SYNTHESIS AND CHARACTERIZATION OF CHLORINE-FREE POLYCYCLOTRIPHOSPHAZENE AS ADHESIVE FOR GLASS

by

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DEDICATION

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LIST OF ABBREVIATIONS AND SYMBOLS

Starting Materials and Products:

BPA	2,2-di(*p*-hydroxyphenyl)propane
$(NPCl_2)_3$	Hexachlorocyclotriphosphazene
Et_3N	Triethylamine
$Et_3N.HCl$	Triethylamine hydrochloride
P1	Chlorine-bound poly[2,2-di(*p*-hydroxophenyl)propane]-cyclotriphosphazene
P2	Chlorine-free poly[2,2-di(*p*-hydroxophenyl)propane]cyclotriphosphazene.

Symbols:

BTEAC	Benzyltriethlyammonium chloride
cm	Centimeter
$CDCl_3$	Deuterated chloroform
DMAC	Dimethylacetamide
DMSO-d	Deuterated Dimethyl Sulfoxide
DTG	Derivative Thermogravimetry
EMA	Ethylmethylamine
EU	European Union
FSPA	Fire Safe Polymeric Adhesive
FT-IR	Fourier Transform Infrared
FT-NMR	Fourier Transform Nuclear Magnetic Resonance
g	Gram
HepG2	Hepatocellular carcinoma
M_n	Molecular weight
Max	Maximum
Min	Minute
MTT	Methyl tetrazolium
NMR	Nuclear Magnetic Resonance
ppm	Part per million
PVC	Polyvinylchloride

PSt	Polystyrene
PMMA	Poly(methyl methacrylate)
PYRMP	Biodegradable polyphosphazene (PYRMP) containing *N*-ethoxypyrrolidone and methoxyethoxyethoxy side groups
PYRP	Poly{bis[2-(2-oxo-1-pyrrolidinyl)-ethoxy]-phosphazene}
RoHS	Restriction of Hazardous Substances
S-1	Hexachlorocyclotriphosphazene
S-2	Hexakis(4-hydroxymethylphenoxy)
S-3	Hexakis(4-hydroxyphenoxy)cyclotriphosphazene
S-4	Hexakis(3,4-methylenedioxyphenoxy)cyclotriphosphazene
S-5	Hexakis[4-(diphenylphosphoroxymethyl)phenoxy]cyclotriphosphazene
S-6	Hexakis[4-(diphenylphosphoroxy)phenoxy]cyclotriphosphazene
S-7	Hexakis(4-methoxymethoxyphenoxy)cyclotriphosphazene
Tg	Glass Transition Temperature
TG	Thermal Gravimetry
TGA	Thermal Gravimetric Analysis

SINTESIS DAN PENCIRIAN POLISIKLOTRIFOSFAZENA BEBAS KLORIN SEBAGAI PEREKAT UNTUK KACA

ABSTRAK

Perekat berasaskan polimer fosfazena tanpa halogen telah disintesis melalui dua langkah yang berlainan. Langkah pertama melibatkan tindakbalas antara heksaklorosiklotrifosfazena dan bisfenol A dengan kehadiran trietilamina kontang yang menghasilkan, selepas pemencilan dan penulenan, polimer pepejal berwarna kuning muda yang dirujuk sebagai P1 (poli[2,2-di(*p*-hidroksofenil)propana]siklotrifosfazena berklorin). Dalam langkah kedua, P1 ditindakbalaskan dengan etil 4-hidroksibenzoat bagi memperolehi pepejal berwarna putih yang dirujuk sebagai P2 (poli[2,2-di(*p*-hidroksofenil)propana]siklotrifosfazena tanpa klorin). Kedua–dua tindakbalas tersebut dijalankan di dalam 1,4-dioksana tulen dalam atmosfera nitrogen kontang. Pencirian P1 dan P2 dilakukan dengan spektroskopi transformasi Fourier "infrared" (FT-IR), spektroskopi transformasi Fourier "Nuclear Magnetic Resonance" (NMR) dan teknik yang mengandungi pencantuman dua system "Thermo gravimetric analyzer dan FT-IR spectrometer" (TGA-FTIR). P2 didapati tidak berbau, stabil terma, tidak mudah terbakar dan kemungkinan besar tidak bertoksik. Bila dilebur dan diletakan di antara dua kepingan kaca, ia akan membentuk satu lapisan perekat lutsinar. Sifat perekat P2 dikaji dengan mengunakan mesin tensil yang dipasang dengan alat penentuan kekuatan perengangan yang direkabentuk khas dengan mengikut speksifikasi tertentu. Sebagai contoh, pengunaan P2 sebanyak 0.50 g memberikan daya perengangan sebanyak 10907.50 N, daya ketegangan sebanyak 11.9 MPa dan tenaga sebanyak 3.38 J pada

muatan maksimum bagi memecahkan ikatan yang kuat disebabkan oleh P2 ke atas kepingan kaca. Untuk memahami sifat perekat P2, 0.25 g P2 dikaji dengan sifat perekat 0.15 g super glue (etil sianoakrilat) yang boleh didapati secara komercial dan didapati sifat perekat P2 adalah selaras dengan permintaan pasaran. Tetapi kelebihan P2 berbanding dengan super glue atau sebarang perekat berasakan epoksi adalah ia bebas daripada komponen iritasi seperti sebatian organik mudah meruap atau hasil penyulingan petroleum. Selanjutnya, sifat perekat P2 boleh dikitarbalikan: permukaan-permukaan yang dilekat dengan lapisan P2 dapat dinyahlekat berulang kali dengan lapisan yang sama. Sifat boleh kitarbalikan ini adalah amat berguna semasa memasang dan memindah penal-penal yang mudah pecah seperti kepingan kaca.

SYNTHESIS AND CHARACTERIZATION OF CHLORINE-FREE POLYCYCLOTRIPHOSPHAZENE AS ADHESIVE FOR GLASS

ABSTRACT

The halogen-free phosphazene-based polymeric adhesive was synthesized via two separate steps. The first step involved the reaction of hexachlorocyclotriphosphazene with bisphenol A in the presence of dried triethylamine that afforded, after isolation and purification, a slightly yellowish solid polymer that is designated as P1 (chlorine-bound poly[2,2-di(*p*-hydroxophenyl)propane]cyclotriphosphazene). In the second step, P1 was reacted with ethyl 4-hydroxybenzoate to obtain a white solid polymer that is designated as P2 (chlorine-free poly[2,2-di(*p*-hydroxophenyl)propane]cyclotriphosphazene). Both reactions were conducted in purified 1,4-dioxane under atmosphere of dried nitrogen. P1 and P2 were characterized by means of Fourier transformed infrared (FT-IR) spectroscopy, ^{1}H and ^{31}P Fourier transformed Nuclear Magnetic Resonance (NMR) spectroscopy, and a hyphenated system comprising Thermo gravimetric analyzer and FT-IR spectrometer (TGA-FTIR). P2 is found to be odorless, thermally stable, non-flammable and likely to be non toxic. When melted and placed in between two pieces of glass, it formed a layer of transparent adhesive. The adhesive properties of P2 were evaluated by using a tensile machine fixed with a custom made shearing fixture to measure its shear strength. For example, usage of 0.50 g of P2 provided an excellent result of 10907.50 N of shearing force, 11.19 MPa of stress and 3.38 J of energy at maximum load to break the strong bond affected by P2 between the glass plates. To

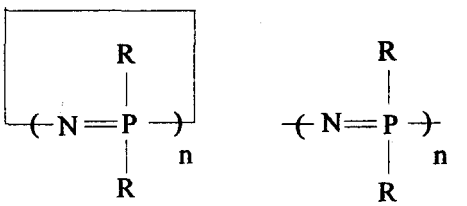
further understand the level of adhesive properties of P2, the result of 0.25 g P2 in glass plates were matched with that of 0.15 g result of super glue (ethyl cyanoacrylate) available commercially. It is concluded that P2 does have a good adhesive properties which is concurrent to the market demands. However, unlike the super glue or any typical epoxy-based adhesive, P2 is free from irritants such as volatile organic compounds or petroleum distillates. Furthermore, the adhesive properties of P2 are reversible: bonded surfaces can be unglued and reglued with the same layer of P2 repeatedly as desired for the purpose of dismantling and transporting shatterable panels such as glass plates.

CHAPTER 1

INTRODUCTION

1.1 Phosphazenes

Phosphazenes are compounds that contain the following unit : $-(N=P(R)_2)_n$, whereby the R group can be organic, organometallic, inorganic or a combination of organic and inorganic groups. They can be prepared as cyclic [1] and linear [2] as shown in Figure 1.1 (Allcock, 1972 ; Mark *et al.*, 1992).



[1] [2]

Figure 1.1 Representation of cyclic [1] and linear [2] phosphazenes

The repeating unit, n for the cyclic is in the range of 3 – 40 (Caminade and Majoral, 1994) and for the linear can be quite large, for example n = 15,000 (Allcock and Kugel. 1965 ; Oakley *et al.*,1985). The basis of the phosphazene notation is parallel to that of carbon, where C–C is alk**ane**, C=C is alk**ene** and C≡C is alk**yne.** The phosphorus – nitrogen compounds that have the repeating unit of H_2N-PH_4 is phosphaz**anes**, $HN=PH_3$ is phosphaz**enes** and $N\equiv PH_2$ is phosphaz**ynes** (Allcock, 1972).

1.2 Literature review

The earliest phosphazene compounds to be synthesized were the chlorophosphazenes, $(NPCl)_n$, which were prepared by the interaction of phosphorus pentachloride with ammonia. This reaction was first studied by Liebig, Wohler and Rose in 1834. The principal reaction product was phospham, $(NPNH)_n$, although Liebig and Wohler isolated a small amount of what appears to have been hexachlorocyclotriphosphazene, $(NPCl_2)_3$. This compound was a white crystalline (Allcock, 1972).

In 1895, Stokes first suggested a cyclic structure of $(NPCl_2)_3$. He also identified a series of higher cyclic homologues, $(NPCl_2)_{4-7}$ and described the thermal polymerization of chlorophosphazenes to inorganic rubber and the subsequent depolymerization of this at higher temperatures and reduced pressures. Since, 1950 there has been an almost explosive increase in research on the substitution of halophosphazenes. During this time, there has been a steadily rising demand by the aerospace industry and other organizations for new and unusual polymers. Three important lines of research have evolved in the polymeric field that are, investigation of polymerization and depolymerization reactions of linear and cyclic species, the synthesis of linear and high molecular weight organophosphazene polymers and the development of cross-linked cyclomatric polymers (Allcock, 1972).

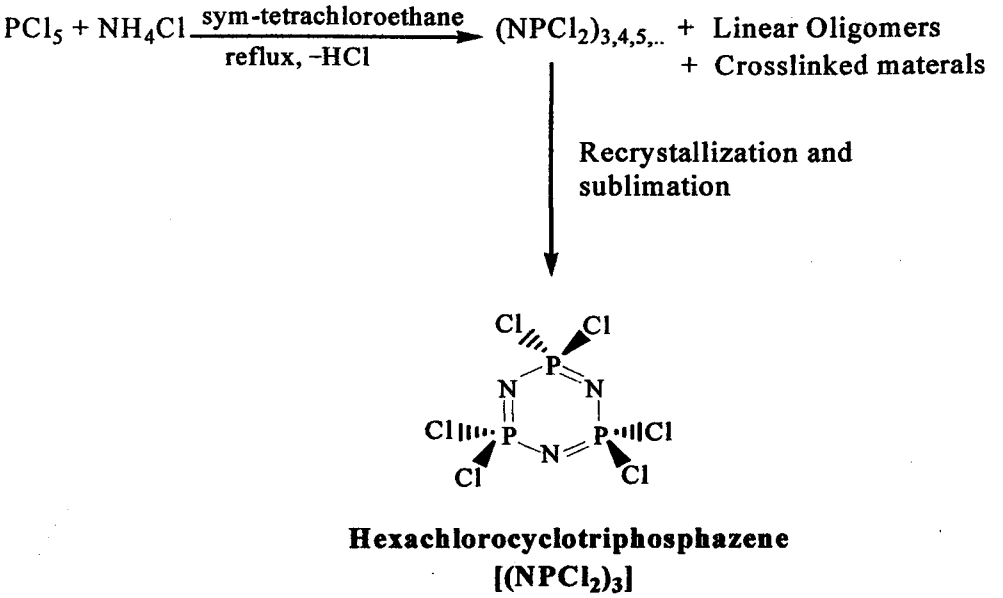
1.2.1 Cyclotriphosphazene

Cyclotriphosphazenes behave as biologically active materials as a result of their antitumor, insect chemostreilant, pesticide and fertilize activities, show potential

applicability as flame retardant additives for cellulose materials, synthetic fibers, textiles, polyurethanes and several different commercial organic macromolecule with a considerably high limiting oxygen index, clathrates for solvent separation or stereoregulated free- radical polymerization and temperature resistant fluid (De Jaeger and Gleria, 1998).

They have been used as pendants, crosslinking agents and additives in an effort to improve thermal properties of organic polymers (Chang, Ji, and Han, 1994). These are imparted mainly by the presence of nitrogen and phosphorus atoms in the ring.

For the synthesis of cyclotriphosphazenes, hexachlorocyclotriphosphazene $[(NPCl_2)_3]$ is the versatile starting material. Hexachlorocyclotriphosphazene $[(NPCl_2)_3]$, can be synthesized from the reaction of phosphorus pentachloride (PCl_5) with ammonium chloride (NH_4Cl) in boiling sym-tetrachloroethane or chlorobenzene (Figure 1.2). Pure $(NPCl_2)_3$ can be obtained from the crude mixture of products by recrystallization and sublimation. $(NPCl_2)_3$ is a white crystalline solid. It melts at 114 °C. $(NPCl_2)_3$ is soluble in polar and non-polar organic solvents. The chloro which are linked to the phosphorus atoms can be replaced with varieties of functional groups via nucleophilic substitution reaction (Allcock, 1972; Gleria and De Jaeger, 2001; Lu and Hamerton, 2002). Figure 1.3, derives some of the reported nucleophilic substitution reactions involving $(NPCl_2)_3$ and different organo-nucleophiles affording different organocyclotriphosphazenes (Gleria and De Jaeger, 2001).



Hexachlorocyclotriphosphazene
$[(NPCl_2)_3]$

Figure 1.2 Preparation of hexachlorocyclotriphosphazene

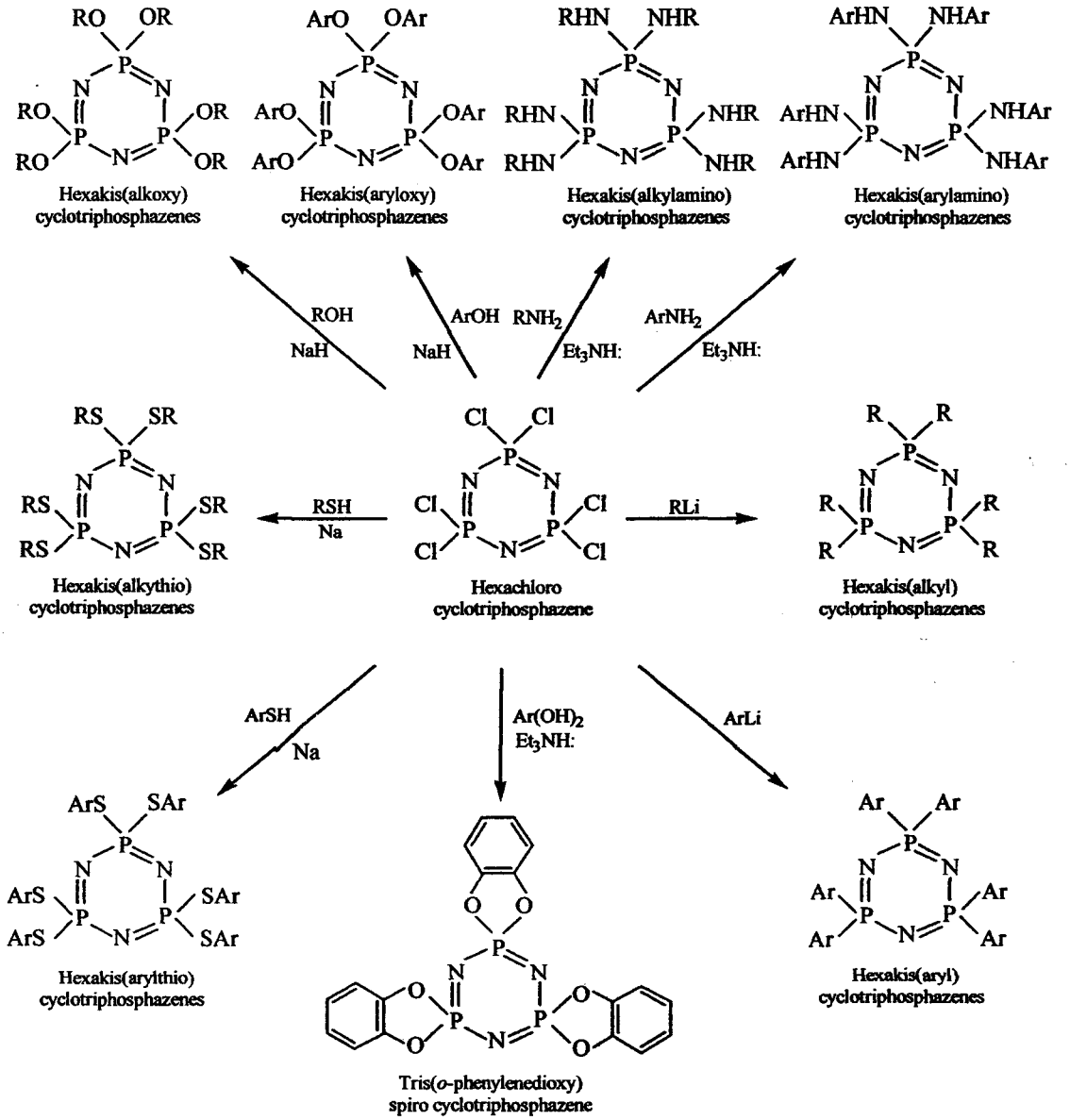


Figure 1.3 Synthesis of some organocyclotriphosphazenes (Gleria and De Jaeger, 2001).

Researchers Muraki *et al.,* 2004, had researched on the enhancement of the thermal stability of polystyrene (PSt) and poly(methylmethacrylate) (PMMA) by blending it with cyclotriphosphazene derivatives (S-3 to S-7). Figure 1.4 outlines the preparation of the organic cyclotriphosphazenes (S-3 to S-7) prepared as stabilizers. The thermal

decomposition of these compounds occurred in the temperature range of 191 -376 °C. For the polymer- stabilizer blend system, high compatibility of stabilizers is an essential requirement for a good physical retention of the additive in a polymer. The effects of S-3 to S-7 on thermal stability of PSt and PMMA were estimated by thermogravimetric analysis in nitrogen and air. The thermal stabilizing ability of the phosphazene derivatives on PSt increased in the following order S-5 (396 °C) > S-6 (386 °C) > S-4 (377 °C) > MOP (376 °C) > S-7 (371 °C). The thermal stabilizing ability of the phosphazene derivatives on PMMA increased in the following order S-3 (272 °C) > MOP (271 °C) > S-4 (269 °C) > S-5 (260 °C)> S-7 (257 °C) > S-6 (244 °C).

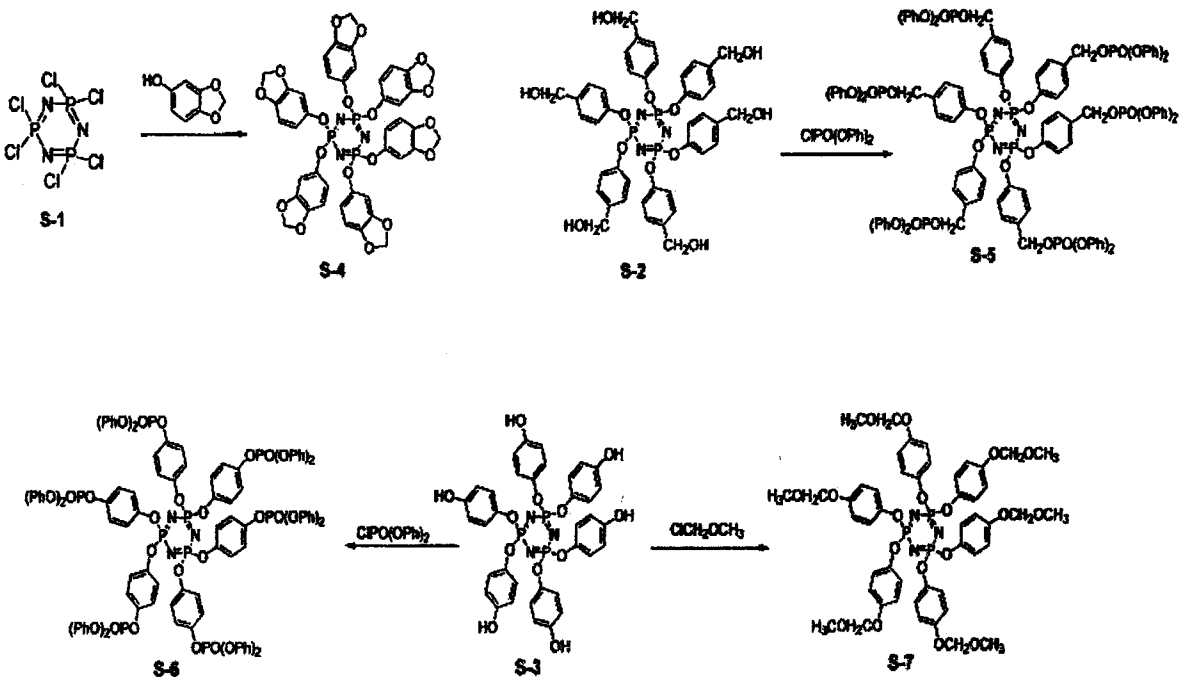


Figure 1.4 Preparation of cyclotriphosphazene-based stabilizers (Muraki *et al.*, 2004)

1.2.2 Polyphosphazene

The field of polyphosphazene consists of a broad range of hybrid inorganic-organic macromolecules, all of which are based on a repeating motif alternating phosphorus and nitrogen atoms, with two organic units attached to each phosphorus (Allcock, 2006). Types of polyphosphazene structures as shown in Figure 1.5 comprise the linear polyphosphazenes [3 and 4], comb-type polyphosphazenes [5 and 6], rings in main chain consist of cyclophosphazene units which are linked together via linkage groups affording either cyclolinear [7] or cyclomatrix [8] poly(cyclophosphazenes) and finally the branched polyphosphazenes [9 and 10] (Murray, 2006 ; Allcock, 2006).

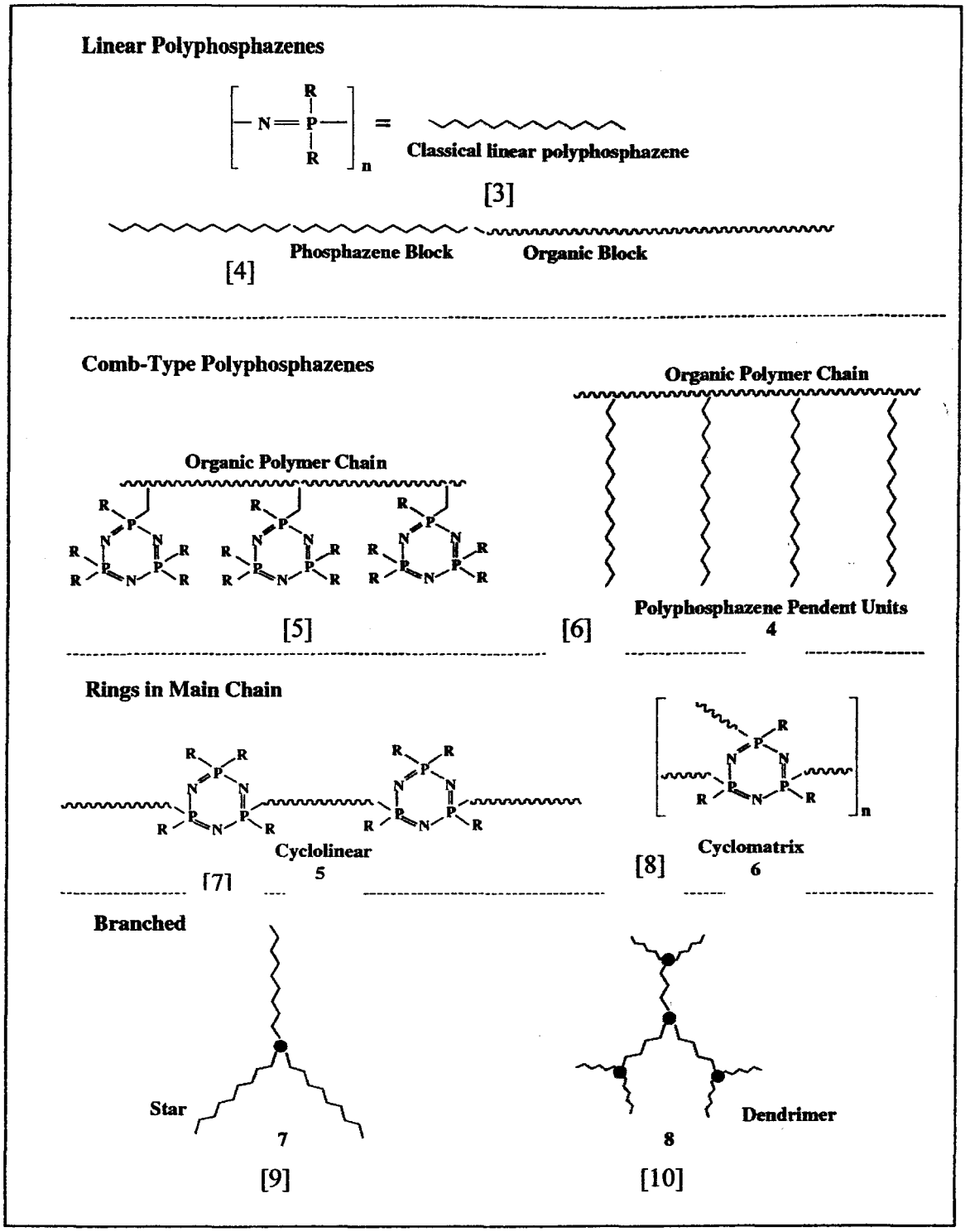


Figure 1.5 Types of polyphosphazene (Allcock, 2006)

1.2.2.1 Linear Polyphosphazenes

Linear polyphosphazenes have a general structure as shown in Figure 1.5, [3]. They are produced by the thermal or catalytic polymerization of cyclic oligomers, followed in many cases, by substitution of halogen ligands by organic, organometallic, inorganic or a combination of organic and inorganic groups (Allcock, 1972).

More than 700 phosphazene polymers and copolymers are described in the literature (Figure 1.6) covering a wide range of practical applications with properties ranging from those of elastomers to glasses (Kireev *et al.*, 1981; Allcock *et al.*, 1996; Vinogradova *et al.*, 1998), from water soluble to hydrophobic polymers (Chang *et al.*, 1994; Stewart *et al.*, 1997; Lee *et al.*, 2002), from bioinert to bioactive materials (Allcock *et al.*, 1982, 1992; Inoue, 1994; Qiu, 2002; Lakshim *et al.*, 2003; Luten *et al.*, 2003), from electrical insulators to conductors (Mark *et al.*, 1992; Yang-Chen *et al.*, 1997; Allcock *et al.*, 1998; Allcock; Kellam, 2003) and from soluble linear copolymer to insoluble crosslinked polymers (in form of both full-IPNs or semi-IPN system) (Inoue, *et al.*, 1993; Visscher *et al.*, 1990; Allcock *et al.*, 1996).

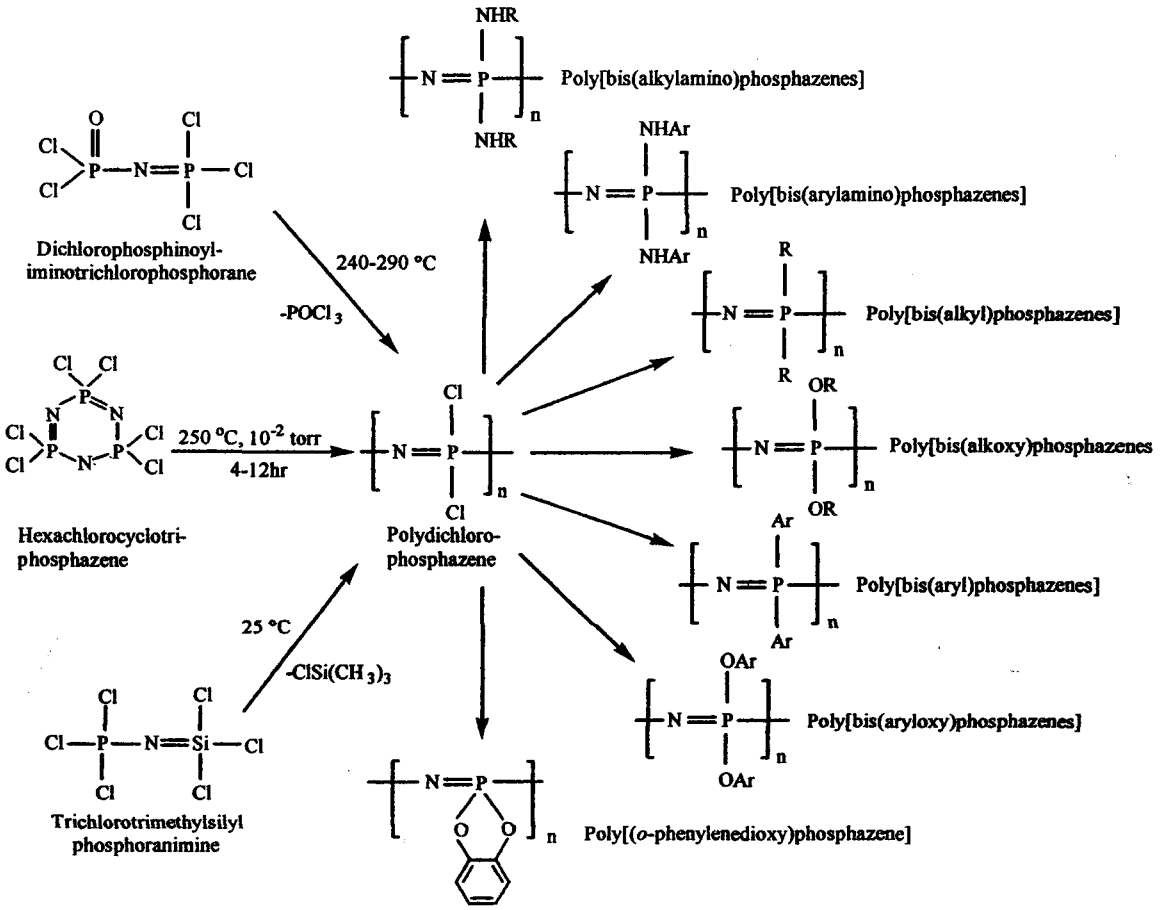


Figure 1.6 Synthesis of some linear poly(organophosphazenes) (Al-Shukri, 2003)

It has been shown that the surface character of this polymer can be altered drastically by environmental plasma treatment (Allcock *et al.*, 2007). Environmental plasma operates at atmospheric pressure and is a convenient method for small scale and medium scale surface modifications. Thus, fluoroalkoxy-phosphazene films and nanofibers have been surface modified with plasmas of CH_4, CF_4, O_2 and N_2 to introduce new functional group at the surface and alter the water contact angels from 5 °C to 151 °C. The use of this technique is to control mammalian cell or microbial adhesion (Allcock, 2006).

One of the most significant developments in recent years have been the access to block copolymers provided by the living cationic condensation polymerization, especially macromolecules in which a polyphosphazene block is linked to an organic polymer or organosilicon block. These include phosphazene blocks with hydrophobic side groups (CF_3CH_2O-, C_6H_5O-, etc) linked to hydrophilic organic polymer blocks such as poly(ethylene oxide), or phosphazenes with hydrophilic side units (such as $CH_3OCH_2CH_2OCH_2CH_2O$-) linked to hydrophobic organic or organometallic polymers such as polystyrene or poly(dimethylsiloxane). These amphiphiles self assemble into micelles that are of interest as drug delivery vehicles in aqueous media and into diverse solid state phase-separated materials, some with unique surface properties (Allcock, 2006).

1.2.2.2 Comb-Type copolymers

In addition to block copolymers, it is possible to synthesize a variety of different macromolecules with either cyclic or linear phosphazenes forming the side groups linked to an organic polymer chain. This type of polymer is possible to be produced in the form of polynorbornenes that bear pendent cyclotriphosphazene side units by using ring opening metathesis polymerization methods as illustrated in Figure 1.7. The organic groups attached to the phosphazene rings can be introduced by chlorine replacement either before or after ring opening metathesis polymerization reactions. If introduced in the final step, a much wider range of side groups and properties are possible because the organic substituent can be chosen without regard to their influence on the ring opening

metathesis polymerization reactions catalyst. Polymers of this type have been investigated extensively for the uses as lithium ion conductors in both rechargeable lithium batteries and lithium seawater batteries and as proton conductors in fuel cell membranes (Allcock, 2006).

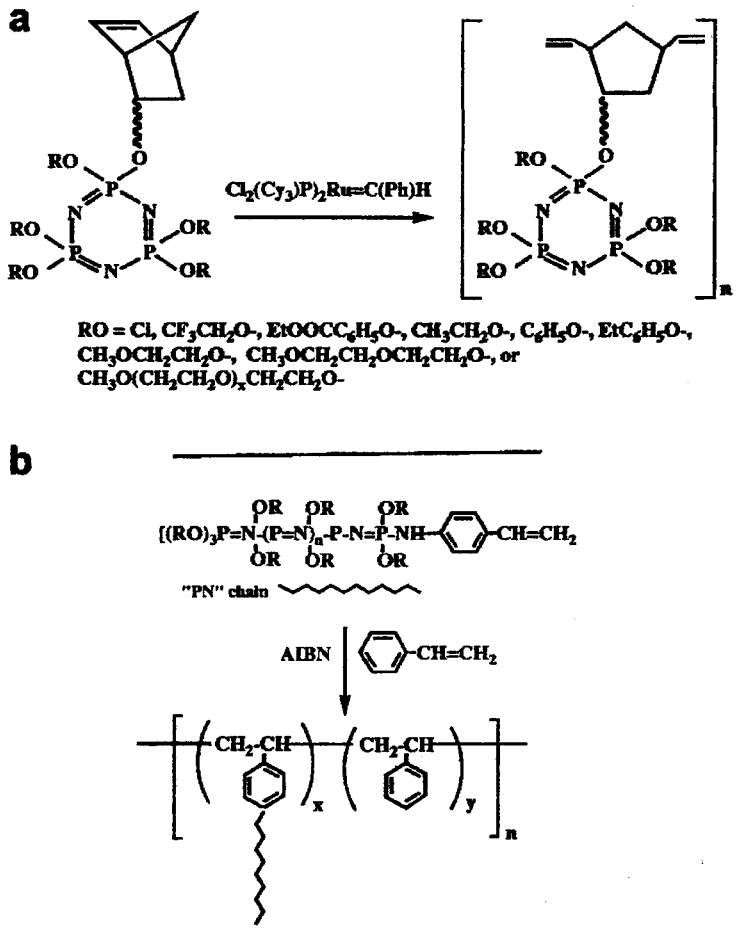


Figure 1.7 Synthesis of comb-type polymers with (a) polynorbornene backbone and cyclic phosphazene side units, and (b) polystyrene with linear phosphazene side groups (Allcock, 2006).

1.2.2.3 Rings in main chain

The six membered phosphazene rings is a uniquely stable and functional entity. In addition enhancing the properties of linear organic polymers through its role as a side group, it can also contribute to the properties of an organic polymer by forming part of the main polymer chain. Two types of these polymers are cyclolinear polycyclotriphosphazenes and cyclomatrix polycyclotriphosphazenes.

1.2.2.3.1 Cyclolinear Polycyclotriphosphazene

Cyclolinear polycyclotriphosphazenes are the focus of this research work. These are prepared by linking together cyclic oligomeric systems by means of difunctional reagents. A typical cyclolinear polycyclotriphosphazene is shown in Figure 1.8. The properties of cyclolinear phosphazene polymers depend upon the nature of the linking group (R'), the nature of the substitution (R) on the cyclophosphazene ring and the polymer backbone structure (R_f) formed by the reaction of the two monomers.

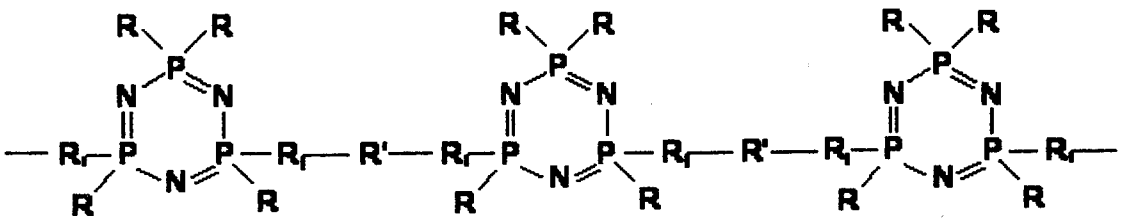


Figure 1.8 Cyclolinear polycyclotriphosphazene

The cyclolinear phosphazene polymers generally have thermoplastic characteristics. In general, the thermoplastic cyclolinear phosphazene polymers are much more thermally

stable than polyorganophosphazenes and possess higher glass transition temperature (T_g > 170 °C). This can be attributed to the presence of the thermodynamically stable cyclophosphazene ring as an integral part of the polymer chain. Cyclolinear phosphazene polymers provide a unique combination of intrinsic properties such as chemical and dimensional stability and resistance to heat and fire, solvents, atomic oxygen, and UV and visible radiation. Cyclolinear phosphazene polymers are suitable for making high performance films and can be processed into composites, laminates and moldings (Salamone , 1996).

Miyata *et al.* (1996) had performed research on cyclolinear phosphazene polymers. Two types of synthesis of polyesters containing cyclotriphosphazene units, [12] have been reported, these are by phase transfer catalyzed two-phase polycondensation and direct polycondensation. The polycondensation of the *trans*-acid chloride, [11] and bisphenol A in the presence of benzyltriethylammonium chloride (BTEAC) as phase transfer reagent afforded a polyester with molecular weight (M_n) of 22,000. An oligomer (M_n = 3,000) was obtained if, the *cis*-acid chloride was used, as shown in Figure 1.9. Based on this result, Miyata *et al.* (1996) concluded that the *trans*-isomer is favorable for effective growth of the polyester. The direct polycondensation using $SOCl_2$ / pyridine and tosyl chloride systems gave only low molecular weight polyesters (M_n = 4,000 - 7,000) even when the *trans*-acid chloride was used.

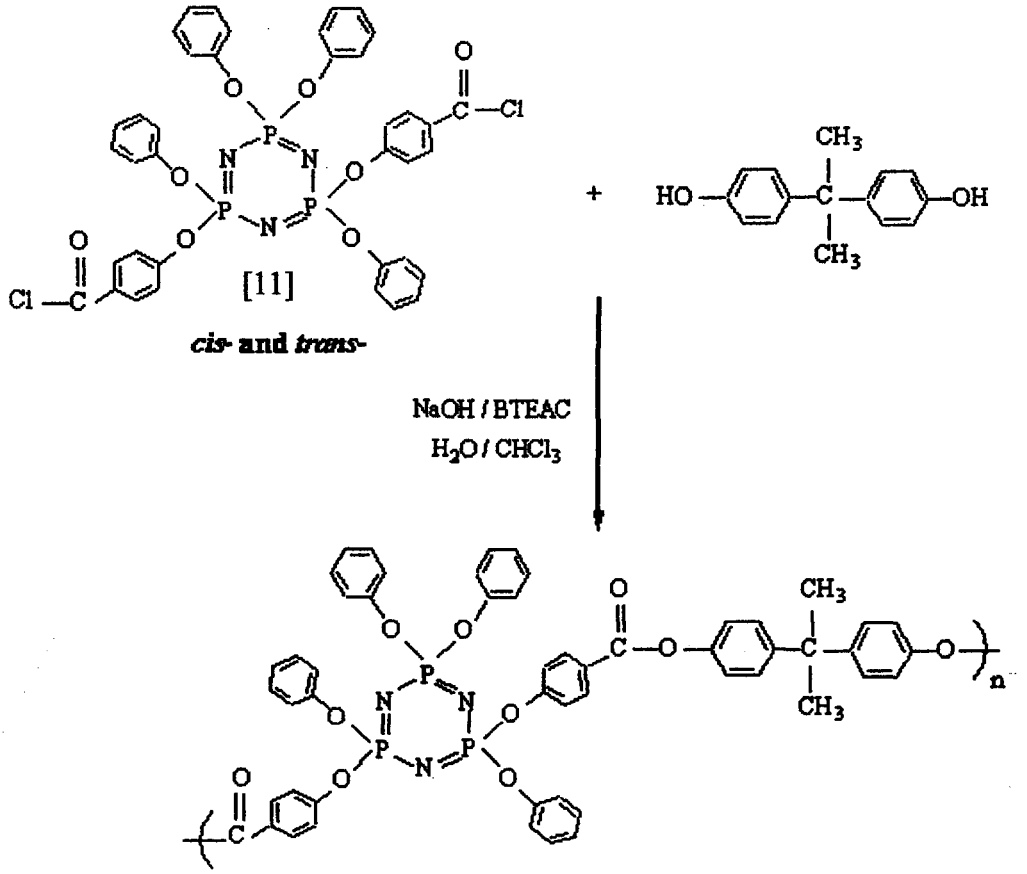


Figure 1.9 Synthesis of polyester-cyclolinear poly(cyclotriphosphazenes)

They also prepared various copolymers (M_n = 13,000 – 25,000) by copolycondensation of bisphenol A with *trans*-[11] and terephthalic acid. The thermal behavior of the polyesters and copolyesters was evaluated by DSC and TGA. The T_g of the polyester prepared from *trans*-[11] and bisphenol A was 65 °C, which was significantly low, compared to that of the copolyesters (T_g in the range of 91 – 220 °C, depending on the contents of *trans*-[11] units). The low T_g value of the homopolymer is attributed to the large degree of conformational freedom than normally present in conventional polyesters. The homopolyester was stable up to 390 °C in a nitrogen atmosphere, and the char yield of copolymer with 5.5 mol % of *trans*-[11] unit was 36 % at 600 °C,

which was seven times higher than that of the polyester without cyclotriphosphazene units. They also noted that the presence of *cis*-[11] units in the polyesters lowered the initial decomposition temperature (e.g. that containing 30 mol % of *cis*-[11] started to decompose at around 330 °C in nitrogen atmosphere), but not the char yields.

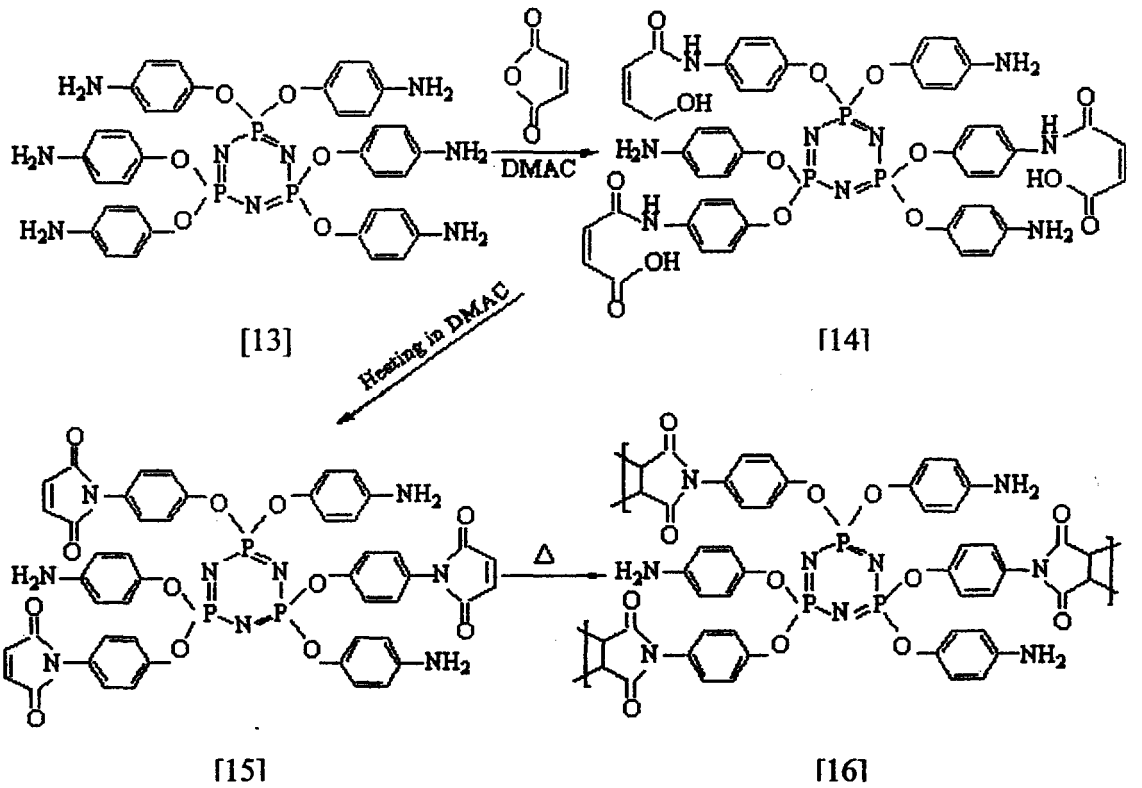
1.2.2.3.2 Cyclomatrix Polycyclophosphazenes

Cyclomatrix phoshazene polymers (Figure 1.5, [8]) are synthesized by chain extension or crosslinking of multifunctional cyclophosphazenes. These polymers are useful in structural applications in the form of coatings, adhesives, composites and laminates. Suitably, synthesized cyclomatrix phosphazene polymers exhibit useful thermal and chemical properties such as fire retardancy at high temperature, resistance to solvents, atomic oxygen and oxygen plasma attack. In addition, the synergism of the phosphorus – nitrogen combination in the form of cyclotriphosphazene offers improved oxidative thermal decomposition and high anaerobic char yields. Also, selection of cyclotriphosphazenes often flexible synthetic methodologies for the preparation of cyclotriphosphazenes with various substituents. It is therefore possible to accomplish molecular design and synthesize multifunctional initiators, terminators, polymer precursors and intermediates (Salamone , 1996).

A key step in development of cyclomatrix phosphazene polymers is to synthesize a cyclophosphazene derivative end-capped with suitable functional group (usually more than two) polymerizable by thermal, photochemical or other reactions. The thermal or photochemical addition polymerization of the suitable end-cap is preferred to minimize

the formation of volatiles during the thermosetting processing step because the liberated volatiles will otherwise cause voids, resulting in poor thermomechanical properties in the material (Salamone, 1996).

Kumar and co-workers (1993 and 1983) had reported the preparation of a wide variety of fire and heat-resistant cyclomatrices based on aromatic cyclotriphosphazenes. Examples are the reaction of cyclotriphosphazene ring consists of aminophenoxy functional groups [13], with maleic anhydride. This affords cyclotriphosphazene containing-maleamic acids [14]. Upon heating the maleamic acid, in a dimethylacetamide (DMAC) solution, the cyclotriphosphazene maleimide [15], was produced. The thermal polymerization of [15] afforded a tough thermoset cyclomatrix polymer (maleimido-substituted cyclomatrix polyphosphazene) [16] as shown in (Figure 1.10). The outcome of this polymer exhibited good thermal stability and high char yield of 82 % and 68 % at 800 °C under nitrogen gas and air, respectively. The observed high char yield may be explained by the presence of unique combination of the cyclotriphosphazene ring and heterocyclic groups. Graphite-fabric laminates prepared with this polymer exhibited superior fire retardant properties, which did not burn in pure oxygen (Limiting Oxygen Index = 100 %) even after heating up to 300 °C. In contrast, the phosphorus-containing poly maleimide-amines exhibited poor thermal and fire retardant properties (Kondo *et al.*, 1980).



[13] [14] [15] [16]

Figure 1.10 Synthesis of cyclomatrix polyphosphazenes containing tris-maleimides

1.2.2.3.4 Stars and Dendrimers

The living cationic polymerization method is useful for the preparation of star polymers. In an example reported, a central core of tris(2-aminoethylamine) was treated with $BrP_2{=}NSiMe_3$ and PCl_5 to give a three site initiator, from which three arms of poly(dichlorophosphazene) were grown (Nelson and Allcock, 1997). Subsequent replacement of the chlorine atoms by trifluoroethoxy groups yielded a stable star structure. The influence of polymer architecture on materials properties is illustrated by the fact that the star polymer with M_n values of 30,000 is an adhesive gum whereas the counterpart's linear polymer with the same molecular weight is a microcrystalline thermoplastic. Four, eight and 16- armed dendrimers with a hydrophobic diamino core

and methoxyethoxyethoxyphosphazene arms are also accessible, and these are candidates for the controlled delivery of hydrophobic drugs (Cho and Allcock, 2007 ;Allcock, 2006).

1.3 Flame retardant, toxicity and adhesive properties of phosphazenes

1.3.1 Flame Retardant

The world of contemporary manufacturing items has a broad array of components derived from polymeric materials. These range from hard, molded objects (thermosets) and flexible items (thermoplastics) to films, fibers and foams. The vast majorities of these polymers are based on organic compounds and consequently are thermodynamically unstable in an oxidative environment. The most common of this instability is toward fire. The flammability of materials presents a general threat to both integrity of the product and human health. Therefore, the search for fire retardants and inherently inflammable polymers represents a major technological challenge. The ideal solution is the utilization of a polymer which itself is resistant to the fire. Unfortunately, these materials are not common or are not economically viable for mass production (specialty polymers). The alternative is incorporation of an additive with flame retardant properties to the mixture of agents which transforms the raw material to a manufacturability material. Traditionally, halogenated materials have played a major role in flame retardant additives. However, the release of toxic materials, particularly dioxins, from incineration of halogenated compounds, has led to the removal of chlorinated material from the market. The obvious move to the corresponding brominated compounds occurred. Recent concerns about the endocrine disrupter activity

and other health related issues of selected brominated flame retardants as well as the potential for release of polybrominated dibenzo-p-dioxins and dibenzofurans under pyrolytic conditions has resulted in the reconsideration of the viability of these materials. The EU has recently placed restrictions on selected brominated flame retardants. The regulatory activity associated with materials which have or are perceived to have a negative impact on the environment will result in considerable pressures to find a "green chemistry" solution to these problems. Phosphorus compounds and compounds containing phosphorus and nitrogen are two major target areas for development of non–halogenated flame retardants. Given this success, phosphazenes represents a logical target of green flame retardant additives and materials (Allen and Rubio, 2004).

1.3.2 Toxicity

Phosphazenes are non toxic and safe to be used on human subjects as stated in the paragraphs below.

Lawrence Gettleman used the polyphosphazene in the dentistry field. Following analysis of the clinical trials, patients were found to prefer the phosphazene denture liner to the silicone rubber denture liner, especially when used in mandibular arch, due in part to the high mechanical modulus of the phosphazene elastomer. Regardless of the location in the mouth, the phosphazene- lined dentures resisted the growth of *Candida albicans* in almost all patients, while more than half of the silicon-lined dentures became fouled. Presentation of evidence of safety (toxicity tests) and effectiveness (results of the

clinical trials) and the reversible nature of use in removable denture resulted in the FDA's approval using 510(k) process to market the phosphazene material in interstate commerce in 1987. This was the first time that a phosphazene material had been approved for a biomedical product in human subjects (Gettleman, 2004).

As depicted in Figure 1.11, a new biodegradable polyphosphazene (PYRMP) containing *N*-ethoxypyrrolidone and methoxyethoxyethoxy side groups was synthesized via a route of macromolecular substitution. The synthetic method of poly{bis[2-(2-oxo-1-pyrrolidinyl)ethoxy]phosphazene} (PYRP) was improved. The thermal properties of the polymers were investigated using differential scanning calorimetry. PYRMP and PYRP have low glass transition temperatures of −68.8 and −59.6 °C, respectively. Degradation studies were carried out *in vitro* with varying pH conditions. The polymers show a higher degradation rate at pH = 5.0 than at both pH = 7.4 and 8.0. The *in vitro* cytotoxicity of PYRMP and its hydrolysis products was evaluated using the methyl tetrazolium (MTT) cytotoxicity test in HepG2 cell culture. The MTT test reveals that PYRMP at concentrations below 800 $\mu g\ mL^{-1}$ and its hydrolysis products are non-toxic to HepG2 cells. Moreover, the hydrolysis products diluted 10 times are able to promote cell proliferation. This study shows that polyphosphazene containing *N*-ethoxypyrrolidone subsituents provides interesting perspectives for various biomedical applications (Bi et *al.*, 2010).

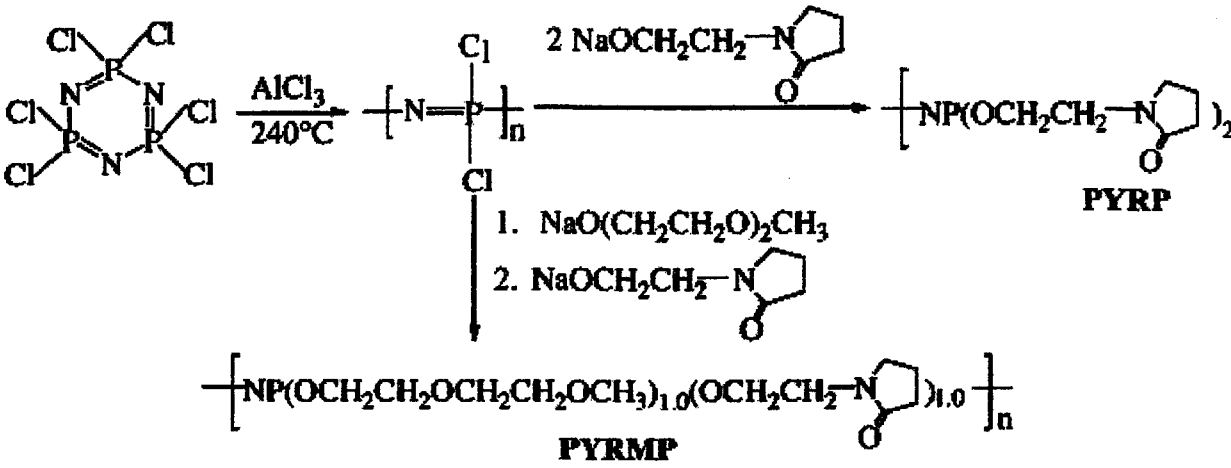


Figure 1.11 Schemes of PYRP and PYRMP

In fact, polycylophosphazenes and cylophosphazenes have been shown to posses interesting biomedical properties and diverse applications such as biomedical materials, membrane hydrogels, biologically active agents and phase transfer catalyst (Uslu et *al.*, 2010)

1.3.3 Adhesive properties

Selecting a structural strength adhesive for a specific application requires performance criteria of several characteristic. First is the bond making properties that determine ease of use and the cost of manufacturing. These includes degree of surface preparation, curing time, cure conditions of heat or room temperature, the degree of pressure and the fixturing to maintain the pressure and finally the viscosity for pumping and staying in place after application. Then, there are the following cured bond properties that are physical properties, environmental resistance and chemical resistance. Several researchers had researched on the adhesive properties by using cyclotriphosphazene as their starting material as stated in the following paragraphs.

Kumar (1998), investigated the synthesis and adhesive strength of organophosphazane compounds having P-O-C linkages formed by the reaction of $(NPCl_2)_3$ with their adhesive properties. Few examples of Kumar's synthesis of the compound along with the adhesive strength of the compounds, measured over duralumin and stainless steel are further discussed in the next paragraphs.

The first example is, reactions were carried out with $(NPCl_2)_3$ and phloroglucinol [17] in molar ratio of 1:3. The equation is shown in Figure 1.12. It is observed that the reaction scheme structure stated in the article is wrong (Figure 1.12). There should be two hydroxyl in each phloroglucinol after the complete reaction. One of the hydroxyl in phloroglucinol is missing. The corrected scheme is shown in Figure 1.13. The shear strength obtained was 5 kg/in^2.

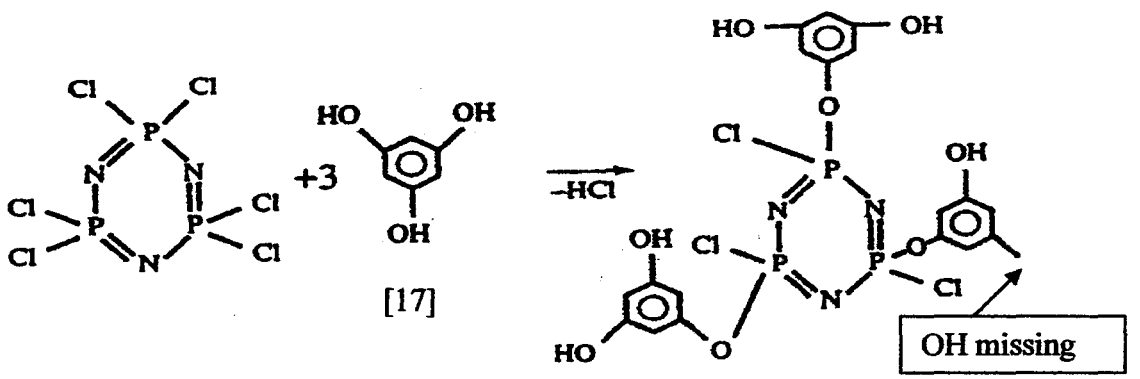


Figure 1.12 Reaction of $(NPCl_2)_3$ with phloroglucinol [17] (1:3) based from the article (Kumar, 1998)

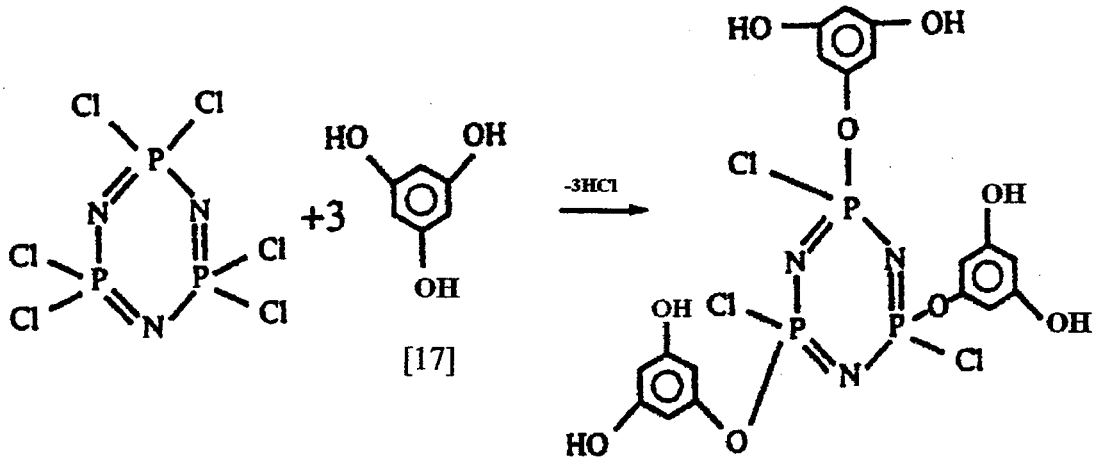


Figure 1.13 Reaction of $(NPCl_2)_3$ with phloroglucinol [17] (1:3), the corrected scheme.

Another reaction was carried out with $(NPCl_2)_3$ and benzilic acid [18] in molar ratio of 1:3. The equation is shown in Figure 1.14. It is observed that the reaction scheme structure stated in the article is wrong (Figure 1.14). The digit 2 is missing in Ph. The corrected scheme is shown in Figure 1.15. The shear strength obtained was 2 kg/in^2.

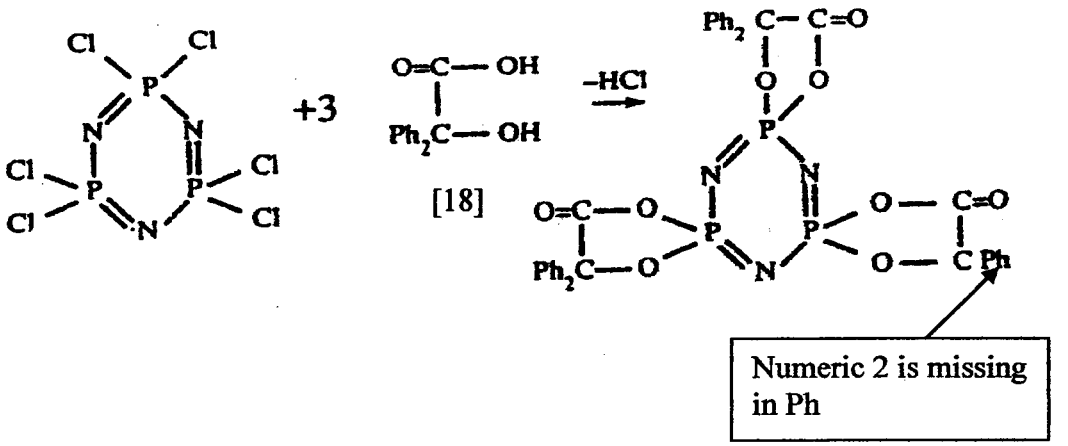


Figure 1.14 Reaction of $(NPCl_2)_3$ with benzoic acid [18] (1:3) based from the article (Kumar, 1998)