

ScOH bonding. Especially in this category fall transitions from the strongly bonding $e_u(Np_\sigma)$ and $b_{1g}(Np_\sigma)$, the latter gaining intensity as the complex goes from D_{4h} to C_{4v} symmetry. Both these possibilities not only destroy approximately 25% of the nitrogen-to-metal 3d overlap population, weakening the covalent bond, but also represent electronic charge transfer which results in excited states with a net negative charge on both the Sc atom and its neighboring nitrogen atoms. The analogous transitions in the vanadyl complex are predicted much to the blue and, because of the more local nature of the $e_g(d_\pi)$ ligand field orbitals, are predicted considerably weaker. As the $e_g(d_\pi)$ orbitals in VO porphyrin are calculated mostly on the vanadyl group, such transitions are not strongly metal-porphyrin antibonding. The implication is that ScOH porphyrins, if made, could photodissociate even if the vanadyl complex which we are using for comparison does not. Although the nature of the $e_g(d_\pi)$ MO's is somewhat sensitive to the assumed geometric relation between the Sc atom and the porphyrin plane, no significant change in this analysis is indicated when this distance is varied from 0.5 to 1.2 Å.

Although the metal character of the $e_g(d_\pi)$ MO's is somewhat sensitive to the location of the Sc atom, its position above the $b_{2g}(d_{xy})$ orbital appears not to be so dependent. For distances between the Sc atom and the porphyrin plane varying from 1.2 to 0.5 Å this orbital energy difference is 0.66 ± 0.03 eV. Likewise the energy gap between the principal $a_{1g}(d_{z^2})$ and $b_{2g}(d_{xy})$

ligand field orbital is rather insensitive to such geometry changes. In contrast to these, the energy of the $b_{1g}(d_{x^2-y^2})$ above that of the $b_{2g}(d_{xy})$ is strongly dependent on the location of the Sc atom above the plane. A similar result was found for VO complexes.³ For the 0.9 Å calculation, the orbital energy difference between the two is estimated at 2.35 eV and is calculated to change ~ 0.2 eV/0.1 Å for distances of 0.9 ± 0.3 Å.

Conclusions

Extended Hückel calculations on ScOH porphyrin have failed to indicate any inherent instability of the molecular ground state. However, these calculations do indicate that the ScOH complex could deviate from the "normal" transition metal porphyrin picture created by the extended Hückel model.³ Foremost among the unusual results noted is that $e_g^*(\pi)$, normally pure porphyrin π , has large $3d_\pi$ character, while $e_g(d_\pi)$ extends considerably into the porphyrin π system. Electronic transitions to these MO's could both alter the normal $\pi \rightarrow \pi^*$ porphyrin spectrum and lead to excited states in which the Sc to porphyrin bonds are greatly weakened.

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Phosponitrilic Compounds. VI.¹ High Molecular Weight Poly(alkoxy- and aryloxyphosphazenes)²

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The synthesis and characterization of the first fully substituted, high molecular weight, uncross-linked poly-(organophosphazenes) is described. Polymers of structure $(NPR_2)_n$ were prepared in which R was OCH_3 , OC_2H_5 , OCH_2CF_3 , and OC_6H_5 , by nucleophilic replacement of chlorine in uncross-linked $(NPCI_2)_n$ with alkoxide or aryloxy ions. Infrared, ultraviolet, nmr, glass transition, and X-ray diffraction data are considered in relation to previous structural interpretations of the polyphosphazene system. The marked depolymerization tendency and the nature of phosphorus-nitrogen bonding in these compounds are also discussed.

Introduction

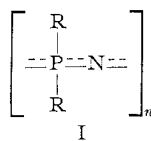
The possibility that high molecular weight, open-chain polymers, comparable in structure and stability

(1) Part V: H. R. Allcock and R. L. Kugel, *Inorg. Chem.*, **5**, 1016 (1966).

(2) For a preliminary account of parts of this work see H. R. Allcock and R. L. Kugel, *J. Am. Chem. Soc.*, **87**, 4216 (1965). The nomenclature used in this paper conforms to the "phosphazene"-based system used previously.¹

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to silicones, might be derived from the phosphazene (phosponitrile) skeleton has intrigued many investigators in recent years. The fact that the phosphorus-nitrogen bond in cyclic trimeric and tetrameric organophosphazenes, $(NPR_2)_3$ and 4 , showed evidence of high thermal and chemical stability provided encouragement for this view. It was also apparent that, if polymers of this type (I) could be synthesized, with a



variety of side groups, R, attached to phosphorus, the physical characteristics of the polymers might provide a valuable insight into both the nature of phosphorus-nitrogen bonding in phosphazenes and the influence of side groups on the bond rotational properties of polymer chains.

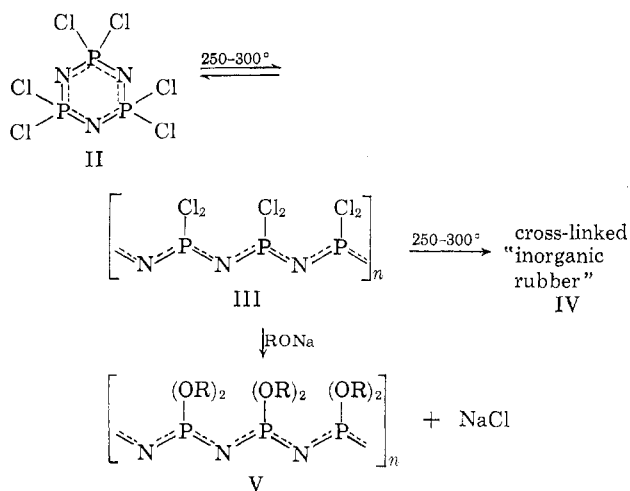
Three principal routes had previously been investigated for the synthesis of macrocyclic or open-chain organophosphazene high polymers. These were as follows: (1) Attempted polymerization of cyclic organophosphazene trimers and tetramers under conditions similar to those required for the ring-cleavage polymerization of the halogen derivatives, $(\text{NPCl}_2)_3$, $(\text{NPF}_2)_3$, and $(\text{NPBr}_2)_3$.⁴⁻⁶ No high molecular weight, open-chain polymers have been prepared by this route. (2) By the reaction of organophosphorus halides with ammonium halides or metal azides.^{7-10a} The polymers produced by this method generally contained no more than about 20 monomer units. The only derivative which was suspected of being a high molecular weight species, $[\text{NP}(\text{CF}_3)_2]_n$, could not be characterized completely, and the degree of polymerization was unknown.⁸ More recently, the polymer, $[\text{NP}(\text{CH}_3)_2]_n$, containing up to 170 repeating units, was synthesized by the pyrolytic condensation of dimethyldiaminophosphonium chloride.^{10b} (3) By thermal polymerization of hexachlorocyclotriphosphazene, $(\text{NPCl}_2)_3$, to hydrolytically unstable, high molecular weight polydichlorophosphazene, $(\text{NPCl}_2)_n$, followed by replacement of the halogen atoms in the polymer by hydrolytically stable organic groups. Previous attempts to employ this method led to the formation of partially substituted, cross-linked, or decomposed products,¹¹⁻¹³ and in no case was a pure polymer obtained which corresponded to structure I.

In the present work, this latter route was employed for the synthesis of fully substituted, high molecular weight organophosphazene polymers of structure I, where R is alkoxy or aryloxy.

Results and Discussion

Syntheses.—The general reaction scheme used for the syntheses involved the steps shown below.

- (4) J. O. Konecny and C. M. Douglas, *J. Polymer Sci.*, **36**, 195 (1959).
- (5) J. O. Konecny, C. M. Douglas, and M. Y. Gray, *ibid.*, **42**, 383 (1960).
- (6) P. Seel and J. Langer, *Angew. Chem.*, **68**, 461 (1956); *Z. Anorg. Allgem. Chem.*, **295**, 316 (1958); N. E. Bean and R. A. Shaw, *Chem. Ind. (London)*, 1189 (1960).
- (7) G. Tesi, C. P. Haber, and C. M. Douglas, *Proc. Chem. Soc.*, 219 (1960).
- (8) G. Tesi and C. M. Douglas, *J. Am. Chem. Soc.*, **84**, 549 (1962).
- (9) D. L. Herring, *Chem. Ind. (London)*, 717 (1960).
- (10) (a) C. P. Haber, "Inorganic Polymers," Special Publication No. 15, The Chemical Society, London, 1961, p 119; (b) H. H. Sisler, S. E. Frazier, R. G. Rice, and M. G. Sanchez, *Inorg. Chem.*, **5**, 326 (1966).
- (11) F. Goldschmidt and B. Dishon, *J. Polymer Sci.*, **3**, 481 (1948).
- (12) M. V. Lenton, B. Lewis, and C. A. Pearce, *Chem. Ind. (London)*, 1387 (1964).
- (13) C. F. Liu and R. L. Evans, U. S. Patent 3,169,933 (1965).



Polymerization.—The thermal polymerization of hexachlorocyclotriphosphazene (II) to the polymeric "inorganic rubber" IV, in the temperature range of 200 to 350°, has been described by many investigators.¹⁴⁻²⁰ In most cases, the descriptions of the polymer indicate that its structure can be rationalized in terms of a cross-linked matrix, although in a few reports¹⁶⁻²⁰ soluble and apparently uncross-linked polydichlorophosphazenes III were mentioned. The present work has shown that the cross-linked polymer IV, frequently obtained from this reaction, is derived from a moderately labile, uncross-linked dichlorophosphazene high polymer III. Both polymeric products may be isolated from the reaction mixture,²¹ but it is the latter, open-chain polymer which is an essential intermediate in the synthesis of high molecular weight, fully-substituted organophosphazenes. The rate of polymerization of II and the ratio of the two polymeric products are particularly sensitive to the experimental conditions employed. Relevant details will be found in the Experimental Section.

The mechanism of cross-linking of III is at present uncertain. Polymerization of II to open-chain species appears to proceed by a cationic chain mechanism.²² However, the possibility also exists that propagation could occur from middle units thermally initiated to $[\sim\text{N}=\text{P}^{\oplus}(\text{Cl})\text{N}\sim][\text{Cl}^{\ominus}]$ ion pairs, and propagation, by electrophilic attack on the nitrogen of a cyclic

(14) References to earlier polymerization work will be found in reviews by R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, **62**, 247 (1962); C. D. Schmulbach, *Progr. Inorg. Chem.*, **4**, 275 (1962); N. L. Paddock, *Quart. Rev. (London)*, **18**, 168 (1964).

(15) J. R. Soulen and M. S. Silverman, *J. Polymer Sci.*, **1**, 823 (1963).

(16) R. Schenck and G. Römer, *Chem. Ber.*, **57B**, 1343 (1924).

(17) A. M. de Fiequelmont, *Compt. Rend.*, **204**, 689, 867 (1937).

(18) F. Patat and F. Kollinsky, *Makromol. Chem.*, **6**, 292 (1951).

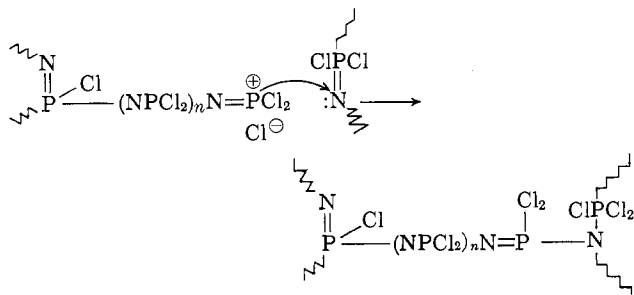
(19) R. Knoessel, J. Parrod, and H. Benoit, *Compt. Rend.*, **251**, 2944 (1960).

(20) F. G. R. Gimblett, *Polymer*, **1**, 418 (1960).

(21) During the course of a polymerization reaction at constant temperature (250 or 300 ± 2°) the yield of uncross-linked polymer rises to a maximum of about 70%, the remainder being heptane-soluble oligomers and low polymer. Formation of cross-linked polymer from the open-chain form then occurs rapidly until, after gelation of the mixture, the concentration of uncross-linked polymer falls to near zero. Before cross-linking occurs, some residual crystalline cyclic oligomers are always present, the amount apparently decreasing with increasing concentration of III. After cross-linking occurs, however, the oligomer concentration falls rapidly to near zero. These results can be interpreted in terms of an equilibrium (reversible) polymerization of the cyclic trimer II to uncross-linked polymer III and a largely irreversible conversion of the latter to the cross-linked polymer IV.

(22) H. R. Allcock and R. J. Best, *Can. J. Chem.*, **42**, 447 (1964).

trimer molecule, would then involve the formation of branches. Reaction of a propagating terminal or middle unit with another chain would lead to cross-linking. Thus, if propagation and cross-linking are



competitive reactions, the latter would occur to a significant extent only when the former is retarded by depletion of the trimer in the final stages of the reaction. The purified, open-chain high polymer cross-links readily at 150–250° in the absence of cyclic species.

Substitution.—Nucleophilic substitution reactions with solutions of III have been carried out with the use of methoxide, ethoxide, trifluoroethoxide, and phenoxide ions. The procedures used were similar to those which have been employed for substitution of cyclic trimeric and tetrameric chlorophosphazenes.²³ In each case, total replacement of chlorine was effected to yield organophosphazene high polymers V. Since the polymers formed by this reaction were particularly sensitive to depolymerization, the reaction temperature (below 130°) was dictated by the need to overcome the steric hindrance to substitution (which was particularly evident with phenoxide ion) and the necessity to avoid depolymerization. The substituted polymers were of comparable chain length to the soluble polydichlorophosphazene (III), and at least 15,000 repeating units were present in the higher molecular weight species. Substitution is not, therefore, accompanied by a significant amount of chain cleavage.

Structural Features. Chain Repeating Distance.—X-Ray diffraction measurements with oriented [NP(OCH₂CF₃)₂]_n and [NP(OC₆H₅)₂]_n showed that the chain repeating distances were 4.8 and 4.9 Å, respectively. These values are very close to the 4.92 Å repeating unit reported for (NPCl₂)_n.²⁴ Since (NPCl₂)_n has been shown to occupy an approximately *cis-trans*-planar configuration,²⁴ it appears likely that the trifluoroethoxy and phenoxy polymers assume a similar conformation.²⁵ This can be rationalized in terms of steric repulsion by the side groups.²⁶

(23) See, for instance, B. W. Fitzsimmons and R. A. Shaw, *Chem. Ind.* (London), 109 (1961); *J. Chem. Soc.*, 1735 (1964); and R. Rätz, H. Schroeder, H. Ulrich, E. Kober, and C. Grundmann, *J. Am. Chem. Soc.*, **84**, 551 (1962).

(24) E. Giglio, F. Pompa, and A. Ripamonti, *J. Polymer Sci.*, **59**, 293 (1962).

(25) Although the most prominent X-ray layer line for [NP(OC₆H₅)₂]_n corresponded to a repeating distance of 4.9 Å (±5%), other very faint meridional arcs were also present. If these are considered to be 001 reflections, a repeating distance of about 10 Å was indicated. These results might possibly be attributed to a slight distortion of the 4.9 Å arrangement (for instance, by a small lateral displacement of the chain from a *cis-trans* planar configuration) which could result in a doubled cell. Attempts to obtain crystalline-type X-ray patterns from [NP(OC₂H₅)₂]_n were unsuccessful.

(26) H. R. Allcock, *Inorg. Chem.*, **5**, 1320 (1966).

Nmr Data.—Proton magnetic resonance values for (NPR₂)_n were as follows (values in σ , with solvent in parentheses): R = OCH₃, 3.64 broad (CDCl₃); OC₂H₅, 4.2 tetrad, 1.2 triad (CDCl₃); OCH₂CF₃, 4.55 tetrad (CD₃COCD₃); OC₆H₅, 6.8 broad (CDCl₃). For [NP(OCH₂CF₃)₂]_n the fluorine resonance was a triplet at ϕ 76.6.

The following ³¹P values were obtained at ~35° (values in ppm relative to triethyl phosphate: R = Cl, +17.4 (benzene); OCH₃, +3.5 (CDCl₃); OC₂H₅, +7.3 (CHCl₃); OCH₂CF₃, +7.5 (DMF); OC₆H₅, +18.6 (benzene). The ³¹P shift values are particularly significant since in each polymer there is a positive shift. The equivalent cyclic trimers show a negative shift. The values for (NPR₂)₃ are as follows (center of spectrum in ppm): R = Cl (-20.8), OCH₃ (-21.7), OC₂H₅ (~-15.3), OCH₂CF₃ (-17.7), OC₆H₅ (-9). In each case, the change from alkoxy or aryloxy cyclic trimer to high polymer involves a shift of approximately 25 ppm toward higher field. The over-all difference between the trimeric and polymeric chloro derivatives is much larger (~38 ppm). For the trifluoroethoxyphosphazene polymer the shift was *not* independent of temperature. In tetrahydrofuran solution the positive ³¹P shift values for [NP(OCH₂CF₃)₂]_n were as follows (with temperature in parentheses): 4.7 (-80°), 4.8 (-69°), 5.2 (-50°), 7.04 (+30°), 7.4 (+50°), 7.8 (+60°), 7.9 (+70°), and 8.2 (+80°). These changes were reversible and reproducible. The effect of temperature variations on the other polymers could not be followed as readily because of the poor solubility at low temperatures.

Infrared Spectra.—The infrared spectra showed no evidence for the presence of OH or POP units. The principal infrared bands for (NPR₂)_n were as follows (in cm⁻¹): R = Cl, 1300, 1230 s (P—N), 745 (P—N); OCH₃, 1330, 1250 s (P—N), 1040, 820 (P—O—C), 755 (P—N); OC₂H₅, 1380 (P—O—C), 1310, 1240 s (P—N), 1050, 965, 800 (P—O—C), 755 (P—N); OCH₂CF₃, 1420 (P—O—C), 1280 s (P—N), 965, 880 (P—O—C), 750 vw (P—N); OC₆H₅, 1200 (P—O—C), 1310, 1240 s (P—N), 940, 800 w (P—O—C), 775 (P—N?), 760, 690 (aryl). An important feature of the spectra concerns the position of the P—N stretching peaks in the 1250 cm⁻¹ region. It is clear that replacement of Cl in (NPCl₂)_n by OCH₃, OC₂H₅, OCH₂CF₃, and OC₆H₅ has no marked influence on the main 1230 cm⁻¹ peak or on the nearby shoulder at 1300 cm⁻¹. However, the surprising result is that the position of this peak in the polymers corresponds closely to that of the equivalent peak in analogous cyclic trimers. For example, the following frequencies (in cm⁻¹) have been recorded for (NPR₂)₃: R = Cl (1190, 1220), OCH₃ (1235, 1275), OC₂H₅ (1220, 1240; 1225²⁷), OCH₂CF₃ (1240, 1280), OC₆H₅ (1160–1200).

The 1250 cm⁻¹ bands were attributed to an out-of-phase stretching mode in the polymer, and the 750 cm⁻¹ band to an in-phase P—N—P stretch. Similar stretching modes can be assigned to the analogous

(27) B. W. Fitzsimmons and R. A. Shaw, *Proc. Chem. Soc.*, 258 (1961).

bands near 1200 and 875 cm^{-1} in the trimer. The splitting of the 1250 cm^{-1} band and the broadening (and possible splitting) of the 750 cm^{-1} band in the chloro, methoxy, ethoxy, and phenoxy polymers can be rationalized in terms of a *cis-trans*-planar polymer conformation rather than a *trans*-planar form.

Ultraviolet Spectra.—The polymers with methoxy, ethoxy, and trifluoroethoxy side groups showed weak, diffuse maxima in the 270–280 $\text{m}\mu$ region of the spectrum in methanol or ethyl acetate ($\log \epsilon < 1.0$ per monomer unit). These corresponded to similar weak absorptions between ~ 400 and 200 $\text{m}\mu$ ($\log \epsilon < 1.0$ per monomer unit) for $[\text{NP}(\text{OCH}_3)_2]_3$ and $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_3$ in methanol. For both polymers and trimers, the optical density varied with the method of purification, and the maxima were attributed to the presence of trace impurities.²⁸ No longer wavelength bands were evident. The phenoxy-substituted polymer showed an absorption in chloroform at λ_{max} 264 $\text{m}\mu$ ($\log \epsilon$ 2.96 per monomer unit) which was attributed to the aryl unit.

Glass Transitions and Polymer Crystallinity.—The glass transition temperature of a polymer is believed to represent the temperature at which rotation of the backbone bonds becomes possible, thereby allowing the material to assume the properties of a rubbery polymer or elastomer. For polyphosphazenes of structure $(\text{NPR}_2)_3$, the glass transition temperatures varied with R as follows: R = Cl (-63°), OCH_3 (-76°), OC_2H_5 (-84°), OCH_2CF_3 (-66°), and OC_6H_5 (-8°). These values corresponded roughly to the barrier height to P–N bond rotation in terms of the maximum steric interactions of the side groups.

The chloro, trifluoroethoxy, and phenoxy derivatives were crystalline and could be oriented by stretching. The optical birefringence of the trifluoroethoxy derivative disappeared reversibly above 242° , as did the crystallinity to X-rays. This temperature probably represents a polymer crystalline melting point.

Depolymerization.—Polydichlorophosphazene, $(\text{NP-Cl}_2)_n$, does not depolymerize below 300–350 $^\circ$.¹⁴ At least part of this stability is due to the fact that the polymer cross-links readily above 100 $^\circ$. The methoxy, ethoxy, trifluoroethoxy, and phenoxy derivatives all underwent a fairly rapid molecular weight decrease below 200 $^\circ$, and with the methoxy, ethoxy, and phenoxy derivatives the depolymerization was perceptible even at 100 $^\circ$ (see Experimental Section). With the methoxy and ethoxy derivatives, depolymerization at 150 and 200 $^\circ$, respectively, was accompanied by decomposition. Although the depolymerization reactions have not been studied in detail, infrared spectral data indicate that the products include low molecular weight cyclic species. In view of this information, it is not surprising that previous attempts to prepare polymers by heating of the equivalent cyclic trimeric

(28) The ultraviolet peaks in the 210– $\text{m}\mu$ region of the solution spectrum of $(\text{NPCl}_2)_3$, reported by N. B. Jurinski, C. C. Thomson, and P. A. D. de Maine, *J. Inorg. Nucl. Chem.*, **27**, 1571 (1965), are similar to those frequently caused as an artifact by scattered light in this region of the spectrum. We find essentially no absorption for solutions of pure $(\text{NPCl}_2)_3$ at wavelengths higher than 199 $\text{m}\mu$.

or tetrameric organophosphazenes were unsuccessful, since the polymers are apparently thermodynamically unstable at temperatures near or above 100 $^\circ$.

Relationship to Current Theories. π -Bond Delocalization in Phosphazenes.—It is generally agreed that the σ -bond framework in phosphazenes is supplemented by some degree of π bonding between phosphorus 3d orbitals and nitrogen 2p orbitals. However, opinions differ as to whether this π bonding is extensively delocalized²⁹ or restricted into nonconjugated “islands” of π character.^{30,31} The previous experimental evidence was inconclusive but, if anything, favored the latter hypothesis. The properties of the high polymers have a particular relevance to this subject. If extensive delocalization exists in phosphazenes, the electronic absorption should be shifted to longer wavelengths as the ring or chain size increases,³² and the force constant of the skeletal bonds should increase at the same time. No evidence of a long wavelength electronic –P–N– absorption band was found for the polymers synthesized here, and the vibrational spectra indicated that the force constants of the skeletal bonds were similar in analogous cyclic trimers, cyclic tetramers, and high polymers. Further indirect evidence about the skeletal bonding can be inferred from the low glass transition values found for the alkoxy and chloro derivatives. These indicate an unusually high flexibility of the backbone and an appreciable degree of torsional or rotational freedom of the skeletal bonds. The skeletal π bonding must, therefore, be sufficiently localized or weak that it confers only negligible resistance to torsional motions on the phosphorus–nitrogen bond. Thus, the over-all picture is one of poor skeletal delocalization in these polymers.

The possibility exists that the side-group bonds from phosphorus could also show some π character due to interaction of a phosphorus d orbital with the lone-pair sp orbital of each adjacent oxygen atom. The infrared results do not provide information on this point since the marginal shift of the main (1230 cm^{-1}) peak toward higher frequencies, when OCH_3 or OC_2H_5 groups are replaced by the OCH_2CF_3 group, can be explained by a purely inductive electron withdrawal from phosphorus, which causes contraction of the d orbitals.

Nmr Spectra.—The interpretation of ^{31}P nmr shifts is complicated.³³ Nevertheless, positive shifts are associated with greater shielding of the phosphorus nucleus, and, for quadruply connected phosphorus, the shift may be connected with a change in the distribution of $d_{\pi}\text{-p}_{\pi}$ bonds among the four δ bonds.³³

(29) D. P. Craig and N. L. Paddock, *J. Chem. Soc.*, 4118 (1962).

(30) M. J. S. Dewar, E. A. C. Lucken, and M. A. Whitehead, *ibid.*, 2423 (1960).

(31) D. P. Craig and K. A. R. Mitchell, *ibid.*, 4682 (1965).

(32) It could be argued that delocalization involving 3d orbitals may not give rise to strong, longer wavelength absorptions. However, D. A. Johnson, G. D. Blyholder, and A. W. Cordes, *Inorg. Chem.*, **4**, 1790 (1965), have shown that the thiothiazyl cation, $(\text{S}_2\text{N}_3)^+$, gives rise to $\pi \rightarrow \pi^*$ transition bands near 340 and 260 $\text{m}\mu$. Apparently this ring is a conjugated system in which sulfur 3d orbitals are employed.

(33) See, for instance, papers by J. R. Van Wazer, C. F. Callis, J. N. Schoolery, and R. C. Jones, *J. Am. Chem. Soc.*, **78**, 5715 (1956); and J. H. Letcher and J. R. Van Wazer, *J. Chem. Phys.*, **44**, 815 (1966).

It was demonstrated earlier that the high polymers, like cyclic tetramers, show positive shifts, but that equivalent cyclic trimers show negative shifts. The most obvious difference between cyclic trimers and higher homologs is that the skeletal bonds in the latter are capable of greater torsional mobility. This could reduce the (localized) π character of the skeletal bonds relative to the side group bonds, improve the π -bond symmetry around phosphorus, and increase the shielding. The temperature-dependent positive shift observed for the trifluoroethoxy derivative in solution may also be due to an enhanced torsional freedom of the chain bonds as the temperature is raised.

Depolymerization.—The instability of the polyorganophosphazenes to thermal equilibration demonstrates the extreme sensitivity of the phosphazene system to side-group steric influences. Replacement of chloro groups in $(\text{NPCl}_2)_n$ by methoxy, ethoxy, trifluoroethoxy, or phenoxy lowers the temperature required for detectable depolymerization to cyclic oligomers by at least 200° . This cannot reflect a purely kinetic influence by the side groups, particularly if depolymerization, like polymerization, requires the ionization of a side group from phosphorus. It is more probable that the side group plays a larger role in influencing the thermodynamics of ring-chain equilibration in phosphazenes.²⁶ The fact that the polymers do not depolymerize in the rubbery phase at 25° can be ascribed to an infinitely slow rate of equilibration at this temperature.

Experimental Section³⁴

Materials.—Hexachlorocyclotriphosphazene (II) (>95% purity) was obtained from Hooker Chemical Corp. and was purified as described below. Methanol (reagent grade) and ethanol (absolute, reagent grade) were dried over aluminum amalgam for 1 week before distillation from the same drying agent. Trifluoroethanol (Halocarbon Products) was used as received. Phenol (reagent grade) was dried by distillation through a short, packed column, and the middle fraction, bp 182° , was taken. The *n*-heptane (Eastman reagent grade) used for recrystallization of II was used as received. However, *n*-heptane employed for the precipitation of III was dried for 48 hr over calcium hydride. Benzene (reagent grade) and xylene (reagent grade) were dried in the same way. The tetrahydrofuran used during the preparation of $[\text{NP}(\text{OC}_6\text{H}_5)_2]_n$ was dried over calcium hydride and was then distilled from the same reagent. Ethyl trifluoroacetate (Aldrich Chemical Co.) required for the light-scattering investigation of $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ was dried over molecular sieves and was then distilled through a spinning-band column (bp 62°). Dioxane (commercial) (5 l.) was refluxed for 16 hr with 1.3 *N* hydrochloric acid (0.9 l.) to hydrolyze ethylene acetal impurity, while a steady stream of nitrogen was passed through

the solution. When cooled, the mixture was shaken with sodium hydroxide pellets to remove acid, water, and peroxides. The aqueous layer was separated from the dioxane and the latter was refluxed for 3 days with sodium (~ 100 g). The dioxane was then distilled directly into the reaction flask after rejection of the forerun.

Equipment.—Polymerization of II was carried out in sealed Pyrex tubes of size 8.5×2.0 cm (20-g scale) or 23×3.5 cm (200-g scale). Evacuation of the tubes prior to sealing was performed on a vacuum line at 0.1 mm pressure. The sealed tubes were heated in a thermoregulated bath of molten Wood's metal ($\pm 2^\circ$ at 250°), although for specific experiments a thermoregulated oven was also used. A nitrogen-filled drybox was employed for the handling of chlorophosphazene polymers and solutions in certain critical experiments. The substitution experiments were performed in standard glass apparatus, with exclusion of moisture by calcium sulfate drying tubes.

Purification of $(\text{NPCl}_2)_3$.—Purification of II (1000 g) was effected by recrystallization from warm *n*-heptane (1500 ml) at a temperature below 75° , after decoloration with activated carbon. The first crop of crystals (~ 621 g) obtained at room temperature was filtered off and dried either *in vacuo* or in air (mp 108 – 113°). This purification procedure ensured the absence of an unidentified polymerization inhibitor which was sometimes present in material recrystallized under alternative conditions. Sublimation of II, irrespective of the method of previous recrystallization, yielded a product (mp 114°) which polymerized at approximately the same rate as the recrystallized material. In one experiment, three successive vacuum sublimations (at 0.0001 mm pressure), the final one directly into an evacuated polymerization tube, did not bring about a noticeable decrease in the polymerization rate. The possibility that polymerization occurs only in the presence of a catalyst seems unlikely, therefore.

Typical Polymerization Procedure.—Recrystallized hexachlorocyclotriphosphazene (200 g) was placed in a 32.5×3.5 cm constricted Pyrex tube. The tube was then evacuated for 30 min at a pressure of 0.1 mm and then isolated from the vacuum line, and the trimer was melted and allowed to resolidify. The stopcock to the vacuum line was opened and evacuation was continued for a further 30 min. The tube was then sealed at the constriction and was immersed in a constant-temperature bath at 250° for 48 hr. When the tube was cooled to 25° , the polymer was a transparent immobile material in which crystallization of residual trimer or other oligomers occurred slowly. The product was then cut into small pieces (~ 0.25 -in. cube), preferably in a stream of dry nitrogen, and was added to dry benzene (1000–3000 ml). The polymer dissolved to a viscous, colorless solution after 24–48 hr of continuous agitation.

Effect of Polymerization Temperature.—The rate of polymerization and the onset of cross-linking were both accelerated by a temperature increase. The following percentage yields of uncross-linked $(\text{NPCl}_2)_n$ were obtained after polymerization of 20-g samples of $(\text{NPCl}_2)_3$ at 250° for specific reaction times, followed by precipitation of the polymer from benzene solution into excess *n*-heptane: 3 hr, 12%; 4 hr, 13.8%; 5 hr, 17.0%; 6 hr, 23.4%; 21 hr, 30.8%; 48 hr, 70%; 96 hr, cross-linked to benzene-insoluble gel. At 300° the polymer yields were: 0.08 hr, 0%; 0.16 hr, 10%; 0.25 hr, 13.7%; 0.33 hr, 15.2%; 0.41 hr, 19.3%; 0.5 hr, 27.3%; 0.66 hr, 37.9%; 1 hr, 50.3%; 1.17 hr, cross-linked to benzene-insoluble gel. It must also be emphasized that not only is the rate of polymerization sensitive to the presence of trace inhibitors but also, as mentioned by other authors,^{4,5} it is sensitive to the influence of small amounts of accelerators. Traces of water on the surface of the polymerization tube may exert a catalytic effect, but the polymerization was inhibited by air. Reproducible polymerization rates are, therefore, very difficult to obtain. Under nonstandardized conditions the rate may vary by a factor of 10. Marked temperature fluctuations during polymerization favored the cross-linking process, and use of benzoic acid as a catalyst at 200° also facilitated the cross-linking reaction.

Properties of Cross-Linked Polydichlorophosphazene.—The

(34) Nmr spectra were measured on a Varian DP 60 apparatus with proton spectra determined at 56.4 Mc and ^{31}P spectra at 16.2 Mc, or on a Varian A 60 apparatus. Infrared spectra of films on rock salt plates were recorded on Perkin-Elmer Model 21 and 137 spectrometers, and ultraviolet solution spectra on a Cary Model 14 automatic recording spectrometer. X-Ray repeat distances were measured using a cylindrical camera of 57.3-mm diameter: stretched fibers of $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ and an oriented film of $[\text{NP}(\text{OC}_6\text{H}_5)_2]_n$ were employed. X-Ray irradiation of $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ was carried out using a 250 KVP unfiltered Maxitron instrument for 6 hr at a dose rate of about 0.25 Mrad/hr. Solution viscosities were measured in modified Ostwald (Cannon) or Cannon Ubbelohde dilution viscometers at 30° . Light-scattering measurements were performed in a Brice Phoenix apparatus, and glass transition temperatures were determined with a Du Pont 900 differential thermal analyzer.

TABLE I
ANALYTICAL DATA

	C, %		H, %		N, %		P, %		F, %		Cl, %		Mol wt ^a	Intrinsic viscosity, dl/g
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found		
(NPCl ₂) _n ^b	12.09	12.35	26.73	26.41	61.18	61.4	c	2.4 (benzene)
[NP(OCH ₃) ₂] _n	22.4	21.76	5.61	5.55	13.09	12.90	29.9	29.34	0	640,000	1.22 (CHCl ₃)
[NP(OC ₂ H ₅) ₂] _n	35.6	35.18	7.41	7.13	10.38	10.40	22.95	22.75	0	d	2.9 (CHCl ₃)
[NP(OCH ₂ CF ₃) ₂] _n	19.77	19.97	1.66	1.94	5.76	5.59	12.74	12.95	46.9	46.85	...	0	1,700,000 ^{e,f}	2.7 (acetone)
[NP(OC ₂ H ₅) ₂] _n	62.3	61.90	4.33	4.60	6.06	6.85	13.42	13.49	0	3,700,000	2.7 (benzene)

^a By light scattering. ^b Soluble polymer, isolated by precipitation from benzene into *n*-heptane. ^c Light-scattering data for (NPCl₂)_n could not be obtained because of the tendency of the polymer to cross-link in benzene solution. ^d In ethyl trifluoroacetate (the only solvent found with a suitable refractive index) a slow gelation reaction occurred which invalidated the data. ^e In ethyl trifluoroacetate. ^f The number-average molecular weight, determined by osmotic pressure, was 90,000, which indicates that the molecular weight distribution is very wide.

cross-linked polymer is a clear, colorless, transparent rubber. When lightly cross-linked it is soft and extensible, but increased cross-linking (brought about by prolonged polymerization) causes a marked toughening and hardening to occur. The polymer is swelled by, but is insoluble in, benzene, toluene, xylene, carbon tetrachloride, nitrobenzene, and chlorobenzene. The degree of swelling appears to be inversely related to the rigidity of the elastomer. These properties are typical of a cross-linked polymer. Treatment of the subdivided, cross-linked polymer with nucleophilic reagents, such as phenol-triethylamine or trifluoroethanol-triethylamine mixtures, yielded uncross-linked (soluble), partially substituted products. The weight-average molecular weights of these products (30,000–70,000) were considerably lower than those prepared from the uncross-linked polymer (~1,500,000), and it must be concluded that nucleophilic reagents cleave not only the cross-links, but also the main chains, possibly at the points of cross-linkage. Sodium alkoxides bring about almost total replacement of chlorine if the cross-linking is minimal. When exposed to atmospheric moisture, the cross-linked chlorophosphazene polymer slowly hardens and finally degrades to phosphate, hydrogen chloride, and ammonia.

Properties of Uncross-Linked Polydichlorophosphazene.—The uncross-linked polymer is a colorless, transparent elastomer which dissolves slowly but completely in benzene, toluene, xylene, or tetrahydrofuran to give viscous solutions. It can be isolated (and separated from low molecular weight cyclic oligomers) by precipitation from benzene or toluene into dry *n*-heptane, but in the rubbery state it is particularly sensitive to cross-linking. For this reason, molecular weight separation was performed on the substituted species and not on the chloro polymer used for substitution.

Solutions of polydichlorophosphazene in dry benzene underwent a slow viscosity increase which culminated in gelation of the solution after about 6 days at 25°. Attempts to exclude water rigorously from the system did not retard the cross-linking process appreciably. Shielding of the solution from light or irradiation with ultraviolet light also appeared to have no influence on the reaction. Addition of stannic chloride (over 0.6 mole % SnCl₄ per NPCl₂ unit) inhibited the cross-linking process, possibly by formation of a complex, $\sim\text{NP}^{\ominus}\text{Cl}_2^{\ominus}\text{SnCl}_4$, at the active chain ends.

Synthesis of Poly(dimethoxyphosphazene).—A solution of polydichlorophosphazene (116 g, 1 unit mole) in dry benzene (600 ml) was added slowly over 1 hr to a stirred solution of sodium methoxide prepared from sodium (57.5 g, 2.5 g-atom) and methanol (400 ml). An exotherm raised the reaction temperature to 60°. Refluxing was continued for a further 12 hr, and the mixture was stirred at 25° for a further 2 days. Methanol was then added and the benzene was removed by azeotropic distillation. The mixture was acidified with concentrated hydrochloric acid and the viscous solution was filtered to remove sodium chloride. The salt was washed with methanol and dried (122 g, theory (NaCl), 117 g). The polymer was then precipitated several times from methanol solution into diethyl ether and into benzene, to remove the lower molecular weight methoxyphosphazene homologs, and the precipitate was dried under vacuum. The product (13 g, 12% based on (NPCl₂)₃) was a

colorless, rubbery material. Analytical data are shown in Table I. The polymer was soluble in methanol, dioxane, tetrahydrofuran, dimethoxyethane, chloroform, pyridine, dimethylformamide, and acetonitrile, but insoluble in water, ethanol, diethyl ether, benzene, and acetone.

Synthesis of Poly(diethoxyphosphazene).—A solution of polydichlorophosphazene (183 g, 1.575 moles) in benzene (2 l.) was added slowly to a stirred solution of sodium ethoxide, prepared from sodium (92 g, 4.0 g-atoms) and ethanol (~2 l.) in a nitrogen atmosphere. The reaction was allowed to proceed at 25° for 5 days. The mixture was then neutralized with concentrated hydrochloric acid and was treated with water to cause separation of an aqueous ethanolic and a benzene layer. The latter was dried (MgSO₄), and the polymer was precipitated from benzene into *n*-heptane. Further purification was effected by partitioning of the polymer in methanol-benzene mixtures. Yields of up to 45% (based on (NPCl₂)₃) were obtained. The polymer was a colorless, elastomeric material which was soluble in alcohols, benzene, ethers, and ketones, but insoluble in aliphatic hydrocarbons and water.

Synthesis of Polybis(trifluoroethoxy)phosphazene.—A solution of polydichlorophosphazene (300 g, 2.58 moles) in benzene (1500 ml) was added over 3 hr to a stirred solution of sodium trifluoroethoxide, prepared from sodium (120 g, 5.22 g-atoms) and trifluoroethanol (600 g, 6 moles) in tetrahydrofuran (600 ml). An exotherm caused the solvents to reflux. The reaction mixture was refluxed for 16 hr, cooled to room temperature, and then acidified (to litmus) with concentrated hydrochloric acid. The solid components were filtered off, washed with large amounts of water to remove occluded sodium chloride, and then washed with aqueous 95% ethanol. The polymer was dissolved in acetone (3 l.), filtered under pressure (because of the high viscosity), and precipitated into water (30 l.) to remove sodium salts. The polymer was air dried and redissolved in acetone. It was then precipitated twice from acetone into benzene to remove oligomers. The polymer (170 g, 27% based on (NPCl₂)₃) was a white, fibrous product. It was soluble in acetone, tetrahydrofuran, ethyl acetate, ethylene glycol, dimethyl ether, and methyl ethyl ketone, but insoluble in diethyl ether, dioxane, ethanol, and aromatic and aliphatic hydrocarbons. Films, formed by evaporation of solvent, were colorless, transparent, and not unlike polyethylene in flexibility and appearance. The solid polymer was unaffected by water, glacial acetic acid, alcohols, pyridine, or concentrated sodium hydroxide solution. However, some decomposition was evident with triethylamine, dimethylformamide, acetonitrile, and concentrated sulfuric acid. The polymer was crystalline to X-rays and to optical polarization up to the crystalline melting point at 242–243°. Differential thermal analysis, X-ray diffraction, and optical polarization experiments revealed the presence of an endothermic crystal transition between 60 and 70°. The density was 1.71. Irradiation of a film of the material for 6 hr with 250 KVP X-rays at a dose rate of approximately 0.25 Mrad/hr appeared to depolymerize the polymer, but did not cross-link it. The polymer was unaffected by prolonged exposure to ultraviolet light.

Synthesis of Poly(diphenoxyphosphazene).—A solution of polydichlorophosphazene (116 g, 1 unit mole) in benzene (500

ml) was added slowly to a stirred solution of sodium phenoxide, prepared from sodium (70 g, 3 g-atoms) and phenol (325 g, 3.5 moles), in tetrahydrofuran (700 ml). The mixture was refluxed at 74° for 4 hr and was stirred at 25° for 2.5 days. Tetrahydrofuran and some benzene (1.5 l.) were then removed by distillation as dioxane (1.5 l.) was added, and the mixture was boiled at reflux for 16 hr and stirred at 25° for 20 hr. An aliquot of the reaction mixture showed that substitution of the polymer was incomplete at this stage. Solvent (1.5 l.) was, therefore, removed from the reaction mixture by distillation as xylene (1.5 l.) was added. The mixture was then refluxed at 126° for 12 hr and then stirred at 25° for a further 16 hr. The semisolid mass was diluted with benzene and acidified to litmus by addition of concentrated hydrochloric acid, before precipitation into *n*-heptane. The solid products were filtered off, washed with acetone until no further color was extracted, and washed with a large volume of water to remove sodium chloride. Water was removed from the residue by washing with acetone, and the residue was dissolved in hot benzene to permit azeotropic removal of the remaining water. The polymer was then purified by precipitation from hot benzene into *n*-heptane and from hot dioxane into water. The polymer obtained in this way was dried by treatment with acetone followed by vacuum drying. Analytical samples were freeze-dried. The polymer was soluble in hot benzene, toluene, dimethylformamide, dioxane, chloroform, chlorobenzene, and tetrahydrofuran, but insoluble in acetone, dimethyl sulfoxide, hexane, ethanol, and water. Films of the polymer, obtained by evaporation from solution, were colorless, transparent, and flexible, and again showed a superficial resemblance to polyethylene. They were stable for 4 months to concentrated aqueous sodium hydroxide solution, esters, alcohols, ethers, ketones, and aliphatic hydrocarbons, but were decomposed by pyridine and concentrated sulfuric acid.

Depolymerization Experiments.—Experiments were performed under vacuum, in nitrogen or air, and in solution. For the reactions under vacuum, approximately 0.5 g of each polymer was vacuum sealed within a 1.9 × 9 cm Pyrex tube. The tubes were then immersed in a thermoregulated bath of dimethylsilicone oil for 8 hr at different temperatures. The trifluoroethoxy and phenoxy derivatives retained their form and integrity as elastomers or thermoplastics at 200°. The methoxy and ethoxy derivatives

were viscous liquids under these conditions. The polymers were then dissolved in benzene (phenoxy derivative), chloroform (methoxy and ethoxy derivatives), or acetone (trifluoroethoxy compound) for solution viscosity measurements. Viscosity data are shown in Table II. It was also shown that at 250° under vacuum the trifluoroethoxy derivative underwent an intrinsic viscosity decrease from 1.73 dl/g to a near-equilibrium value of 0.18 dl/g within 4 hr. The infrared spectrum did not change during this process.

TABLE II
DEPOLYMERIZATION OF POLYPHOSPHAZENES (NPR₂)_n^a

R	Initial soln viscosity, dl/g	—Viscosity (dl/g) after 8 hr at—		
		100°	150°	200°
OCH ₃	1.02	0.095	<i>b</i>	<i>b</i>
OC ₂ H ₅	1.63	1.090	0.158	<i>b</i>
OCH ₂ CF ₃	2.50	2.50	1.20	0.48
OC ₆ H ₅	4.24	2.06	0.62	0.43

^a Reduced specific viscosity at 0.5% concentration in benzene (R = OC₆H₅), chloroform (R = OCH₃ and OC₂H₅), or acetone (R = OCH₂CF₃). ^b Depolymerization accompanied by decomposition or rearrangement.

Depolymerization of the trifluoroethoxy and phenoxy derivatives also occurred in nitrogen (~1.5 atm pressure) at 150° and when exposed to the air at 200°. In tetrahydrofuran solution (2 wt %) at 66°, the phenoxy polymer underwent an approximately 33% decrease in average chain length in 24 hr, while the trifluoroethoxy derivative underwent only a 2% decrease under the same conditions. Qualitative evidence was also obtained that the ethoxy derivative depolymerized slowly in ethanol solution at 25°.

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