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Harry R. Allcock

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CHAPTER 7

Ring-Opening Polymerization in Phosphazene Chemistry

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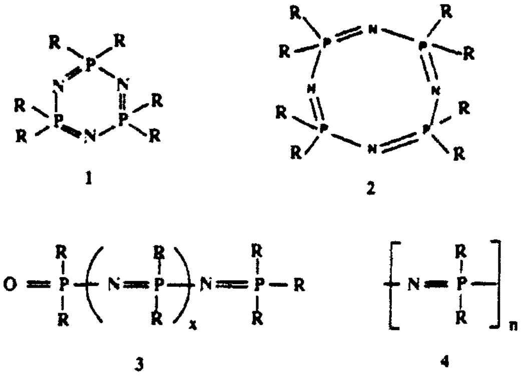
7.1 WHAT ARE PHOSPHAZENES?

Phosphazenes comprise a broad range of cyclic or linear small-molecules and high polymers that occupy an important place in the chemistry of heterocyclic compounds and new macromolecules. Typical structures are shown in Table 7.1. In these molecules the side groups, R, attached to phosphorus can vary over a very broad range, from halogen or pseudohalogen units such as fluorine, chlorine, bromine, iodine, cyano, or isothiocyano, to simple or complex organic groups such as alkoxy-, aryloxy-, amino-, alkyl-, aryl-, sugar units, amino acid ester groups, oligopeptides, transition metal complexes, porphyrins, phthalocyanines, organosilicon units, liquid crystalline, nonlinear optical, and photosensitive side groups, and a whole range of biologically active side groups.

Table 7.1. Different Types of Phosphazenes



In this chapter the emphasis is on the chemistry of cyclic trimers (**1**) and on their conversion by ring-opening polymerization to polymers of structure **4**. Linear short chain species of type **3** are monomers for condensation polymerizations or are reaction models for the high polymers. Their chemistry will not be considered here. Thus, the main starting point for this discussion is the ring-opening polymerization of halogenophosphazene trimers, such as **5** to high polymers of structure **6**.

The structural diversity found for species **1–4** is a consequence of the unusual chemistry developed for these compounds. Some of the most useful reactions are summarized in Schemes 1–3,[1–9] and are based on the ease with which halogeno side groups attached to phosphazene rings or chains can be replaced by interactions with a broad range of nucleophilic-type reagents. Note that these reactions at both the small-molecule and high polymeric levels allow the facile introduction of two or more different organic side groups by sequential or simultaneous substitution reactions. Thus, the known small-molecule phosphazenes number in the thousands,[10,11] and at

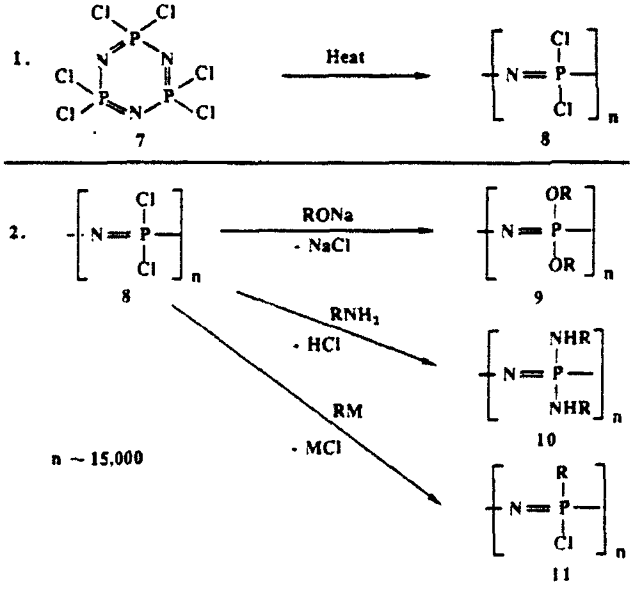
5

6

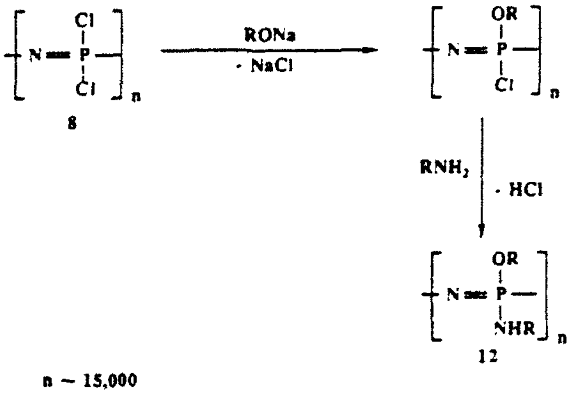
X = F or Cl

n ~ 15,000

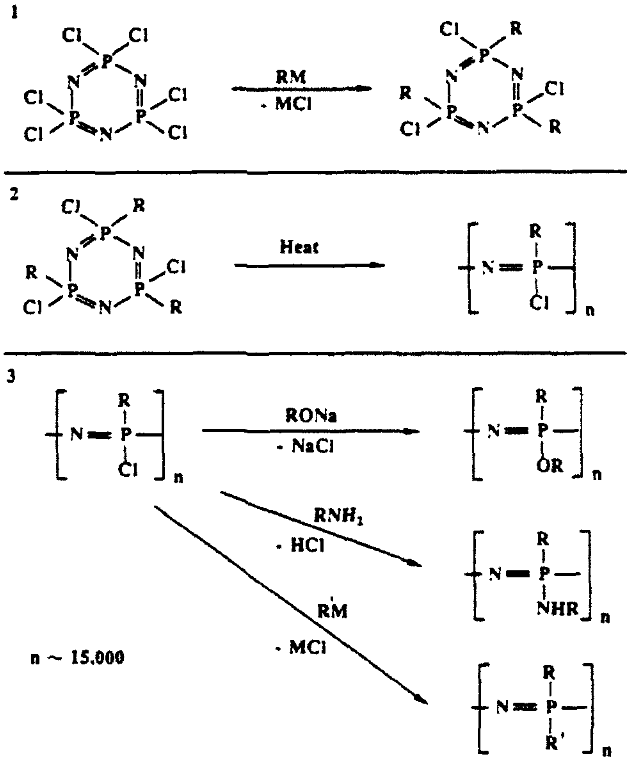
least 300 different high polymers have been reported in the literature.[12] This molecular diversity is one of the main reasons for the widespread interest in phosphazene polymers both for their intellectual significance and their practical applications. It is also important to note that macromolecular intermediate **8**, because of its high reactivity, is sensitive to atmospheric moisture. However, replacement of the chlorine atoms by organic groups generally converts the macromolecules to species with impressive resistance to moisture, oxygen, and a wide variety of other reagents.[1–9]



Scheme 1. Two step synthesis.



Scheme 2. Sequential substitution.



Scheme 3. Three step synthesis.

7.2 IMPORTANCE OF PHOSPHAZENE RING-OPENING POLYMERIZATION

Perhaps the most critical reaction in Scheme 1 is the ring-opening polymerization of hexachlorocyclotriphosphazene (**7**). This compound was first synthesized in the early 1800s from phosphorus pentachloride and ammonia or ammonium chloride.[13] By 1897 Stokes[14] had reported that heating of this heterocyclic compound brought about its conversion to a rubbery material ("inorganic rubber") subsequently (in the 1960s) identified as a cross-linked form of poly(dichlorophosphazene) (**8**).[1-3] Thus, this conversion, although not understood at the time, represents one of the earliest, if not the earliest, description of a ring-opening polymerization.

Second, even today the polymerization of **7** remains one of the most intriguing ring-opening polymerization processes known. For one thing, it is an *inorganic* ring-opening polymerization, and is one of the few examples (along with the polymerization of cyclosiloxanes and cyclothiazenes) of this genre. The reaction is also unusual because of the critical role played by the side groups in facilitating or preventing polymerization (see later). Also, a glance at the molecular structure of phosphazene cyclic trimers and tetramers such as **1** or **2** raises the question of how an unsaturated, and apparently electron-delocalized, "monomer" undergoes a ring-opening polymerization in view of the resistance of benzene, *s*-triazine, or borazine to participate in similar transformations.

Finally, the topic is important because of the growing industrial and manufacturing dependence on the polymerization of **7** to give polymeric intermediates for the large-scale production of organo-substituted phosphazene high polymers (**9–12**).[15,16] These polymers are used increasingly as high-performance elastomers in the aerospace and related high technology fields. Their utilization in biomedicine is also under way.[17-21]

7.3 THE PROTOTYPE REACTION: RING-OPENING POLYMERIZATION OF $(NPCl_2)_3$

7.3.1 *Conditions for the Polymerization*

The most thoroughly studied ring-opening polymerization in phosphazene chemistry is the one shown in step 1 of Scheme 1. As developed initially,[12,13] this is a melt-polymerization, in which cyclic trimer **7** is heated at about 250°C in a sealed system for several hours. During this time the mobile, colorless molten trimer is converted first to a highly viscous solution of the high polymer in residual molten trimer, and then to an immobile rubbery elastomer. This final stage represents the formation of a cross-linked polymer and is to be avoided if halogen-replacement reactions are planned. Thus, the most important requirement in this polymerization is to terminate the reaction when the yield of polymer has risen to perhaps 70%, but before cross-linking occurs.[1-3] It is also important to ensure that moisture is excluded from the system, since the reaction of P—Cl bonds with water also leads to cross-linking by the formation of intermolecular

P—O—P bonds. The uncross-linked polymer produced by the melt-polymerization process has a very high molecular weight—with weight average values in the region of 2×10^6. This corresponds to a chain length of about 15,000 repeating units.

The polymerization of 7 can also be carried out in solution, although the reaction rates and degrees of polymerization are usually lower than those obtained in the molten reaction medium. Solvents such as chlorinated hydrocarbons,[22] or carbon disulfide[23] have been studied. An advantage of the solution process is that the polymerization rates are more easily controlled.

Various catalysts have been identified that accelerate the polymerization, or are used to lower the temperature required for polymerization and, at the same time, lower the average molecular weight of the polymer.[24] Traces of water appear to function as catalytic species, but the reproducibility of the effect is not predictable.[25] By far the most effective catalyst reported to date, for both the melt and solution polymerizations, is a complex formed between boron trichloride and triphenyl phosphate.[26] This initiator appears to function by assisting the ionization of chloride ions from phosphorus.[27]

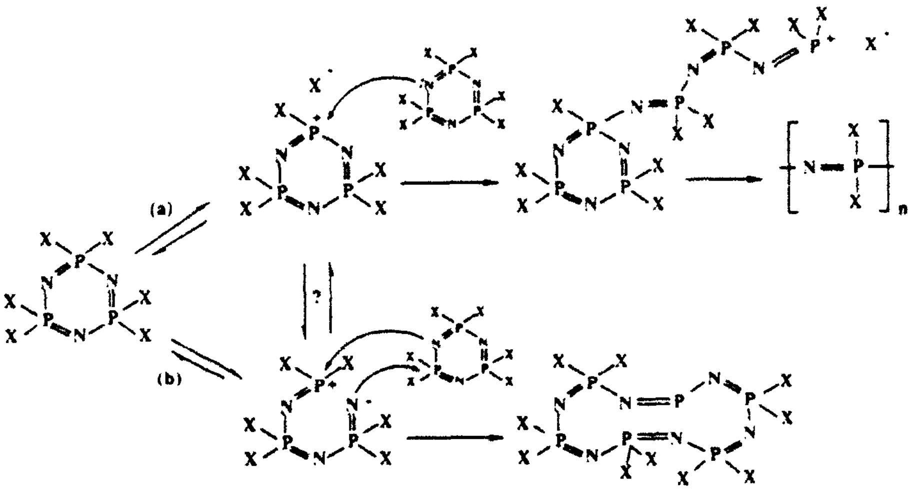
7.3.2 *The Polymerization Mechanism*

The mechanism proposed for the polymerization of 7 is unique.[28,29] It supposes that the initiation process requires the thermally induced ionization of a chloride ion from phosphorus, followed by an attack by the resultant phosphazenium cation on a nitrogen atom of another trimer molecule. This then initiates a cationic ring-opening chain growth process that continues until the concentration of free trimer falls below a critical limit and the viscosity of the system rises to the point that growing chains can no longer encounter freely diffusing trimer molecules. This process is summarized in pathway (a) of Scheme 4. An alternative mechanism, that appears to operate in specialized cases, is shown in pathway (b) of Scheme 4.

The evidence on which the mechanism shown in pathway (a) is based is as follows.[28] First, in the uncatalyzed reactions, it has been shown that the electrical conductivity of the molten cyclic trimer is low until the liquid is heated to the temperature range where polymerization begins. Above this temperature (about 210–220°C), the conductivity rises in a way that indicates the presence of ions as conducting species. These ions are assumed to be those formed by the thermal ionization of P—Cl bonds. The capacitance of the system also rises in a manner that is compatible with the formation of linear from cyclic species.

Second, those compounds that function as accelerators for the polymerization are species that might reasonably be expected to assist the ionization of chloride from phosphorus–reagents such as boron trichloride, traces of water, metals, etc. Free-radical initiators have no discernible effect on the speed of polymerization.

Third, variations in the type of halogen attached to the cyclophosphazene ring bring about changes in the rate of polymerization in ways that suggest a critical involvement by the halogen in the polymerization process. This aspect is discussed in a following section.



Scheme 4. Pathway (a) would be favored if X is a readily ionizable group such as Cl, F, or perhaps OCH_2CF_3. Pathway (b) would be preferred if X is alkyl, aryl, or perhaps OCH_2CF_3.

Fourth, complete replacement of the chlorine atoms in 7 by organic groups generally blocks the polymerization process. It is assumed that organic side units do not ionize from phosphorus at the temperatures normally used for the polymerization. This aspect is also considered in more detail in a later section.

7.3.3 *Unanswered Questions*

The pathway described above for the thermal or catalyzed polymerization of 7 fits most of the known experimental facts, but not all. For example, the mechanism outlined in Scheme 4 implies that every polymer chain should bear a cyclophosphazene unit at one terminus. Attempts to detect such end groups by ^{31}P NMR spectroscopy have so far been unsuccessful. The cyclic end groups may be present in such low concentrations in each molecule that they fall below the 5% sensitivity limit for the ^{31}P NMR method. Alternatively, they may not be present at all. No end groups of any type have been detected by NMR spectroscopy, and this raises the possibility that most of the polymer molecules are macrocyclic rather than linear.

A second puzzling feature of this reaction is that, although the total replacement of the chlorine atoms by organic groups, such as methyl or phenyl units, blocks the polymerization process, it still permits ring expansion reactions to take place. Thus, the anomaly exists that polymerization and ring expansion reactions may follow different mechanistic pathways. This too will be discussed later.

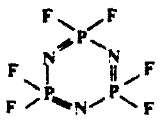
7.4 EXTENSION OF THE POLYMERIZATION PROCESS TO $(NPF_2)_3$, $(NPBr_2)_3$, $[NP(NCS)_2]_3$, TO CYCLIC TETRAMERS, AND TO PHOSPHAZOPHOSPHAZENES

Small-molecule cyclic fluorophosphazenes can be synthesized by fluorination of the corresponding chlorophosphazene (Table 7.2). The cyclic trimer, $(NPF_2)_3$ (**13**), undergoes a ring-opening polymerization when heated, but the minimum temperature needed for polymerization is as high as 350°C.[30–32] Again, cross-linking occurs in the final stages of the polymerization, but this can be avoided by a careful control of the time and temperature relationships. Poly(difluorophosphazene) is also used as a macromolecular intermediate for halogen replacement reactions, but its reactivity is lower than that of the chloro derivative, and it is soluble only in specialized fluorinated solvents.[31–34] The slower rate of polymerization of the fluorophosphazene compared with the chloro derivative can be ascribed to the greater bond strength of the P—F bonds and to a correspondingly higher temperature needed for halogen separation as fluoride ion.

The bromophosphazene, $(NPBr_2)_3$ (**14**), is prepared by the reaction of PBr_5 with ammonium bromide. This compound polymerizes at a lower temperature (200–220°C) than does the chlorophosphazene, and this may reflect the lower bond strength of the P—Br bond. The ease of ring-opening polymerization of the bromo derivative is also paralleled by a greater tendency for cross-linking. An uncross-linked variety of $(NPBr_2)_3$ has not yet been reported. Several iodophosphazenes have been reported.[48] These are gem-$N_3P_3Cl_4IR$, where R = Me, Et, *n*-Bu, *i*-Pr, and *t*-Bu. Attempts to polymerize these compounds led to decomposition of the structures, probably as a consequence of iodine free-radical elimination reactions.

The isothiocyano group is generally considered to be pseudohalogen and as such might be expected to initiate phosphazene ring-opening polymerization in the same way as chlorine, fluorine, or bromine. Indeed, compound **15** undergoes ring-opening polymerization when heated at temperatures above 100°C.[36–38] All three cyclophosphazenes, **13–15**, copolymerize with chlorophosphazenes.

Table 7.2. Other Polymerizable Cyclophosphazenes



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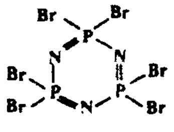

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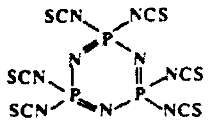

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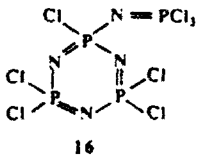

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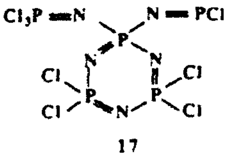

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The presence of branched structures, as in the phosphazophosphazenes **16** and **17**, also allows ring-opening polymerization to take place.[39] Indeed, the temperatures required for the onset of melt polymerization are surprisingly low (150°C). The polymers prepared from these cyclic trimers retain the phosphazo branch units. Replacement of the halogen atoms in the polymers by alkoxy or aryloxy groups has yielded an interesting group of new polymers.

Phosphazene cyclic tetramers (**2**) with halogen or pseudohalogen side groups also undergo thermal ring-opening polymerization reactions, but often at a slower rate than the corresponding cyclic trimers. This is ascribed to a lower degree of ring strain in the tetramers than the trimers.

7.5 CYCLIC TRIMERS WITH BOTH ORGANIC AND HALOGENO SIDE GROUPS

7.5.1 Reasons for Studying Organo-Halogeno-Substituted Phosphazenes

If the ring-opening polymerization mechanism discussed above [Scheme 4, pathway (a)] is correct, cyclic phosphazenes that bear organic side groups as well as halogen atoms should still be capable of polymerization since "initiation" sites (the P–halogen bonds) are still present. However, it is of interest to determine the extent to which the successive replacement of halogen atoms affects the reaction since, as will be discussed later, replacement of all the halogen atoms by organic units prevents polymerization.

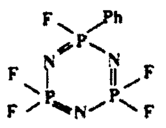
A second motive for studying the polymerization behavior of organo-halogenophosphazenes is the opportunity they provide for the synthesis of high polymers that contain side groups that cannot be incorporated solely by a macromolecular substitution process. For example, the reactions of poly(dichlorophosphazene) with Grignard, organolithium, or other organometallic reagents often lead to polymer chain cleavage as well as halogen replacement by alkyl or aryl groups. [This is less true for poly(difluorophosphazene) than for the chloro system, but it is still a persistent difficulty.] However, organometallic halogen replacement reactions can be carried out fairly easily with the cyclic trimers, and hence a trimer substitution, followed by a ring-opening polymerization process, and a final halogen-replacent step by oxo- or nitrogen-nucleophiles, is an appealing prospect. Copolymerization of organo-halogeno-cyclophosphazenes with trimers such as **7** would provide additional opportunities for structural diversity within this polymer system.

7.5.2 Types of Organo-Halogeno Cyclic Phosphazenes

Cyclic chloro- or fluorophosphazenes undergo a wide range of halogen replacement reactions with organometallic reagents to give derivatives with alkyl, aryl, or organometallic side groups, as well as unreacted halogen atoms.[40–67] Reactions of this type have been used to synthesize cyclic phosphazenes with the structures shown in Tables

Table 7.3. Phenyl-cyclophosphazenes[a]

A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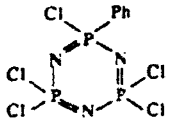
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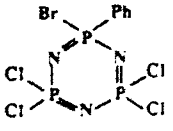
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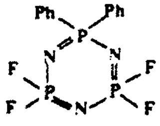
B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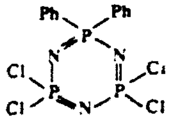
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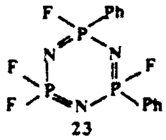
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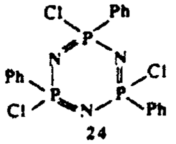
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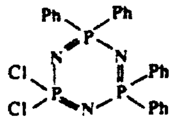
C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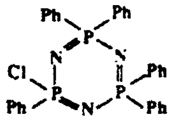
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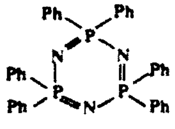
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[a] A, polymerize thermally, and copolymerize with $(NPCl_2)_3$. Compound 18 also undergoes ring expansion. B, do not homopolymerize, but copolymerize with $(NPCl_2)_3$, and undergo ring expansion. C, do not homopolymerize, and inhibit polymerization of $(NPCl_2)_3$. Undergo ring expansion.

7.3–7.5. Note that substitution reactions offer the possibility of wide variations in the molecular structure, including geminal or nongeminal side group arrangements, *cis*- or *trans*-nongeminal configurations, and compounds that, for cyclic trimers, contain from one to six organic side groups per molecule. These variations, together with changes in the types of side groups present, offer many opportunities for probing the scope and details of the ring-opening polymerization process.

7.5.3 *Response of Different Cyclic Species to Heating*

The thermolysis of phosphazene cyclic species can lead to a number of different reactions. These include polymerization to high-molecular-weight macromolecules, ring expansion to give higher cyclic homologues, side group condensation reactions to link the ring systems together, or general fragmentation and decomposition. It is also possible that high polymers or higher cyclic oligomers, once formed, may depolymerize or "equilibrate" to give lower homologues. The reaction pathway followed depends

Table 7.4. Polymerization and Ring-Equilibration Reactions of Nongeminal Alkyl-cyclophosphazenes

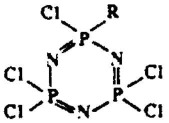
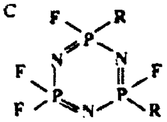
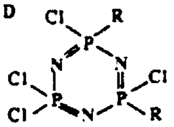
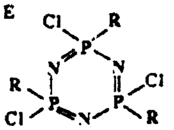
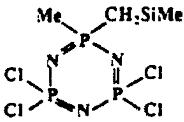
A		When R = Me, Et, *t*-Bu, or Ph, both polymerization and ring expansion occur
B		When R = Me, Et, *n*-Pr, *n*-Bu, CH_2CMe_3, CH_2SiMe_3, or phenyl-*o*-carborane, polymerization occurs. However, when R = *i*-Pr or *t*-Bu, side group reactions take place
C		When R = CMe_3, or Ph, ring expansion is the main reaction
D		When R = Me or Et, both polymerization and ring expansion occur
E		When R = Me, polymerization and ring expansion are found, and the compound also copolymerizes with $(NPCl_2)_3$. However, when R = Et, ring expansion predominates and polymerization occurs only during copolymerization with $(NPCl_2)_3$

Table 7.5. Geminal Organosilyl-cyclophosphazenes



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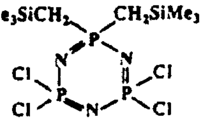

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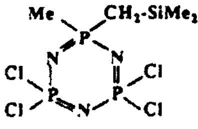

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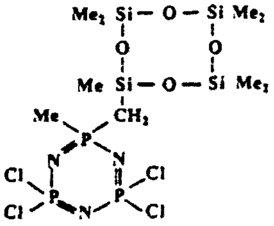

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critically on the type and number of organic side groups attached to the phosphazene ring.

Consider the phenyl-halogeno-phosphazenes shown in Table 7.3.[40,52,61,62] These are divided into three groups that reflect structural and polymerization differences. The three compounds in group A possess only one phenyl group per ring. All three polymerize to high polymers when heated, and also copolymerize with $(NPCl_2)_3$. Compound **18** also forms ring-expansion cyclic oligomers concurrent with polymerization. An interesting feature of compound **20** is that polymerization is accompanied by scrambling of the bromine atoms among the various possible phosphorus sites.[52] It was established that the scrambling occurred during an initial halogen exchange reaction at the cyclic trimer level, and this reinforces the view that halogen ionization takes place as a prelude to or concurrent with the initiation of polymerization.

The four compounds shown in group B of Table 7.3 do not polymerize when heated, but they can participate in ring-expansion reactions. However, **21**, **22**, and **24** copolymerize with **7** to give high polymers. The addition of further phenyl groups to the ring (**25–27**) also prevents homopolymerization, but allows ring expansion to cyclic tetramers and higher species. Copolymerization with **7** is now blocked. Thus, the overall pattern is one of inhibition of high polymer formation as successive halogen atoms are replaced by phenyl groups, but with no inhibition of the ring-expansion reactions. This series of comparisons is important because the phosphorus–phenyl bond is particularly stable at elevated temperatures, and side group condensation processes seem not to be significant, at least in the 200–300°C temperature range.

A second series of comparison trimers is shown in Table 7.4. Here the organic side units are alkyl groups with varying steric dimensions.[43,45,61–63] As before, the trimers are grouped according to their structures and behavior when heated. In general, the presence of one alkyl group per ring (Groups A and B) allows polymerization to occur, usually accompanied by ring expansion reactions to give cyclic tetramers, pentamers, hexamers, etc. Exceptions are found when the alkyl group is an isopropyl or *tert*-butyl unit and the halogen atoms are chlorine. Under these circumstances the alkyl groups react with phosphorus–halogen bonds to eliminate alkyl halide. Trifluoroethoxycyclotriphosphazenes such as $N_3P_3Cl_5(OCH_2CF_3)$ or nongem-$N_3P_3Cl_4(OCH_2CF_3)_2$, also polymerize at 200°C. As the degree of steric crowding increases, the tendency is for ring expansion processes to predominate over polymerization. This is evident with the bulky alkyl units present in the two compounds shown in Group C, and especially in the triethyl derivative shown in Group E.

Finally, the geminal-disubstituted compounds shown in Table 7.5[55,57,58] underwent ring-opening polymerization when heated at 210–250°C in spite of the steric crowding evident at one phosphorus atom, and this illustrates the difficulty of making predictions based on intuitive steric arguments.

7.5.4 Utility of the Polymers Prepared by This Approach

Virtually all the polymers prepared by the polymerization of the trimers shown in Tables 7.3–7.5 are elastomers. However, as long as the halogen atoms remain in the structure the macromolecules are sensitive to reaction with atmospheric moisture. This problem can be overcome by replacement of the halogen atoms by treatment with alkoxide nucleophiles, and particularly with sodium trifluoroethoxide. Many of the resultant trifluoroethoxy-alkyl- or aryl-phosphazene polymers are also rubbery elastomers, often with low glass transition temperatures. These elastomers have the potential to be used in a wide variety of engineering and biomedical applications.

7.6 TOTALLY ORGANIC-SUBSTITUTED PHOSPHAZENE RING SYSTEMS

7.6.1 Reasons for Interest

It follows from the earlier comments that a primary reason for attempting to polymerize cyclophosphazenes that bear only organic side groups is the prospect that they may be polymerized directly to fully organo-substituted high polymers without the need for a subsequent macromolecular substitution step. Polymers produced by this method would also bear alkyl or aryl groups bonded to the chain through phosphorus–carbon bonds, rather than the normal phosphorus–oxygen–carbon or phosphorus–nitrogen–carbon linkage units. Other methods are available to prepare polymers of this type[68,69] but these involve condensation-type reactions.

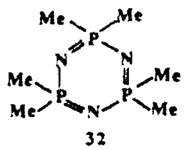
7.6.2 Typical Compounds That Have Been Studied

Table 7.6 contains the structures of several cyclophosphazenes that lack phosphorus–halogen units, and which form the basis of investigations on this topic.[63,64,70,71]

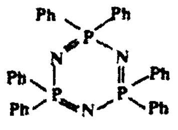
7.6.3 Thermal Behavior

None of the compounds shown as **32–36** undergoes ring-opening polymerization when heated. Instead, they participate in ring-expansion reactions to give higher ring systems based on the same repeating unit structure, as depicted in Scheme 5. For example, the methyl derivative, **32**, generates a trimer–tetramer equilibrium system when heated at 250–350°C.[70] A similar situation exists for the phenyl derivative, **33**. Indeed, the thermal equilibration process is a preferred method for synthesis of the two cyclic tetramers. The trifluoroethoxy derivative, **34**, undergoes ring expansion at 275°C to yield a mixture of cyclic trimer, tetramer, pentamer, and hexamer.[71] This equilibration is accelerated by the presence of traces of chlorophosphazenes or CsCl. Although ring–ring equilibration of the phenoxy–trimer, **35**, does occur, this reaction is overshadowed by the tendency of these molecules to undergo side group condensation reactions at elevated temperatures to link phosphazene rings into an ultrastructure.[63] Finally, the organosilicon derivative, **36**, is inert under thermolysis conditions.[64] It neither polymerizes nor undergoes ring–ring equilibration. The stability of this compound has been ascribed to side group steric crowding which thermodynamically favors the cyclic trimer, and protects the ring from reagents that might initiate ring-opening reactions.

Table 7.6. Fully Organo-Substituted Cyclophosphazenes



32



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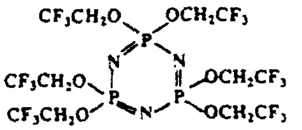
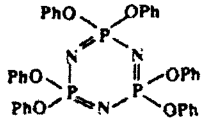
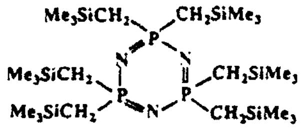


34



35



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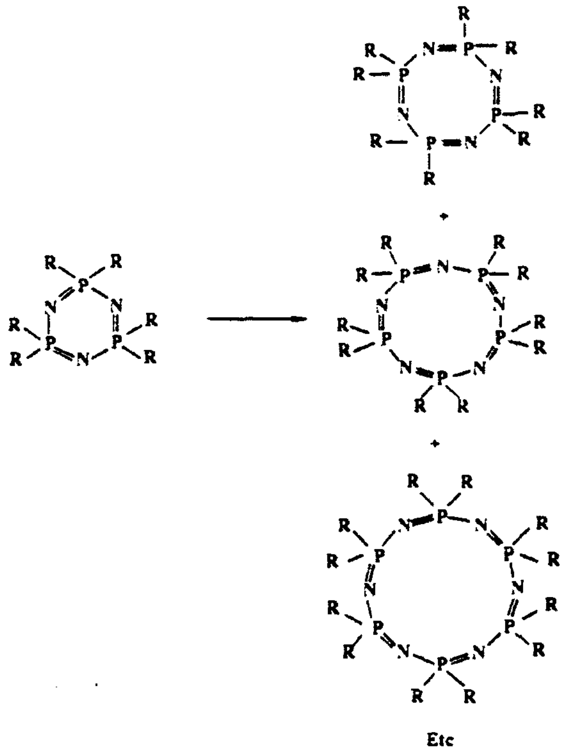
7.6.4 *Factors That Tip the Balance between Polymerization and Ring–Ring Equilibration*

The argument can be made that polymerization is favored by the presence of relatively small, ionizable side groups attached to the phosphazene ring. Polymerization would become progressively more difficult as the halogen atoms were replaced (1) by non-ionizable groups, and (2) by side groups that are bulky. It can be shown that bulky side groups thermodynamically favor small-molecule rings over linear, polymeric chains because, in the phosphazene system at least, polymerization allows molecular conformations that bring the side groups closer together and this, in turn, generates steric hindrance. Thus, in an equilibrating system in which both small-molecule rings and high polymers can be formed, the bulkiest side groups would favor the formation of rings. This is a plausible argument so long as halogen initiation sites are present around the ring. However, the presence of ring–ring equilibria in systems that bear no halogen atoms raises a serious question. If the reasonable assumption is made that polymerization and ring–ring equilibration follow similar mechanisms, why do molecules such as **32–35** undergo ring-expansion reactions? The possibility must be considered that two separate mechanisms give rise to polymers or ring-expanded oligomers. A plausible second mechanism is shown as pathway (b) in Scheme 4. It is assumed that two types of bonds can undergo heterolytic cleavage at moderate temperatures—phosphorus–halogen or phosphorus–nitrogen bonds. The latter process would generate a zwitterion



Scheme 5

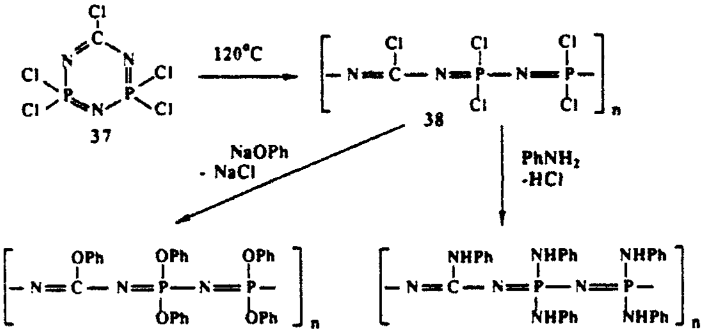
which could attack another trimer molecule by a ring-cleavage or ring-fusion process. For those cyclic trimers that bear both halogeno and organic side groups, the preference for one pathway over another will depend on the ease of the initial chain propagation process, which would be retarded by the presence of bulky end groups. A second question is whether the chloride ionization route is the only mechanism that can lead to high polymer, or whether macrocyclic high polymers are accessible via the ring expansion route. This aspect is considered in a later section.

7.7 THE ROLE OF RING STRAIN

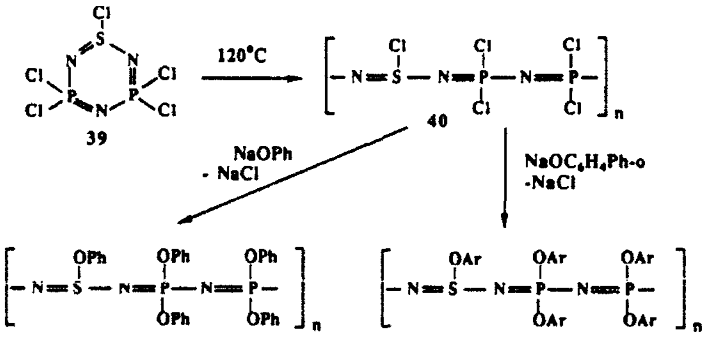
7.7.1 *Ring Strain through Skeletal Heteroatoms*

The position of a ring–polymer equilibrium, will depend on several factors including the relative side group steric hindrance in small-molecule rings compared to the corresponding linear or macrocyclic high polymers. In addition, destabilization of a small-molecule ring, for example by ring strain, should favor polymers (or higher cyclic species) rather than cyclic trimers or tetramers. Such destabilization has been achieved in two ways—first by the introduction of heteroelements into the rings of cyclic "monomers," and second by spanning the phosphazene ring by a transannular unit that imparts ring strain to the molecule. The introduction of heteroelements into the ring is considered first.

The first example of this effect is shown in Scheme 6.[72,73] The cyclic carbophosphazene **37** can be prepared from phosphorus pentachloride, ammonium chloride, and cyanamide.[74] When heated at 120°C, compound **37** undergoes a ring-opening polymerization to give polymer **38**.[72,73] This temperature is more than 120°C lower than that needed to bring about the polymerization of hexachlorocyclotriphosphazene (**7**). Polymer **38** serves as a macromolecular intermediate for halogen replacement reactions in the manner discussed earlier for poly(dichlorophosphazene) (**8**).[72,73] A second example is illustrated in Scheme 7.[75] Here, cyclic thiophosphazene **39** polymerizes to the corresponding high polymer, **40**, when heated at 120°C. A related cyclic thiophosphazene with an —S(O)Cl— unit in place of the —SCl— unit in **39** has also been reported to polymerize.[76] Again, chlorine atoms in the polymers can be replaced by organic units. In all of these ring-opening polymerizations it appears that the unusually facile polymerizations reflect a release of ring strain imparted by the carbon or sulfur. Indeed, an X-ray crystal structure of **37** revealed considerable ring distortion that is consistent with this interpretation.



Scheme 6. Poly(carbophosphazene) synthesis.

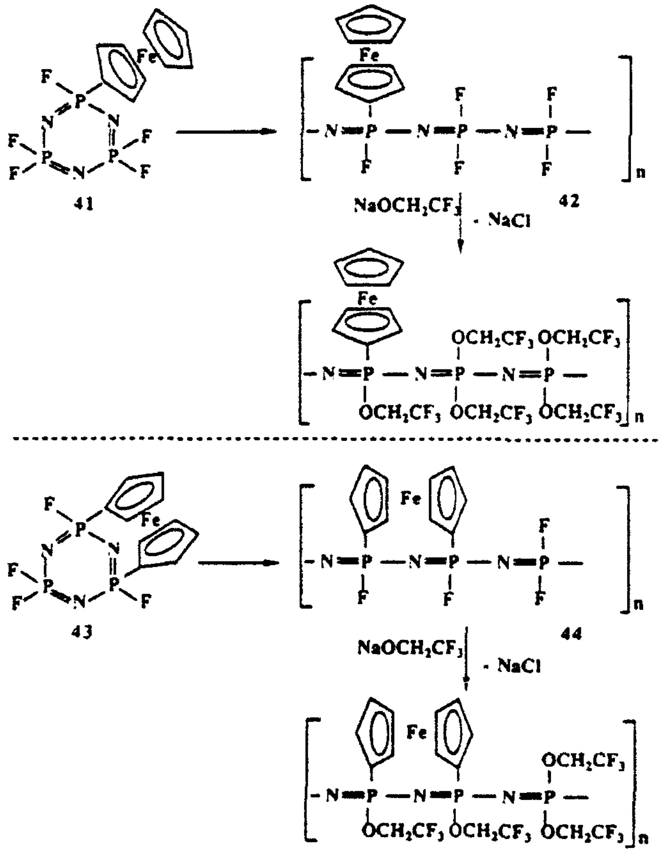


Scheme 7. Poly(thiophosphazene) synthesis.

7.7.2 Ring Strain through Transannular Linkage Group

Recent synthetic advances in our program have allowed the preparation of phosphazene cyclic trimers that bear ferrocenyl or ruthenocenyl groups linked to the phosphazene ring.[77–86] These compounds are prepared by the reactions of lithio- or dilithioferrocene or -ruthenocene with halogen-cyclophosphazenes such as **5**. The products are of two types—those in which the metallocenyl group is linked to the phosphazene through one bond, and those in which the metallocene unit is linked to two different phosphorus atoms to form a transannular arrangement. The other side groups can be chlorine or fluorine or, by halogen replacement reactions, a variety of alkoxy or aryloxy groups. In the interest of brevity, only the ferrocenyl system will be discussed here.

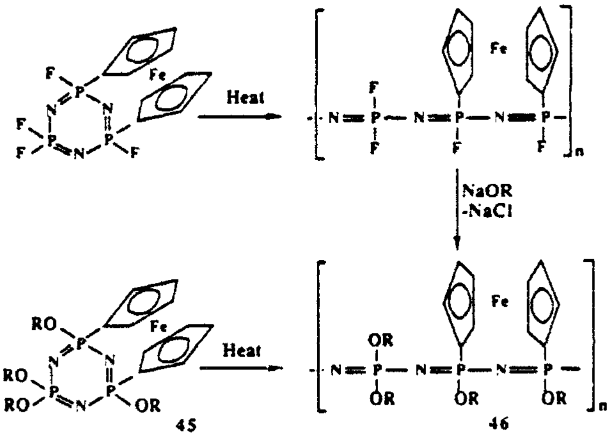
First, as shown in Scheme 8, both the singly-linked compound **41** and the transannular compound **42** polymerize when heated, but the transannular species polymerizes faster at 250°C than does **41**. An X-ray crystal structure of both compounds revealed that the transannular structure alone contained a highly puckered phosphazene ring, which is an indication of considerable ring strain. Note that both compounds contain



Scheme 8. Metallocenylphosphazenes.

fluoro cosubstituent groups which, according to the concepts discussed earlier, would provide a mechanism for initiation.

However, it has been found that a derivative of **43**, which contains trifluoroethoxy units in place of the fluoro atoms (**45**), also polymerizes when heated to give macromolecules with molecular weights in the region of 1.2×10^5 (Scheme 9).[84,85] Thus, polymers of type **46** can be prepared by the two alternative pathways shown in Scheme 9. Other derivatives of type **45** with different organic cosubstituent groups behave similarly. The polymerizations are accelerated by the presence of traces of $(NPCl_2)_3$, but the catalyst is not essential for the polymerization to take place. This suggests that species such as **45** are capable of forming high polymers by a mechanism that does not require the presence of ionizable halogen and may, in fact, represent an example of polymerization to macrocycles via pathway (b) shown in Scheme 4.



Scheme 9. Poly(ferrocenylphosphazenes).

7.8 CONCLUSIONS, QUESTIONS, AND FUTURE PROSPECTS

It will be clear that the ring-opening polymerization of cyclic phosphazenes is a diverse subject with a complex interrelationship among many factors such as side group ionization, skeletal cleavage reactions, side group steric bulk, polymer to cyclic oligomer depolymerizations, and ring strain. For a few side groups the question of side reactions, such as side group condensation and ring coupling, must also be taken into account. Nevertheless, as shown, the polymerization of $(NPCl_2)_3$ underlies an emerging technology, and an understanding of the nuances of the polymerization is one of the most important requirements in advancing that technology. The development of this class of reactions to include the polymerization of organo-substituted trimers has important long-range consequences. Perhaps most significantly, these reactions provide access to new generations of phosphazene elastomers that are not available via the classical route. Second, they provide a powerful method for probing and understanding the details of the polymerization process in ways that would not be possible using $(NPCl_2)_3$ alone. Most important is the possibility that these studies may point the way to the development of methods for the polymerization of other inorganic and organometallic ring systems that would provide access to entirely new macromolecular systems.

ACKNOWLEDGMENTS

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