Polymerization of cyclic phosphazenes

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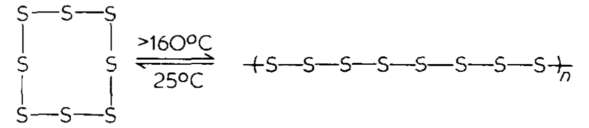
(Received 10 September 1979)

The synthesis of inorganic macromolecules is a subject that has attracted sporadic attention since the 1940s. Activity in this area has waxed and waned in phase with new discoveries and seemingly insurmountable synthetic problems. Yet the long-range promise still exists that polymers based on chains of inorganic atoms offer the only solutions to many of the scientific and technological problems that will confront us during the next 15 or 20 years. One reason for the slow progress in this area has been the lack of interaction between organic polymer chemists on the one hand and small-molecular inorganic chemists on the other. The two conspicuous successes in the field so far [the poly(organosiloxanes) and the poly(organophosphazenes)] have resulted from a blending of these two disciplines. It is convenient to view the synthesis of inorganic macromolecules in terms of three different approaches: (1) the use of inorganic ring systems as polymerization 'monomers'; (2) the study of small-molecule inorganic ring systems as 'models' to test exploratory reactions that would be much more difficult to perform on a macromolecule; (3) the use of preformed inorganic macromolecules as reactive intermediates for the substitutive synthesis of stable polymeric derivatives. All three aspects will be mentioned in this review. However, the model compound concept (2) has recently been reviewed in detail (Allcock, ref 1), and only an introductory description will be given here. Similarly, the use of preformed inorganic macromolecules as substrates for substitution reactions has been discussed elsewhere (Allcock, refs 2–4). In this article, the use of inorganic ring systems as polymerization monomers is reviewed.

PERSPECTIVE

All the major inorganic polymer systems known today are derived from small-molecule inorganic rings. This is well-known, and only a few examples will be mentioned here merely to provide a perspective for the later discussion.

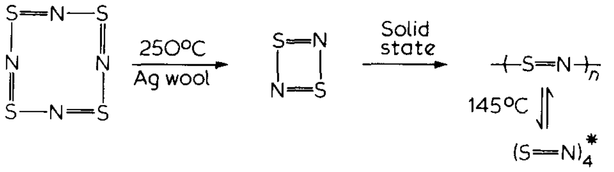
Perhaps the simplest and best known system is the one which involves the thermal polymerization of S_8 to high polymeric sulphur (reaction 1):



(1)

A free-radical, ring-opening mechanism is believed to operate in this transformation, although, under certain reaction conditions, an anionic mechanism can occur. Two special features of this polymerization have been observed. First, the reaction is an equilibration process in which rings, such as S_6, S_8, S_{10} etc., are in equilibrium with chains. Second, because of the facile bond interchanges that occur in this system, the process is dominated by thermodynamic factors. At low temperatures (25°C) small rings such as S_8 are thermodynamically preferred over long chains: at higher temperatures (near 160°C), long chains are formed at the expense of rings: at still higher temperatures, the equilibrium shifts again to favour small rings[5]. The high polymer is flexible and elastomeric at temperatures above 70°C or when plasticized by rings, but it is hard and microcrystalline at 25°C when pure.

Consider now the ring–polymer behaviour exhibited by the sulphur nitride (polythiazyl) system (equation 2)[6–9]:



(2)

Here again a polymeric series exists which contains both small rings, unstable short chains, and stable long chains. The stable species formed initially by synthetic procedures is the eight-atom cyclic tetramer. Heating this species to high temperatures brings about a conversion to the unstable cyclic dimer which, after being condensed as a solid at liquid nitrogen temperature and warmed to 25°C or higher temperatures, undergoes a solid-state polymerization to a high polymer, $-(S{=}N)-_n$., This polymer is now well-known as a fibrous, gold-coloured 'covalent metal', showing conductivity at moderate temperatures and superconductivity at temperatures near absolute zero. The polymer can be 'depolymerized' to reactive (probably linear) oligomers when heated at 145°C, and these fragments repolymerize

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* This article is based on a plenary lecture given at the 2nd International Symposium on Inorganic Ring Systems, Gottingen, 1978

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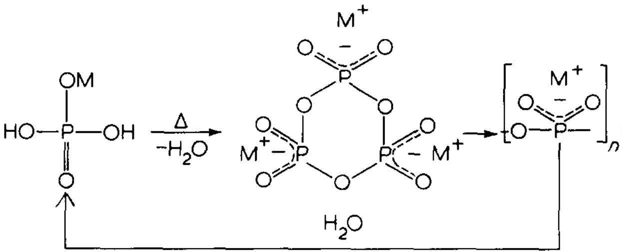
when cooled. It is interesting to note that the related system, N≡SF, participates in a monomer–trimer equilibrium[10].

Three more examples will serve to illustrate some additional general principles. The polyphosphate system has been known for many years[11,12] (reaction 3):

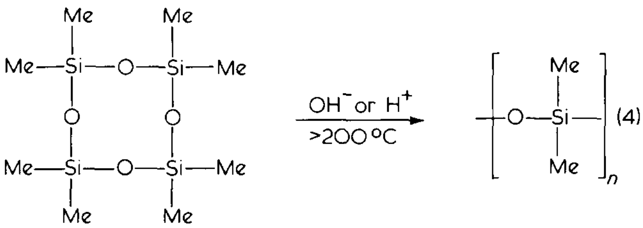


(3)

(M = an alkali metal)

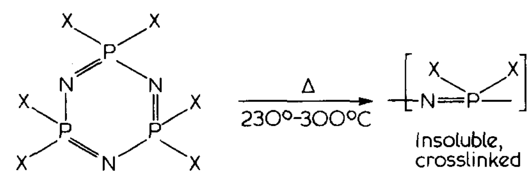
The high polymers are fibrous materials formed by a condensation polymerization. The polymers are sensitive to chain cleavage by hydrolysis. However, if the ratio of univalent metal cation to phosphorus is less than 1:1 (i.e. if more than two functional groups are present), the condensation reaction will yield *crosslinked* polymers.

The poly(dimethyl siloxane) equilibration, illustrated in reaction (4), has been studied in greater detail over the past thirty-five years:



For our present purposes it is sufficient to note three features of this reaction. First, the cyclic trimer and tetramer undergo an ionic ring-opening polymerization when treated with traces of base or acid, but the polymer depolymerizes back to cyclic oligomers when heated above 200°C. Second, the polymerization is really an *equilibration* in which the reaction products form a *polymeric series* of rings and chains that extend from the cyclic trimer and tetramer to the linear high polymer. Third, replacement of methyl groups by higher alkyl or aryl groups shifts the equilibrium to favour small rings at the expense of long chains.

The final example – the polyphosphazene system – is the main subject of this review. It has been known for 70 years[13] that hexachlorocyclotriphosphazene (prepared from ammonium chloride and phosphorus pentachloride) polymerizes when heated (reaction 5) and that the rubbery high polymer depolymerizes to cyclic oligomers when pyrolysed at 350°C [14–19]. The polymers prepared in earlier work were insoluble, crosslinked, and hydrolytically unstable. This is a key point that will be referred to later.



(5)

(X = F, Cl, Br)

Many other inorganic polymer systems exist; for example, the carborane siloxanes, silazanes, ferrocene polymers, metal phosphinates, etc. Indeed, the chemistry of most of the elements in the Periodic Table can be viewed in terms of rings, cages, and chains. Moreover, a discussion of inorganic polymers cannot be separated from a consideration of related organic polymers produced by the ring-opening polymerization of epoxides, cyclic sulphides, tetrahydrofuran, trioxane, caprolactam, etc. However, the inorganic systems mentioned above illustrate the following key general principles that apparently apply to a wide range of ring-polymer systems.

(1) The interconversions between small rings, short chains, and linear high polymers are usually governed by thermodynamic effects. These effects (particularly the influence of translational entropy) favour small rings at the expense of long chains at high temperatures or at moderate temperatures in dilute solution. Moreover, inorganic compounds are especially prone to 'scrambling' reactions at elevated temperatures. These lead to an interchange of molecular parts and the formation of new atomic clusters.

(2) Bulky side-groups attached to the main chain often favour small rings at the expense of polymer chains.

(3) Ionic side-groups, particularly those bound to di- or trivalent cations, cause ionic crosslinking and intractability.

(4) Polar bonds in the main chain or connected to the main chain favour hydrolytic instability.

(5) The synthesis of polymers via tri- or higher functional monomers leads to the formation of highly crosslinked, three-dimensional matrices.

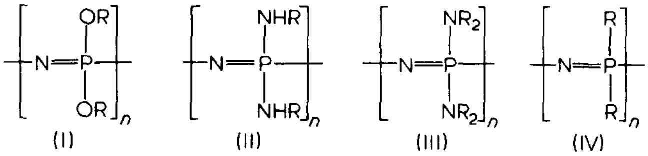
(6) General *linearity* of the macromolecular structure **is** needed if the polymer is to be soluble, flexible, or elastomeric.

PHOSPHAZENE HIGH POLYMERS

Long-range objective

The possibility that a broad new class of macromolecules based on an inorganic backbone of alternating phosphorus and nitrogen atoms has been explored in our laboratory during the last 15 years. The motivation for this search was both our fundamental interest in the synthesis and discovery of new substances, and the recognition that such polymers, if they could be prepared, might provide answers to many important practical problems. Thus, the basic hypothesis underlying our studies can be summarized in the following three precepts:

(i) if the high polymers with the structures shown in I–IV could be synthesized, together with those with two or more different substituents attached to each chain, they would constitute an extremely large class of stable new macromolecules with an almost unprecedented range of properties.

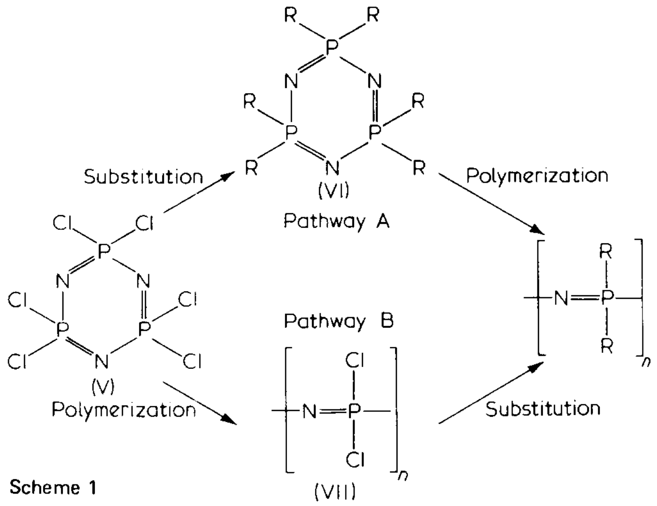


$$\left[-N{=}P(OR)_2-\right]_n \quad \left[-N{=}P(NHR)_2-\right]_n \quad \left[-N{=}P(NR_2)_2-\right]_n \quad \left[-N{=}P(R)_2-\right]_n$$

(I) (II) (III) (IV)

(R = alkyl or aryl)

(ii) two alternative approaches could be anticipated for the synthesis of high polymers of types I–IV based on the two reaction pathways shown in *Scheme 1*.



Scheme 1

In the first (pathway A), the readily available hexachlorocyclotriphosphazene (V) would be converted to hydrolytically stable organocyclotriphosphazenes (VI), which would then be polymerized. In the second, V would be polymerized to poly(dichlorophosphazene) (VII), which would then be subjected to substitution reactions to yield the hydrolytically stable poly(organophosphazenes), I–IV. The polymerization of the cyclic species V and VI would thus constitute critical steps in the sequence.

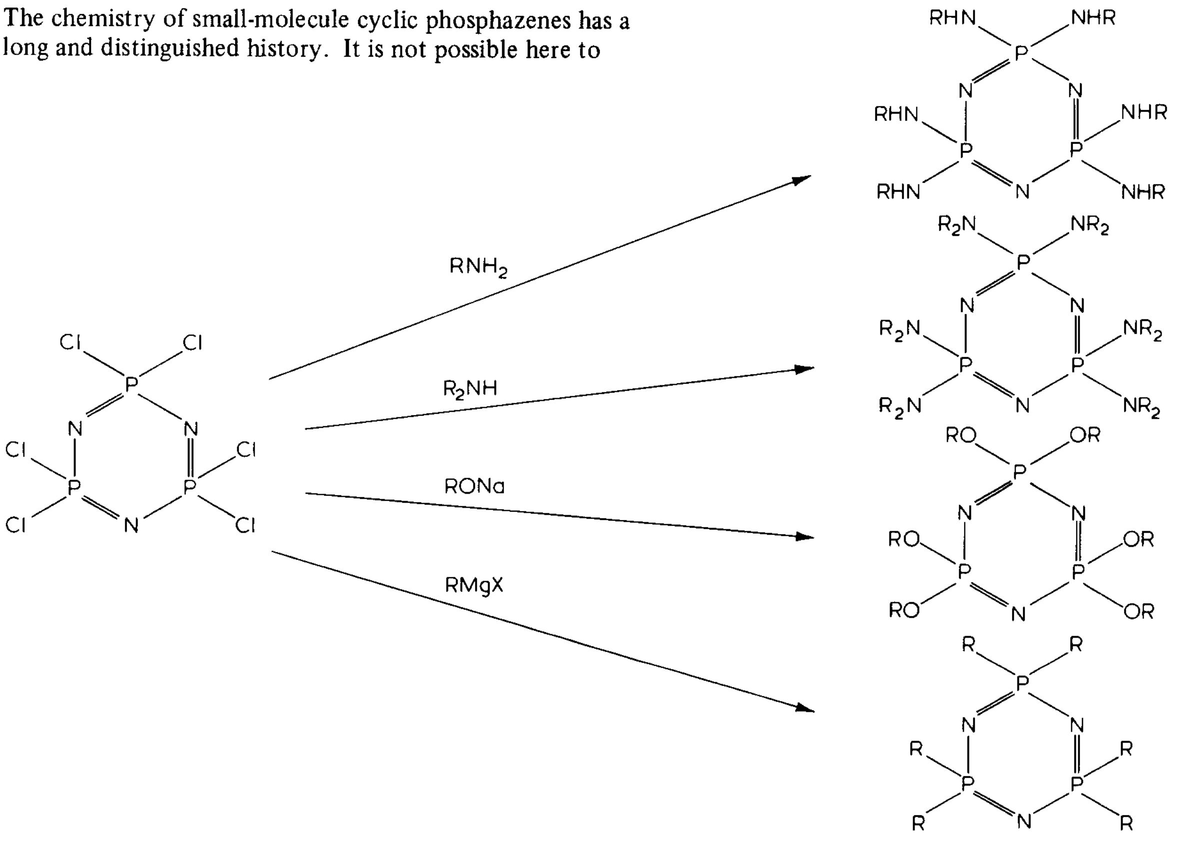
(iii) An understanding of the substitution reactions of V and VII was an essential prerequisite for the success of this undertaking and, because of the complexities expected with the substitution reactions of VII, the reactions of V would be important as model studies for the reactions of VII. This aspect is amplified in the following section.

REACTIONS OF SMALL-MOLECULE CYCLIC PHOSPHAZENES

The chemistry of small-molecule cyclic phosphazenes has a long and distinguished history. It is not possible here to review this earlier work in detail, but numerous reviews have been written on the subject[20–25], and it continues to be an active area of research, with many mechanistic problems remaining to be solved. However, certain key developments in that field both in our laboratories and elsewhere were crucial for the high polymeric work, and these will be mentioned briefly.

It will be clear from the following sections that some of the critical steps in the synthesis of phosphazene high polymers involve the replacement of halogen atoms attached to phosphorus in phosphazenes by organic groups. The first small-molecule reactions of this type were reported between 1885 and 1948 by Hofman, Couldridge, and Bode[26–28] (reaction 6, $RNH_2 = C_6H_5NH_2$), and the second set (reaction 8, $RONa = CF_3CH_2ONa$) were described in 1959 by McBee, Allcock, Caputo, Kalmus, and Roberts[29]. Reaction (9), the interaction of an organometallic reagent with hexachlorocyclotriphosphazene, was explored first by Bode and Bach in 1942[30]. Since that time, the mechanisms of these small-molecule reactions have been investigated in detail, principally by Becke-Goehring, Shaw, Paddock, Moeller, and our own research group.

In our group, we have viewed these *cyclo*phosphazene reactions as synthesis reactions for the preparation of organophosphazene monomers and as model systems for the less accessible high polymers. Indeed, our experience has been that the synthesis of a new phosphazene high polymer via Pathway B (*Scheme 1*) usually must be preceded by a detailed study of the related reaction carried out with a cyclic, trimeric, or tetrameric 'model'. Otherwise, formidable problems are encountered with the more complex macromolecular systems. Hence, during recent years we have divided our attention between small-molecule studies on the one hand and macromolecular syntheses on the other, with the two being closely synchronized.



(6)

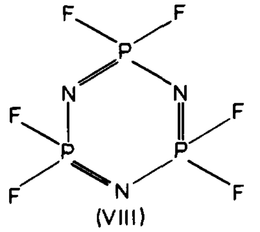
(7)

(8)

(9)

POLYMERIZATION OF HALOGENOCYCLOPHOSPHAZENES

As mentioned earlier, halogenocyclophosphazenes such as V, VIII, or IX polymerize when heated (reaction 10).



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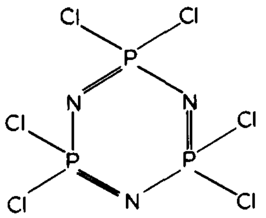

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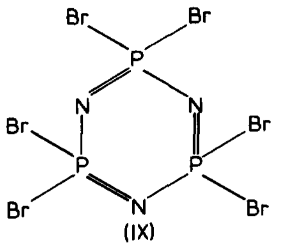


(IX)

The polymeric products in each case are rubbery elastomers which are sensitive to hydrolysis in contact with atmospheric moisture because of the presence of phosphorus–halogen bonds. This hydrolytic instability provided the main motivation for the synthesis of *organo*phosphazene high polymers. The rubber elasticity is an unusual and (on theoretical grounds) unexpected property. Poly(dichlorophosphazene) is virtually an ideal elastomer in a physical sense.

The experimental conditions required for polymerization of these three cyclophosphazenes are as follows: the compounds must be free from organic solvent impurities; they must be handled without excessive contact with atmospheric moisture; and they should be polymerized in a closed system, preferably in glass reaction vessels and with the exclusion of air. On a laboratory scale, the polymerizations can be carried out conveniently in evacuated sealed glass tubes. The fluoro-derivative (VIII) polymerizes only when heated to 350°C [31–33], a temperature at which the trimer generates considerable vapour pressure[33]. Hence, a compensating external pressure inside an autoclave, and the exercise of sensible safety precautions is mandatory. The chloro-derivative (V) is the easiest of the three to polymerize (reaction 10). The trimer is normally purified by recrystallization and sublimation techniques, and is then heated at ≃250°C for several hours[34–37]. The bromo-derivative polymerizes at 220°C [38–40].

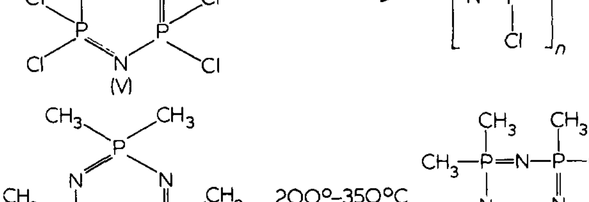
In all three cases, the final polymer is a crosslinked insoluble elastomer unless specific precautions are taken. The two principal precautions are: (a) the need for a high purity of the trimer, and (b) a termination of the polymerization reaction before the reaction is complete – i.e. before 100% of the trimer is converted to polymer. Typically, if the polymerization is terminated (by cooling to 25°C) before 70–75% of the trimer has been converted to polymer, the macromolecular product will be soluble in organic media. Beyond that stage, it will be crosslinked. The recognition of this fact[34,35] was the critical key to the development of poly(organophosphazenes) by the polymeric substitutive route (Pathway B in *Scheme 1*). The mechanism of these polymerizations will be discussed in a later section.

POLYMERIZATION OF ORGANOCYCLOPHOSPHAZENES

The polymerization of organic-substituted cyclic phosphazenes (reaction 11) is, in principle, the simplest route to the preparation of poly(organophosphazenes). The interactions of halogenocyclophosphazenes with organic nucleophiles, Friedel–Crafts systems, or organometallic reagents have been studied in detail[24,25]. Moreover, small-molecule organophosphazenes can be manipulated, purified, and characterized with much greater ease than can a reactive polymer such as VII. However, it is significant that no cyclic phosphazenes containing *only* organic side groups have yet been induced to polymerize to a high polymer. The following examples are illustrations of this problem.

First, the phenyl-substituted cyclic phosphazene, $[NP(C_6H_5)_2]_3$, yields no high polymers when heated to 250°–300°C [41] Second, the methyl-derivatives, $[NP(CH_3)_2]_3$ and $[NP(CH_3)_2]_4$, participate in a trimer–tetramer ring–ring equilibration reaction at temperatures between 200° and 350°C, either alone or in the presence of acidic accelerators (reaction 11). The proportion of trimer in the equilibrate increases markedly as the temperature is raised[42], but no high polymers are formed. A similar phenomenon is observed when the trifluoroethoxy-substituted derivatives, $[NP(OCH_2CF_3)_2]_3$ or $[NP(OCH_2CF_3)_2]_4$ are heated at 275°C. For example, the cyclic trimer undergoes a ring expansion reaction to yield a mixture of cyclic trimer, tetramer, pentamer, and hexamer[43]. Again, no high polymer is formed under these reaction conditions. The phenoxy-substituted trimer, $[NP(OC_6H_5)_2]_3$, is inert at high temperatures[44]. When the side group is NHC_6H_5, $NHCH_3$, NHC_4H_9 or $N(CH_3)_2$, side group decomposition occurs at only moderate temperatures[45].

These results are in striking contrast to the behaviour of the analogous methyl cyclosiloxanes. The mechanistic implications of this will be discussed later. However, the difference between the polymerizability of V, VIII, or IX, and the behaviour of $[NP(CH_3)_2]_3$, $[NP(C_6H_5)_2]_3$, or



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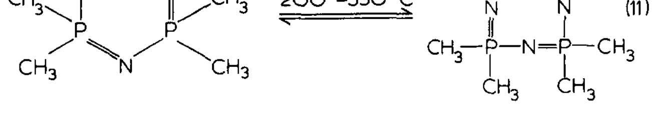

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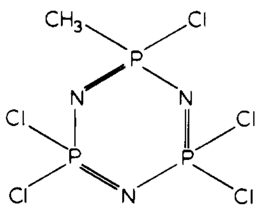

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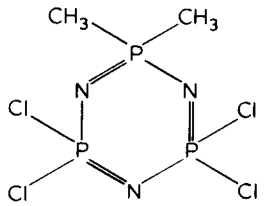

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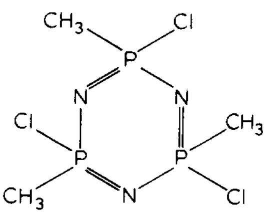

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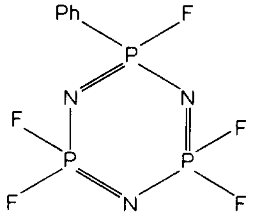

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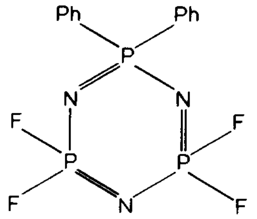

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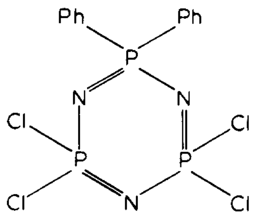

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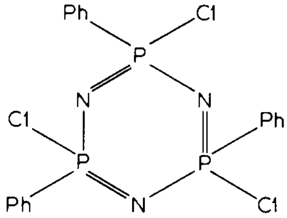

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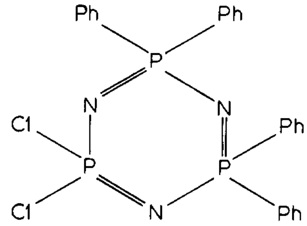

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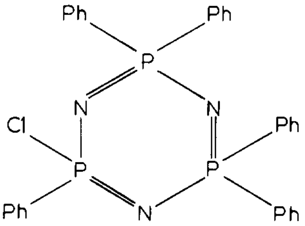

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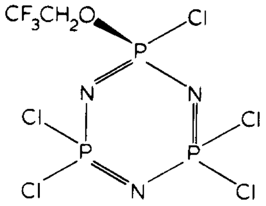

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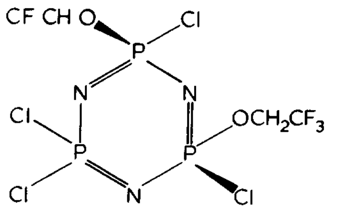

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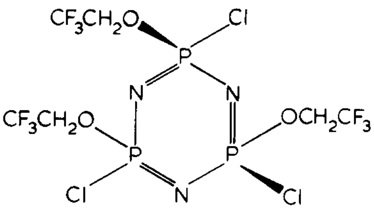

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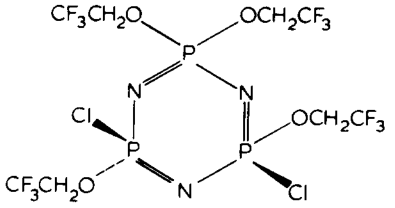

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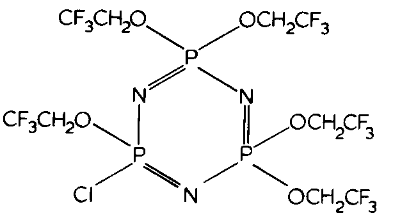


(XXIII)

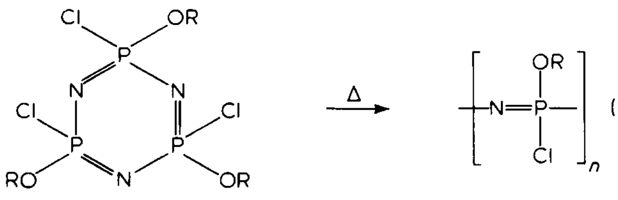
$[NP(OCH_2CF_3)_2]_3$, suggests the conclusion that the presence of halogen atoms may be a requirement for the establishment of extensive chain growth. Hence, cyclic phosphazenes which contain *both* organic and halogen side groups have been studied with some interest.

The molecules shown in X–XXIII have been synthesized specifically as possible polymerization 'monomers'.

The introduction of only one methyl group per trimer ring, as in X, does not inhibit polymerization at 250°C [46]. However, the presence of two methyl groups geminal to each other (XI) brings about a marked reduction in the ease of polymerization. Only low polymers are formed at 200°C and decomposition reactions occur at higher temperatures[47]. It has been reported that the non-gem-trimethylcyclotriphosphazene, shown in XII, does polymerize thermally[48].

A similar deactivation effect occurs when the chlorine atoms in V are replaced by phenyl groups[41]. The introduction of one phenyl group (XIII) does not inhibit polymerization. (The related compound, $N_3P_3Cl_5C_6H_5$, has not yet been isolated). However, polymerization is inhibited when two or more phenyl groups are attached to the same trimeric rings (XIV–XVIII). Potential catalysts, such as traces of water, or gamma-irradiation of the solid trimers, failed to induce polymerization.

The introduction of trifluoroethoxy groups in place of chlorine in V leads to a more complex polymerization pattern[43]. The presence of from 1 to 3 trifluoroethoxy groups in XIX, XX, and XXI, allows polymerization to take place at 200° or 225°C (reaction 12). However, the presence of 4 or 5 trifluoroethoxy groups (XXII or XXIII) blocks the polymerization process, although ring–ring interconversion (to tetramers, pentamers, etc.) occurred rapidly when XXI–XXIII were heated at 200°–250°C [43]. These reactions are complex because the polymerization



(12)

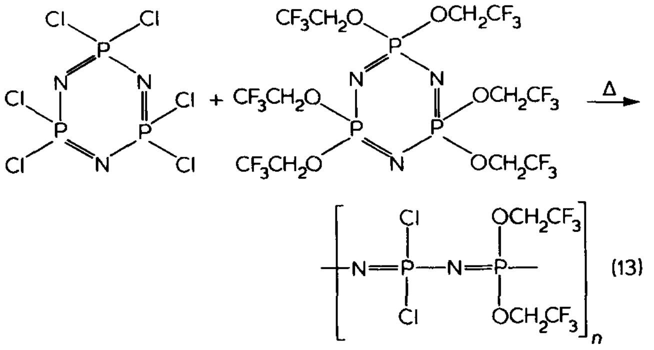
process is in competition with decomposition and ring-coupling reactions. These reactions are discussed later.

COPOLYMERIZATIONS

An analysis of the data just presented leads to the conclusion that the replacement of halogen atoms in V by organic groups interrupts the chain propagation steps but does not inhibit either initiation or ring–ring equilibration. Thus, the possibility existed that those phosphazene ring systems which participate in ring–ring equilibrations might yield high polymers in copolymerization reactions with species such as V: this is indeed the case.

Copolymerizations take place between $(NPCl_2)_3$ and the phenyl halocyclotriphosphazenes, XIII, XIV, XV, or XVI, but *not* with species, XVII, XVIII, or with $[NP(C_6H_5)_2]_3$[41]. In general, those copolymers that are formed have lower molecular weights than the homopolymer derived from $(NPCl_2)_3$. Hence, it appears that the presence of phenyl side groups attached to a phosphazene ring reduces the reactivity to copolymerization as well as to homopolymerization. Explanations for this will be presented later.

More extensive copolymerization reactions are possible with trifluoroethoxy-substituted cyclophosphazenes, such as XIX–XXIII. Even the compound $[NP(OCH_2CF_3)_2]_3$ copolymerizes with $(NPCl_2)_3$ at 200°C (reaction 13)[43]. When the $(NPCl_2)_3$ is present in a lower concentration than $[NP(OCH_2CF_3)_2]_3$, the $(NPCl_2)_3$ functions mainly as an accelerator for the ring-expansion equilibration of $[NP(OCH_2CF_3)_2]_3$. But if the two cyclophosphazenes are present in equimolar amounts, or if the $(NPCl_2)_3$ is present in excess, genuine copolymerization reactions take place. However, the copolymerization reactivity of $[NP(OCH_2CF_3)_2]_3$ is lower than that of $(NPCl_2)_3$. These copolymerizations are complicated by side reactions, and these are discussed in the next section.



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SIDE REACTIONS DURING POLYMERIZATION OR COPOLYMERIZATION

Inorganic systems differ from their organic counterparts with respect to an increased tendency for 'scrambling'-type reactions to occur at elevated temperatures. This is partly a consequence of the relatively high polarity of bonds that link inorganic-type atoms and the low activation energies for bond interconversions. Consequently, thermodynamic factors often play a predominant role in determining the products from the reactions of inorganic systems, and mechanistic factors may be less important.

Whether a particular ring system will polymerize or not often depends on a subtle interplay of three factors.

(1) The stability of rings *versus* long chains as the temperature is raised;

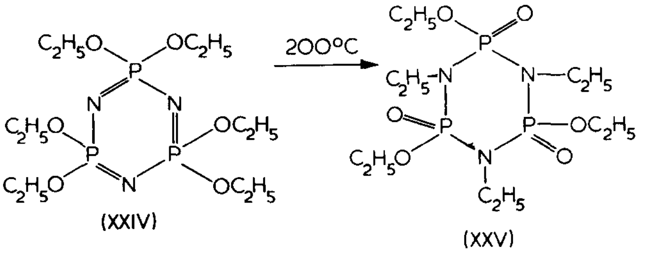
(2) The activation energy for ring-opening or chain propagation;

(3) The temperature at which unwanted side reactions (such as ligand scrambling, side group rearrangements, general decomposition, etc.) become serious.

For example, suppose that a particular ring-opening polymerization process has a sufficiently high activation energy for initiation or propagation so that polymerization does not occur at temperatures below the decomposition temperature of the side groups. Clearly, if such circumstances exist, the expected polymer cannot be formed. This is an extreme case, but evidence exists that organic-substituted cyclic phosphazenes (particularly those that contain *both* organic and halogen side groups) fall close to this barrier condition.

Consider first the methyl-substituted cyclophosphazenes, $[NP(CH_3)_2]_{3\text{ or }4}$, $N_3P_3Cl_5CH_3$ (X), and $N_3P_3Cl_4(CH_3)_2$ (XI). It was mentioned earlier that increases in temperature shift the equilibrium between $[NP(CH_3)_2]_3$ and $[NP(CH_3)_2]_4$ to favour the trimer. Thus, it would be anticipated that high polymers would not be formed even at higher temperatures. However, this hypothesis cannot be tested because decomposition of the system (scrambling) occurs at 350°C or higher temperatures[42]. The products are $(CH_3)_3P$, $(CH_3)_2PH$, $CH_3(H)P{-}P(H)CH_3$, and $(CH_3)_2P{-}P(CH_3)_2$. The rate of decomposition at 350°C is quite slow (less than 2% per week), but it is presumed to accelerate at higher temperatures. When both methyl groups and chlorine atoms are attached to the same ring, decomposition occurs at elevated temperatures by the elimination of hydrogen chloride[46].

Polymerization of alkoxycyclophosphazenes, such as $[NP(OC_2H_5)_2]_3$, cannot occur because the side groups undergo a rearrangement reaction at moderate temperatures[49]. This is illustrated in the conversion of XXIV to XXV.

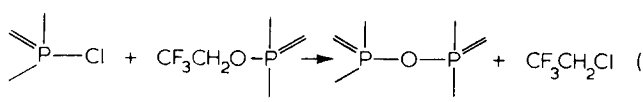


(XXIV)

(XXV)

Side group decomposition to yield amines and 'phosphams' occurs when aminophosphazenes which contain NH_2, $NHCH_3$, or $N(CH_3)_2$ side groups are heated at 310°C[35]. In general, those compounds that contain NH_2 side groups yield ammonia, those with $NHCH_3$ groups yield methyl amine, and those with $N(CH_3)_2$ groups give trimethyl amine. These products are formed by condensation-type reactions which lead to the linking of rings or chains.

Finally, side group elimination reactions can place severe restrictions on the conditions which can be used for the polymerization or copolymerization of cyclic phosphazenes containing both halogeno and alkoxy or aryloxy groups. Consider the example mentioned earlier of the copolymerization of $(NPCl_2)_3$ (V) and $[NP(OCH_2CF_3)_2]_3$[43]. These copolymerizations are carried out at 200°C. At 300°C the sealed glass polymerization tubes, used for these experiments, explode because of the high internal pressures generated by the formation of gaseous CF_3CH_2Cl. The same gas is formed when compounds XIX–XXIII are heated at temperatures above 225°C. The product is believed to be formed by an elimination reaction between P–Cl and P–O–CH_2CF_3 side group systems, with the concurrent formation of P–O–P crosslinks (reaction 14):



$$\geqslant P{-}Cl + CF_3CH_2O{-}P\leqslant \rightarrow \geqslant P{-}O{-}P\leqslant + CF_3CH_2Cl \quad (14)$$

It is this reaction which places an upper limit on the temperatures that can be used for the attempted polymerization of a wide variety of alkoxy- or aryloxy-substituted phosphazenes.

MECHANISTIC AND THERMODYNAMIC ASPECTS

The mechanism of polymerization of halocyclophosphazenes, such as V, VIII, IX, X, XIX, or XX, and the ring–ring equilibration of species, such as $[NP(CH_3)_2]_3$ or $[NP(OCH_2CF_3)_2]_3$, are not fully understood. A number of different mechanistic pathways have been proposed, but the four shown in *Scheme 2* deserve special consideration. These mechanisms are discussed in turn.

Side group ionization mechanism

From the information presented earlier, it will be clear that the phosphorus–halogen bonds may play an important role in the polymerization process. The evidence for this participation is summarized as follows. (1) The progressive replacement of halogen atoms by organic groups reduces the tendency for polymerization. (2) The temperature required for the onset of polymerization rises in the order: $(NPBr_2)_3 < NPCl_2)_3 < (NPF_2)_3$, the same as the increase in phosphorus–halogen bond strength. (3) The electrical conductivity of molten $(NPCl_2)_3$ remains low until the temperature is raised to the point at which polymerization begins. At that temperature, the conductivity rises dramatically in a manner consistent with the ionization of P–Cl bonds to yield $\geqslant P^+$ and Cl^- ions[44]. (4) Organic groups, such as CH_3 or C_6H_5 groups, have a lower tendency to ionize from phosphorus than do chloride ions, and this is compatible with the inability of organic-substituted trimers to yield high polymers.

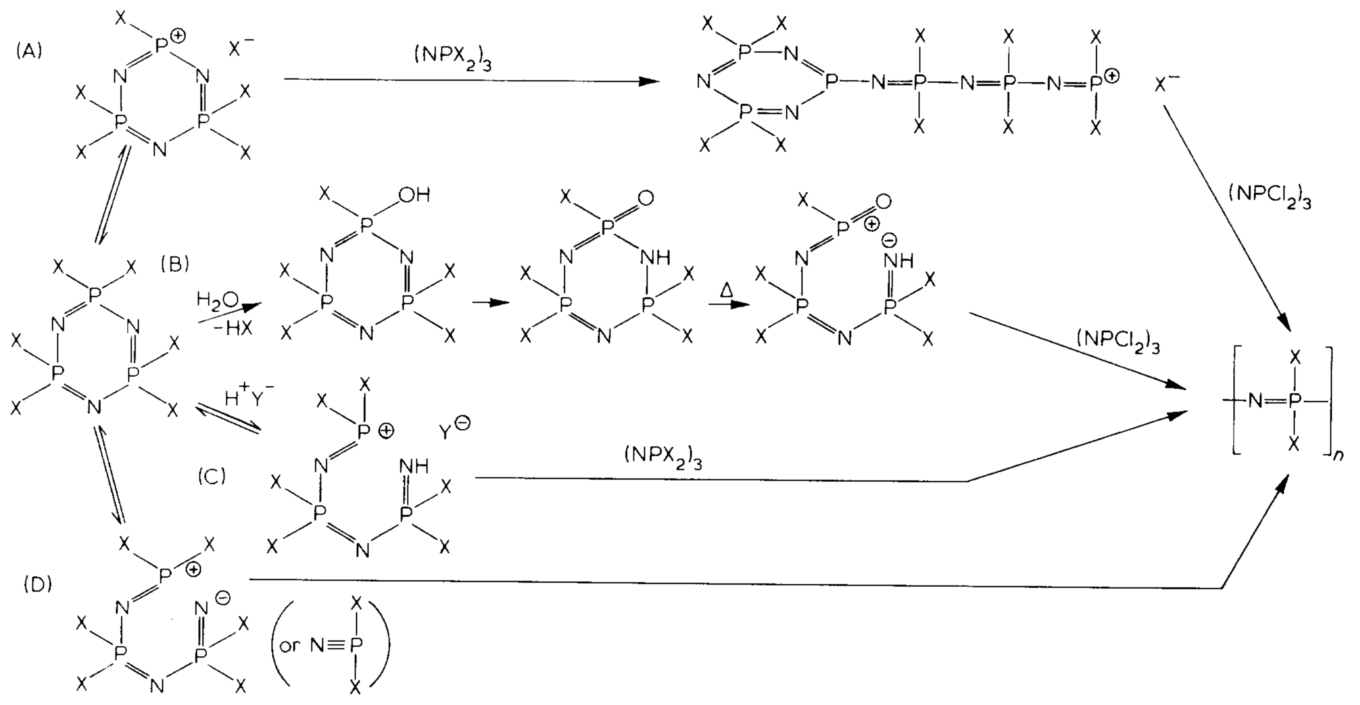
If such an ionization process does occur at elevated temperatures, it is conceivable that the cyclophosphazenium cation formed in this step can initiate a cationic propagation process, as depicted in Pathway A of *Scheme 2*[37].

However, evidence *against* a special role played by P–halogen bonds is the observation that $[NP(CH_2)_2]_3$[42] and $[NP(OCH_2CF_3)_2]_3$[43] both undergo ring expansion reactions when heated. Thus, if the initiation process for ring–ring equilibration and for polymerization is the same, then ionization of a side group may not be a prerequisite for either process. This remains an anomaly of the side group ionization mechanism.

Side group hydrolysis mechanism

At low concentrations, water is a powerful catalyst for the polymerization of $(NPCl_2)_3$[37]. Phosphorus–chlorine bonds are known to be sensitive to hydrolysis, yielding hydroxyphosphazenes and phosphazanes, as shown in Pathway B of *Scheme 2*. Evidence exists that the phosphazane linkage is weaker than the phosphazene bond. Hence, ring cleavage may be facilitated to initiate a polymerization or ring expansion process.

However, once again, the ability of $[NP(CH_3)_2]_3$ or $[NP(OCH_2CF_3)_2]_3$ to undergo ring expansion is incompatible with this process. Although it is conceivable that trifluoroethoxy groups might be displaced from phosphorus by high temperature hydrolysis, it is highly unlikely that a methyl group could be displaced in the same way.



Scheme 2

Chemical cleavage of the phosphorus–nitrogen ring

The ring expansion of $[NP(CH_3)_2]_3$ is totally inhibited by bases such as sodium amide or sodium methoxide, but it is accelerated by acids such as hydrogen chloride, ammonium chloride, $HCl \cdot AlCl_3$, FSO_3H, or $SbF_5 \cdot FSO_3H$[42]. Moreover, treatment of $[NP(CH_3)_2]_{3 \text{ or } 4}$ with large amounts of the acids yielded linear species of the type $HN{=}P(CH_3)_2{-}N{=}P(CH_3)_2{-}N{=}P(CH_3)_2{-}Y$. The possibility exists that such species may function as intermediates for ring–ring equilibrium reactions or, in other systems, for polymerization reactions.

Thermal ring cleavage

The thermal cleavage of a phosphazene ring to yield a zwitterionic chain or even a monomer molecule is an intuitively appealing possibility. However, no direct experimental evidence exists for the formation of such intermediates. The only indirect evidence is the existence of the limited trimer–tetramer equilibrium with $[NP(CH_3)_2]_{3 \text{ and } 4}$; higher cyclic species are virtually absent from the equilibrate.

All four initiation pathways would be affected by changes in the side group structure either directly (by influencing ionization ability or hydrolysis sensitivity) or indirectly (by affecting the strength of the skeletal bonds as a consequence of electron supply or withdrawal). However, the influence of the side group would become manifest in two other ways. First a bulky side group, such as a phenyl group, could retard chain propagation if that group were located at the growing chain end or at a site near the point of attack by that active chain end. Second, bulky organic groups, such as phenyl or trifluoroethoxy favour the formation of rings rather than long chains by intramolecular steric hindrance effects[50]. Thus, the steric size of the side group would lower the ceiling temperature to the point where chains would always be unstable relative to small rings. However, the methyl group has roughly the same steric size as a bromine atom. The trimer $(NPBr_2)_3$ polymerizes readily at 200°C, but $[NP(CH_3)_2]_3$ does not.

Thus, it will be clear that the polymerization of cyclophosphazenes presents a riddle that has broad mechanistic and practical ramifications. It is clear that more experimental work is needed before this process can be understood.

POLYMER SUBSTITUTION ROUTE

Although the synthesis of poly(organophosphazenes) by the direct polymerization of organocyclophosphazenes is an appealing prospect for the future, the problems are sufficiently serious that an alternative synthesis route has been devised.

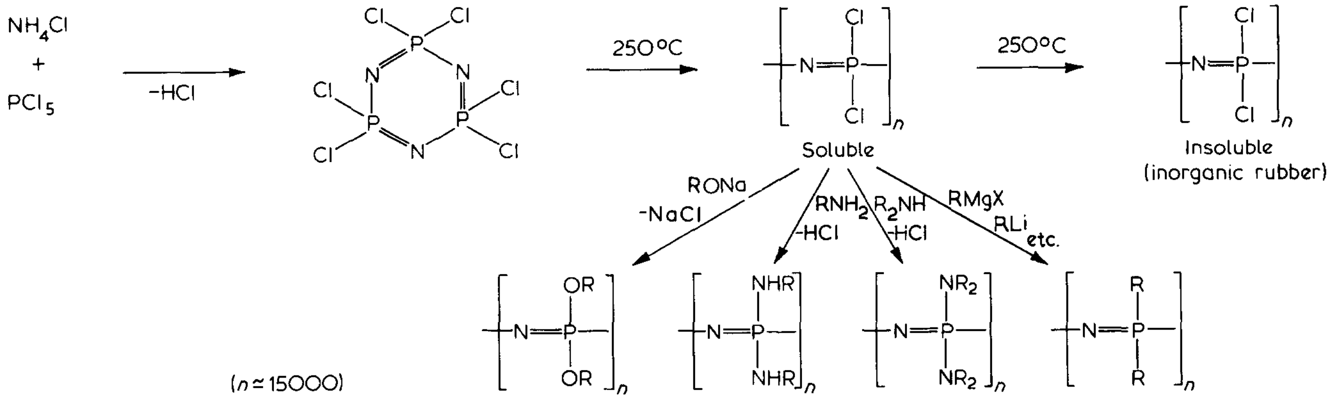
In this route, the high molecular weight poly(dihalophosphazenes), $(NPCl_2)_n$ and $(NPF_2)_n$ are used as substrates for reactions with nucleophiles in order to replace the halogen atoms by organic residues (*Scheme 1*, Pathway B). The analogy with the model-compound studies is obvious. This synthetic method was developed by the author and coworkers, mainly to circumvent the difficulties outlined in the preceding sections. This work has been reviewed elsewhere[2–4,22,24,51], and the following brief summary is intended mainly to provide perspective.

This reaction route makes use of the halogenophosphazenes as *polymeric reactive intermediates*. This is an uncommon procedure in polymer synthesis. Attempts to perform substitution reactions on organic polymers are often unsuccessful because of the coiling of the chains in solution and the resultant incomplete substitution. A failure to achieve complete substitution in the polyphosphazene system would yield a hydrolytically unstable polymer. At the time when we began our macromolecular work the only samples of high molecular weight $(NPCl_2)_n$, $(NPF_2)_n$, or $(NPBr_2)_n$ that had been prepared were crosslinked and insoluble in all solvents. Complete replacement of all the halogen would be impossible if the substrate were insoluble.

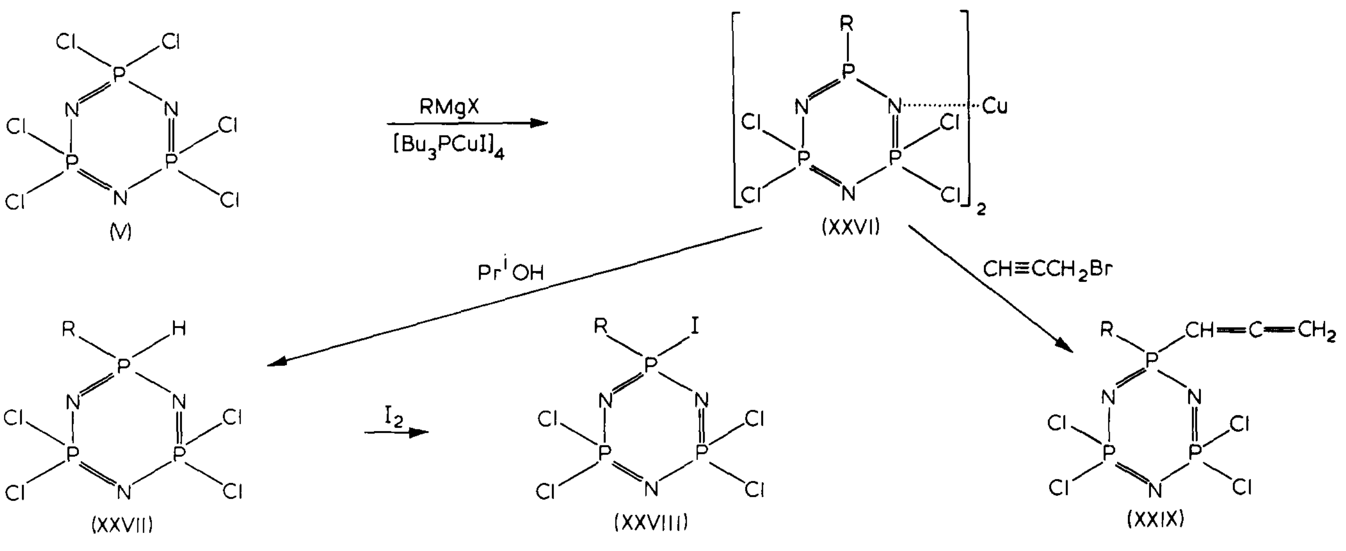
As discussed earlier, soluble $(NPCl_2)_n$ and $(NPF_2)_n$ can be prepared under suitable experimental conditions[33–37].

Solutions of poly(dichlorophosphazene) react rapidly and completely with a wide range of different nucleophiles[34–36]. Apparently the extremely high reactivity of the phosphorus–chlorine bonds in the polymer (higher than observed for most cyclic oligomers) more than compensates for the restrictions of the coiled macromolecular substrate. The reaction sequence shown in *Scheme 3* summarizes the overall reaction pathways. The product macromolecules are hydrolytically stable and exhibit an unusual range of different properties.

Given the enormous variety of alcohols, phenols, primary or secondary amines and organometallic reagents that can be utilized in this reaction, and the fact that two or more different substituent groups can be attached to the same chain, it is clear that an almost incalculable number of new polymers is accessible by this reaction route. To date, roughly 90 different polymers have been synthesized[34–36,52–58], but in principle, the number of different polymers that are accessible for the polyphosphazene system rivals or exceeds that of all the known organic polymers. This synthetic versatility is perhaps the most intrigu-



Scheme 3

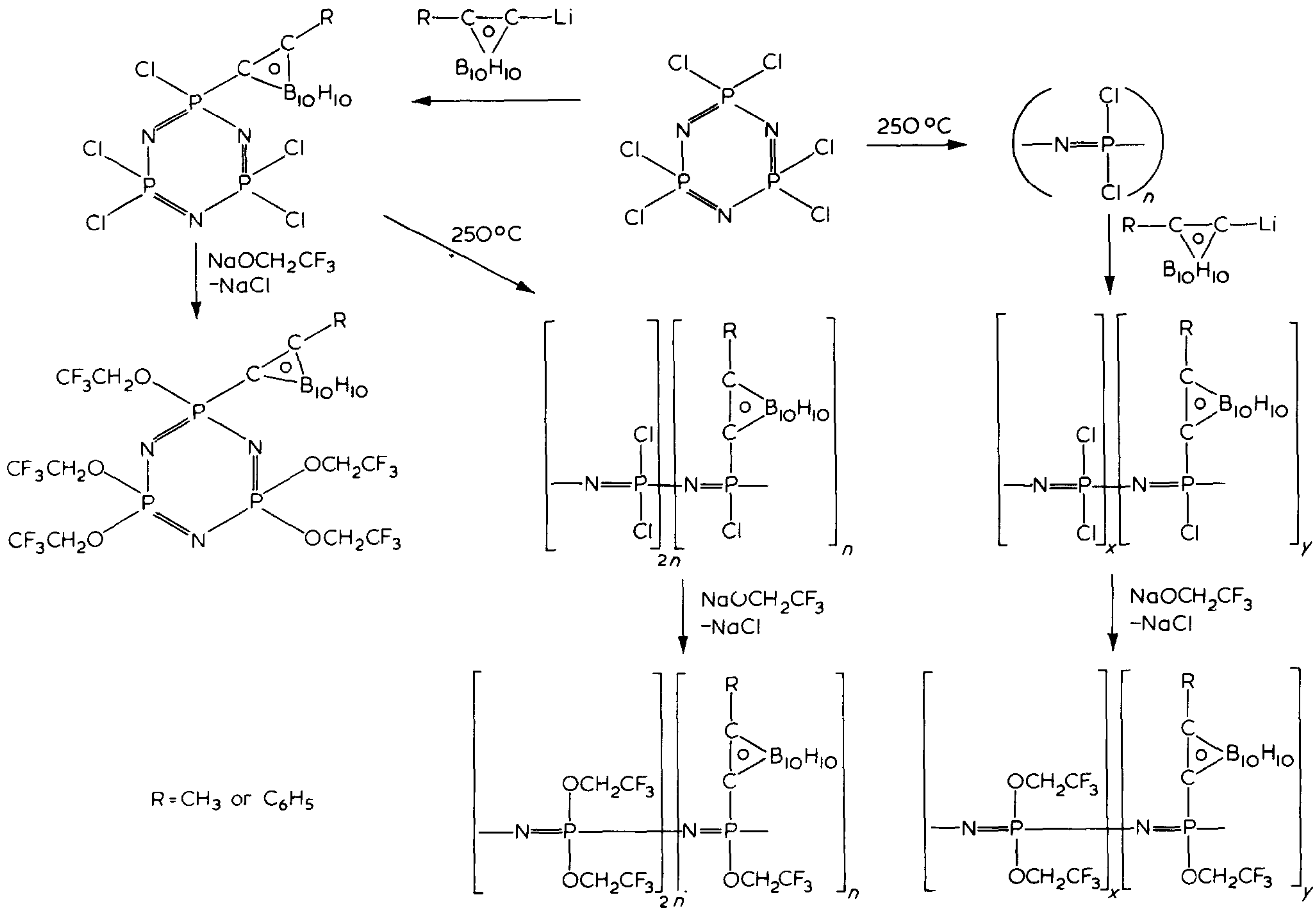


Scheme 4

ing feature of polyphosphazene chemistry. In retrospect, it is interesting to note that the first poly(organophosphazene) synthesis was of poly[bis(trifluoroethoxy)phosphazene], $[NP(OCH_2CF_3)_2]_n$ [34,35] mainly because of our earlier experience with the first synthesis of the cyclic model compounds, $[NP(OCH_2CF_3)_2]_3$ and 4 seven years previously[29]. This remains today the easiest of all the phosphazene high polymers to prepare.

FUTURE

Future developments in polyphosphazene chemistry will revolve around all three of the approaches outlined at the start of this review – continued attempts to find suitable reaction conditions for the polymerization of cyclic trimers or tetramers and to understand the polymerization mechanisms; the development of new reactions at the small-



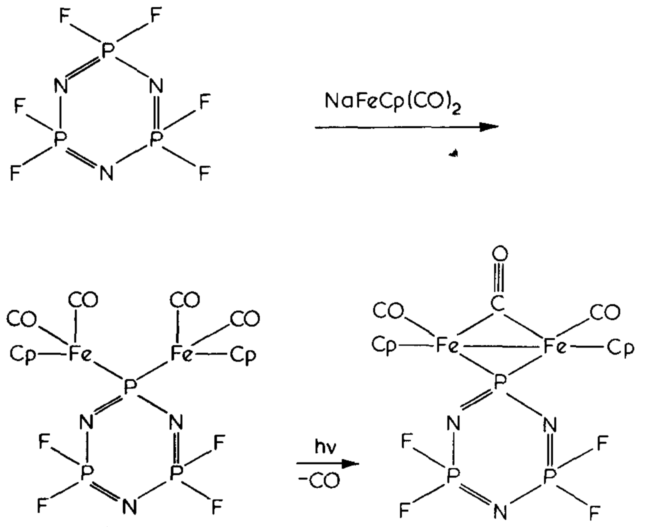
Scheme 5

molecule model system level; and an even broader exploration of the reactions of $(NPCl_2)_n$ and $(NPF_2)_n$. However, the small molecule work will provide the key to future advances. For this reason, a number of recent developments are summarized here.

First, organocopper reagents are now being used for the synthesis of a range of unusual new cyclophosphazenes. The reaction between $(NPCl_2)_3$ and Grignard reagents in the presence of the tributylphosphine adduct of copper iodide leads to the formation of a reactive phosphazene–copper intermediate (*Scheme 4*)[62–65].
This species provides a reaction pathway to the synthesis of XXVII, XXVIII, and XXIX.

Second, carborane residues have been linked to both cyclic and polymeric phosphazenes, and the cyclic derivatives have been polymerized (*Scheme 5*)[66]

Finally, the first members of an entirely new class of phosphazenes have been synthesized; these have transition metal units linked directly to the skeletal phosphorus atoms. These are exemplified by species, such as XXX and XXXI, prepared by the reaction of $(NPF_2)_3$ with sodium cyclopentadienyldicarbonyl ferrate[67].



(XXX) (XXXI)

Model reactions of these kinds are expected to provide a new dimension to the development of polyphosphazene chemistry.

ACKNOWLEDGMENTS

The research described in this review was supported by the US Army Research Office, Office of Naval Research, National Institute of Health, The Firestone Tire and Rubber Company, and NASA.

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