solvents within experimental error. This may imply that the optically active polymers have no special conformation, although the strong peaks in the CD and ORD spectra are due to a rigid structure.[17] The optical data depend very much on the conformations of two carbonyl groups on the cyclopropane and cyclohexane rings. Probably the conformations in the polymers are not varied in all the solvents. However, the DSH unit in the polymers can rotate the amide groups clockwise or counterclockwise by 90° as shown in Figure 6. Since there are no differences in the steric interactions and the dipole–dipole interactions between the two structures, the rotation may be random in the polymers. This may be the reason why the optically active polymers and the racemic polymers demonstrated the same viscosity behavior.

In the cases of (+)-C3 • piperidane and (+)-C3 • *trans*-2,5-dimethylpiperadine polyamide, the solution viscosities in TFE and MSA were somewhat different; the viscosity in MSA was much greater than that in TFE.[18] The difference in the viscosity behavior also indicates that (+)-C3 • DSH may have a different conformation from (+)-C3 • piperadine and (+)-C3 • *trans*-2,5-dimethylpiperadine polyamides as stated in the solvent effect on the CD spectra.

The nmr studies of the polymers and the model compounds, especially I and III, will be reported in a future publication.

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Polymerization of Hexachlorocyclotriphosphazene. The Role of Phosphorus Pentachloride, Water, and Hydrogen Chloride[1]

H. R. Allcock,* J. E. Gardner,[2] and Karen M. Smeltz

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802.

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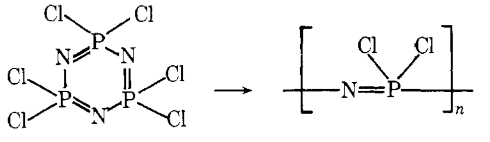
ABSTRACT: The polymerization of hexachlorocyclotriphosphazene (I) (also known as phosphonitrilic chloride trimer) to high molecular weight poly(dichlorophosphazene) (II) has been studied in the presence of phosphorus pentachloride, water, and hydrogen chloride. Phosphorus pentachloride is a powerful polymerization inhibitor, water is a polymerization catalyst or cocatalyst, and hydrogen chloride is a mild inhibitor. The results are discussed in terms of possible reaction mechanisms.

The thermal polymerization of hexachlorocyclotriphosphazene (phosphonitrilic chloride trimer) (I) to the rubbery, high molecular weight poly(dichlorophosphazene) (II) was first reported by Stokes in 1897.[3] More recently a number of investigators have studied this reaction with a view to understanding the reaction mechanism,[4–14] yet the details of this process are still only poorly understood. Interest in this polymerization reaction has grown rapidly in recent years, mainly because poly(dichlorophosphazene) is now a critical intermediate in the substitutive synthesis of high molecular weight poly(organophosphazenes).[9,15–20] These latter polymers constitute an important new class of applicable elastomers and thermoplastics.



I II

The thermal polymerization of hexachlorocyclotriphosphazene (I) is a complex reaction. The pure, molten trimer polymerizes at an observable rate only at temperatures above 230°, with the rate accelerating as the temperature is raised to 300°. However, polymerization is eventually accompanied by the formation of an insoluble modification.[9,15] This latter species is unsuitable as a substrate for substitution reactions, and the choice of a time–temperature relationship for polymerization requires a delicate assessment of the relative rates of polymerization and insolubilization.

The overall reaction is further complicated by the fact that traces of impurities appear to function as powerful accelerators or inhibitors for the polymerization. Catalysts are known which permit polymerizations to be effected at temperatures as low as 200°.[6,7,21] Finally, it is known that, at temperatures near 350°, the polymer breaks down to yield lower molecular weight cyclic species.[2,22,23] In this work we have attempted to clarify some of the factors which influence the polymerization of the trimer, $(NPCl_2)_3$.

Experimental Section

Materials. Hexane (Baker) was dried overnight over anhydrous sodium carbonate before storage over molecular sieves. Acetone (Baker), anhydrous ether (Fisher), xylene (Baker), and trifluoroethanol (Halocarbon Products) were used as received. Benzene (Fisher) was dried by boiling at reflux over calcium hydride, followed by distillation just before use. Phosphorus pentachloride (Allied Chemical) was either used as received or was purified by vacuum sublimation at 65°. Tetrahydrofuran (Baker) was distilled from lithium aluminum hydride. Gaseous helium and hydrogen chloride (Matheson) were used as received. Nitrogen gas (Wolf) was dried in one of two ways. First, for use as a purging gas to remove air from reaction vessels, the nitrogen was passed through sulfuric acid bubblers and through tubes containing anhydrous sodium carbonate. Second, for use in glove bags, the nitrogen was passed through a 90 by 4 cm column packed with glass and phosphorus pentoxide.

Hexachlorocyclotriphosphazene (I). Hexachlorocyclotriphosphazene (El Monte Chem. Co., Pasadena, Calif.) was purified by sublimation at 50° (0.7 mm). The sublimate was then recrystallized twice from dry hexane, was dried for 15 hr in vacuum, and was resublimed at 50° (0.7 mm). During this sublimation, only 60–70% of the material was allowed to sublime in order to ensure the absence of the cyclic tetramer from the sublimate. Trimer used for the study of the influence of water was subjected to further purification. After the second sublimation, the sublimed trimer was transferred within a dry bag to another sublimator without exposure of the compound to the atmosphere. A third fractional sublimation was then carried out and the sublimate was again removed from the sublimator in a dry bag prior to filling of the polymerization tubes in a dry nitrogen atmosphere. The melting point of the purified trimer was 113–114°.

Polymerization Technique. The type 7740 Pyrex glass polymerization tubes were of two sizes: a larger size with a 200 g trimer capacity and dimensions of 310 mm long, 33 mm inside diameter, 2 mm wall thickness, with a constriction 90 mm from the open end; and a smaller size with an 18 g capacity and with the dimensions, 210 mm long, 13 mm inside diameter, 3 mm wall thickness and a constriction 70 mm from the open end. Most of the reactions were carried out with the smaller tubes. The open ends of the tubes were sealed on to 24/40 outer ground glass joints.

The tubes were soaked for 15 hr in "Micro" cleaning solution, followed by 10–11 washings with distilled water and drying at 140° in an oven. After the drying procedure, the tubes were attached to a vacuum line, were evacuated, and then were flamed out and allowed to cool on the vacuum line. The tubes were subsequently removed from the vacuum line, filled with trimer, stoppered, returned to the vacuum line, degassed for 20 min, and then sealed.

The sealed, evacuated tubes were heated at 250° in a Freas Model 104 thermoregulated oven. The polymerization times varied from experiment to experiment (see Results and Discussion sections). Agitation of the tubes during a run was accomplished by means of a geared-down electric motor and arm assembly attached to the top of the oven. A wire from the arm entered the oven and was attached to one end of a wire mesh basket which contained the tubes. A complete rocking motion of the tubes took place once every minute.

Technique Modification for the Introduction of Additives. Addition of Phosphorus Pentachloride. Weighed amounts of sublimed PCl_5 were placed in dry polymerization tubes in a nitrogen-filled dry bag. A weighed amount of trimer was then added, the tube was stoppered, and the contents were mixed by shaking. The tubes were then degassed on the vacuum line and sealed after cooling in liquid nitrogen to prevent sublimation of PCl_5.

Addition of Water. Water vapor was measured by pressure and volume on the vacuum line and was then condensed into the trimer-filled tubes. The tubes were cooled in liquid nitrogen during condensation and sealing. The addition of water did not result in the generation of colored species.[11]

Addition of Hydrogen Chloride. Hydrogen chloride vapor was measured by pressure and volume within the vacuum line system. Measured samples were then condensed into a polymerization tube at liquid nitrogen temperature.

Derivatization Procedure. Poly(dichlorophosphazene) is subject to rapid hydrolysis in contact with atmospheric moisture. For this reason the polymer was converted to the hydrolytically stable trifluoroethoxy derivative by the following typical procedure. A mixture of poly(dichlorophosphazene) and unchanged hexachlorocyclotriphosphazene (15 g) was removed from the polymerization tube in a nitrogen-filled dry bag and then added to 400 ml of freshly distilled dry benzene. The flask was tightly stoppered and the contents were stirred by means of a magnetic stirrer for 15 hr to dissolve the polymer.

A solution of sodium trifluoroethoxide was then prepared by the addition of trifluoroethanol (~110 ml) to a stirred mixture of sodium (16 g) and ether (300 ml) in a 3000 ml, three-necked flask, continuously flushed with dry nitrogen. The sodium had previously been separated from adhering oxide and hydroxide by a melting procedure in the vapor of boiling xylene in a dry nitrogen atmosphere. Following the preparation of the sodium trifluoroethoxide, dry tetrahydrofuran (300 ml) was added.

The solution of chlorophosphazenes in benzene was then filtered through a course porosity, sintered glass funnel into a pressure equalizing addition funnel, from which it was added slowly to the stirred sodium trifluoroethoxide solutions. After completion of addition, the mixture was stirred at reflux for 24 hr.

The mixture was then allowed to cool to room temperature and was vacuum filtered through a medium porosity sintered glass funnel. The filtrate contained derivatized low molecular weight cyclic phosphazenes and these were isolated by removal of most of the solvent, followed by precipitation into 5–10 l. of acidified water, with subsequent filtration and drying.

Those insoluble components of the reaction mixture that had been isolated by the initial filtration included sodium chloride, poly[bis(trifluoroethoxy)phosphazene], and derivatized cyclic species. This mixture was washed with dilute hydrochloric acid (2–3 l., pH ~6) and then allowed to dry. The phosphazenes were dissolved in acetone, the mixture was filtered, the filtrate was added to a large volume of dilute hydrochloric acid, and the precipitate was removed and dried. Further purification was effected by precipitation of the polymer from acetone into hexane. Finally, the polymer was redissolved in acetone and cast as a film. This ensured homogeneity of the sample during subsequent GPC analysis. Samples used for solution viscosity experiments were reprecipitated twice from acetone into benzene to remove the cyclic species.

Equipment. Solution viscosity measurements were made with a Cannon-Ubbelohde 75-E-157 viscometer at 30°. Acetone was used as the solvent for the derivatized polymers and chloroform was the solvent for underivatized poly(dichlorophosphazene).

Infrared spectra were measured with the use of a Beckman IR5A spectrometer. ^{31}P nmr spectra were measured on a Varian 100 Mc instrument or on a JEOL spectrometer. Cyclic phosphazenes were studied on the Varian spectrometer as solutions in benzene and low molecular weight linear species as benzene or nitrobenzene solutions. With the JEOL instrument, the reference compounds and solvents were $CDCl_3$ or $(CD_3)_2CO$. Chemical shifts are reported in parts per million relative to aqueous 85% phosphoric acid.

Gel permeation chromatograms were obtained with the use of a Waters Associates ALC 201 instrument fitted with a refractive index detector. Acetone was used as the solvent. Sample concentrations were 0.25 or 0.125%. The columns consisted of Corning porous glass beads with four 2 ft lengths of $\frac{3}{8}$ in. wide sections of 75, 175, 700, and 2000 Å stationary phase. Typical analyses were conducted with 1× attenuation, positive polarity, 400–500 psi pressure, and 1.8–2.0 ml/min flow rate. The instrument was calibrated with narrow molecular weight polystyrene standards (Waters Associates). Thus, the $\bar{M}_n$ values for these polyphosphazenes are considered to be approximate.[1b]

Results and Discussion

The Fundamental Polymerization Process. The polymerization of hexachlorocyclotriphosphazene (I) is a highly unpredictable process. Different batches of this compound, obtained from the same source and purified by an identical sequence of operations, nevertheless polymerize at widely differing rates. For example, the time required for ~70% conversion to polymer can vary from 12 hr to 2 weeks. The onset of "cross-linking" is similarly unpredictable. Some of the reasons for this behavior will be discussed later. At this point it is sufficient to note that serious reproducibility

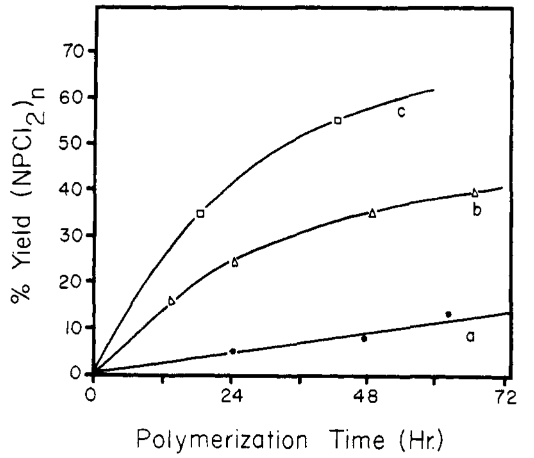
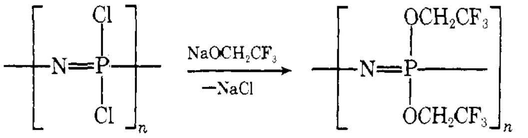


Figure 1. Variation of polymer yield as a function of time from the polymerization of: (a) $(NPCl_2)_3$ protected from atmospheric moisture during final purification steps and during storage and transfer procedures; (b) $(NPCl_2)_3$ exposed to the atmosphere during 2 days storage; and (c) $(NPCl_2)_3$ polymerized after exposure to the atmosphere for 4 days.

problems are encountered unless all comparative reactions are performed with the use of trimer from exactly the same batch, and preferably with all the polymerization tubes being filled and sealed at the same time. The neglect of these precautions undoubtedly explains many of the puzzling contradictions about this reaction that are found in the literature.

A reliable analysis of this reaction is made more difficult by the hydrolytic lability of poly(dichlorophosphazene) (II). It is not uncommon, for example, for minute traces of water to cause cross-linking of this polymer *during* a gel permeation chromatography (GPC) experiment, during a solution viscosity measurement, or while the polymer solution is being stored in a sealed flask. For this reason, most of the GPC and solution viscosity results reported in this paper are for polymers that were derivatized by conversion to the hydrolytically stable trifluoroethoxy compound (III) by the reaction[9,15]



$$\left[-N=\overset{Cl}{\underset{Cl}{P}}-\right]_n \xrightarrow[-NaCl]{NaOCH_2CF_3} \left[-N=\overset{OCH_2CF_3}{\underset{OCH_2CF_3}{P}}-\right]_n$$

II III

The cross-linking reaction that occurs when poly(dichlorophosphazene) comes into contact with water may follow a different mechanism from the insolubilization which normally takes place toward the end of the thermal polymerization (see section on the reaction mechanism).

With the above factors taken into consideration, a number of polymerizations were carried out with a view to determining the relationship between polymerization time at 250° and the yield of polymer and degree of polymerization. Curve b in Figure 1 illustrates the percentage conversion to soluble[24] high polymer as a function of time in a typical experiment. Occasionally, up to 75% yields of soluble polymer were obtained, but continued reaction beyond that point generally resulted in conversion of the polymer to the insoluble modification.

Gel permeation chromatography (GPC) and solution viscosity measurements were then obtained for the polymers isolated after different reaction times and after derivatization. No appreciable differences could be detected in the GPC curves of polymers isolated at different stages in the polymerization. A typical GPC curve is shown in Figure 2A. In each case the center of the polymer distribution curve corresponded to an estimated degree of polymerization of ~10,000 repeating units, irrespective of the degree of conversion. Polymer samples isolated late in the polymerization process (after ~40% conversion) showed a slight broadening of the peak, but this change was very small.

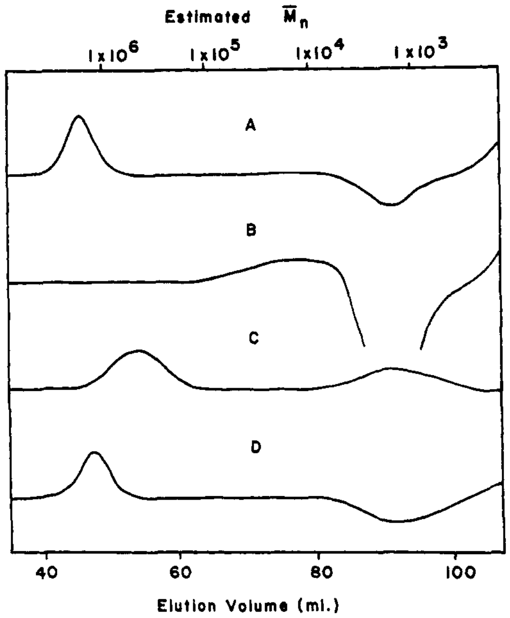


Figure 2. Gel permeation chromatography for *derivatized* samples of: (A) polymer prepared by the normal thermal polymerization technique at 250°; (B) polymer prepared by the thermal polymerization of $(NPCl_2)_3$ at 250° in the presence of 0.10 mol % PCl_5; (C) preformed polymer after treatment at 250° for 24 hr with 11.1 mol % PCl_5 (relative to $NPCl_2$); (D) polymer prepared in the presence of 0.62 mol % water.

In general, the width of the GPC peak corresponded to an estimated degree of polymerization range from ~3000 to ~30,000. It is possible that some of the polymer molecules had molecular weights above the exclusion limit of the GPC columns. However, it is particularly significant that *no medium or low molecular weight polymer fractions were detected from any of the reaction products.* This was *not* an artifact of the derivatization and reprecipitation process, since it was shown that medium molecular weight species reprecipitate with the high polymers. Thus, the components of a polymerization system included the cyclic trimer (I), possibly the cyclic tetramer, and the high polymer. Medium molecular weight polymers were seen only in depolymerization experiments[2,25] or when the PCl_5 was present. The mechanistic significance of this fact is discussed later.

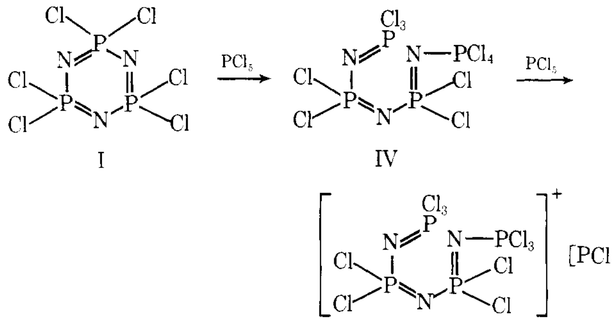
The solution viscosities in acetone were consistent with the GPC results, the values being almost independent of the degree of conversion. Specifically, the μ_{sp}/c values of the derivatized polymers at 1% concentration were in the region of 3.5 dl/g, and the intrinsic viscosities were in the range of 2.0 to 3.5 dl/g. A similar pattern was observed for underivatized, $(NPCl_2)_n$ polymer but the results were less reliable for the reasons discussed previously.

The Role of Phosphorus Pentachloride. Because phosphorus pentachloride is used in the synthesis of chlorophosphazenes,[4] the strong likelihood exists that traces of this reagent can be carried through the trimer purification process and may be present in the polymerization system. Phosphorus pentachloride was thus a prime suspect as an impurity which could be responsible for the erratic polymerization behavior. Arguments could be formulated for the participation of PCl_5 either as a polymerization catalyst or as an inhibitor. Experiments were, therefore, performed in which rigorously purified $(NPCl_2)_3$ (see Experimental Section) was heated in sealed, evacuated glass tubes with varying amounts of PCl_5 under conditions identical to those used for a typical polymerization process (24 hr reaction at 250°). The reaction products were then analyzed by ^{31}P nmr spectroscopy and, after derivatization, by gel permeation chromatography and solution viscosity.

Higher PCl₅ Concentration Range. Within the concentration range of 1.9 to 80.5 mol % of PCl_5 in $(NPCl_2)_3$,[26] after 24 hr at 250°, the reaction products separated into two layers: an upper colorless liquid (at 250°) and a yellow liquid. When cooled to 25°, both products crystallized. The amount of the yellow layer increased in proportion to the concentration of PCl_5 in the system. Neither of these layers contained any detectable amounts of chlorophosphazene high polymer even though control reactions, which contained no PCl_5, gave 50–70% yields of high polymer under the same reaction conditions.

^{31}P nmr spectroscopy permitted the identification of the principal components of both layers. The colorless layer consisted principally of unchanged $(NPCl_2)_3$. The yellow layer also contained $(NPCl_2)_3$ together with low molecular weight end-capped linear phosphazenes.[27] These species had properties consistent with the structures $[Cl(Cl_2P{=}N)_nPCl_3]^+PCl_6^-$ or $Cl(Cl_2P{=}N\text{-})_nPCl_4$,[28-30] in which n was 3–8. The PCl_6^- ion was also detected in some samples.

The results indicate that, at these higher PCl_5 concentrations, the principal reaction is a cleavage of trimer rings by PCl_5 to yield species such as IV or V. Apparently, some minimal interchange of repeating units can occur to give the n = 4–8 oligomers. However, a genuine polymerization process does not occur under these conditions, and this is consistent with the observation that a mixture of V (prepared and purified separately) and a 20-fold excess of $(NPCl_2)_3$ yielded no polymer when heated for 24 hr at 250°. Thus, V is not a catalyst for the polymerization.



I IV V

Lower PCl₅ Concentration Range. When the PCl_5 concentration was reduced to ~1.2 mol % or less, the reaction products formed a homogeneous system. A total of 14 different PCl_5 concentrations in this range were examined,[31] and the products were again compared with control reactions which contained no PCl_5.

After 24 hr at 250°, those samples which contained more than 0.1 mol % of PCl_5 were mobile liquids which crystallized to white or pale yellow solids at temperatures below 114°. ^{31}P nmr spectra of the underivatized reaction mixture indcated the presence of unchanged trimer only, and solution viscosity experiments confirmed that no high polymer was present. The control experiments, which contained no PCl_5, gave 50–70% yields of high polymer.

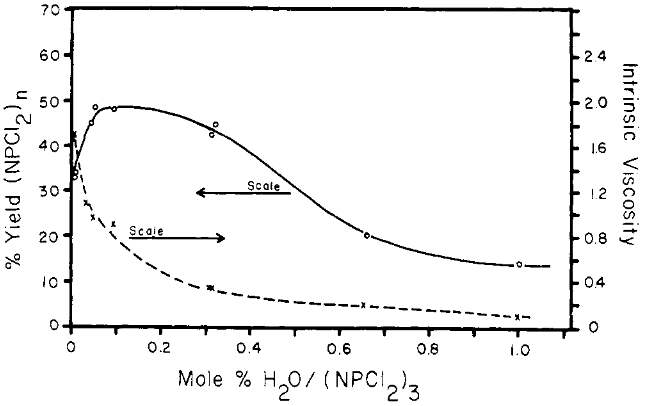


Figure 3. Variation in the yield (solid line) and intrinsic viscosity (broken line) of poly(dichlorophosphazene) as a function of water concentration after polymerization of $(NPCl_2)_3$ after 15 hr at 250°.

However, at PCl_5 concentrations near or below 0.10 mol %, some poly(dichlorophosphazene) was formed. Gel permeation chromatography of derivatized samples demonstrated the presence of small amounts of medium molecular weight polymer, with an estimated $\overline{DP}$ centered around 30. A control reaction without PCl_5 gave a 15% yield of polymer with an estimated $\overline{DP}$ of about 10,000. Prolonged polymerization at 250° in the presence of 0.02 mol % PCl_5 resulted in a 30% conversion to chlorophosphazene polymer. The ^{31}P nmr spectra of the chlorophosphazene polymers formed in the presence of PCl_5 showed peaks at +16, and +18 ppm, presumably from polymer middle units, and at −19.4 ppm from unchanged cyclic trimer.

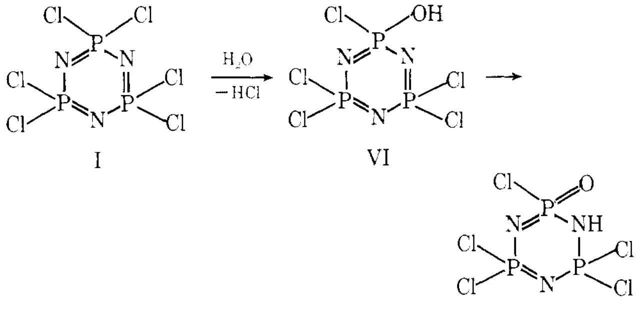
Addition of PCl₅ to (NPCl₂)ₙ High Polymer. The foregoing evidence suggests that PCl_5 functions as a skeletal cleavage and end-capping reagent. If this is so, it should be possible to reduce the chain length of a high molecular weight poly(dichlorophosphazene) by the addition of PCl_5.

Mixtures of PCl_5 and poly(dichlorophosphazene) (11.7 and 28 mol % of PCl_5 relative to $NPCl_2$) were, therefore, heated at 250° for 21 hr and these were compared with the behavior of a control reaction which contained polymer only. The control polymer became insolubilized but the polymer in the presence of PCl_5 formed a yellow oil. Gel permeation chromatograms of the derivatized oil showed a marked decrease and broadening of molecular weight, especially toward the lower molecular weight end of the spectrum (Figure 2C). The solution viscosity data for the derivatized polymer indicated a lowering of this intrinsic viscosity from 1.5 dl/g to about 0.14 dl/g (11.7% PCl_5 reaction).

Thus, PCl_5 can cleave the skeletal systems of chlorophosphazene rings or chains. When present in a polymerization system, PCl_5 functions either as a polymerization inhibitor or, at low concentrations, as a molecular weight controlling agent. It serves the latter function also when added to a chlorophosphazene high polymer after the normal polymerization process has been terminated. These facts partly explain why the observed polymerization behavior of $(NPCl_2)_3$ is markedly dependent on the source of the trimer and on the method of purification.

The Role of Water. Rigorously purified hexachlorocyclotriphosphazene polymerizes much faster after exposure to the atmosphere than material that has been stored under vacuum. For example, highly purified $(NPCl_2)_3$ that has been protected from the atmosphere may require 2 weeks reaction at 250° before appreciable yields of polymer are obtained (Figure 1, curve a). The same material, after exposure to the atmosphere, polymerizes rapidly to give high yields of polymer in less than 20 hr (Figure 1, curves b and c). Furthermore, trimer that has been exposed to the atmosphere accelerates the polymerization of trimer that has been stored under vacuum. This behavior suggests that water may be a polymerization catalyst or cocatalyst or that hydrolysis of $(NPCl_2)_3$ by atmospheric moisture may generate catalytic species.

Chlorophosphazenes, both cyclic and polymeric, are hydrolytically unstable.[32] The cyclic trimer is probably the least sensitive member of the series to hydrolytic attack and, indeed, the crystalline trimer appears superficially to be stable in the atmosphere. However, in solution $(NPCl_2)_3$ undergoes rapid hydrolysis in the presence of water to give hydroxyphosphazenes such as VI, oxophosphazanes (VII), and eventually phosphoric acid, ammonia, and hydrochloric acid. Furthermore, samples of crystalline $(NPCl_2)_3$ stored in a closed container for several days in contact with air evolve traces of hydrogen chloride. Thus, the possibility existed that even a brief exposure to atmospheric moisture could generate catalytic sites on the surface of the crystals which, after melting, could initiate or accelerate polymerization.



I VI VII

Therefore, experiments were carried out to examine the influence of small amounts of water on the polymerization behavior of $(NPCl_2)_3$. Details of the procedure are given in the Experimental Section. Both derivatized and underivatized polymers were examined. In several series of reactions a broad range of water concentrations was examined, from 0.02 to 2.57 mol % water in $(NPCl_2)_3$ with comparisons made with the behavior of the pure trimer for each series of runs. The data shown in Figure 3 represent a typical set of results.

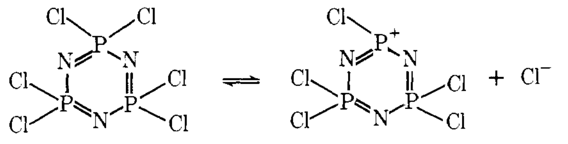
First, it was found that at very low water concentrations, within the range of 0.02 to ~0.1 mol % water in $(NPCl_2)_3$, increasing amounts of water increased the rate of polymerization. This was established from the weight of polymer isolated after 12, 14, or 21 hr at 250°, followed by derivatization. When more than 0.2 mol % of water was present, the polymerization process was retarded. At the highest water concentrations (>1% water) cross-linked polymer was often formed.

Gel permeation chromatograms showed only a very small shift in the peak position toward lower molecular weights as the water concentration was raised from 0 to 2.57% (Figure 2). However, the intrinsic viscosities of the polymers decreased with increasing water concentration. The mechanism of action of water is discussed later.

Influence of Hydrogen Chloride. Hydrogen chloride is evolved when chlorophosphazenes react with water. For this reason an assessment was made of the role played by hydrogen chloride in this polymerization. Figure 4 demonstrates the influence of hydrogen chloride on the yield of poly(dichlorophosphazene) at constant temperature (250°) and reaction time (24 hr). Increasing amounts of hydrogen chloride (over the range of 0 to 0.083 mol % HCl in $(NPCl_2)_3$) reduced the rate of polymerization and lowered the intrinsic viscosity in chloroform of the underivatized polymer from 2.8 to 1.4 dl/g.

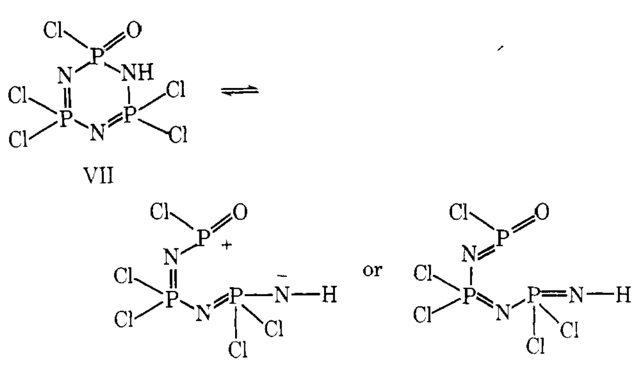
The Reaction Mechanism. Ultraviolet irradiation of the polymerization tubes had no discernible influence on the polymerization rate. Moreover, no free radicals could be detected during esr experiments carried out on samples at 250°.[8] Thus, a free-radical mechanism appears unlikely.

Earlier published work favored the view that the polymerization of $(NPCl_2)_3$ proceeded *via* an ionic mechanism which involved a prior ionization of chloride ion from phosphorus (VIII).[6–8,10] The evidence for this initiation step was as follows. First, those compounds which function as catalysts for the reaction (metals, carboxylic acids, alcohols, ethers) have in common the presumed ability to facilitate the ionization depicted in VIII.[6,10] Second, it can be shown that the conductance of molten $(NPCl_2)_3$ rises dramatically when the temperature is raised above 230° into the range in which polymerization occurs.[8] Subsequent steps in the mechanism were assumed to involve electrophilic attack by VIII on the nitrogen atom of another trimer molecule to generate a cationic chain mechanism, although concrete evidence for this was lacking.[6,8] An alternative, anionic chain mechanism has also been proposed.[10]


I VIII

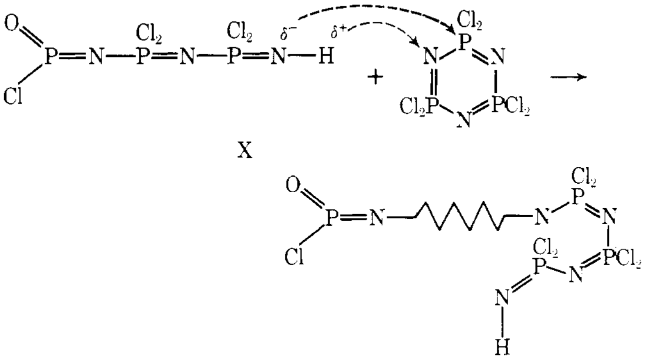
It now seems certain that the mechanism of polymerization is more complex than is implied by any of the above steps. The catalytic influence by water described in this work raises the possibility that, in a *totally* dry system, polymerization may not occur, or may take place by a different mechanism.

The exact role played by water is difficult to assess, but the following possibilities are plausible. (1) Water could facilitate the ionization of chloride ion from phosphorus. (2) Water could function as a cocatalyst. (3) Water may facilitate chain branching, coupling, or cross-linking. (4) Water could react with $(NPCl_2)_3$ to yield hydroxyphosphazenes or oxophosphazanes such as VI or VII. The latter compounds could presumably undergo thermal chain cleavage to yield species such as IXa or IXb.



VII IXa IXb

The available evidence does not preclude any of these possibilities. However, alternative (4) has much to recommend it as a primary initiation and propagation process. Species IXa or IXb could initiate the chain propagation process *via* an attack by the terminal N–H bond on the ring of an $(NPCl_2)_3$ molecule (X and XI). The conversion of VII to XI could, in fact, be a synchronous process, without the independent formation of IXa or IXb. Thus, the N–H grouping would constitute the true catalytic unit during propagation. A mechanism of this type is also consistent with the observation that $(NPCl_2)_3$ purified by a sulfuric acid route[18] in general polymerizes faster than trimer which has not received this treatment. Presumably traces of hydroxyphosphazenes or oxophosphazanes formed during this process could be carried through the subsequent purification and could function as catalysts. Furthermore, a mechanism of this type would explain why halo- or pseudohalocyclophosphazenes, such as $(NPCl_2)_3$, $(NPBr_2)_3$, $(NPF_2)_3$, or $[NP(NCS)_2]_3$, polymerize when heated, but hexaorganocyclotriphosphazenes do not. Bonds between phosphorus and halogen or pseudohalogen are broken readily by water, but bonds between phosphorus and side-group oxygen, nitrogen, or carbon atoms are not. If this mechanism is correct, it implies that other compounds which contain the N–H group (or OH group) should function as catalysts for the polymerization of halophosphazenes.



X

XI

The mechanistic role played by PCl_5 in this system is ambiguous. Although PCl_5 can cleave phosphazene rings and chains, it is also possible that added PCl_5 can scavenge traces of water from the system and hence retard polymerization by a secondary effect. The inhibiting effect shown by hydrogen chloride could be ascribed to 1,6 addition to the terminal units of species such as IX or to a suppression of chloride ionization from phosphorus in VIII.

Particular attention is drawn to the molecular weight distribution characteristics of this polymerization. No medium molecular weight polymers were detected (except in the presence of PCl_5) and the high polymers all showed similar molecular weight distributions (by GPC analysis) irrespective of the degree of conversion. By any standards, the polymerization of $(NPCl_2)_3$ at 250° is a slow reaction. It appears likely, therefore, that the initiation process is the slowest step in the reaction for, if propagation were rate controlling, the molecular weight of the polymer would be expected to increase perceptibly with time. Thus, the suspicion exists that initiation requires the presence of a P–OH or P(O)–NH unit or a low probability event involving ionic species such as VIII, that propagation is relatively fast, and that propagation ceases when the chain length reaches a certain high value. The very high viscosity of the medium beyond a certain point could reduce the rate at which trimer molecules can reach the chain ends and this effect could limit the chain length.

Finally, the question remains as to the exact nature of the so-called "cross-linked" insoluble polymer formed in the later stages of the polymerization. All that is really known about this material is that it is insoluble in organic media, such as benzene, toluene, or tetrahydrofuran, but is swelled by many organic solvents. The possibility exists that highly branched poly(dichlorophosphazene) could display properties similar to those expected for a cross-linked matrix. If the ionization of chloride ion from phosphorus constitutes an initiation process, propagation sites could be generated at polymer middle units and appreciable opportunities for branching would exist. Furthermore, if P–OH units are present along the chain, coupling of chains by the mechanism depicted in XII would be a facile process. Only if all the water is consumed during initiation, and if the formation of VI and VII results in rapid skeletal cleavage, would linear unbranched polymer predominate.

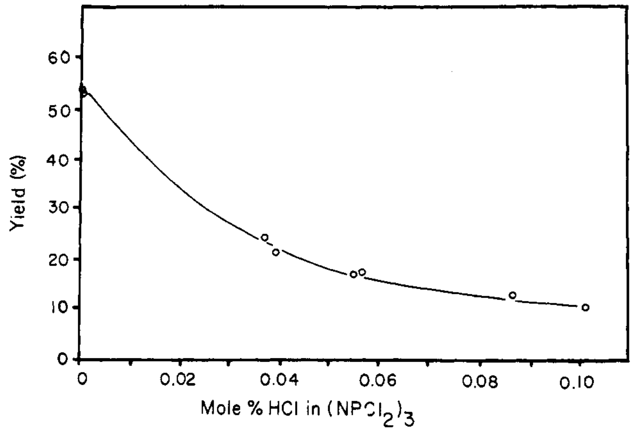
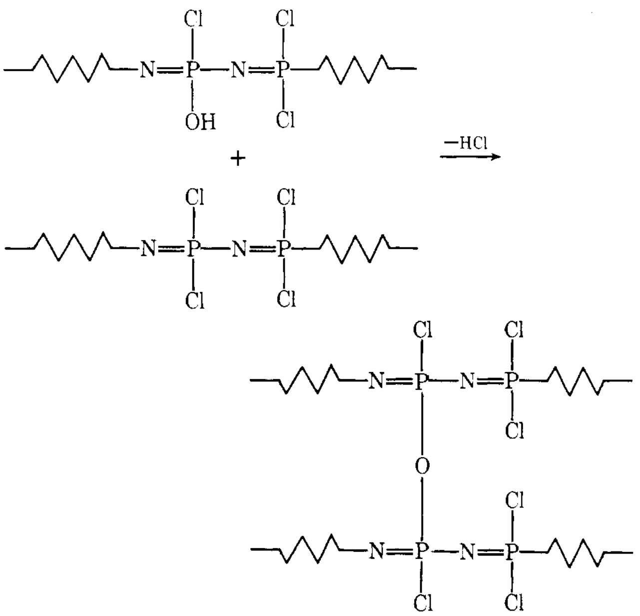


Figure 4. Variation in the yield of poly(dichlorophosphazene) as a function of hydrogen chloride concentration after 24 hr reaction at 250°.



XII

Acknowledgments. We thank the National Heart and Lung Institute, the Army Research Office (Durham), and the Firestone Tire Company for the support of this work.

References and Notes

(1) (a) This paper is Part XXI in a series on phosphorus-nitrogen compounds; (b) Part XX: H. R. Allcock, G. Y. Moore, and W. J. Cook, *Macromolecules*, **7**, 571 (1974).

(2) James E. Gardner, Jr., died suddenly and tragically on August 31, 1974. He was an outstanding research worker whose scientific and personal attributes are deeply missed by his colleagues.

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(23) J. R. MacCallum, *J. Macromol. Sci., Chem.*, **5**, 653 (1971).
(24) The term "soluble" high polymer refers to material that is soluble in benzene or THF, in contrast to "insoluble" material that is swelled by but not soluble in these solvents. Unless specified otherwise, the polymerization conditions were such that no insoluble polymer was formed.
(25) H. R. Allcock and W. J. Cook, *Macromolecules*, **7**, 284 (1974).
(26) A total of 15 different concentrations were investigated, with the following initial mole ratios (%) of PCl_5 in $(NPCl_2)_3$: 80.5, 34.3, 20.1, 18.9, 16.1, 15.7, 8.5, 6.9, 5.4, 4.2, 3.6, and 1.9.
(27) ^{31}P nmr shifts (in ppm relative to 85% H_3PO_4 in water) were correlated with the presence of the following species: −19.4 $(NPCl_2)_3$; −11.4, terminal PCl_3 group; +7 $(NPCl_2)_4$ or $(-NPCl_2-)_4$ units; +15.3 to 17.24 $(-NPCl_2-)_{5\text{ or }6}$ units; +18 $(-NPCl_2-)_{7\text{ or }8}$ units; +300, PCl_6^- (probably as an end-capping unit).
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(31) The following initial mole per cent concentrations of PCl_5 in $(NPCl_2)_3$ were studied: 1.8, 1.2, 0.85, 0.75, 0.37, 0.31, 0.24, 0.18, 0.10, 0.057, 0.031, 0.028, 0.021, 0.018. Those which contained less than 0.1% PCl_5 were carried out with 200 g of trimer in each tube.
(32) Reference 4a, Chapter 5.

Effects of Mercaptides on Anionic Polymerization. IV. Polymerization of Styrene by Thiophenoxides in Polar Aprotic Solvents

Yuji Minoura* and Takuji Hirahara

Research Institute for Atomic Energy, Osaka City University, Sugimoto-cho, Sumiyoshi-ku, Osaka, Japan.

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ABSTRACT: It was found, surprisingly, that sodium thiophenoxide initiates the polymerization of styrene in polar aprotic solvents such as *N,N′*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and hexamethylphosphoramide (HMPA). It initiated nearly no polymerization in less polar solvents such as benzene, toluene, dioxane, dimethoxyethane, and tetrahydrofuran. The active species that initiated the polymerization of styrene in the polar aprotic solvents was found to be sodium thiophenoxide itself by means of the identification of end groups of the oligomers. The activation energy for the polymerization of styrene by the mercaptide in DMF was 5.7 kcal/mol. Kinetic studies on the polymerization of styrene by the mercaptide in DMF were also made, and it was found that a living type polymerization occurred. The initiation reaction was found to be very slow and increased with increasing polymerization time. The rate constant of the propagation reaction (k_p) was 1.00×10^4 l. mol^{-1}/hr^{-1} (in DMF at 20°).

Styrene has been known to polymerize anionically when initiated by many organometallic compounds in solvents such as tetrahydrofuran, dimethoxyethane or dioxane to form living polymers.[1] The anionic polymerization of styrene (Alfrey–Price *e* value of styrene = −0.80), however, does not occur so readily compared with that of monomers having higher +*e* values such as methacrylonitrile (*e* = +0.81),[2] acrylonitrile (*e* = +1.20),[2] and vinylidene cyanide (*e* = +2.58),[2] etc., that easily polymerize anionically even by the weak bases.[3] Thus, anionic polymerization of styrene necessitates the use of strongly basic initiators.

As described briefly in our previous papers,[3,4] sodium thiophenoxide, having a lower pK_a value than the general anionic initiators hitherto known, was also found surprisingly to initiate the polymerization of styrene in polar aprotic solvents such as *N,N′*-dimethylformamide (DMF), hexamethylphosphoramide (HMPA), or dimethyl sulfoxide (DMSO) under ordinary polymerization conditions. It did not, however, initiate polymerization in less polar solvents, such as benzene, toluene, dioxane, or tetrahydrofuran. These results suggest that new active species are formed by reactions between the mercaptide and polar aprotic solvents.

In this paper, the active species in the polar aprotic solvents that initiated the polymerization of styrene was confirmed by the same fashion as the previous papers.[4] The activation energy was also investigated for the polymerization of styrene in DMF between 0 and 30°. The kinetics of the polymerization of styrene by sodium thiophenoxide in DMF solvent were also studied.

Experimental Section

Reagents. Polar Aprotic Solvents. Commercially available products were refluxed over finely divided calcium hydride overnight and then distilled at reduced pressure just before use: hexamethylphosphoramide (HMPA), 66° (0.5 mm); dimethyl sulfoxide (DMSO), 86° (25 mm); *N,N′*-dimethylformamide (DMF), 76° (39 mm).

Styrene. Commercially available monomer was washed several times with 10% sodium hydroxide solution and then water. The monomer was dried with anhydrous calcium chloride and then distilled under nitrogen at reduced pressure. The middle fraction was freshly distilled immediately before use over calcium hydride at 48° (20 mm).

Sodium Thiophenoxide. This mercaptide was prepared in a three-necked flask, equipped with a stirrer, an argon gas inlet, and a condenser protected by a calcium chloride tube, by the addition of thiophenol to freshly cut sodium in dry ether, under an argon atmosphere. After refluxing and vigorous stirring for about 10 to 20 hr, the solvent was distilled off under a stream of argon.[5,6]

Polymerization. The polymerizations were carried out in sealed glass tubes. Precautions were taken to remove traces of moisture and air. To the glass tube was added styrene and aprotic solvent. This solution was cooled to −78° and the sodium thiophenoxide solution was added. Polymerization at 30° proceeded slowly and