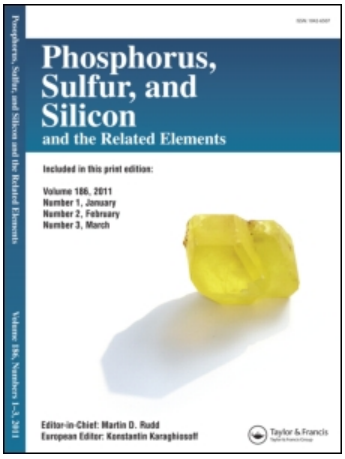

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THE CRUCIAL ROLE OF INORGANIC RING CHEMISTRY IN THE DEVELOPMENT OF NEW POLYMERS

Harry R. Allcock[a]
[a] The Pennsylvania State University, University Park, Pennsylvania, USA

Online publication date: 12 August 2010

To cite this Article Allcock, Harry R.(2004) 'THE CRUCIAL ROLE OF INORGANIC RING CHEMISTRY IN THE DEVELOPMENT OF NEW POLYMERS', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 4, 661 — 671
To link to this Article: DOI: 10.1080/10426500490426386
URL: http://dx.doi.org/10.1080/10426500490426386

Phosphorus, Sulfur, and Silicon, 179:661–671, 2004

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490426386

Taylor & Francis
Taylor & Francis Group

THE CRUCIAL ROLE OF INORGANIC RING CHEMISTRY IN THE DEVELOPMENT OF NEW POLYMERS

Harry R. Allcock
The Pennsylvania State University, University Park, Pennsylvania, USA

(Received August 17, 2003; accepted October 3, 2003)

The field of phosphazene high polymers has developed into a large area of more than 700 different types of macromolecules with novel combinations of properties and diverse applications. Small-molecule phosphazene rings have played a major role in these developments, first as starting materials for polymer synthesis, second as synthetic and structural models for the high polymers, and third as components of hybrid inorganic-organic macromolecules. These three aspects are reviewed, with examples taken from our recent work, together with some thoughts on the development of this and related fields in the future.

Small-molecule six- and eight-membered phosphazene rings have been studied intensively since the 1950s, mainly from the viewpoint of reaction mechanisms and x-ray crystal structures. Indeed, in our program at The Pennsylvania State University over the past 37 years we have synthesized and studied the chemistry of more than 250 new small-molecule phosphazenes, but usually as a means to an end rather than as an end in itself. Our long-range objective has been the synthesis of high polymers based on the phosphazene platform, followed by investigations of the properties and uses of these new macromolecules. This has developed into a major branch of polymer chemistry, with more than 700 different polyphosphazenes now known, and applications evident in areas as diverse as high performance elastomers, lithium ion- and proton-conductive membranes (batteries and fuel cells), opto-electronic materials, and a variety of biomedical uses that include responsive

Address correspondence to Harry R. Allcock, Department of Chemistry, The Pennsylvania State University, 152 Davey Laboratory, University Park, PA 16802, USA. E-mail: hra@chem.psu.edu

membranes, controlled drug delivery devices, tissue regeneration matrices, and biosensors.[1]

All these developments would have been difficult or impossible without knowledge gained from small-molecule ring chemistry. Small-molecule cyclophosphazenes are of interest for three reasons. First, they are employed as "monomers" for ring-opening polymerization to phosphazene high polymers. This is one of the main pathways for the syntheses of phosphazene macromolecules. Second, small-molecule cyclic phosphazenes are crucial model systems for halogen replacement and secondary transformations that are to be applied to the high polymers and for x-ray structure determinations that provide a starting point for polymer structural investigations. Third, new methods are now available that allow small-molecule phosphazene rings to be incorporated into linear polymers either as side groups linked to an organic polymer chain or as components in the main chains of cyclolinear polymers. These three aspects will be discussed in turn.

RING-OPENING POLYMERIZATION

In has been known since 1897 that hexachlorocyclotriphosphazene, $(NPCl_2)_3$ (**1**), when heated, is transformed into an insoluble, hydrolytically unstable, rubbery material known as "inorganic rubber."[2] This crosslinked material cannot be used for subsequent reaction chemistry. In 1965 and 1966 we showed that $(NPCl_2)_3$ can be polymerized thermally to uncrosslinked, and therefore soluble, high molecular weight poly(dichlorophosphazene), $(NPCl_2)_n$ (**2**), and that this polymer can be used as a reactive macromolecular intermediate for the production of a large number hydrolytically stable organic-substituted derivatives (**3–5**).[3–5] This primary reaction pathway is shown in Figure 1. The polymerization process is believed to involve chloride ionization from phosphorus followed by a cationic chain growth process.

In later research a substantial number of other cyclophosphazenes have been shown to undergo similar ring-opening polymerization to uncrosslinked macromolecules, and these too have been used as substrates for macromolecular substitution processes.[1] Some examples of these cyclic "monomers" are shown in Figure 2.

Two points are important. First, polymerization normally requires the presence of halogen atoms attached to the ring, presumably to allow the halogen ionization mechanism to operate. Thus, rings with one, two, or three organic side groups polymerize easily, but six-membered rings with six organic side groups (Figure 3) do not, unless the inorganic ring is destabilized by ring strain. Strain can be imposed by the presence

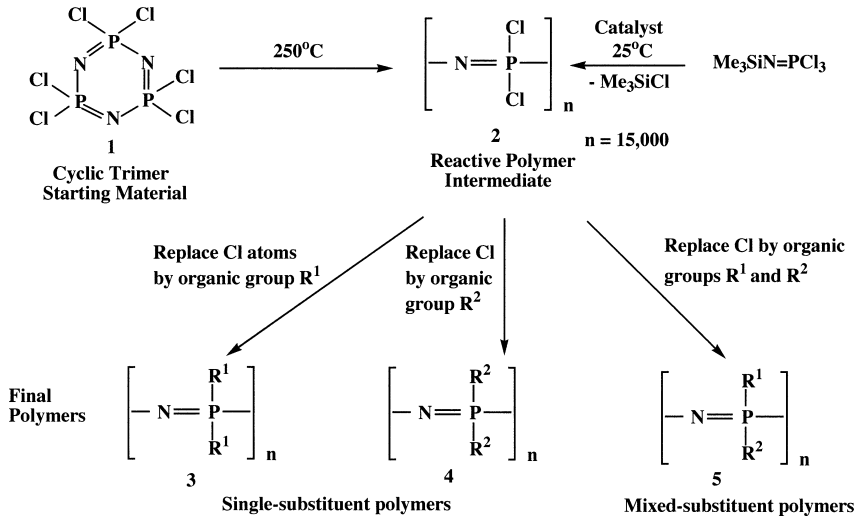

FIGURE 1 The synthesis of most polyphosphazenes involves two steps: (1) ring-opening polymerization of a halogeno phosphazene cyclic trimer or tetramer and (2) nucleophilic replacement of the halogen atoms in the high polymer by organic or organometallic groups. Typical reagents for the halogen replacement step are alkoxides, aryloxides, or primary or secondary amines. A few organometallic nucleophiles can also be used. An optional third step is to carry out substitution or deprotection reactions on the organic side groups to give functional macromolecules. Poly(dichlorophosphazene) is also accessible through a living cationic polymerization of the phosphoranimine, $Me_3SiN{=}PCl_3$.

of heteroelements such as carbon or sulfur in the ring[6–8] or by the presence of trans-annular organic or organometallic side groups.[9,10] In the absence of ring strain a cyclic trimer or tetramer may undergo *ring-expansion* but not polymerization. Of special interest is the fact that a number of spirocyclic phosphazene trimers resist polymerization when heated, but form the basis of a unique class of crystalline nano-tunnel clathrates which are used for small-molecule and polymer separations and as templates for addition polymerizations.[11,12]

MACROMOLECULAR SUBSTITUTION REACTIONS

General Considerations

As illustrated in Figure 1, a key step in the synthesis of hydrolytically stable macromolecules is the replacement of chlorine (or fluorine) in the macromolecular intermediate by organic side groups. Normally all the

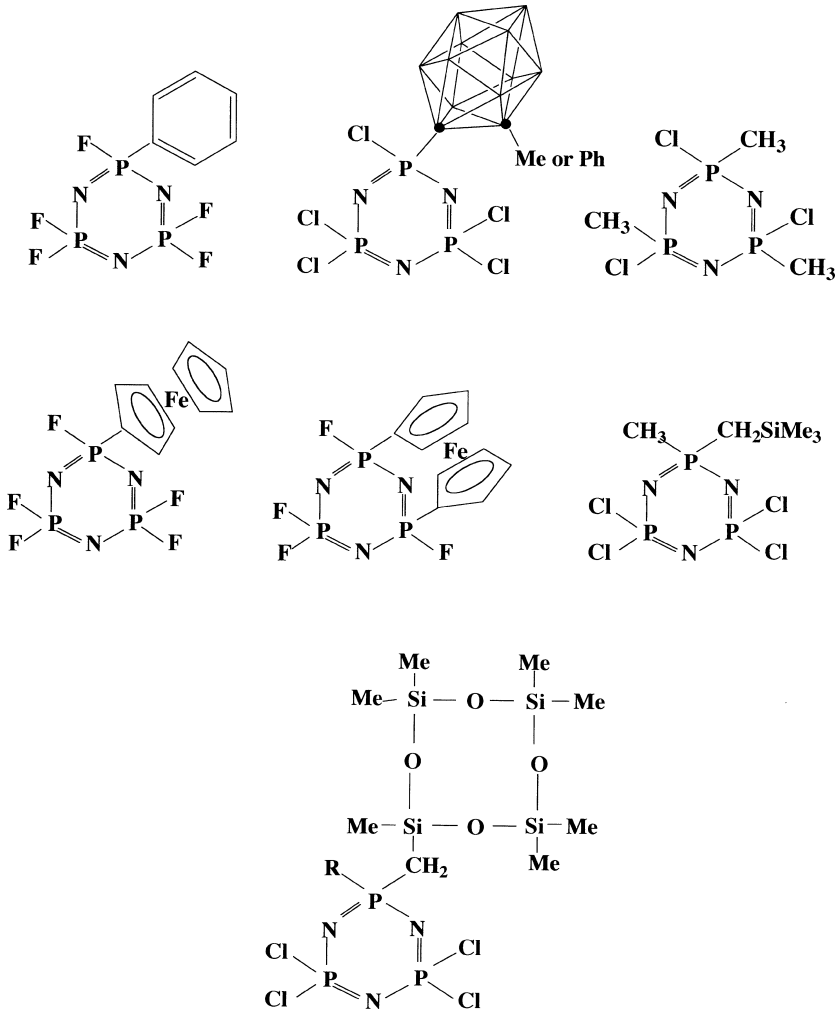

FIGURE 2 Examples of phosphazene cyclic trimers that bear both organic or organometallic side groups and halogen units and which undergo ring-opening polymerization.

halogen atoms must be replaced because unreacted chlorine or fluorine will be sites of hydrolytic instability. This means that, for a typical polymer with 15,000 repeating units, 30,000 halogen atoms must be replaced in each molecule. The fact that this is possible is an indication of the extremely high reactivity of the P—Cl or P—F bonds.

However, these polymer substitution reactions are not trivial. If the halogen replacement reagent is small and reactive, such

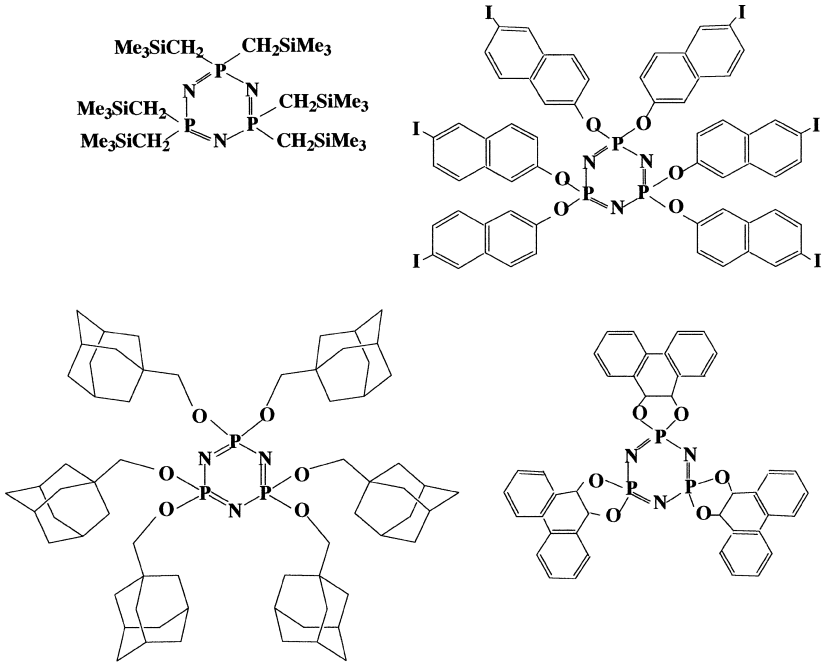

FIGURE 3 Examples of halogen-free cyclic phosphazenes with bulky organic side groups. These do not undergo ring-opening polymerization.

as trifluoroethoxide or *n*-propoxide, or even the sodium salt of methoxyethoxyethanol, rapid, complete replacement of all the halogen atoms along each chain is likely. Use of two or more suitable nucleophiles leads to mixed-substituent polymers. However, if the incoming nucleophile is bulky, such as diethylamine, sodium 2-phenylphenoxide,[13] sodium naphthaleneoxides,[14] adamantylmethoxide,[15] or chlorinated phenoxy groups,[16] steric hindrance effects may prevent complete halogen replacement. Often, only one chlorine atom per phosphorus will be replaced, but the remaining halogen can usually be displaced by use of a smaller or more reactive alkoxide or amine to give mixed-substituent polymers.

Phosphazene ring systems play a critical role in all the polymer substitution reactions we have pioneered. First, trial reactions with $(NPCl_2)_3$, $(NPF_2)_3$, or $N_3P_3F_5Ph$ indicate if complete halogen replacement with a particular nucleophile is possible, and if side reactions are likely. For example, in principle, nucleophilic attack at phosphorus could lead to P—Cl or P—N skeletal bond cleavage. At the macromolecular level P—N bond cleavage would be highly detrimental to the

chain length and hence to the properties of the final polymer. The reactions of $(NPCl_2)_n$ with organometallic reagents are difficult because of P—N cleavage reactions, and extensive model compound work has been required to identify conditions that minimize chain cleavage.[17] Thus, model reactions carried out with phosphazene cyclic trimers and tetramers provide either a green light for subsequent macromolecular reactions or suggest caution. Although most of the model compound work carried out to date has been with cyclic trimers, cyclic tetramers may be better models because of their inherent skeletal flexibility, and the bond angles approximate more closely to those of the high polymer. Cyclic pentamers or hexamers would be even more useful models.

Example Small Molecule Model Reactions and Structures

The following examples illustrate some of the principles described above. First, steric hindrance in an incoming nucleophile complicates the synthesis of a number of polymers that bear bulky high refractive index aryloxy,[13,14,16] liquid crystalline,[18] nonlinear-optical,[19] photochromic,[20] steroidal,[21] or bulky amino acid ester[22] side groups. In nearly all cases, complete replacement of all the chlorine atoms in $(NPCl_2)_3$ is difficult or impossible except under forcing reaction conditions. The model reactions suggest whether or not those conditions are acceptable for the corresponding macromolecular substitution. The model reactions also indicate the pattern of substitution (gem, non-gem, cis or trans) that might be expected if similar mechanisms are followed for the high polymers. X-ray crystal structures of phosphazene cyclic trimers and tetramers with fused aromatic rings or linked aryl side groups suggest ways in which these same side units might direct the chain packing patterns in the solid high polymers.[23]

The linkage of organometallic side groups to a polyphosphazene chain is particularly challenging. Model compound work, carried out by us in the 1990s to link organometallic clusters to the phosphorus atoms of $(NPCl_2)_3$ or $(NPF_2)_3$, has not yet been transposed to the macromolecular level. However, organic nucleophiles with transition metals, such as (η^6-phenoxyethoxy)chromium tricarbonyl, react directly with both the cyclic trimer and with the high polymer to give species with the (η^6-arene)$Cr(CO)_3$ units pendent to the phosphazene skeleton.[24,25]

Models for Secondary Reactions

The macromolecular substitution synthesis of phosphazene high polymers requires the use of *mono*-functional organic or organometallic

nucleophiles. Otherwise a reagent with di- or higher-functionality would crosslink the chains and cause precipitation of the polymer before halogen replacement was complete. However, many of the most useful polyphosphazenes bear functional units on the organic side groups, and these must be introduced by secondary reactions. Functionalization often requires the use of aggressive reagents to bring about oxidation,[26] nitration and reduction,[27] or sulfonation,[28,29] which could lead to cleavage of the polymer backbone. Sulfonation and phosphonation reactions at the high polymer level are needed for the formation of phosphazene fuel cell membranes.[30,31] It is essential to perform model reactions of this kind at the small molecule level before proceeding to secondary reactions on the high polymers.

Deprotection of functional groups has been widely used in recent work. For example, the formation of arylcarboxylic acid groups, as shown in Figure 4 requires hydrolysis of an ester to the free acid. Protected hydroxy or amino groups in a side chain are deprotected by standard techniques. Polymers produced by these techniques are

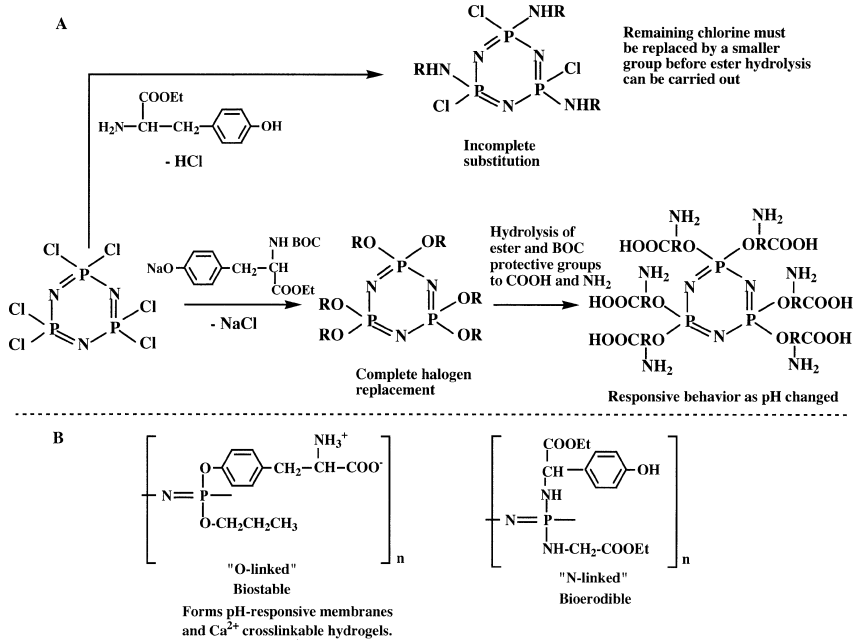

FIGURE 4 (A) Illustration of the use of a cyclic trimeric model to develop conditions for reactions with a complex nucleophile (L-tyrosine) and the subsequent deprotection reactions. (B) Two polymers synthesized following procedures developed in the model compound work.

important for biological experiments. For example, one of the tyrosine-substituted polymers shown in Figure 4 forms hydrogels that expand and contract with pH changes or in the presence or absence of di- or trivalent cations.[32] The other polymer shown is designed to bioerode either for controlled drug release or for tissue regeneration experiments.

All these are conventional organic chemistry reactions, but they are often challenging when carried out on the corresponding high polymer. Hence, prior studies with small molecule cyclic analogues are essential to establish reaction conditions and avoid polymer decomposition.

PHOSPHAZENE RINGS AS COMPONENTS IN ORGANIC POLYMERS

Organic polymers with pendent cyclophosphazene rings, that are produced by polymerization of vinyl or allyl-substituted cyclophosphazenes, have been studied in detail by C. W. Allen and coworkers.[33,34] We have recently developed two alternative ways to produce polymers in which cyclic phosphazene units are pendent to an organic polymer chain. The first approach involves the reaction of a mono-azido-penta-organo-cyclotriphosphazene with polystyrene molecules that bear diphenylphosphine units in the para position of the aryl rings (Figure 5).[35] The second method involves the ring-opening-metathesis polymerization (ROMP) of unsaturated organic rings to which are attached organic-substituted phosphazene rings.[36,37] An example is

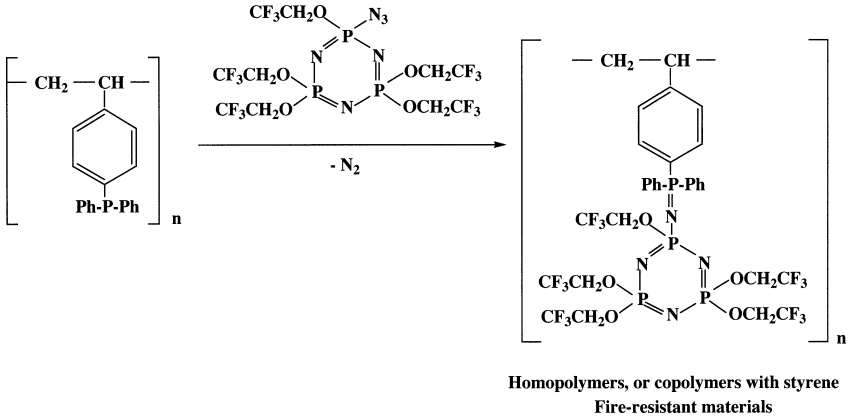

FIGURE 5 Synthesis of a fire-resistant polystyrene with pendent cyclophosphazene units with use of an azide coupling reaction. The resultant polymers can bear one cyclophosphazene on every phenyl ring, or they can be spaced along the chain.

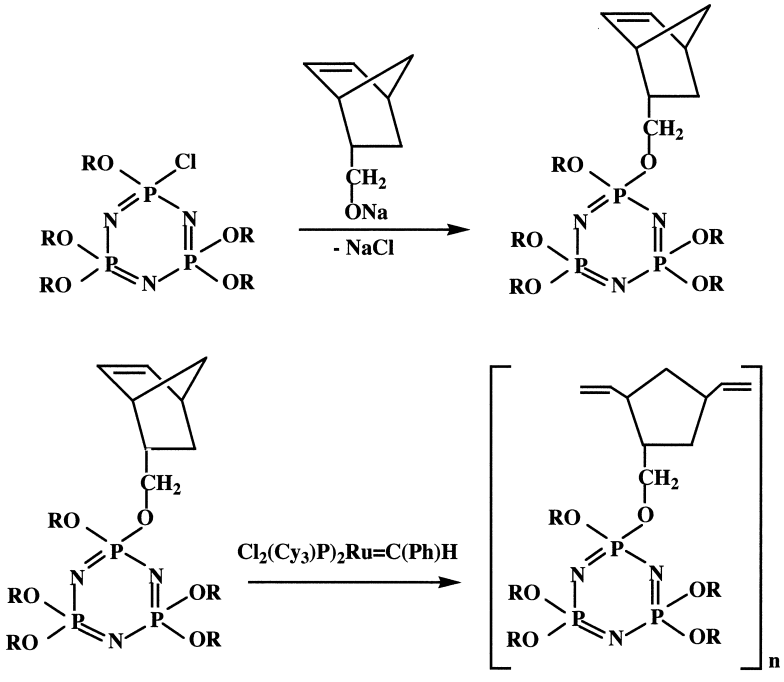

FIGURE 6 Synthesis of polynorbornenes with pendent cyclophosphazene groups using ROMP techniques. The polymers can be fire-resistant polynorbornenes or lithium ion conductors depending on the substituents linked to the phosphazene rings.

shown in Figure 6. The side groups on the phosphazene can vary over a wide range. When CF_3CH_2O-units are the cosubstituents on the ring, the phosphazene confers resistance to combustion on the normally highly flammable polynorbornene. When oligoethyleneoxy side chains are present, the polymer is a good lithium ion conductor that is of interest in solid or gel rechargeable lithium batteries.

Cyclolinear polymers are now available via acyclic diene metathesis (ADMET) polymerization carried out on cyclophosphazenes that bear two terminally unsaturated non-gem alkoxy side groups (Figure 7).[38] These polymers can be used as synthesized, or the organic unsaturation in the main chain may be removed by reduction to yield polymers that are essentially short strands of polyethylene linked by phosphazene

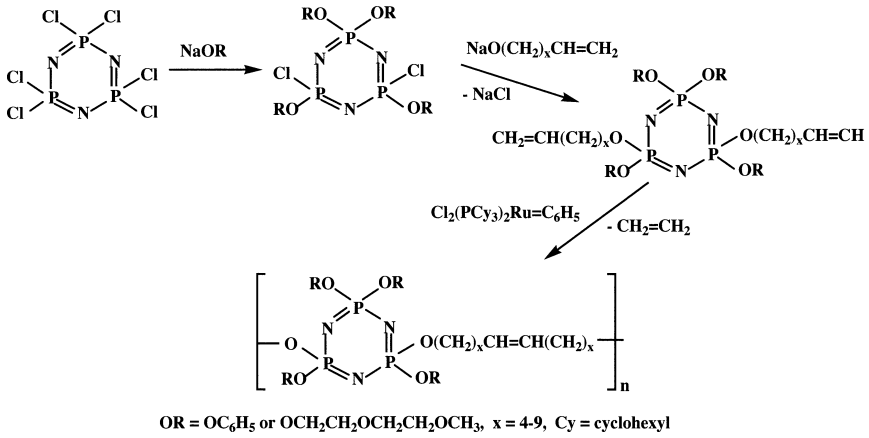

FIGURE 7 Formation of a cyclolinear polymer using ADMET polymerization of a difunctional cyclotriphosphazene.

rings. The properties can be controlled by the choice of the other organic side groups on the phosphazene rings.

FINAL COMMENTS

Small-molecule cyclic phosphazene chemistry attracted enormous attention in the 1960s and 1970s directed mainly toward questions of substitution reaction mechanisms and the detailed structures of the substitution products. This phase ran its course and slowed in recent years. In its place has come the realization that the chemistry of cyclic phosphazenes has another purpose—to provide starting materials for polymer synthesis, model compounds for high polymer research, and components for incorporation into organic polymers. It is through these three aspects that the renaissance of this field is taking place. There may be a lesson here for the future of other inorganic ring systems, especially those based on boron, silicon, germanium, aluminum, and the transition metals, where the polymer chemistry and materials science aspects may eventually come to dominate research in these areas.

REFERENCES

[1] H. R. Allcock, *Chemistry and Applications of Polyphosphazenes* (Wiley-Interscience, Hoboken, 2003).
[2] H. N. Stokes, *Am. Chem. J.*, **19,** 782 (1897).
[3] H. R. Allcock and R. L. Kugel, *J. Am. Chem. Soc.*, **87,** 4216 (1965).

[4] H. R. Allcock, R. L. Kugel, and K. J. Valan, *Inorg. Chem.*, **5,** 1709 (1966).
[5] H. R. Allcock and R. L. Kugel, *Inorg. Chem.*, **5,** 1716 (1966).
[6] H. R. Allcock, S. M. Coley, I. Manners, G. Renner, and O. Nuyken, *Macromol.*, **24,** 2024 (1991).
[7] H. R. Allcock, J. A. Dodge, and I. Manners, *Macromol.*, **26,** 11 (1993).
[8] M. Liang and I. Manners, *Macromol.*, **29,** 29 (1996).
[9] I. Manners, G. H. Riding, J. A. Dodge, and H. R. Allcock, *J. Am. Chem. Soc.*, **111,** 3067 (1989).
[10] H. R. Allcock and M. L. Turner, *Macromol.*, **26,** 3 (1993).
[11] A. P. Primrose, M. Parvez, and H. R. Allcock, *Macromol.*, **30,** 670 (1997).
[12] H. R. Allcock, A. P. Primrose, N. J. Sunderland, et al., *Chem. Mater.*, **11,** 1243 (1999).
[13] H. R. Allcock, M. N. Mang, A. A. Dembek, and K. J. Wynne, *Macromol.*, **22,** 4179 (1989).
[14] M. A. Olshavsky and H. R. Allcock, *Macromol.*, **28,** 6188 (1995).
[15] H. R. Allcock and W. E. Krause, *Macromol.*, **30,** 5683 (1997).
[16] H. R. Allcock, J. D. Bender, Y. Chang, M. McKenzie, and M. M. Fone, *Chem. Mater.*, **15,** 473 (2003).
[17] H. R. Allcock, J. L. Desorcie, and G. H. Riding, *Polyhedron*, **6,** 119 (1987).
[18] H. R. Allcock and C. Kim, *Macromol.*, **22,** 2596 (1989).
[19] A. A. Dembek, C. Kim, H. R. Allcock, et al., *Chem. Mater.*, **2,** 97 (1990).
[20] H. R. Allcock and C. Kim, *Macromol.*, **24,** 2846 (1991).
[21] H. R. Allcock, T. J. Fuller, and K. Matsumura, *J. Org. Chem.*, **46,** 13 (1981).
[22] H. R. Allcock, A. Singh, A. M. A. Ambrosio, and W. Laredo, *Biomacromol.*, **4,** (2003), in press.
[23] H. R. Allcock, S. Al-Shali, D. C. Ngo, K. B. Visscher, and M. Parvez, *J. Chem. Soc., Dalton Trans.*, **21,** 3521 (1995).
[24] H. R. Allcock, A. A. Dembek, J. L. Bennett, et al., *Organometallics*, **10,** 1865 (1991).
[25] H. R. Allcock, A. A. Dembek, and E. H. Klingenberg, *Macromol.*, **24,** 5208 (1991).
[26] H. R. Allcock, R. J. Fitzpatrick, and L. Salvati, *Chem. Mater.*, **4,** 769 (1992).
[27] H. R. Allcock and S. Kwon, *Macromol.*, **19,** 1502 (1986).
[28] E. Montoneri, M. Gleria, G. Ricca, and G. C. Pappalardo, *Makromol. Chem.*, **190,** 191 (1989).
[29] H. R. Allcock, R. J. Fitzpatrick, and L. Salvati, *Chem. Mater.*, **3,** 1120 (1991).
[30] Q. Guo, P. N. Pintaro, H. Tang, and S. O'Connor, *J. Membr. Sci.*, **154,** 175 (1999).
[31] H. R. Allcock, M. A. Hofmann, and R. M. Wood, *Macromol.*, **34,** 6915 (2001).
[32] H. R. Allcock, A. Singh, A. M. A. Ambrosio, and W. R. Laredo, *Biomacromol.*, **4,** (2003), in press.
[33] C. W. Allen, *Coord. Chem. Rev*., **130,** 137 (1994).
[34] C. W. Allen and M. Bahadur, *J. Inorg. Organometal. Polym*., **8,** 23 (1998).
[35] T. J. Hartle, N. J. Sunderland, M. B. McIntosh, and H. R. Allcock, *Macromol.*, **33,** 4307 (2000).
[36] H. R. Allcock, W. R. Laredo, C. R. deDenus, and J. P. Taylor, *Macromol.*, **32,** 7719 (1999).
[37] H. R. Allcock, W. R. Laredo, and R. V. Morford, *Solid State Ionics*, **139,** 27 (2001).
[38] H. R. Allcock, E. C. Kellam, and M. A. Hofmann, *Macromol.*, **34,** 5140 (2001).