EFFECT OF ORGANIC SOLVENT ON THE ENTRAPMENT OF 25 MOLE PERCENT EPOXIDIZED NATURAL RUBBER IN PREFORMED CYCLOMATRIX POLY(1,3-DIOXYBENZENE) CYCLOTRIPHOSPHAZENES

OH CHENG CHEOW

UNIVERSITI SAINS MALAYSIA

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by

OH CHENG CHEOW

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LIST OF ABBREVIATIONS AND SYMBOLS

Starting Materials and Products

ADMET	Acyclic Diene Metathesis
CH_2Cl_2	Methylene Chloride
Copolymers CP1: CP2	Poly{[2-(2-oxo-1-pyrrolidinyl)ethoxy](4-carboxylatophenoxy) phosphazene}
ENR-25	25 mole percent epoxidised natural rubber
ENR-50	50 mole percent epoxidised natural rubber
Et_3N	Triethylamine
$(NPCl_2)_3$	Hexachlorocyclotriphosphazene
P5	Chlorine-bound poly(1,3-dioxybenzene)cyclotriphosphazene resulted from 1:3 mole ratio reaction of $(NPCl_2)_3$ with 1,3-dihydroxybenzene
$[P5/ENR\text{-}25]_b$	Polymeric material obtained from blending P5 with ENR-25
$[P5/ENR\text{-}25]_b$-Cyclohexane	Polymeric material obtained from blending P5 with ENR-25 using cyclohexane as solvent
$[P5/ENR\text{-}25]_b$-1,4-dioxane	Polymeric material obtained from blending P5 with ENR-25 using 1,4-dioxane as solvent
$[P5/ENR\text{-}25]_b$-Methylene Chloride	Polymeric material obtained from blending P5 with ENR-25 using methylene chloride as solvent
$[P5/ENR\text{-}25]_b$-THF	Polymeric material obtained from blending P5 with ENR-25 using tetrahydrofuran as solvent
$[P5/ENR\text{-}25]_b$-Toluene	Polymeric material obtained from blending P5 with ENR-25 using toluene as solvent
$[P5/ENR\text{-}25]_s$	Polymeric material obtained from formation of P5 in the presence of ENR-25
PCPP	Poly[di(carboxylatophenoxy)-phosphazene]
PVP	Poly(vinylpyrrolidone)

PYRP	Poly{di[2-(2-oxo-1-pyrrolidinyl)ethoxy]-phosphazene}
THF	Tetrahydrofuran

Symbols

cm	Centimeter
DSC	Differential Scanning Calorimetry
DTG	Derivative Termogravimetry
FTIR	Fourier Transform Infrared
g	Gram
LOI	Limiting Oxygen Index
min	Minute
mm	Millimeter
NMR	Nuclear Magnetic Resonance
T_g	Glass Transition Temperature
TG	Thermal Gravimetry
TGA	Thermal Gravimetric Analysis
TGA/FTIR	Thermal Gravimetric Analysis combined with Fourier Transform Infrared
T_m	Melting Temperature

KESAN PELARUT ORGANIK TERHADAP PEMERANGKAPAN 25 MOL PERATUS GETAH ASLI TEREPOKSIDA DALAM SIKLOMATRIKS POLI(1,3-DIOKSIBENZENA)SIKLOTRIFOSFAZENA PRA-SEDIA

ABSTRAK

Pengadunan 25 mol peratus getah asli terepoksida (ENR-25) dengan siklomatrik, poli(1,3-dioksibenzena)siklotrifosfozena pra-sedia (P5) dilakukan dalam toluena, diklorometana, tetrahidrofuran, sikloheksana dan 1,4-dioksana. Kajian pemerangkapan dengan bantuan Analisa Kalorimetri Imbasan Pembezaan (DSC) dan Analisa Termogravimetri (TGA) menunjukkan P5 boleh memerangkap rantai ENR-25. Data DSC dan TGA untuk [P5/ENR-25]$_b$ yang disintesis dalam semua jenis pelarut dalam kajian kecuali toluena menunjukkan kehadiran rantai ENR-25 bebas. Tiada ENR-25 bebas diperolehi dalam keputusan analisa DSC dan TGA untuk produk sintesis dalam toluena, [P5/ENR-25]$_b$-Toluene. Oleh itu, kesimpulan dibuat bahawa sintesis dalam toluena menghasilkan pemerangkapan ENR-25 secara lengkap dalam P5. Pengembungan P5 dalam toluena mendorong pemerangkapan rantai ENR-25 secara efektif ke dalam P5. Keputusan analisa DSC menunjukkan peningkatan dalam sifat termal untuk [P5/ENR-25]$_b$-Toluena, dengan suhu lebur (T_m) yang lebih tinggi pada 125 ^oC, berbanding dengan bahan permulaan (dengan T_m 117 ^oC untuk P5 dan T_g -44 ^oC untuk ENR-25). Keputusan analisa FTIR ke atas berbagai produk yang diperolehi dalam kajian ini menunjukkan tiada perubahan terhadap kumpulan fungsi untuk

ENR-25 yang terperangkap dalam P5, seperti yang ditunjukkan oleh anjakan frekuensi jalur penyerapan yang tidak signifikan. Keputusan ini menunjukkan kemungkinan besar tiada berlaku tidakbalas kimia dalam pemerangkapan rantai ENR-25 dalam P5.

EFFECT OF ORGANIC SOLVENT ON THE ENTRAPMENT OF 25 MOLE PERCENT EPOXIDIZED NATURAL RUBBER IN PREFORMED CYCLOMATRIX POLY(1,3-DIOXYBENZENE) CYCLOTRIPHOSPHAZENES

ABSTRACT

Blending of 25 mole percent epoxidized natural rubber (ENR-25) with preformed cyclomatrix poly(1,3-dioxybenzene)cyclotriphosphazene (P5) was carried out in toluene, methylene chloride, tetrahydrofuran, cyclohexane and 1,4-dioxane. Entrapment studies with the aid of Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) revealed that P5 can trap ENR-25 chains. The DSC and TGA data for $[P5/ENR\text{-}25]_b$ synthesized in all the studied solvents except toluene, revealed the presence of untrapped ENR-25. No untrapped ENR-25 is obtained in the DSC and TGA analysis results of the product synthesized in toluene, $[P5/ENR\text{-}25]_b$-Toluene. As such, it can be concluded that synthesis in toluene lead to complete entrapment of ENR-25 in P5. The swelling of P5 in toluene facilitates the effective entrapment of ENR-25 chains into P5. The results of DSC analysis revealed the improvement in thermal properties of $[P5/ENR\text{-}25]_b$-Toluene, with higher melting temperature (T_m) of 125 ^oC, as compared to that of the starting materials (with T_m of 117 ^oC for P5 and T_g of -44 ^oC for ENR-25). The results of FTIR analysis of the different products revealed no change in the functional groups of the ENR-25 entrapped in P5, as indicated by the insignificant shift of the absorption frequencies. Therefore it is

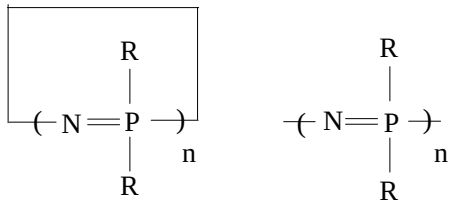
likely that there is no chemical reaction involve in the entrapment of the ENR-25 chains in P5.

CHAPTER 1

INTRODUCTION

1.1 Phosphazene

Phosphazenes are compounds that consist of alternating sequence of phosphorus and nitrogen atoms, with 2 side groups, R, being attached to each phosphorus atom. The side group may be organic, organometallic or inorganic units. Phosphazenes can exist as cyclic [1] and/or linear [2] forms, as depicted in Figure 1.1. Each macromolecule typically contains range of 3 – 40 repeating units for the cyclic and for the linear, the repeating units ranges from 15,000 or more (Allcock and Kugel, 1965). Therefore the molecular weights for the linear phosphazes are in the range of 2 million to 10 million. The bonding structure is formally represented by as a series of alternating single and double bonds.



[1] **[2]**

Figure 1.1 Schematic structures of phosphazenes: cyclic [**1**] and linear [**2**], (Al Shukri, 2003)

Polyphosphazenes comprise by far the largest class of inorganic macromolecules. At least 300 different polymers of this type have been synthesized, with a range of

physical and chemical properties that rivals only to synthetic organic macromolecules (Mark *et al.*, 1992).

1.2 History

The beginning of this field can be traced back more than 170 years to the observation by Rose in 1834 that phosphorus pentachloride (PCl_5) reacts with ammonia to yield a stable, white, crystalline solid (Mark *et al.*, 1992). Only sporadic interest in this product existed during the next 50 years and it was concluded that the formula was $(NPCl_2)_3$ (Mark *et al.*, 1992). It is now known that the reaction is as shown in Figure 1.2.

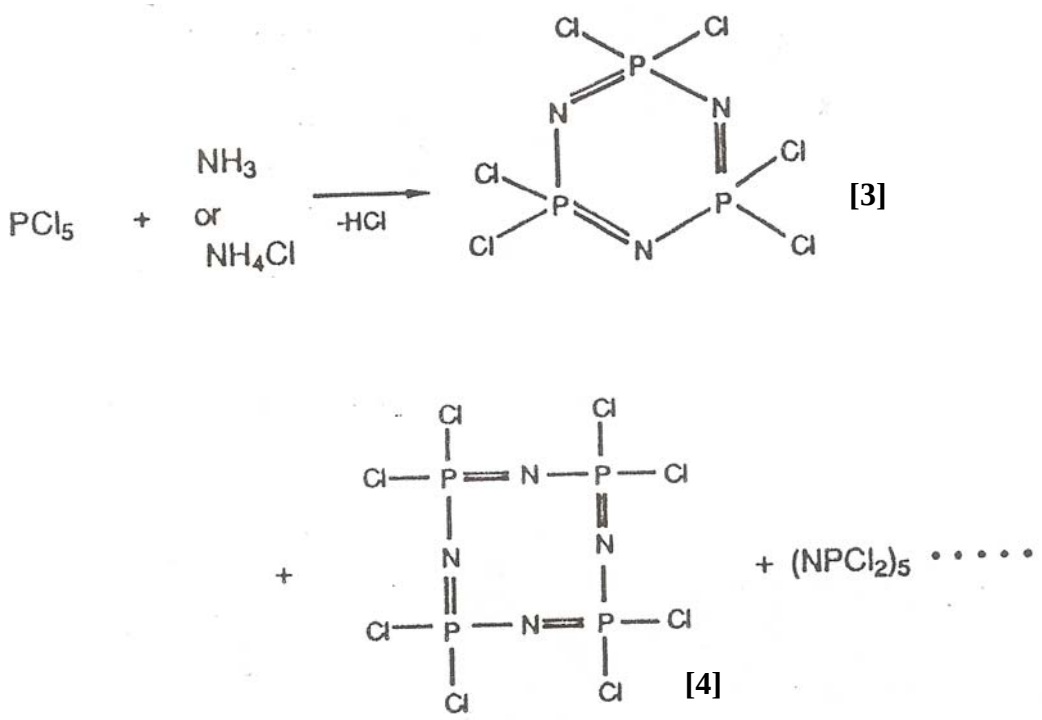


Figure 1.2 Reaction of PCl_5 with ammonia, (Mark *et al.*, 1992)

The principal early contributor was an American Chemist, H.N. Stokes, who at the turn of the century, first suggested the cyclic structure of [3], identified cyclic homologs

such as [4] up to the species $(NPCl_2)_7$, and reported that chlorophosphazenes, when heated, were transformed into an elastomeric known subsequently as “inorganic rubber”, (Mark *et al.,* 1992). Stokes also described how inorganic rubber decomposed to reform the cyclic compounds when heated to high temperatures under reduced pressure. Considering the laboratory conditions under which Stokes probably worked, it is remarkable that he achieved so much. All the compounds he worked with are sensitive to a moist atmosphere, in which they hydrolyze to ammonium phosphate and hydrochloric acid.

The reading of Stokes’s papers about 100 years after publications is an uncanny experience. He could not have known that “inorganic rubber’ was a high polymer with thousands of repeating units linked end to end. His material was insoluble in all solvents and was probably highly cross-linked (Mark, *et al.,* 1992). Nevertheless, one senses he understood the uniqueness of the transformation of a molten small-molecule system to an insoluble, rubbery elastomeric solid. It took another 70 years before it could be fully understood or utilized for the synthesis of a broad range of useful polymers.

During the next 40 years, “inorganic rubber” was mentioned sporadically as a laboratory curiosity, but was largely ignored by the mainstream scientists of the day. Staudinger’s idea that long-chain macromolecules could exist (Mark *et al.,* 1992) and the demonstration by Meyer and Mark in the 1920s and 1930s that natural rubber is a linear macromolecule, stimulated a brief resurgence of interest in “inorganic rubber” (Mark *et al.,* 1992). X-ray diffraction experiments by Meyer, Lotmar and Pankow in

1936 strongly suggested that this material contained linear high polymeric chains with a repeating structure (Mark *et al.,* 1992). Once again, it was the insolubility of the polymer in all known solvents and its hydrolytic instability in the atmosphere that discouraged a more serious interest in this material.

This situation persisted until the mid 1960s when a series of three papers by Allcock, Kugel and Valan were published. The theme of these papers was as follows.

The hydrolytic instability of “inorganic rubber” might be utilized as its principal advantage. The hydrolytic sensitivity implied a high reactivity of the P-Cl bonds, a characteristic that might be translated into reactions that could be used to replace chlorine atoms by hydrolytically stable organic groups. Thus, the halogenophosphazene high polymer might be used as a macromolecular reactive intermediate, providing access to a very broad range of stable organic derivative polymers.

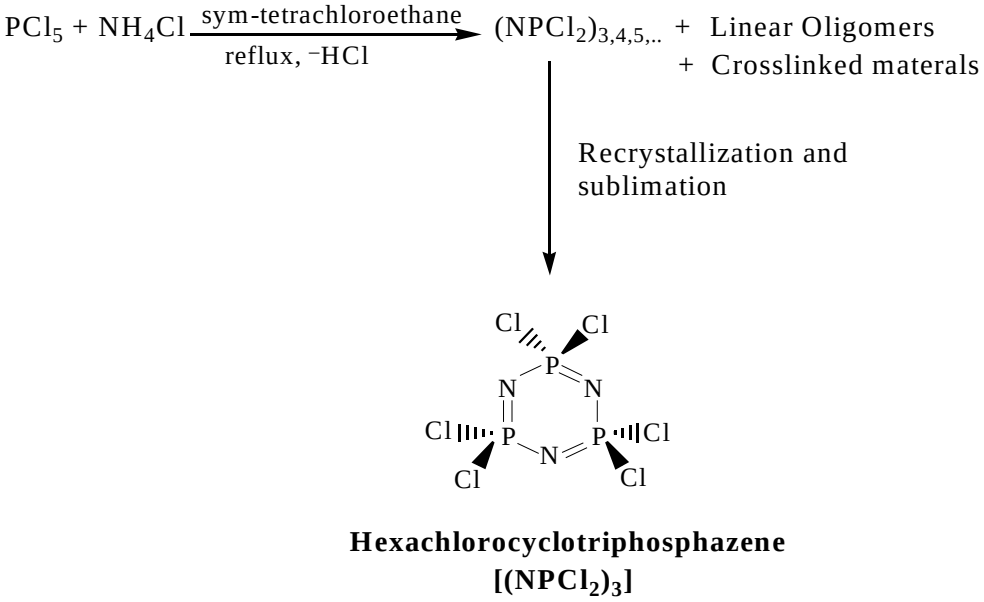
It was known that Stokes’s polymer swelled in organic solvents such as benzene, but it did not dissolve (Allcock, Kugel and Valan, 1966). This is a characteristic of a cross-linked polymer. Reactions carried out on this swollen polymer provided encouragement for the idea of chlorine replacement reactions, but the substitutions were never complete because of the insolubility. Thus, a critical need existed for a polymerization process that would yield an uncross-linked polymer. It was during a mechanistic study of the polymerization of hexachlorocyclotriphosphazene that the answer was found. Careful control of the time, temperature and trimer purity and termination of the reaction before it reached a stage of 70% polymerization, yielded an essentially linear

high polymer, $(NPCl_2)_n$ that dissolved completely in organic solvents such as benzene, toluene or tetrahydrofuran. Further heating of this polymer caused cross-linking of the chains and yielded the insoluble “inorganic rubber” described by Stokes.

When dissolved in a suitable solvent, poly(dichlorophosphazene) was found to behave as a remarkable macromolecular reactant (Allcock and Kugel, 1966). Treatment with organic nucleophiles such as the sodium salts of alcohols, or phenols, or with primary or secondary amines, brought about total replacement of the chlorine atoms by the organic units. These derivative polymers proved to be hydrolytically stable and to possess a broad range of unusual, interesting and useful properties. In later years, this synthesis route has been used to prepare several hundred different types of polyphosphazenes.

1.3 Cyclotriphosphazene

Hexachlorocyclotriphosphazene $[(NPCl_2)_3]$ is the most widely used starting material in phosphazene chemistry. This material is prepared on industrial scale by the interaction of phosphorus pentachloride (PCl_5) with ammonium chloride (NH_4Cl) in an organic solvent such as chlorobenzene or tetrachloroethane, as depicted in Figure 1.3 (Al Shukri, 2003).



Hexachlorocyclotriphosphazene
$[(NPCl_2)_3]$

Figure 1.3 A route for the preparation of hexachlorocyclotriphosphazene, (Al Shukri, 2003)

The balls and sticks representation of the structure of $(NPCl_2)_3$ is shown in Figure 1.4, (Bullen, 1971). Crystallographic data also show that the P–N bonds are all equal in length, *ca*. 1.581 Å (158.1 nm) and the P–Cl bond lengths range from 1.991- 1.995 Å (199.1 – 199.5 nm). The chlorine atoms of $(NPCl_2)_3$ can be readily replaced with a wide variety of groups via nucleophilic substitution reaction.

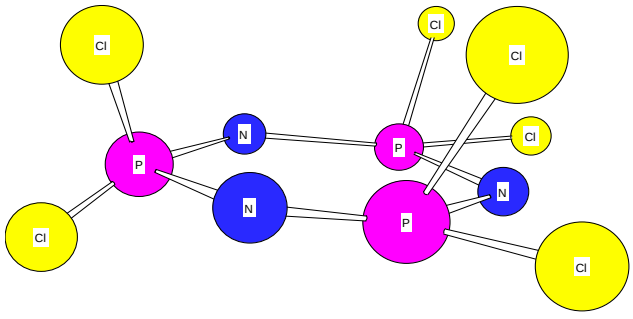


Figure 1.4 Balls and sticks representation of the molecular structure of $(NPCl_2)_3$, (Bullen, 1971)

Figure 1.5 depicts some of the reported nucleophilic substitution reactions involving $(NPCl_2)_3$ and different organo-nucleophiles affording different **organocyclotriophosphazenes** (Gleria and De Jaeger, 2001).

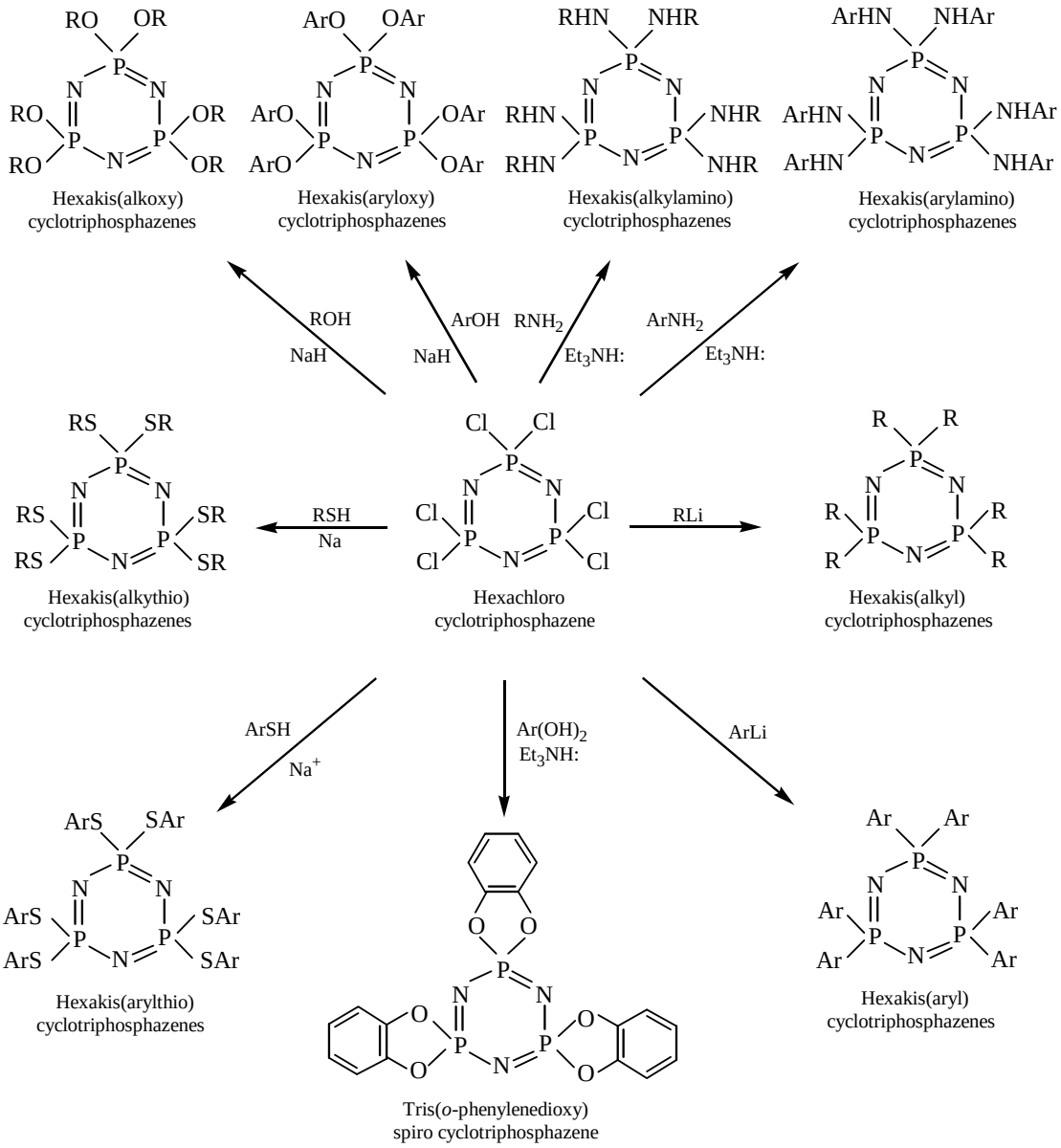


Figure 1.5 Synthesis of some organocyclotriphosphazenes, (Gleria and De Jaeger, 2001)

1.4 Polyphosphazene

Some of the most rapid advances in inorganic polymer research and technology are occurring in the field of phosphazene polymers. The polymers are a versatile class of hybrid organic-inorganic materials that have many remarkable properties. Soluble and hydrolytically stable phosphazene polymers have a variety of uses, including as membranes for the removal of water from aqueous solutions, for organic separations, and as solid polymer electrolytes. They may be formed as water-soluble high polymers, or as non-flammable fluids. Because of the presence of alternating phosphorus and nitrogen atoms in the backbone, polyphosphazenes are inherently flame retardant and exhibited high thermal stability (Kumar *et al*., 1993a,b,c; Lu and Hamerton, 2002). Polymerization of phosphazene material potentially can be performed to yield three distinct backbone structures: **linear**, **cyclolinear** and **cyclomatrix.**

1.4.1 Linear Polyphosphazene

The linear polyphosphazenes have been the most extensively studied. The synthesis of linear polyphosphazene involves a two step process. The first step involves the thermal ring opening polymerization of a cyclic trimer, hexachlorocyclotriphosphazene in the melt at 250 ^{o}C, to form the linear high molecular weight polymer, poly(dichlorophosphazene). This route was perfected by Allcock and Kugel in 1965 by carefully controlling the time and temperature of the ring opening polymerization. The intermediate, poly(dichlorophosphazene) is unstable due to the highly reactive phosphorus-chlorine bonds present in the polymer (Laurencin and Nair, 2003). Consequently, the polymer hydrolyzes rapidly upon exposure to atmospheric moisture, to form phosphoric acid, ammonia and hydrochloric acid. The second step in the

synthesis is the macromolecular substitution reaction which involves the replacement of the reactive chlorine atoms of poly(dichlorophosphazene) with hydrolytically stable nucleophiles such as alkoxy, aryloxy or amino groups. The synthesis of the first hydrolytically stable, high molecular weight linear polyphosphazene was reported by Allcock et al in 1966. Different classes of polyphosphazenes have been synthesized so far by replacing the chlorine atoms of poly(dichlorophosphazene) by alkoxides/aryoxides, primary/secondary amines and organometallic reagents. The different synthesis routes are as depicted in Figure 1.6.

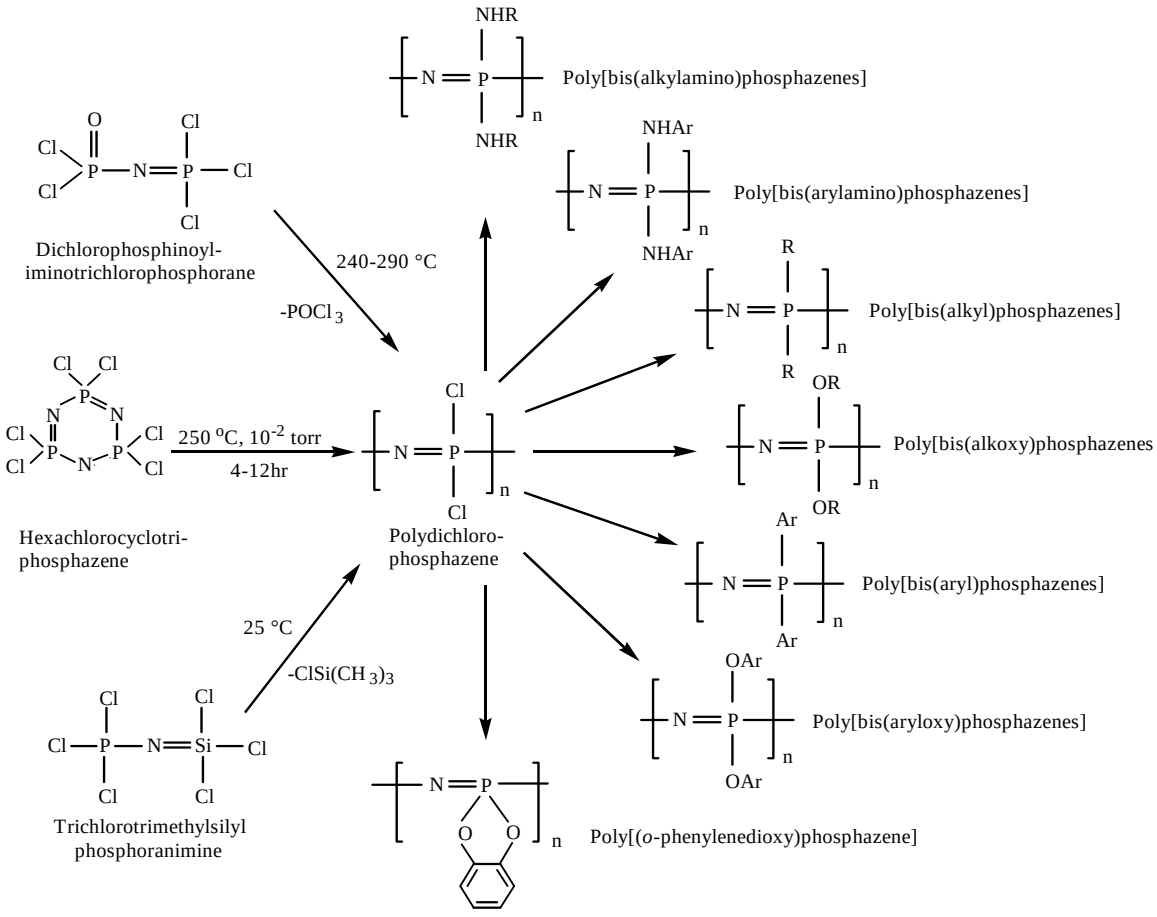


Figure 1.6 Synthesis of some linear poly(organophosphazenes) (Al Shukri, 2003)

In 2000, Ravi Kumar reported on the applications of polyphosphazene derivative as controlled drug delivery devices. Allock and co-workers (Allcock *et al.,* 1991, 1994 and 1997) developed derivatives of the phosphazene polymers suitable for biomedical applications. PEO-coated nanoparticles of the poly(organophosphazenes) containing amino acid, have been prepared and the chemical structures as depicted in Figure 1.7.

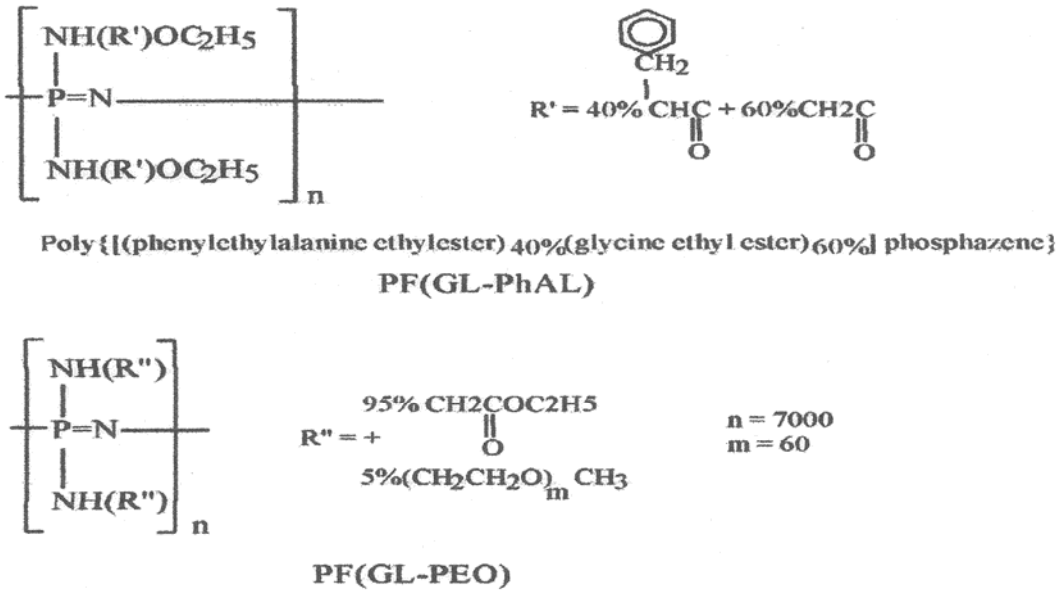


Figure 1.7 Polyphosphazenes for medical applications (Ravi Kumar, 2000)

In 2003, Laurencin and Nair reported some preliminary studies on polyphosphazene nanofibers for biomedical applications. By combining the advantages of nanoscale fibers with the unusual property profile available with polyphosphazenes, novel materials with excellent properties can be developed. Biodegradable polyphosphazenes such as amino acid ester polyphosphazenes are perhaps the most extensively investigated polyphosphazenes for biomedical application. One of the active areas of research in biomedical field is in developing controlled drug delivery systems

(Laurencin and Nair, 2003). Several biodegradable polyphosphazene drug conjugates were developed, in which drugs such as naproxen have been immobilized and released in a controlled manner by the hydrolytic degradation of the backbone. Biodegradable polyphosphazenes due to the non-toxic and neutral degradation products and other versatile properties could form a potential candidate for developing nanofiber based scaffolds for tissue engineering (Li *et al.,* 2002).

Wolf *et al.* reported the application of a novel biodegradable polymer, poly (2-dimethylamino ethylamino)-phosphazene for use in non-viral gene delivery to tumors (Wolf *et al.*, 2005).

In 2005, Maher and Allcock have reported the synthesis of co-substituted polyphosphazenes via the sequential addition of sodium hexoxide and sodium trifluoroethoxide to poly(dichlorophosphazene). This order of reaction was used to prevent displacement of trifluoroethoxy side groups, already linked to the polymer chain, by sodium hexoxide. The reaction is depicted in Figure 1.8. A wider range of compositions (10 % or higher hexoxy units) may be useful as elastomers in aqueous environments, and possible applications as biomedical materials are foreseen.

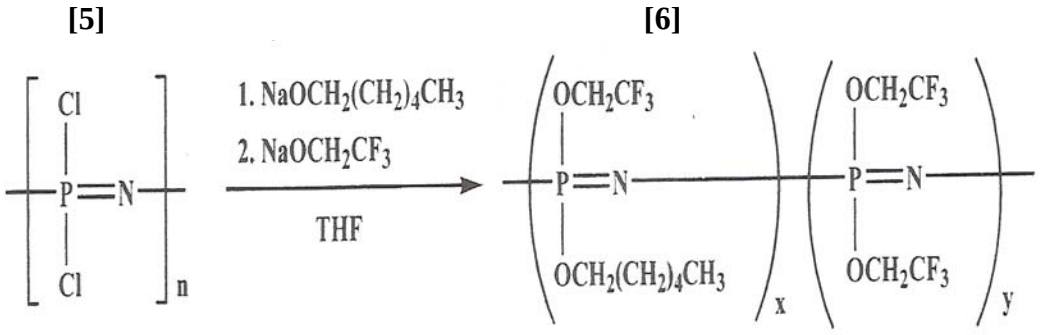


Figure 1.8 Synthesis of Co-substituted Polyphosphazenes (Maher and Allcock, 2005). The 'n' refers to the number of repeat units of the dichlorophosphazene monomer in the poly(dichlorophosphazene), while 'y' refers to the number of repeat units of the copolymer block of poly[bis(trifluoroethoxy)phosphazene] and 'x' refers to the number of repeat units of the copolymer block with the hexoxy side group.

Bhattacharyya reported the development of nanofibers from a biodegradable and biocompatible polyphosphazene, poly[bis(ethyl alanato)phosphazene] by electrospinning (Bhattacharyya *et al.,* 2006). These nanofiber matrices could find a number of biomedical applications including issue engineering and drug delivery.

In 2005, Andrianov *et al.* have reported on the preparation of novel water-soluble biodegradable polyphosphazenes, to mimic the structure of poly(vinylpyrrolidone), PVP (Andrianov *et al.,* 2005). Poly{di[2-(2-oxo-1-pyrrolidinyl)ethoxy]-phosphazene}, PYRP, [7] and its co-polymers containing biologically active carboxylatophenoxy side groups have been synthesized, as depicted in Figure 1.9. Mixed substituent copolymers containing ionic moieties, [8], CP1: CP2, poly{[2-(2-oxo-1-pyrrolidinyl)ethoxy](4-carboxylatophenoxy) phosphazene} and PCPP, [9], poly[di(carboxylatophenoxy)-phosphazene] were also synthesized.

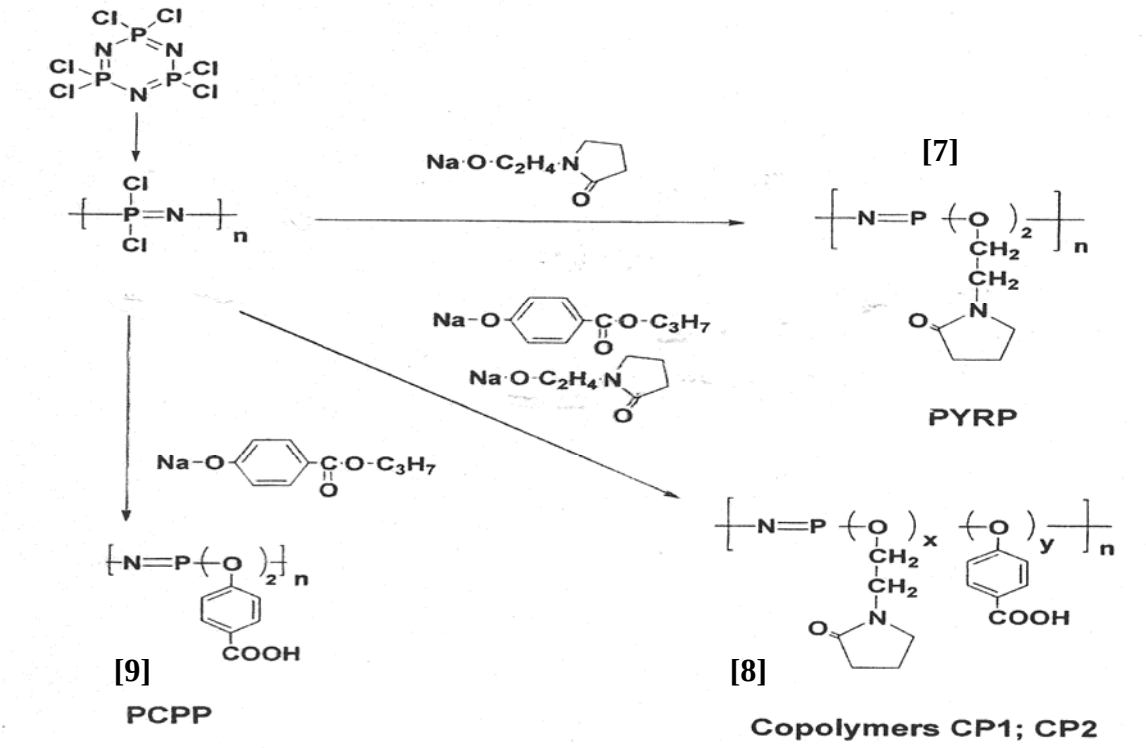


Figure 1.9 Synthesis of N-Ethylpyrrolidone Containing Polyphosphazenes and PCPP (Andrianov *et al.*, 2005). The 'x' refers to number of repeat units for the copolymer block of PYRP, while 'y' refers to the number of repeat units for the copolymer block of PCPP and 'n' refers to number of repeat units of copolymers CP1: CP2.

Orme *et al.* reported the application of polyphosphazenes as membranes for gas and liquid separations (Orme *et al.,* 2005). Specific ratios of differing pendant groups were placed on the phosphazene backbone, with the objective of demonstrating the control of solubility, chemical selectivity and the effects on gas transport properties.

1.4.2 Cyclolinear Poly(cyclotriphosphazenes)

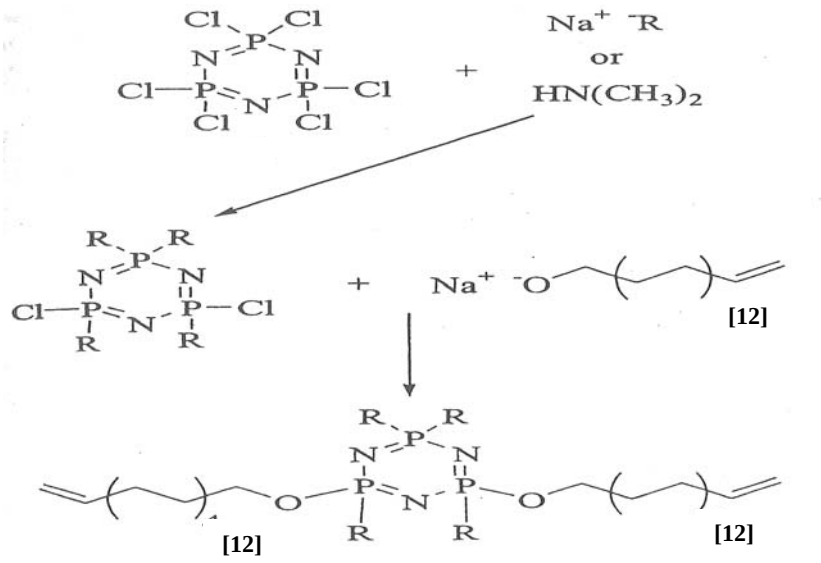
Cyclolinear poly(cyclotriphosphazenes) are polymers containing cyclotriphosphazene as part of the backbone structure. Cyclolinear structures have been least studied among the phosphazene polymers, due to the complexity of the synthesis. Two requirements must be met for the synthesis of polymers of this type (Mark *et al.*, 1992).

(a) The cyclophosphazene must have only 2 functional sites (usually P-Cl bonds).

(b) A difunctional linkage molecule is needed to form the chain. Aromatic or aliphatic diols or their sodium salt or diamines can serve this purpose.

In 2001, Allcock *et al.* reported a new method for the synthesis of cyclolinear organic-inorganic polymers with phosphazene rings in the main chain structure by the use of acyclic diene metathesis (ADMET) polymerization. In their work, cyclic phosphazene trimers bearing two non-geminal alkene chains were prepared. Both of the alkene chains have a terminal double bond that together form the diene structure required for ADMET polymerizations. The remaining four substituents were varied to include phenoxy, benzyloxyphenoxy, methoxyethoxyethoxy and dimethylamino groups. The resultant polymers are well-defined, low-polydispersity materials with phosphazene cyclic trimers uniformly incorporated into the backbone structure.

Four different small molecule cyclic phosphazene trimers bearing different organic groups were prepared with the diene structure required for the ADMET monomers. The reaction is as depicted in Figure 1.10.



[10], [11], [12]

[10] R = O O CH_2

[11] R = O

[12] R = O O O

[13] R = $N(CH_3)_2$

Figure 1.10 Synthesis of Acyclic Diene Metathesis (ADMET) Monomers (Allcock *et al.*, 2001)

ADMET polymerizations are driven by the elimination of ethylene under reduced pressure. All the polymerizations were carried out with the addition of the classical Grubbs catalyst as depicted in Figure 1.11.

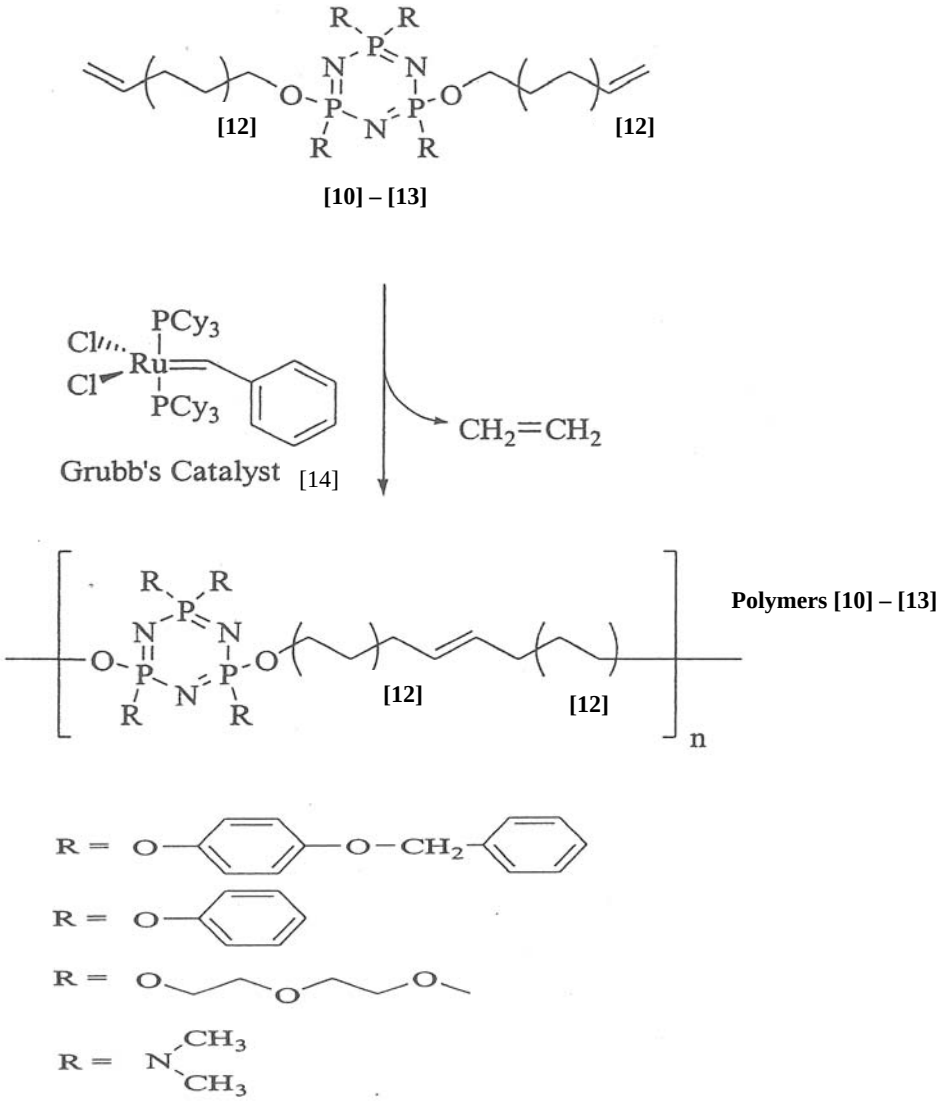
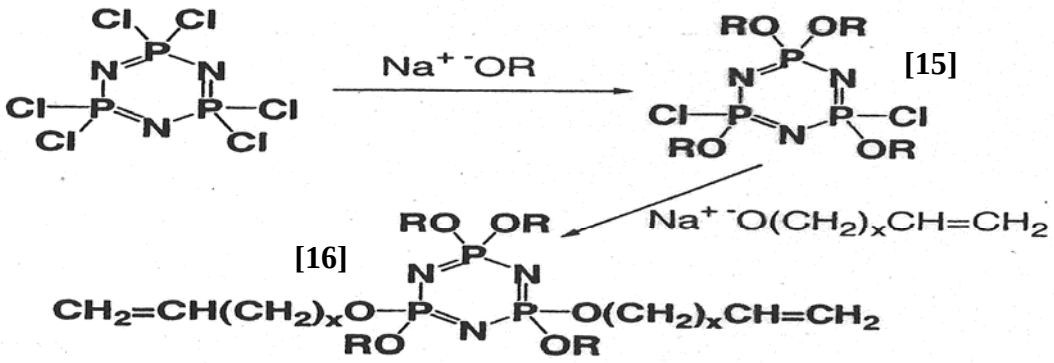


Figure 1.11 General Synthesis of ADMET Polymers (Allcock *et al.*, 2001)

Further studies on ADMET polymerization have been reported (Allcock and Kellam, 2002). This work extends the range of propertiesachievable in cyclolinear phosphazenes synthesized via ADMET and provides an assessment of the synthetic limitations. In that studies by Allcock and Kellam, a series of tetraphenoxy and tetramethoxyethoxyethoxy functionalized phosphazene trimers have been synthesized. The alkene chains vary in length from three carbons to 11 carbons. This has allowed the

influence of the negative neighboring group effect to be examined as well as steric factors.

The synthesis of monomers is depicted in Figure 1.12. The starting material, hexachlorocyclotriphosphazene was treated with either sodium phenoxide or sodium methoxyethoxymethoxide to yield a mixture of cyclic phosphazenes with four or five substituents.



OR = OPh

x	Monomer
1	3
2	4
3	5
4	6
8	7
9	8

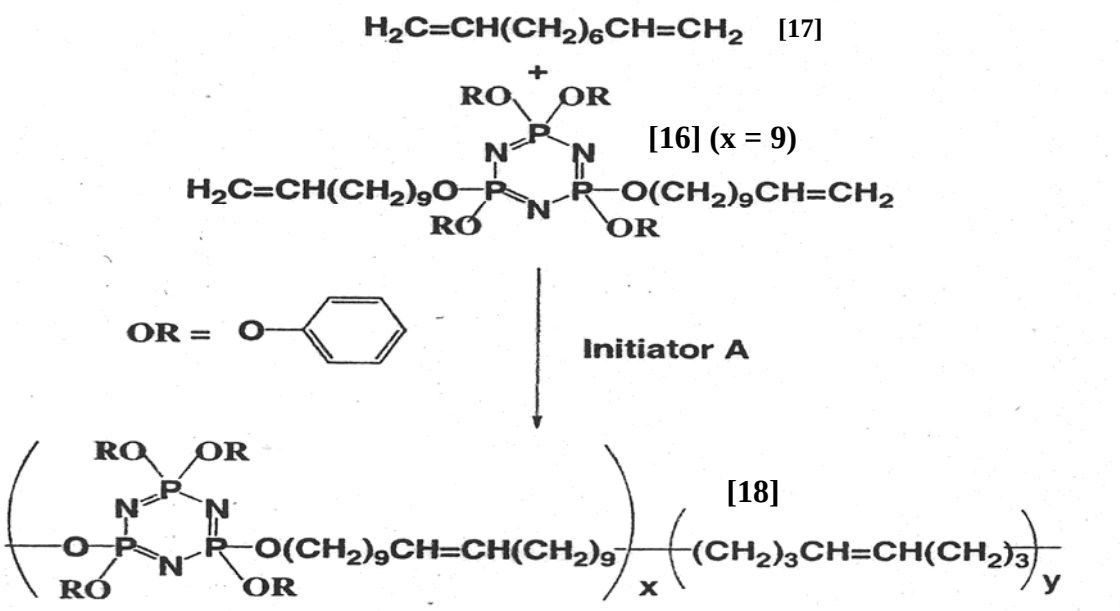
OR = $OCH_2CH_2OCH_2CH_2OCH_3$

x	Monomer
1	10
2	11
3	12
9	13

x refers to the number of repeat units of methylene group and determine the length of the olefinic side group.

Figure 1.12 Synthesis of Phosphazene Monomers (Allcock and Kellam, 2002)

The monomers were polymerized with the use of Grubbs catalyst through the reaction as depicted in Figure 1.13.



OR = OPh

x refers to number of repeat units of phosphazene derivatives forming the copolymer block

y refers to the number of repeat units of octene forming the copolymer block

Figure 1.13 Synthesis of Copolymers of 1,9-Decadiene and Monomer (Allcock and Kellam, 2002)

1.4.3 Cyclomatrix Poly(cyclotriphosphazenes)

Cyclomatrix poly(cyclotriphosphazenes) are polymers containing cyclotriphosphazene as part of a three-dimensional structure. Cyclomatrix polymer is formed when the cyclotriphosphazene precursor molecule has more than 2 reactive sides. These materials are reported to have very high thermal stability as a result of the three-dimensional framework of cross-links.

A polyester containing cyclomatrix phosphazenes have been synthesis and patented in United States in June 2002 by Stewart, Luther and Harrup (Stewart *et al.*, 2002). This

invention provided a method for using cyclomatrix phosphazene as a subunit in phosphazene-containing polyester molecules. A feature of this invention is the trimeric structure of the cuclomatrix phosphazene comprising a core, an aromatic region surrounding the core and an aliphatic moiety directed away from the core. The reactions are depicted in Figure 1.14 and 1.15, while the polyester obtained is depicted in Figure 1.16.

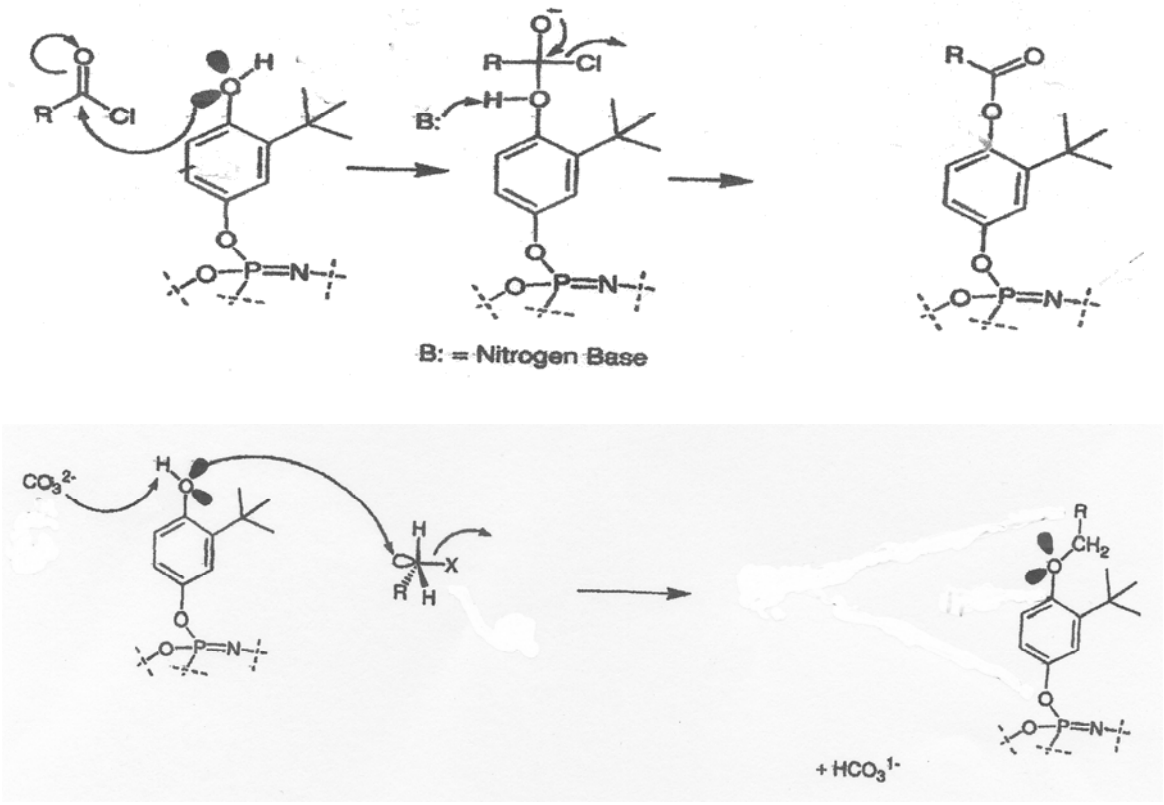


Figure 1.14 Esterification Processes of Trimer Sub-units (Stewart *et al.*, 2002)

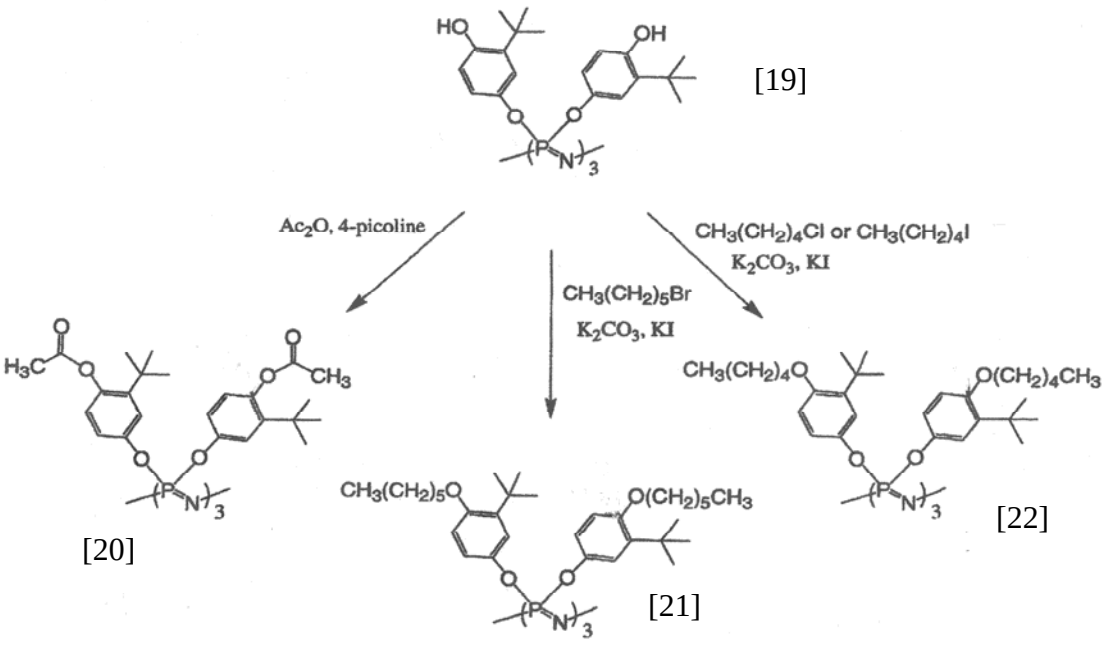


Figure 1.15 Phosphazene Sub-units Used for Creating the Invented Polyesters (Stewart *et al.*, 2002)

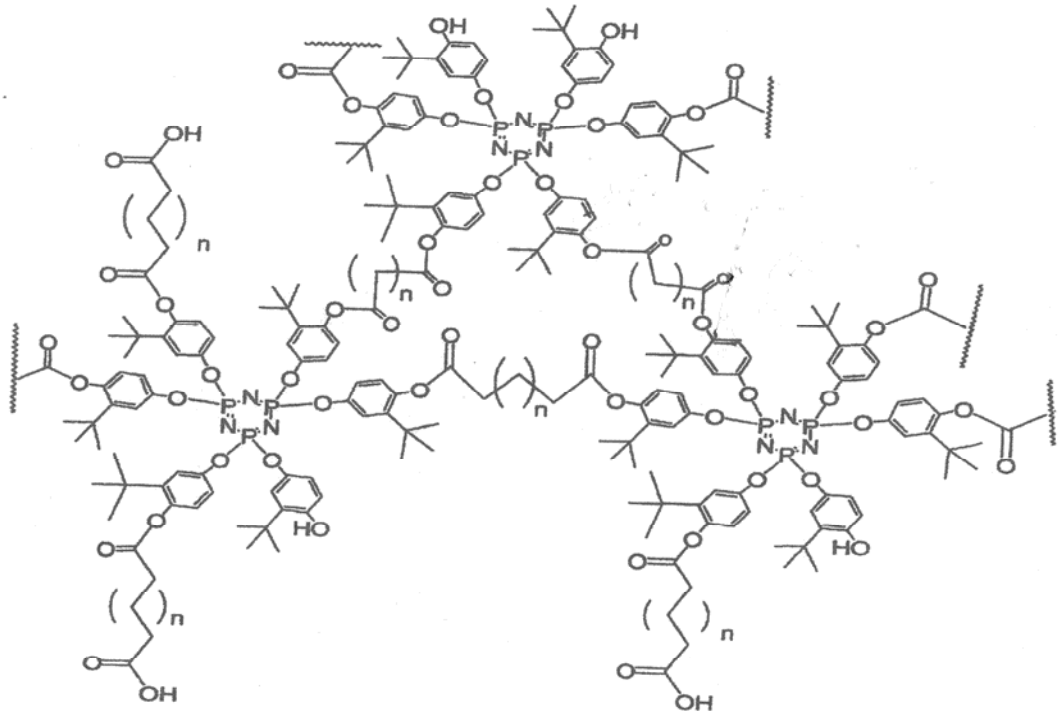


Figure 1.16 Polyester formed via reaction of tertbutyl phosphazene sub-units with diacid chlorides (Stewart *et al.*, 2002). The 'n' refers to the number of carbon atoms in length and can be designed with minimum of 2 carbon atoms or up to maximum of 20 carbon atoms.

The product is fully soluble in common polar organic solvents such as acetone and tetrahydrofuran, and therefore can be used as thin films in applications such as membranes. This invention discloses new pathways for the synthesis of soluble cyclomatrix polymers.

Fu *et al.,* (2008) have reported a method for preparation of a multi-walled carbon nanotubes (MWCNTs) cyclomatrix-type polyphosphazenes, poly(cyclotriphosphazene-co-4,4'-sulfonyldiphenol) nanocables based on a hard template mechanism. The synthesis is as shown in Figure 1.17. The synthesis method involves polymerization of the co-monomers, cyclotriphosphazene and 4,4'-sulfonyldiphenol through condensation.

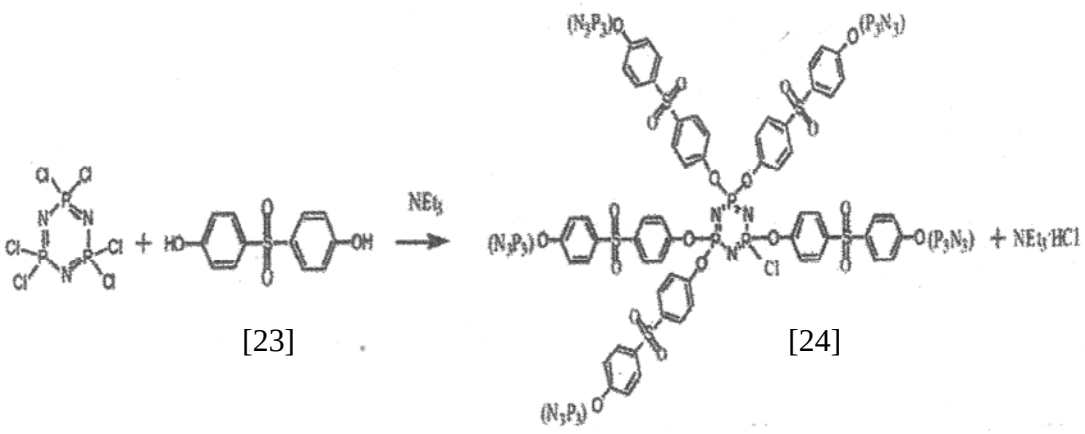


Figure 1.17 Polycondensation of co-monomers, cyclotriphosphazene and 4,4'-sulfonyldiphenol (Fu *et al.,* Supplementary Material, 2008)

1.5 Organic Polymers with Cyclotriphosphazenes as Pendant Groups

Most organic polymers have poor fire retardant properties. Once ignited, they usually burn with an uncontrollable flame to completion under normal atmospheric conditions. The presence of phosphorus and nitrogen provide protection against burning of the material. Thus organic polymers that contain cyclotriphosphazene have a much lower flammability than their counterparts in which phosphazene is absent (Mark *et al.*, 1992). One approach is to synthesis organic polymers that have cyclotriphosphazene units bound chemically as pendant groups or side groups to the organic chain. Incorporation of cyclotriphosphazenes as pendant groups to the backbone of organic polymers is an approach of considerable interest to both the academic and industrial sectors for preparing organic-inorganic hybrid polymers with markedly improved flame retardancy. Cyclotriphosphazenes can be attached to organic polymers via either a Phosphorus-Oxygen (P–O) or a Phosphorus-Carbon (P–C) bond.

Example of cyclotriphosphazenes attached to organic polymers by Phosphorus-Oxygen (P–O) bond is as shown in Figure 1.18, This polymer is prepared by polymerization of vinyl monomer (Mark *et al.*, 1992).

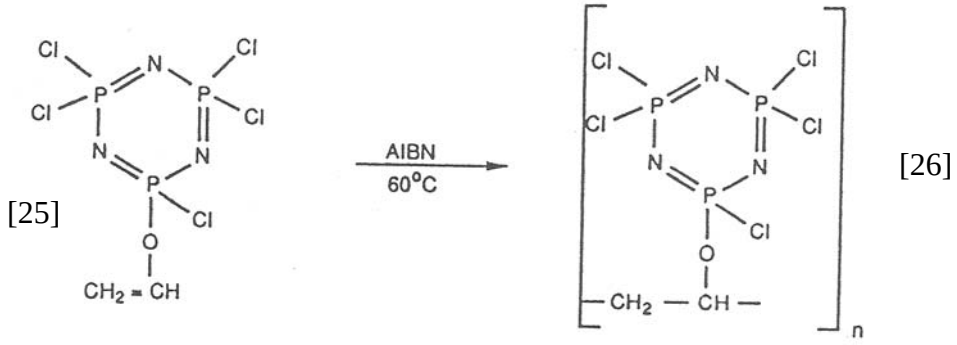


Figure 1.18 Cyclotriphosphazenes attached to organic polymers (Mark *et al.*, 1992)

In 2001, Brown *et al.* reported on the homopolymerization of both the monovinyloxypentachlorocyclotriphosphazene and the heptachlorocyclotetraphosphazene under conditions of radical initiation leads to polymers having cyclotriphosphazene and cyclotetraphosphazene ring as substituent on a carbon-carbon backbone. The reaction is depicted in Figure 1.19. The resulting, air stable, materials are soluble in a broad range of organic solvents and are easily cast into thin films, which are inflammable in simple flame tests.

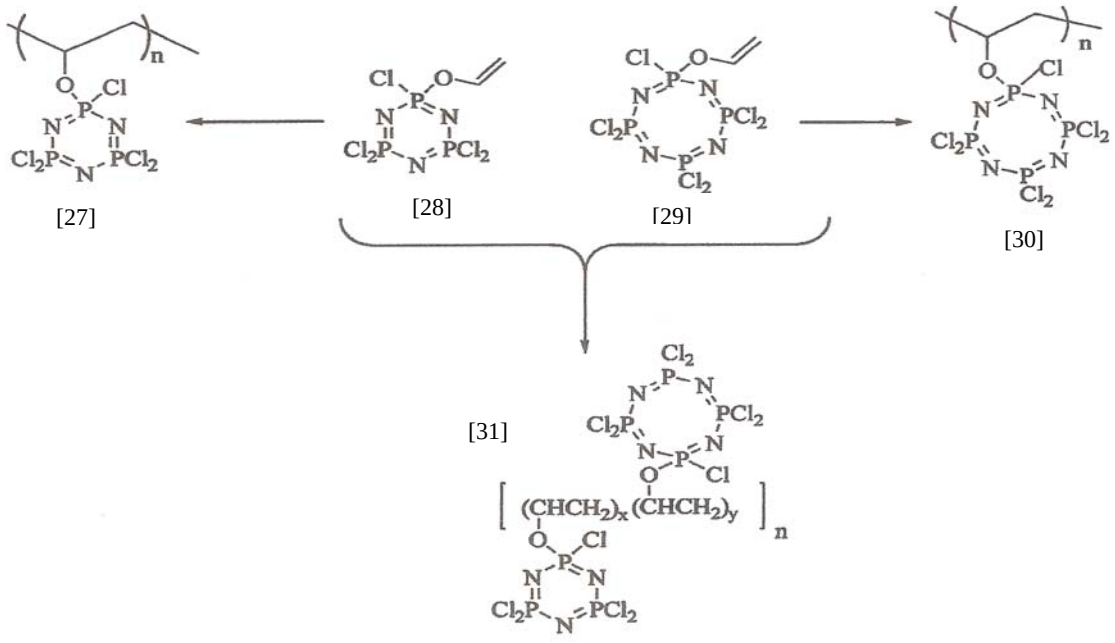


Figure 1.19 Polymerization of monovinyloxypentachlorocyclotriphosphazene and heptachlorocyclotetraphosphazene (Brown *et al.*, 2001)

Copolymerization represents another approach to elucidation of the behavior of the olefinic center in vinyloxycyclophosphazenes (Brown *et al.*, 2001). The formation of a series of copolymers is reasonable in light of the expected electronic similarity between the two monomers. Chlorocyclotri- and tetraphosphazenes with a vinyloxy substituent

are converted to high molecular weight homo and copolymers by radical addition polymerization.

In 2001, Allcock *et al.,* reported on the preparation of polystyrene and poly(methyl methacrylate) copolymers with cyclophosphazene pendant groups by the reaction of azidocyclophosphazenes with diphenylstyrylphosphine residues in the copolymer structures. The reactions are depicted in Figure 1.20 and Figure 1.21.

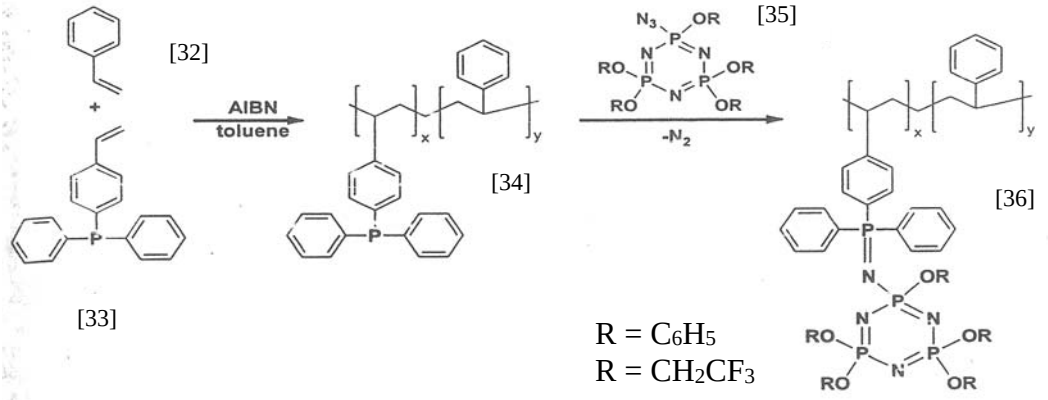


Figure 1.20 Preparation of polystyrene copolymers with cyclophosphazene pendant groups (Allcock *et al.,* 2001)

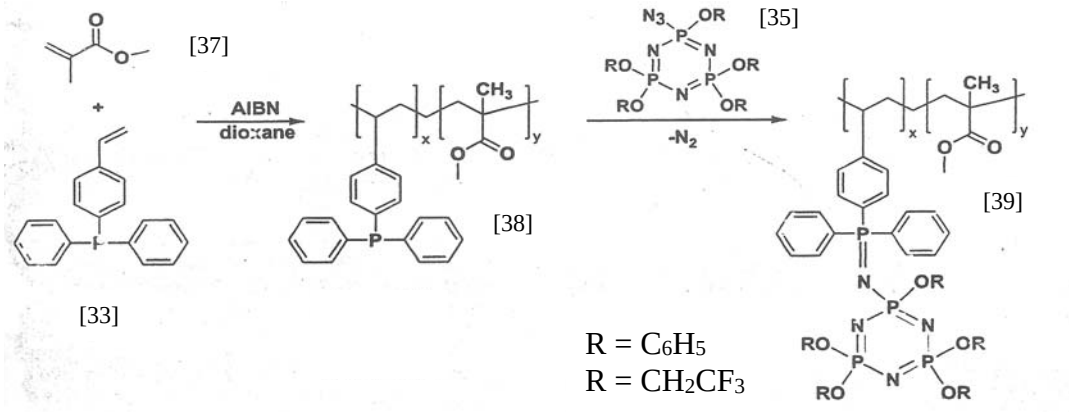


Figure 1.21 Preparation of poly(methyl methacrylate) copolymers with cyclophosphazene pendant groups (Allcock *et al.*, 2001)

Pendant phosphazene cyclic trimers inhibit the thermal degradation of polystyrene by increasing the char yield at high temperatures through cross-linking reactions. The fire resistance of polystyrene is improved, and the aryloxy phosphazene is more effective than trifluoroethoxy phosphazene in this system.

In 2005, Allcock *et al.*, reported on the synthesis of novel polyoctenamers with pendant functionalized cyclotriphosphazenes as amphiphilic lithium ion conductive membranes. Two different types of monomer units, one with oligoethyleneoxy cation coordination pendant groups and the other with hydrophobic fluoroalkoxy pendent groups were prepared. The synthesis route employed to produce the monomers is shown in Figure 1.22. Nucleophilic replacement of the chlorine atoms by the appropriate sodium alkoxide was carried out to obtain single-substituent monomers.