sampling procedures employed on the instrument. However, it was possible to calculate the *relative* concentrations of the volatile photolysis products for each sample independently. [b] Estimated from measurement of parent ion intensity and normalized to the instrumental sensitivity for the parent peak of known amounts of *n*-butane at 70 eV accelerating potential. [c] No meaningful ratios could be measured because of the low volatility of phenol and biphenyl at 25 °C. [d] Detected only after warming of the polymer to 75 °C. [e] Trace amount, defined as less than 20% of the peak intensity of naturally occurring ^{40}Ar in the background.

Scheme I



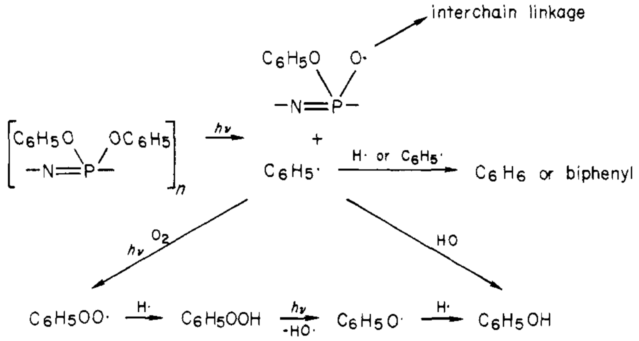
stracted from the polymer side-group structure. An alternative decomposition route, in which a hydroperoxide, such as CF_3CH_2OOH, decomposes to $CF_3CH_2O\cdot$ and $\cdot OH$ cannot be precluded, but it would be expected to yield detectable amounts of CF_3CH_2OH and H_2O. It was not possible to conclusively detect changes in the water vapor concentrations before and after photolysis because of the large number of mass spectral fragments that contributed to the spectrum in the lower mass region. However, water was detected from the photolysis of polyethylene. The lower reaction sequence shown in (a) (Scheme I) depicts a pathway that might be operative for a direct attack by singlet oxygen on the polymer. Further decomposition of the intermediates formed by this reaction could account for the observed volatile photolysis products.

It seems clear that P–Cl units markedly enhance the susceptibility of the molecule to radiation damage (see later sections). However, it is not known if the initial absorption of radiation (sequence (b)) leads to P–Cl cleavage or to P–N scission. Certainly the isolation of the cyclic trimers, $[NP(OCH_2CF_3)_2]_3$ and $N_3P_3Cl_2(OCH_2CF_3)_4$, suggests the ultimate involvement of a "backbiting" mechanism in which a radical or ionic intermediate cleaves at a point adjacent to a PCl_2 residue. As discussed later, the tetramer, $(NPCl_2)_4$, was the only cyclic compound studied that showed evidence of extensive skeletal cleavage.

It is emphasized that these reactions with $[NP(OCH_2CF_3)_2]_n$ represent damage to only a very small fraction of the total polymer present. Nevertheless, these products do suggest the reaction pathways that may be involved in more prolonged radiation exposure.

$[NP(OC_6H_5)_2]_{n\text{ and }4}$. Photolysis of a film of high polymer $[NP(OC_6H_5)_2]_n$ resulted in a slightly discolored, soluble polymeric product. The intrinsic viscosity increased from 0.74 to 1.8 dL/g during irradiation and the relative molecular weight increased from 400 000 to 1 200 000. This suggested that interchain linkage predominated over chain scission. The volatile photolysis products included carbon dioxide (the major product) and small amounts of benzene, phenol, and biphenyl. Particular care was taken to ensure that the phenol and biphenyl were photolytic products rather than trace impurities introduced during the synthesis process. Thus, after irradiation of the polymer under vacuum at 2537 Å for 1 week, the concentration of phenol was eight times that in the unirradiated polymer, and the concentration of biphenyl was at least five times greater. The cyclic tetramer, $[NP(OC_6H_5)_2]_4$, irradiated under the same conditions, yielded benzene and biphenyl. No carbon dioxide was detected. However, irradiation of the tetramer in oxygen yielded appreciable amounts of carbon dioxide as well as phenol and biphenyl.

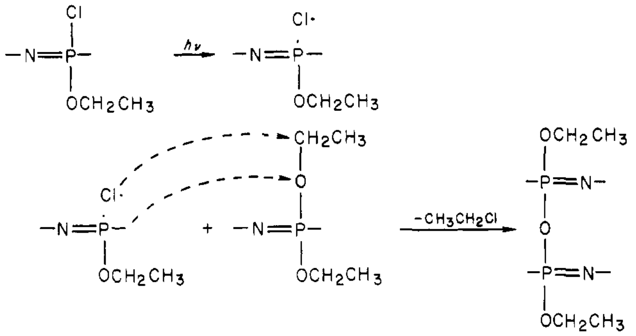
Scheme II



It seems clear from the comparisons between the polymer and the cyclic tetramer that dissolved oxygen is responsible for the formation of carbon dioxide from the polymer. This photolytic reaction is characteristic of nearly all organic polymers, including polyethylene (Table II). The other products can be accounted for by the reaction sequence outlined in Scheme II. Reactions of this type, involving peroxo intermediates, have been suggested for the photooxidation of poly(dimethylsiloxane),[23] polypropylene,[24] polystyrene,[25] and polyethylene.[26] The phenyl peroxo radical formed in this sequence could be the main source of carbon dioxide. Benzene itself photooxidizes to unsaturated linear aldehydes[27] and such species could undoubtedly degrade further to yield carbon dioxide.

$[NP(OCH_2CH_3)_2]_{n\text{ and }4}$. It is exceedingly difficult to synthesize samples of $[NP(OCH_2CH_3)_2]_n$ that correspond to the idealized formula. In particular, the low reactivity of the ethoxide ion makes it almost impossible to replace 100% of the chlorine atoms in $(NPCl_2)_n$ by ethoxy groups under mild reaction conditions. More drastic reaction conditions bring about a rearrangement of ethyl groups from oxygen to skeletal nitrogen. Thus, the polymer used in this study contained 1.1 wt % of chlorine in the form of residual P–Cl bonds. Photolysis of $[NP(OCH_2CH_3)_2]_n$ caused a color change from colorless to brown and an insolubilization that was indicative of light cross-linking. The volatile reaction products were carbon dioxide and smaller amounts of n-butane, ethane, and chloroethane.

Scheme III



Particular care was taken to verify that the observed photolysis products were derived from the polymer and not from traces of residual solvents. Thus, polymers isolated from benzene or tetrahydrofuran solvents gave the same photolysis products. Apart from the normal C–H, C–C, and C–O homolytic cleavage processes to yield the ethane and butane expected in this system, the photolytic decomposition mechanism undoubtedly is facilitated by the presence of P–Cl bonds. This is reflected in the mechanism shown in Scheme III, which accounts for the formation of both chloroethane and cross-link sites. However, facile cross-linking mechanisms can also be expected via radicals formed by C–H and C–C cleavage of the ethoxy side groups.

The cyclic tetramer, $[NP(OCH_2CH_3)_2]_4$, underwent an extremely low yield photolysis to generate a trace amount of butane. Once again, this indicates the photolytic stability of these systems in the absence of P–Cl bonds or oxygen.

$[NP(OCH_2CH_3)_{0.4}(OCH_2CF_3)_{1.6}]_n$. Irradiation of this polymer at 25 °C caused cross-linking and a slight discoloration. Carbon dioxide, 1,1,1-trifluoroethane, and trifluoromethane were the principal volatile products detected. Butane or other recombination products expected from the ethyl groups were not detected.

$(NPCl_2)_4$ and $[NP(N(CH_3)_2)_2]_4$. The photolysis behavior of $(NPCl_2)_4$ was investigated in order to examine further the role played by P–Cl bonds in enhancing the sensitivity of phosphazenes to photolytic decomposition. The principal volatile product from the photolysis of this compound was phosphorus trichloride, which clearly indicated a skeletal cleavage process. This is the only example found among the *cyclic* model compounds studied in which skeletal cleavage products were detected. The details of this decomposition mechanism are not clear, but the initial reaction is very probably a homolytic cleavage of a P–Cl bond, followed by skeletal rupture.

By contrast, the compound $[NP(N(CH_3)_2)_2]_4$ showed no evidence of skeletal scission during photolysis. The principal product was hydrogen. Thus, it can be inferred that even P–N bonds that connect the skeleton to side-group structures are relatively stable to photolysis.

Conclusions. Any attempt to rationalize the photochemical behavior of high polymers must take into account (1) the ability of the polymer to sustain radiation damage by absorption of the incident radiation, (2) the bond dissociation energies of the various linkages in the molecule, and (3) the accessible reaction pathways.

First, it seems clear from this study that the phosphazene skeleton (either polymeric or cyclic oligomeric) is not itself a significant absorber of light in the 2400–3000-Å spectral region. Thus, skeletal cleavage reactions that result from direct light absorption are generally insignificant in these systems. However, P–Cl bonds and P–O–aryl units do absorb in this general region of the spectrum and they function as internal sensitizers. It must also be recognized that a small amount of surface radiation damage that generates strong chromophores may in fact form a surface "filter" that protects the rest of the polymer sample.

Table III
Relative Concentrations of Gaseous Products[a] to the Natural Concentrations of Atmospheric Argon in the Mass Spectral Background

sample	photoproduct	peak measured[b]	*d*
$[NP(OC_6H_5)_2]_4$	C_6H_6	78	0.5
$[NP(OC_6H_5)_2]_n$	C_6H_6[c]	78	0.2
$[NP(OCH_2CF_3)_2]_4$	CF_3CH_3	65	0.2
$[NP(OCH_2CF_3)_2]_n$	CF_3CH_3[c]	65	0.1
$[NP(OCH_2CH_3)_2]_4$	$CH_3CH_2CH_2CH_3$	43	0.1
$[NP(OCH_2CH_3)_2]_n$	$CH_3CH_2CH_2CH_3$	43	22.0
$[NP(OCH_2CH_3)_{0.4}(OCH_2CF_3)_{1.6}]_n$	CF_3CH_3	65	8.0
$[NPCl_2]_4$	PCl_3	101	8.0
$[NP(N(CH_3)_2)_2]_4$	H_2[c]	2	~12.0
$[-CH_2-]_n$	H_2	2	22.7

[a] 10-g sample in a 150-mL cell, sealed at 10^{-5} mm Hg. [b] Corrected for background. [c] A smaller than 10-g sample used in this determination but, in order to achieve internal comparison, the result is estimated for a 10-g sample. [d] Peak height of photoproduct/peak height of Ar.

Table IV
Published Bond Dissociation Energies or Bond Energies for Poly(organophosphazenes)

bond	compd	dissociation energy, kcal/mol	bond energy, kcal/mol
C-C	CH_3CH_3	83[a]	
C-H	CH_3CH_3	96[a]	
C-F	CF_4	121[a]	
C-O	C_2H_5OH	~90[a]	
C-N	CH_3NH_2	80[a]	
P-N	$(NPCl_2)_4$		73[b,c]
P-N	$(Me_2N)_3P$		~69[b]
P-Cl	PCl_3		78[a]
P-O		125[a,b]	
P-O	$[NP(OC_6H_{11})_2]_3$		135[d]

[a] Reference 29. [b] Questionable value. [c] Reference 30. [d] Reference 31.

Second, in order for direct photolytic bond scission to occur, it is necessary for the photon energy to equal or exceed the dissociation energy of the bond. Table IV lists possible bond dissociation energies and bond energies for linkages of the types found in these particular phosphazenes.[8] The photon energy of 2537-Å radiation corresponds to approximately 113 kcal/mol. Because of the sharp spectral distribution of the irradiation source employed (>90% at 2537 Å), bonds with dissociation energies greater than 113 kcal/mol should be relatively insensitive to direct photolytic cleavage. Thus, P–O and C–F bonds should be relatively stable, whereas C–C, C–H, C–O, and P–Cl bonds would be the most sensitive to photolytic scission. The bond dissociation energy for a –P=N– skeletal bond is not known but, based on this study, it would appear to be greater than the ~70 kcal/mol values previously assumed for the bond energies. If not, it has an unusual capacity to dissipate absorbed energy by processes other than bond cleavage.

Third, an equally important but more complex factor is the nature of the energy transfer pathways that are accessible in a particular system. In alkoxy- or aryloxyphosphazenes, the primary process appears to be cleavage of a C–O bond to generate an alkyl or aryl radical and a macroradical. As in all similar photochemical reactions, the more mobile alkyl or aryl radicals could in principle participate in hydrogen abstraction, recombination with other radicals, reaction with molecular oxygen, or elimination of a hydrogen radical to form an alkene. The reactions discussed here are extremely *low yield* processes that can best be explained by the interaction of radicals with nearby units within a polymer "cage". Radical–radical recombinations appear to be unlikely outside the polymer matrix. This interpretation explains the absence of propane or hexane from $[NP(OCH_2CH_3)_2]_{n \text{ or } 4}$, or hexafluoropropane from $[NP(OCH_2CF_3)_2]_{n \text{ or } 4}$, and the formation of butane from $[NP(OCH_2CH_3)_2]_n$ and biphenyl from $[NP(OC_6H_5)_2]_n$.

It should be noted that, with the sole exception of carbon dioxide generation, the cyclic model compounds behave on irradiation in a virtually identical manner to the high polymers. Thus, in future work, photolysis experiments on other cyclic phosphazenes may offer an excellent method for the preliminary screening of phosphazene high-polymer systems.

Based on this study, it appears that polyphosphazenes as a class have the capability to withstand appreciable exposure to near-ultraviolet radiation without sustaining appreciable skeletal cleavage or depolymerization to cyclic oligomers, *provided that phosphorus–chlorine bonds are absent*. Because the C–O bonds in alkoxy- and aryloxyphosphazenes constitute one of the weakest linkages in the system (Table IV), the recently synthesized polyphosphazenes that contain direct P–C bonds to the side group[32] are of considerable interest for future photolysis work.

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Chain Scission and Cross-Linking in the Radiation Degradation of Polymers: Limitations on the Utilization of Theoretical Expressions and Experimental Results in the Pregel Region

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ABSTRACT: An appraisal is made of current methods of determining radiation–chemical yields for main-chain scission and cross-linking of a polymer from measurements of molecular size distributions and average molar masses after high-energy radiation doses D below the gel dose D_g. Calculation of molecular size distributions by a single cycle of successive scission and cross-linking is shown to give significant errors. A multicycle procedure that uses iterative, numerical solutions of the fundamental scission and cross-linking equations is developed and shown to be superior. On the basis of theoretical calculations of likely experimental errors in measurements of $\bar{M}_w$ and $\bar{M}_z$ it is recommended that radiation doses be restricted to the region $D < 0.4D_g$ for evaluation of scission and cross-linking yields from the dose dependence of average molar masses.

High-energy (ionizing) radiation causes a variety of chemical reactions to occur in polymers and results in permanent molecular changes including scission and cross-linking of backbone chains.[2,3] These two effects are of particular importance because of resultant changes in the physical and mechanical properties of the irradiated

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