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Polyphosphazenes

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Phosphazene polymers, their methods of production, properties, and uses are considered. A new classification for polyphosphazenes is proposed. 298 references.

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I. INTRODUCTION

The chemistry of the phosphazenes, derived initially from the work of Liebig[1], has shown considerable developments in recent years, due on the one hand to the scientific interest in this independent class of compounds and on the other to the great practical value of many phosphazene compounds, especially the polymers. A review[2] published in 1943 cited 73 references; the exhaustive review of Shaw and coworkers[3] published 19 years later had 397 references and after four more years the number of publications and communications in this region had increased almost twofold[4].

The reviews published earlier[2-10] did not contain thorough and critical considerations of the phosphazene polymers. The published reviews of phosphazene polymers[11-14] are restricted to an examination of the various types and classes of polyphosphazenes.

In recent years much new material on the synthesis, structure, and properties of polymeric phosphazenes has accumulated and shows the separation of this division of phosphazene chemistry into a separate branch of the chemical science of polymers, a branch which is of independent interest.

The present article is an attempt at a more detailed review of the latest approaches in the chemistry of phosphazene polymers without considering cyclic and linear oligomers and methods of obtaining them, and a new classification for these polymers is also proposed.

II. CLASSIFICATION OF POLYPHOSPHAZENES

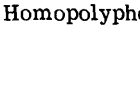
The first attempt at the classification of the phosphazene polymers was made by Shaw[15], who proposed to divide them into two classes: (1) polyphosphazenes obtainable by the polymerisation of cyclic phosphazenes; (2) polyphosphazenes obtainable by polycondensation; the latter, in turn, are subdivided into those which can be synthesised by the homopolycondensation of only phosphazene monomers (for example, phosphams) and the polycondensation of them with other monomers.

Another classification[4] is based on the nature of the substituents connected with the phosphorus atom in phosphazene polymers; according to this they are divided into purely inorganic (polyhalogenophosphazenes, polythioisocyanatophosphazenes) and organo-substituted phosphazenes. However, in using the above two classifications it is difficult to systematise all the various phosphazene polymers.

We think that the appearance in recent years of new and numerous types of phosphazene polymers enables the classification proposed earlier to be reconsidered and the classification adopted to be based on the structure of the macromolecule of the polymers and not on their method of production or the nature of their lateral substituents.

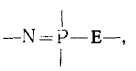
We think that the structural-chemical classification of high-molecular-weight compounds proposed by Korshak[16] is more correct in principle for systemising the polyphosphazenes. In accordance with this principle all the polyphosphazenes can be divided into three large classes: homopolyphosphazenes, heteropolyphosphazenes, and polymers with phosphazene groupings in the side-chain.

Homopolyphosphazenes are polymers of the type

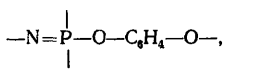


the main chain of the macromolecules of which is constructed from alternating phosphorus and nitrogen atoms, and the lateral radicals can be inorganic (halogens, isothiocyanate groups), or organic, or organoelemental. Examples of homopolyphosphazenes are the polydichlorophosphazene, polydimethylphosphazene, polydialkoxyphosphazenes, etc.

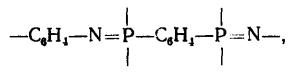
Heteropolyphosphazenes are polymers, the macromolecules of which consist of units of the type



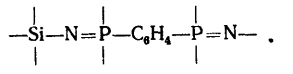
where E represents atoms or groups of atoms other than the phosphazo-group. Examples of the second class of phosphazene polymers include the polyoxyphenyleneoxyphosphazenes



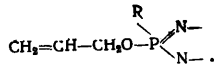
the polyphenylenephosphazenes



and the polyphenylenesilylphosphazenes



Polymers with phosphazene groupings in the side-chain contain macromolecules with a main carbo- or hetero-chain and phosphazene groups in the side-chain. Such polymers are obtained by the polymerisation of unsaturated organic derivatives of phosphazenes, for example:

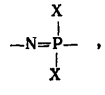


Our proposed classification of the polyphosphazenes is analogous to that generally accepted in the chemistry of organic and organoelemental polymers; it is mainly based on a constant criterion of these polymers—the structure of the macromolecules. This classification allows both the known phosphazene polymers and polymers which may appear in future to be systematised.

III. HOMOPOLYPHOSPHAZENES

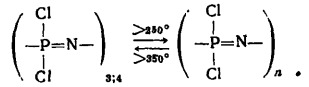
1. Polyhalogenophosphazenes

Linear polyhalogenophosphazenes are inorganic polymers with an elemental unit of the macromolecule of the structure



where X is Cl, Br, or F. These polymers are distinguished primarily by high thermal stability and fire resistance, although they are of limited practical use owing to low stability towards hydrolysis. Nevertheless the finding of the main rules for the formation of halogenophosphazene polymers always was and is still an extremely important task. A knowledge of these rules could open the path to the production of such linear polymers and rubbers with highly elastic macromolecules, combined with good thermal stability, materials which are needed by modern technology.

As long ago as 1870 Wichelhaus[17] observed the formation of a resinous substance on heating hexachlorocyclotriphosphazotriene (HCP). Later, Stokes[18] noted, in studying the polymerisation of cyclochlorophosphazenes with 6–12 atoms in the ring, that it proceeds very slowly at 250°C and rapidly at 350°C, while depolymerisation of the polymer starts at not much above 350°C:

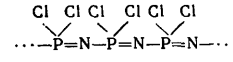


Stokes also noted the decomposition of polychlorophosphazene by hot water.

Schenk and Romer[19] observed the polymerisation of HCP and octachlorocyclotetraphospazotetraene (OCP) from 250° to 350°C and described the physical properties of the polychlorophosphazene rubber, which is colourless when pure, transparent, insoluble in organic solvents, but swells strongly in benzene and is stable in the cold to the action of inorganic acids. Under the action of water this polymer loses its elasticity, being converted into a brittle mass. It was also found that linear oily oligomers can also be converted into a rubber but below 200°C.

Renaud[20–23] studied the polymerisation of HCP and made an X-ray diffraction investigation of the polymers which are formed; according to his results these polymers had an amorphous or a crystalline structure. The effect of the polymerisation temperature on the molecular weight of the polymers formed was noted; their glass formation temperature was −47°C.

Detailed study of the physical properties of the polychlorophosphazene rubber were carried out by Meyer and coworkers[24–27]. Various polyhalogenophosphazenes were examined. Meyer[24] found the most probable position of the phosphorus and nitrogen atoms in the macro-chain. On the basis of the X-ray diffraction investigations of chlorophosphazene rubber, a fibrous structure was proposed for it, amorphous in the unextended state and crystalline when stretched. As was shown, the main valencies of the macromolecule



are arranged in a direction parallel to the axis of the fibre with an identity period of 5.16 Å, which corresponds with two elemental units.

The thermoelastic properties of the polychlorophosphazenes suggest the existence of spiral, flexible, long chains[25–27], with the molecular weight, calculated from the thermoelastic properties, equalling 20 000.

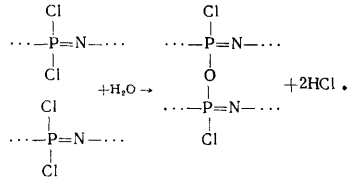
From the X-ray results the P–N–P bond angle in a rubber macromolecule was found to be equal to the N–P–N angle, 124°.[28] From its physico-mechanical properties, freshly-prepared chlorophosphazene rubber is not inferior to organic rubbers[26,27].

Ficquelmont suggested[29] that the polychlorophosphazenes consist of cross-linked macromolecules and the gradual decrease in their elasticity is connected with the crystallisation processes. When heated carefully to 500°C the rubber is converted into a black, infusible, insoluble product. Later[30], a tendency to a more rapid crystallisation of the polymerisation product from pure HCP than of the polymer from a mixture of low-molecular-weight homologues was observed.

In a subsequent paper Ficquelmont[31] noted that the polymerisation of cyclic chlorophosphazenes and the depolymerisation of the rubber are equilibrium processes. Schmitz-Dumont[32,33] concluded that in the polymerisation of HCP and OCP true equilibrium exists only in the gas phase. When cyclochlorophosphazene vapour was heated to 600°C a rubber was not formed, but a mixture of HCP, OCP, and higher homologues in crystalline and liquid states was obtained.

These results were confirmed by Moureu and Ficquelmont[34], who determined the molar heat of vaporisation on the elemental unit $PNCl_2$, equal to 15.5 kcal, and showed the impossibility of reaching high polymerisation coefficients in the gas phase.

Specker[35,36] investigated the physico-mechanical properties of the polychlorophosphazene rubber in the light of Kuhn's kinetic theory. The elasticity modulus was found to be proportional to the temperature in the range from −60° to 160°C, Specker found the elasticity modulus of rubber to be 2–4.2 kgf cm^{-2}. Values of the elasticity modulus close to these limits were also found later[37,38]. The molecular weight of rubber calculated by Kuhn's formula was 80 000, which corresponds to 700 $-PNCl_2-$ units. Specker considers[36] that the increase in the elasticity modulus of polychlorophosphazene is connected not with the crystallisation of the rubber but with the hydrolysis of the polymeric molecules and the formation of a lattice structure:



The first investigations of the kinetics of the thermal polymerisation of HCP were made by Schmitz-Dumont[33]. Systematic and detailed studies in this direction were made by Patat and coworkers[39–42].

Patat and Kolinskii[39] investigated the polymerisation of cyclic chlorophosphazenes in hydrocarbon solvents in the presence of oxygen at 250–350°C. They thought that the oxygen was responsible for the initiation of polymerisation, breaking of the chain, and the cross-linking of the macromolecule. However, it was found later[41] that polymerisation of sufficiently pure cyclochlorophosphazenes in the absence of oxygen takes place by a radical mechanism with homolytic breaking of the P–N bond in the ring as a second-order reaction with an activation energy of 42 kcal mole^{-1}.

Abel[43], who found that the reaction order of block polymerisation of cyclochlorophosphazenes is between 1 and 2, doubted the radical mechanism of this process.

Patat and Derst[42] found that depolymerisation of polychlorophosphazene rubber is a first-order reaction with an activation energy of 26 kcal mole^{-1} and a rate independent of the presence of oxygen. Nevertheless they stated that the depolymerisation had a radical character but with peculiarities connected with the structure of the rubber. They suggested that polychlorophosphazene is constructed from small cyclic molecules connected with one another. Such a structure for the rubber explains its high molecular weight and insolubility. In depolymerisation, as a result of the homolytic breaking of bonds these rings are freed from one another forming small cyclic molecules. The depolymerisation of higher linear halogenophosphazenes can generally be used as an effective method for obtaining the lower cyclic homologues[44,45], the yields of the individual phosphazenes decreasing with increase in the size of the ring, so the amounts of the cyclic tri-, tetra-, penta-, hexa-, and hepta-mers formed in the depolymerisation of the polychlorophosphazene are[44] in the ratio 20 : 15 : 8 : 5 : 1.

In investigating the block polymerisation of HCP at 275–350°C and the hydrolysis of polychlorophosphazenes Gimblett[46] concluded that polymerisation takes place in the gas phase by a radical mechanism and the breaking of the chain is effected in the block as a result of recombination. Chain-transfer reactions should also take place in the block through the polymer molecule with the formation of branch and lattice structures[46]. The effect on the thermal polymerisation of HCP of its concentration, the temperature of the process, and the reactor material has been shown[47]. The polymerisation is described by an S-shaped kinetic curve.

Shaw[48] suggested that if this reaction also involves free radicals their concentration is very low.

The radical mechanism of polymerisation came under even greater doubt after an investigation of the radical polymerisation of industrial HCP under the influence of γ-radiation[49] and of the polymerisation of pure HCP under the action of ultraviolet radiation[50] or of a beam of accelerated electrons[51], since in every instance of polymerisation either polymerisation was not observed or low-molecular-weight oligomers were obtained.

As is well known, cyclochlorophosphazene molecules contain P–N and P–Cl polar bonds. Therefore the initiation of polymerisation is probably connected with the heterolysis of some bond and the ionic initiation of chain growth. This view was first advanced by Konecny and coworkers, who studied the catalytic polymerisation of cyclochlorophosphazenes[52], and by Gimblett[53] who, in studying the thermal polymerisation of HCP, suggested that the act of initiation is the breaking of the P–Cl bond in HCP by the reaction:

$$P_3N_3Cl_6 \rightleftarrows P_3N_3Cl_5^+ + Cl^-,$$

and the chloride ion is responsible for the chain growth.

Further investigations of the electrical conductivity of HCP[54], its ability to form pyridinium salts[55] and pyridine complexes with Lewis acids[56] confirmed the suggestions about the possibility of heterolytic breaking of the P–Cl bond in HCP.

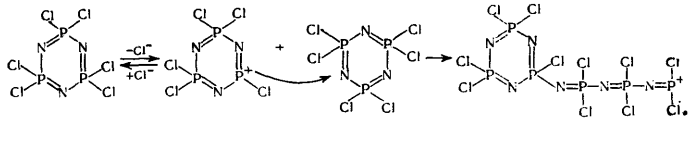
A study of the mechanism of thermal polymerisation of HCP with the aid of the EPR method and by measurements of the capacity, electrical conductivity, and dipole moments of HCP melts at various temperatures, also confirmed the ionic nature of the thermal polymerisation of the cyclochlorophosphazenes[57].

Table 1. Electrical conductivity of $(PNCl_2)_3$ and $[PN(OC_6H_5)_2]_3$, 10^{11} mΩ cm^{-1}.

$P_3N_3Cl_6$		$(PN(OC_6H_5)_2)_3$		$(PN(OC_6H_5)_2)_3$	
°C	conductivity	°C	conductivity	°C	conductivity
120	1.7	120	1.5	163.5	4.8
163	1.7	165	3.5	139	2.4
203	33	203.5	4.3	350	316
253	6250	252	17.7	120	17.7
202	2900				

Measuring the EPR in the range from 25° to 250° did not show free radicals in a melt of the trimer; the dielectric constant alters slightly under these conditions (from 2.52 to 4.85). However, the conductivity changes very sharply, especially above 200°C (Table 1). For comparison, Table 1 gives the change in conductivity of a control compound—hexaphenoxycyclotriphosphazotriene which does not polymerise in the temperature range studied[57].

These results convincingly support an ionic mechanism for the polymerisation of HCP. Unlike Gimblett's hypotheses[53], Allcock and Best[57] consider that the growth of the chain of cyclic cations is brought about by the positive charge on the phosphorus atom, which attacks a nitrogen atom of a new phosphazene ring, starting chain growth:



This mechanism also provides a reason for the formation of a three-dimensional polymer: the terminal group of the growing chain is a ring, which can also undergo electrophilic attack by the growing end of another macrochain, giving the beginning of branching.

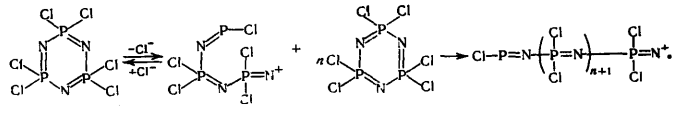
A mass-spectrometric study of the products of the decomposition of cyclochlorophosphazenes by Brion and Paddock[58] showed that a compound of ionic type $P_nN_{n+1}Cl^-_{2n+1}$ is formed predominantly.

Heterolysis of the P–Cl bond in linear molecules of polychlorophosphazenes is evidently also the reason for their depolymerisation at higher temperatures. It cannot be ruled out that this process can be effected at any part of the chain. The following results suggest that polymerisation and depolymerisation of chlorophosphazenes are equilibrium reactions[59]: (1) when held separately at 600°C the linear polychlorophosphazene and a mixture of the trimer with tetramer (HCP and OCP) both form a mixture of linear and cyclic chlorophosphazene oligomers of the same composition[33]; (2) with increase in the temperature the proportion of the polymer in the equilibrium mixture drops and that of the lower rings rises; (3) an increase in pressure favours the formation of a polymer[60]; (4) the polymerisation of cyclic chlorophosphazenes $(PNCl_2)_{3-7}$ is endothermic and ΔH_{polym} decreases with increase in the size of the ring, amounting to 1.39 kcal mole^{-1} for the trimer and 0 for the hexamer[61].

Evidently, as for other inorganic polymers the polymerisation of chlorophosphazenes and depolymerisation of polychlorophosphazenes includes an equilibrium between all the homologues $(PNCl_2)_n$ with n from 3 to 15 000 and the direction of the process is determined by the change in free energy $\Delta G = \Delta H - T\Delta S$, that is, by the change in the entropy and enthalpy of the system[62]. Kinetic factors must also be taken into account[63].

Probably the depolymerisation of polychlorophosphazenes takes place with participation of ionic terminal groups; possibly the high polarity of the bonds in the main chain of the macromolecules of the polychlorophosphazene also permits the rearrangement of the bonds, as is observed with the polysiloxanes[64].

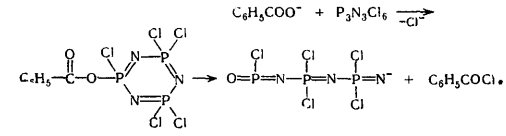
Konecny and Douglas[50] first observed the catalytic action of many organic compounds and metals in the polymerisation of cyclochlorophosphazenes. It was noted that the polymerisation of GCP is also brought about by t-butyl peroxide, but here the catalysis cannot be ascribed to the decomposition of peroxide into radicals, since at 210°C its half-decomposition period is very short whereas the polymerisation occurs in a few hours. The reaction also proceeds similarly in the presence of ammonium persulphate[65]. The investigation of the polymerisation of cyclochlorophosphazenes in the presence of benzoic acid, diethyl ether, and alcohols[52] suggested that the initiating act of chain growth is the heterolysis of HCP molecules (or other rings) at the P–N bond with formation of an active electrophilic centre at the nitrogen atom



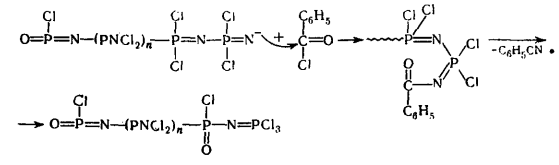
Gimblett found that oxygen does not affect the rate of catalytic polymerisation of HCP in the presence of benzoic acid; this polymerisation can be described by a first-order equation with an activation energy of 27.3 kcal mole^{-1}.[66]

A study of the kinetics of block polymerisation of HCP at 240–250°C showed it to be a second-order reaction with activation energy of 57 kcal mole^{-1}.[67]

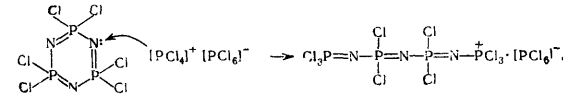
An investigation of the effect of benzoic acid and its salts on the polymerisation of HCP was made[67]. On the basis of the analysis of the volatile products of the polymerisation and of the previously established nature of interaction of salts of benzoic acid and HCP[68] it was suggested that the most probable mechanism includes attack by the benzoate anion on the HCP molecule and its opening by the scheme



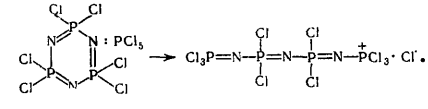
The linear anion formed reacts with HCP molecules starting the chain growth. The breaking of the chain is represented as follows:



This anionic mechanism is evidently specific for the action of benzoic and other carboxylic acids. Sometimes cyclochlorophosphazenes are polymerised in the presence of Lewis acids. The first report of the conversion of cyclic chlorophosphazenes into linear ones on heating with PCl_5, $AlCl_3$, $FeCl_3$, and other chlorides appeared in 1959.[69] Later it was stated in a patent[70] that such a process is brought about by heating cyclochlorophosphazenes in an autoclave at temperatures above 250°C with various iron, phosphorus, aluminium, and antimony chlorides, etc. After Becke-Goering and coworkers[71,72] had established the structure and mechanism of formation of linear chlorophosphazenes, the nature of the processes thus occurring became evident, which for PCl_5 can be represented as follows. Cyclochlorophosphazene (for example, HCP) are attacked by the $[PCl_4]^+$ cation with opening of the ring:

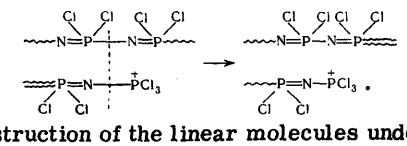


Chain growth takes place similarly with attack by a linear growing cation of the cyclic molecules until disappearance of the cyclophosphazene. Ring opening may precede its formation of a complex with PCl_5:



Here there is a chloride anion instead of a hexachlorophosphate anion. With other chlorides there is evidently similar opening of the rings[73].

Probably the terminal cationic groups of linear molecules react not only with cyclic molecules but also with linear macromolecules especially after the chlorophosphazenes have been used up:



This destruction of the linear molecules under the action of the terminal groups will, as for many polycondensation organic polymers, lead to the formation of an equilibrium mixture containing linear and cyclic chlorophosphazenes[74].

Even in the preparation of chlorophosphazenes by the ammonolysis of PCl_5 part of the linear oligomers can split off cyclised short-chain fragments [75].

Above 250°C equilibrium is reached rather rapidly—after 1–2 h. [70] The amount of chloride in the reaction mixture will determine the molecular weight of the linear chlorophosphazenes which are formed.

Considering the above possibility of polychlorophosphazene distribution as a result both of terminal group reactions and the intrachain rearrangement of bonds, the possibility of interchain exchange leading to the formation of an equilibrium mixture of linear molecules must also be admitted. Catalytic breaking of the macromolecules under the action of other reagents, for example, chlorine, is also possible at the same time.

The ability of phosphorus, aluminium, and iron chlorides etc. to stabilise linear chlorophosphazenes is sometimes used in the preparation of chlorophosphazenes by the ammonolysis of PCl_5. The ammonolysis was carried out in the presence of these chlorides [77,78] or even in the presence of metals [79–81] which form chlorides during ammonolysis.

The mechanisms of the thermal and catalytic polymerisation are thus very similar, especially at the chain growth stage--in every instance this is the process of growth of a polymeric ion.

Among other methods of polymerisation mention must be made of attempted solid-phase polymerisation of HCP and OCP. [82,83] Although radiation polymerisation of HCP does not take place [49–51], irradiation of the solid trimer with 50 kV X-rays at 40–120°C leads to the formation of a polymer [83]. However, the rate of polymerisation is low and reaches a maximal value of 0.8% h^{-1} at the melting point of HCP. By the action of γ-radiation for 300 h and a dose of 10^6–10^7 roentgen a degree of conversion of HCP into polymer of ~ 15% could be reached, which decreases in the presence of water, oxygen, solvent, and even OCP. [82] Unlike HCP the tetrameric chloride is not polymerised under the action of X-rays and γ-radiation. This difference in their capability for radiation polymerisation is evidently connected with the structural features of HCP (the greater capability of HCP for polymerisation was noted earlier [41]) and agree well with the calculated heat of polymerisation [61]. The identity of the polymers obtained by thermal and radiation polymerisation of HCP has been noted [82]. In the common solid-phase polymerisation of isomorphous HCP and hexabromocyclotriphosphazotriene the rate of polymerisation is lower than during their separate polymerisation [84].

It should be noted that in the determination of the quantitative rules for the polymerisation of cyclic chlorophosphazenes there are significant differences in the results of different authors (Table 2) even when the polymerisation is carried out under identical conditions. This characterises the complexity of the process of polymerisation of cyclochlorophosphazenes and the influence of many factors on this process.

Assuming that the most accurate values of the activation energy for the polymerisation of trimeric cyclochlorophosphazene is 27.3 kcal $mole^{-1}$ [66] and that for depolymerisation is 26 kcal $mole^{-1}$, [42] Paddock [10] considers that their difference accurately corresponds to the molar heat of polymerisation of HCP (1.39 kcal $mole^{-1}$), determined by differential thermal analysis [61].

There have been some reports of the polymerisation of oily homologues of chlorophosphazenes which also form chlorophosphazene rubber when heated above 130°C. [18,85,86] However, in estimating their polymerisation tendency it is necessary to take into account that these homologues can contain higher cyclic chlorophosphazenes with terminal NH groups [85] capable of polycondensation with liberation of HCl [86] and also that partial hydrolysis by small quantities of water with the formation of high-molecular-weight compounds in which the chlorophosphazene blocks are linked by P–O–P bonds can occur [85,87]. Linear polychlorophosphazenes with terminal ionic groups of the $\ldots P^+Cl_3.An^-$ type are thermally stable; their molecular weight does not change up to the depolymerisation temperature (although destruction processes with participation of terminal groups can occur in it). If these linear chlorophosphazenes have a low molecular weight and are not capable of being cyclised they are stable to temperatures above 500°C. [77]

Table 2. Results of the kinetic investigations of the polymerisation of hexachlorocyclotriphosphazotriene and depolymerisation of polydichlorophosphazene.

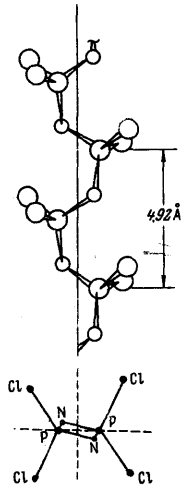
Process	Temp., °C	Kinetic order of reaction	Activation energy, kcal $mole^{-1}$	Reference
Polymerisation in the absence of air	250—300	2	42	41
Depolymerisation (traces of oxygen)	250—500	1	26	42
Polymerisation in benzene in the presence of various catalysts	210	1	—	52
Polymerisation in the presence of benzoic acid	200—210	1	27.3	66
Polymerisation in a block	240—255	2	57	67
Polymerisation in the presence of benzoic acid and sodium benzoate	235	1	—	67
Polymerisation in a block	250—300	1	51	47

An original method for obtaining linear polychlorophosphazenes was developed by Yakubovich and coworkers [88–90]. Heating low-molecular-weight linear compounds of the type $Cl[PNCl_2]_n$–$P(O)Cl_2$ and $R[PNCl_2]_n$–$P(O)Cl_2$ (where R is Cl, OR, or other groups and $n \geq 1$) at 150–200°C leads to the release of $POCl_3$ and the formation of a linear chlorophosphazene polymer of the general formula $P_XN_XCl_{2X} - mR_m$ free from lateral intermolecular bonds which are present in the polymers obtainable by thermal polymerisation of cyclochlorophosphazenes.

Since the hydrolytic stability of polychlorophosphazene is low, an attempt was made to improve it by various additions and modifiers, for example, silicone rubber, barium and tin stearates, and other salts [91] and also by carrying out the polymerisation of HCP in the presence of 2,6-di-t-butyl-*p*-cresol [92]; although in the last instance the hydrolytic stability of the polychlorophosphazene was increased ten times it was still unsatisfactory. The molecular weight of the linear polychlorophosphazenes was determined by various methods: by osmometry and viscometry [39–42], by viscometry and light scattering [93], and also from the temperature dependence of the elasticity modulus [35,36]. A comparison of the values of the osmometric and viscosimetric measurements made by Patat and coworkers [39,41] gave the following relation for solutions of polychlorophosphazenes in toluene: $[\eta] = 0.165 \times 10^{-4} M^{0.69}$. The values of the molecular weights of the polychlorophosphazene calculated by this formula were [41] ~ 10^6. Later [93] in an investigation of polychlorophosphazene isolated by precipitation into several fractions other values of the coefficients K and α in the equation $[\eta] = KM^{\alpha}$ were found for this polymer: in toluene $K = 3.89 \times 10^{-3}$ and $\alpha = 0.71$; in chloroform $K = 1.32 \times 10^{-1}$ and $\alpha = 0.56$. The difference between the values of the constants and those found earlier [99,41]

were explained[99] by the polydispersity of the products which Patat and coworkers had used. Nevertheless the absolute values of the molecular weights of the polychlorophosphazenes found by various authors agree satisfactorily and are ~ 10^5.

X-Ray diffraction studies of the polychlorophosphazene[94] suggested that its macromolecules do not have a spiral structure[27] but are almost planar. The conformation of the chain (see Figure) of the polychlorophosphazene is characterised by angles of rotation around the P–N and N–P bonds of 156° and 4° respectively, which is close to a *cis*-planar conformation. The identity period is 4.92 Å and includes two $PNCl_2$ links; the bond angles are PNP = 127° and NPN = 119° the length of the P–N bond is 1.74 Å.



Space model of a linear polychlorophosphazene.

Other halogenocyclophosphazenes are also capable of thermal polymerisation. At 250°C or over bromocyclophosphazenes form elastomeric products[95–97] which when heated subsequently form a brittle solid substance stable to the action of acids and alkalis. Polyfluorophosphazenes[98,99] form cyclofluorophosphazenes on heating above 300°C.

Of the other methods for making polyhalogenophosphazenes mention must be made of the "azide" method, which is being greatly developed. Thus, by heating PBr_3 with sodium azide at 170°C in the absence of a solvent, Herring[100] obtained polybromophosphazene:

$$PBr_3 + NaN_3 \xrightarrow[-NaBr]{} Br_2PN_3 \xrightarrow[-N_2]{} 1/n\,[-PNBr_2-]_n,$$

which forms an elastomer when heated to 200°C.

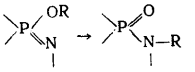
2. Polyorganophosphazenes

The chemical inertness of the P–C, P–O–C, and other bonds and above all their hydrolytic stability suggests that thermostable and chemically stable polyorganophosphazenes with these bonds in the side-chain can be obtained.

Two synthetic paths for such high-molecular-weight polymers are possible in principle: polymerisation of cyclic organophosphazenes and the replacement of the halogens in the polyhalogenophosphazenes by corresponding groups.

Polymerisation of cyclo-organophosphazenes. Most of the investigations in this field relate to attempts to polymerise alkyl, aryl, alkoxy, and aryloxy-cyclophosphazenes. Lipkin tried to convert the most accessible and easily obtainable in high yields of the alkoxy- and aryloxy-cyclophosphazenes into linear polymers[101]. By heating the products of the condensation of cyclochlorophosphazenes with phenoxides, alkoxides, and their thio-analogues, Lipkin obtained water-resistant polymers insoluble in organic solvents. Braun[102] repeated Lipkin's experiments but was unable to isolate pure products. When the aryloxyphosphazenes he had obtained were heated above 320°C their viscosity increased, they lost their solubility, but their composition did not change. Braun suggested that here polymerisation of cycloaryloxyphosphazenes took place with the formation of linear polymers.

Study of the thermal polymerisation of alkyloxy- and aryloxy-cyclophosphazenes in air and in nitrogen at 150–350°C showed that under these conditions low-molecular-weight polymers are formed[103]. Many authors[3] have noted the resinification and formation of polymeric products when alkoxycyclophosphazenes are heated in a vacuum, but it was found later[104] that the formation of polymers on heating alkoxycyclophosphazenes is due to side-reactions connected with the insufficient purity of the monomers. Shaw and coworkers[105–107] showed that at 200°C and above cyclic alkoxyphosphazenes undergo the phosphazene–phosphazane rearrangement:



but here there is no polymerisation as a result of the opening of the phosphazene ring, as occurs with halogenocyclophosphazenes. This is also characteristic for cyclophosphazenes with alkyl and aryl substituents at the phosphorus atom.

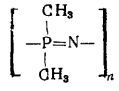
One of the first attempts at the polymerisation of the aryl-cyclophosphazenes was made by Bode and coworkers[108,109]: heating $(C_6H_5)_4P_3N_3Cl_2$, $(C_6H_5)_2P_3N_3Cl_4$ and $(C_6H_5)_8P_4N_4$ at 250–300°C for several hours leads, in their opinion, to the formation of polymers, but these polymers do not exhibit rubber-like properties. However, detailed investigation of the thermal polymerisation of $(C_6H_5)_6P_4N_4$ in the temperature range from 320° to 500°C showed[110] that there is hardly any polymerisation but a mixture of lower cyclic phenylphosphazenes is formed. The cyclic $(CH_3)_6$. $.P_3N_3$ and $(CH_3)_8P_4N_4$,[111] and $(C_2H_5)_6P_3N_3$ and $(C_2H_5)_8P_4N_4$[112] also do not polymerise on heating but start to decompose at 350–400°C. Similar results are also obtained in the polymerisation of the isopropyl- and phenyl-phosphazenes in air and in nitrogen[113].

Only two instances are at present known of the formation of high polymers from substituted cyclophosphazenes: at 150°C the trimeric and tetrameric isothiocyanate cyclophosphazenes form rubbery polymers[114–116]; tris-(*o*-phenylenedioxy)cyclotriphosphazatriene and tris-(2,2-dioxybiphenyl)cyclotriphosphazatriene also polymerise on heating[117,119].

Gimblett[53] thinks that the ability of thioisocyanatocyclophosphazenes to polymerise is due to the possibility of the ionisation of the P–NCS bond. However, as was correctly noted by Shaw and coworkers[120], both polymerisation as a result of the breaking of the phosphazene rings and also polymerisation with participation of thioisocyanato-groups

are possible here and it is still not yet known which of these two processes actually takes place. The same can also be said in respect of tris-(*o*-phenylenedioxy)- and tris-(2,2-dioxybiphenyl)-cyclotriphosphazotrienes: in addition to the polymerisation of the phosphazene rings[119] opening of the five-membered heterocycles is also possible and this can lead to the formation of polymers constructed from compounds with oxyaromatic units of substituted phosphazene structures.

Hence the direct thermal polymerisation of organocyclophosphazenes cannot yet be used for obtaining the corresponding homopolyphosphazenes. The catalytic polymerisation of these compounds shows greater promise. Rice and coworkers[121] heated a mixture of $(CH_3)_2P(NH_2)_2Cl$ and NH_4Cl and obtained the polymer



with a molecular weight of ~ 12 000, together with the corresponding trimer and tetramer. They suggest that the polymer is formed by the proton-catalysed polymerisation of cyclic phosphazenes. Polydimethylphosphazene is a crystalline polymer stable on heating to 300°C.[121]

It can be assumed that in the future the ionic polymerisation of many organocyclophosphazenes will be effected.

Synthesis of polyorganophosphazenes from polyhalogenophosphazenes. The reactivity of the halogens in the polyhalogenophosphazenes allows them to be readily replaced by various radicals.

The first attempt in this direction was made in 1948 when, by the action of alcohols in the presence of pyridine on polychlorophosphazenes with a polymerisation coefficient of 200, Goldschmidt and Dishon[122] obtained the corresponding polyalkoxy-derivatives, however, not all the chlorine was replaced, the proportion of alkoxy-groups was low and could not be increased by replacing the alcohol–pyridine mixture by alkoxides. Becke-Goering and Koch[85] obtained the corresponding polymethoxyphosphazene by the action of sodium methoxide on a linear chlorophosphazene oligomer with a polymerisation coefficient of 11. High-molecular-weight organo-oxyphosphazenes have been obtained by the action on polychlorophosphazenes of a mixture of alcohols and pyridine[123-126], alkoxides of alcohols and phenoxides[127-130], glycols or alkoxides of glycols[131,132].

The alcoholysis of polydichlorophosphazene favours its dissolution[125] or swelling[127] in an inert solvent. Under these conditions 93–95% of the chlorine atoms could be replaced by alkoxy-groups and polyalkoxyphosphazenes stable to hydrolysis obtained. The action of solutions of alkoxides or phenoxides in alcohol and also of amines[133] on polychlorophosphazene in benzene[129] gave the corresponding polyalkoxy-, aryloxy-, and amino-phosphazenes with high molecular weights. It was found that the process is not accompanied by appreciable destruction of the main chain of the initial polychlorophosphazene (see Table 3). X-Ray structural investigation of oriented linear alkoxy- or aryloxy-phosphazenes showed the identity period of their chains to be 4.8–4.92 Å, on the basis of which they were assigned a planar zig-zag structure[129]. With the aim of obtaining polymers which were more inert chemically, fluorinated[125-127,130,134] or chlorinated[124,128] alcohols were used for the alcoholysis of the polychlorophosphazenes, and polyalkoxyphosphazenes can be obtained by polyreesterification of the lower alkoxy-derivatives[125]. All the alkoxy-, aryloxy, and aminophosphazene polymers prepared exhibit comparatively low thermal stability—at 150–200°C and above they rapidly undergo destruction with the formation of low-molecular-weight linear and cyclic oligomers[129].

The greater ability of the high-molecular-weight organophosphazenes to undergo depolymerisation in comparison with the polychlorophosphazenes was related by Allcock[119,135] to the structure of the chain and the increase in the intramolecular interaction on replacing chlorine by larger organic radicals, which makes the cyclic compounds more stable thermodynamically. However, it is possible that the high flexibility and polarity of the bonds of the polyphosphazene chains[27] can also facilitate the destruction of the macromolecule and the formation of cyclophosphazenes, owing to the intramolecular redistribution of bonds, analogous to that observed in polyorganosiloxanes[64].

Polydimethylphosphazene could also be obtained by the action of CH_3MgBr or CH_3Li on polychlorophosphazene[136].

Table 3.

Elementary unit of the polymer	Mol. wt. $\times 10^{-3}$	T_c, °C	Solvent
$PN(OC_2H_5)_2$	2 000	—84	ethanol
$PN(OCH_2CF_3)_2$	1 700	—66	ketones
$PN(OC_6H_5)_2$	3 700	—8	benzene
$PN(OCH_3)_2$	640	—76	methanol
$PN(NHC_6H_5)_2$	1 650	91	benzene
$PN[N(CH_3)_2]_2$	363	—4	aqueous solution of acid
$PN(NC_5H_{10})_2$	697	19	benzene

Other methods of making polyorganophosphazenes. Methods of obtaining polyorganophosphazenes are known which are based on the use of alkali metal azides. This method was first proposed for obtaining chlorophenyl[100] and perfluoromethyl[137] polyphosphazenes and then extended also to phenyl polyphosphazenes[138,139]:

$$R_3PX + MN_3 \rightarrow [R_3PN_3] \rightarrow 1/n\ [-R_2P=N-]_n + N_2.$$

When R = CF_3 only a polymeric, solid, waxy product with a softening point of 95°C and good resistance to strong acids and oxidants is formed[137]. When R = CH_3 lower cyclic homologues are mainly formed.

Linear oligomeric fluorine-containing organophosphazenes with yields of up to 40% (remainder: cyclic phosphazenes) are formed by the following reaction[140]:

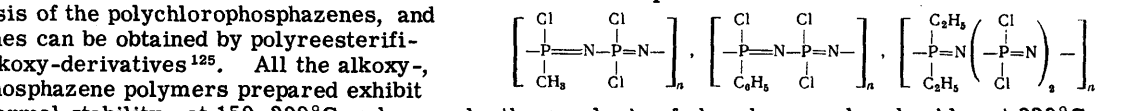
$$R_2PNH_2 + Cl_2 \rightarrow R_2PCl_2(NH_2) \xrightarrow{R'_3N} 1/n\ [-R_2P=N-]_n + R'_3N \cdot HCl.$$

The polyfluoromethylphosphazene obtained by this method is similar to those made by the azide method[137]. By heating hydrazinophosphines at 200°C mixed polyarylaminoalkylphosphazenes of the formula:



were obtained[141].

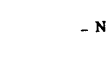
Yakubovich and coworkers[142] obtained insoluble polymers of the composition



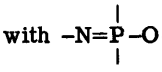
by the pyrolysis of phosphazene phosphoxides at 220°C.

IV. HETEROPOLYPHOSPHAZENES

In this class of polyphosphazenes we put the polymers which contain a main chain of phosphazene groups or structures linked by various organic, organoelemental, or inorganic radicals and groups of atoms:



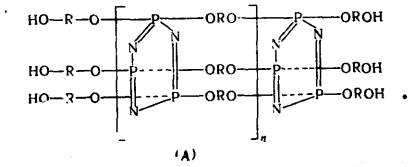
where E is alkylene, arylene, oxyalkyleneoxy, or oxyaryleneoxy radicals, residues of amines, diamines, the –NH– and O–B– groups, etc.

1. Polymers with  Bonds in the Main Chain

This type of heteropolyphosphazenes obtained on the basis of cyclic and linear halogenophosphazenes and polyoxy-compounds is one of the most promising polymers in practical respects, similar in structure to phenolic resins but differing from them by higher thermal stability and fire resistance.

Three methods for obtaining such polymers are now known[143]: the reaction of chlorophosphazenes with dihydricphenols[144-147], with phenoxides of diphenols[148,149] and the polyre-esterification of alkoxyphosphazenes with polyhydric phenols[150-152].

Although the reaction of chlorophosphazenes with alcohols and phenols has long been known[3], the preparation of polymers based on chlorophosphazenes and polyhydric phenols was first patented by Redfarn in 1957[144]. This method involved heating (at 170–190°C) a mixture of crystalline chlorophosphazenes, predominantly the trimer and tetramer, with resorcinol, hydroquinone, 2,2-di-(4-hydroxyphenyl)propane and other aromatic polyhydroxy-compounds, amounting to 75–100% of the weight of the chlorophosphazenes. The process was accompanied by the release of HCl and the formation of a resin capable of solidifying when heated with paraform or hexamethylenetetramine. However, the resins thus formed have low solubility owing to the high functionality of the original chlorophosphazenes; furthermore, the high temperature of the process facilitates the partial destruction of the phosphazene rings in these resins by the action of the HCl liberated. These drawbacks could be avoided by carrying out the polycondensation of the initial substances in organic solvents at temperatures below 130°C in the presence of acceptors of HCl—tertiary amines[145-146]. The use of an excess of dihydricphenols and their restricted solubility in the reaction mixture leads to gradual successive replacement of the chlorine atoms in the cyclochlorophosphazenes and the formation of resins predominantly containing structure of the type (for HCP):



(A)

However, these resins nevertheless contain up to 10% residual chlorine and are often sparingly soluble. The molecular weight of the soluble resins varies within the range 10 000–15 000; they are freed from traces of tertiary amines by precipitation with aqueous solutions of acids[153] and harden when heated with substances which are donors of formaldehyde[154] or in the presence of organosilicon or organotin hardeners[155].

An investigation of the reaction of HCP with dihydricphenols[143,147,156-158], made with the aim of finding the optimal conditions for the formation of polymers based on them showed that when pure the initial substances hardly react below 180°C whether in the melt or in organic solvents. Appreciable reaction starts above 190°C and its rate depends significantly on the polarity of the medium which also affects the composition and structure of the reaction products when the reaction is carried out in the presence of tertiary amines[143,156-158].

The order and rate constants of the reaction of equimolecular amounts of HCP and dihydricphenols were determined and it was assumed that both without catalysts and in the presence of tertiary amines the reaction is unimolecular with heterolysis of the P–Cl bond[157]. This assumption agrees well with the formation of pyridine complexes of HCP and $SnCl_4$ [56] and of phosphazenepyridinium salts[55].

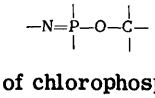
Bispentachlorocyclotriphosphazetrienes—the simplest homologues of the polyphosphazenes being considered—were isolated from the products of the reaction of equimolecular amounts of HCP and dihydricphenols by liquid absorption chromatography and characterised[159]. Their study allowed some conclusions to be drawn concerning their mode of formation[157,158].

To obtain only soluble resins, equimolecular amounts of cyclochlorophosphazenes and dihydricphenols were made to react and then the chlorine atoms left in the oligomers were replaced by various groups of atoms and radicals[160,161].

For the same purpose the functionality of the initial substances can be reduced by using monohydric phenols instead of the dihydricphenols[162] or by replacing some of the chlorine atoms in the original cyclochlorophosphazenes by inert phenyl[163-165] or phenoxy[166,167] radicals. Thus linear polymers with a softening point of 110–120°C and molecular weight of ~ 12 000 are obtained by heating dichlorohexaphenylcyclotetraphosphazotetraene and resorcinol in a vacuum at 310°C; when hydroquinone is used under the same conditions the molecular weight of the polymer is 5000.[163] Polymers of higher molecular weight were obtained from the same cyclophosphazene and 4,4-dihydroxydiphenyl oxide; the molecular weight of the polymer before purification was 42 000 when the reaction was effected in a melt and 115 000 when in a solvent; the molecular weights of the other fractions exceeded 250 000–500 000.[164]

Yokoyama and coworkers[168] repeated Redfarn's experiments[144] and also obtained resins insoluble in most solvents. The use of 2,6-bishydroxymethyl-*p*-cresol[169,170] leads to the formation of polymers similar to those described above. It was found that up to 200°C only the hydroxymethyl groups react with cyclochlorophosphazenes[169] but above 200°C the phenolic OH groups also start to react; homocondensation of the hydroxymethyl groups does not occur[170].

The release of HCl and the presence in the resinous products of some residual chlorine are the principal drawbacks of the method of making the heteropolyphosphazenes with



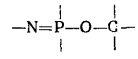
bonds by the reaction of chlorophosphazenes with polyhydroxycompounds. These drawbacks can be circumvented by the use instead of chlorophosphazenes of their alkoxy-derivatives[150-152]. The kinetics of the polyre-esterification of hexabutoxycyclotriphosphazotriene with diphenols was investigated and it was shown that the polymers thus formed are analogous to those synthesised from cyclochlorophosphazenes[152].

Instead of the completely substituted alkoxycyclophosphazenes, phosphazene compounds of the general formula

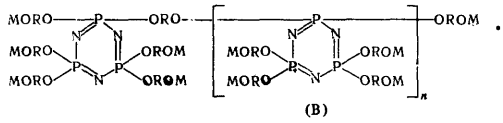
$$[PN(OR)_m(OH)_{2-m}]_n,$$

where $m \leqslant 2$, n is an integer $\geqslant 3$, and R = CH_3, C_2H_5, or C_4H_9, which are made by the alcoholysis of cyclochlorophosphazenes with lower alcohols, also react with diphenols. When these phosphazenes condense with dihydroxy-compounds water-soluble polymers are formed[171] which contain OH groups connected with phosphorus atoms. Such polymers can also be obtained by the hydrolysis of resins with cyclic phosphazene structures which contain residual P–Cl bonds[172,173].

An extremely promising method for obtaining polyphosphazene polymers with



bonds is by the reaction of chlorophosphazenes with phenoxides of polyhydric phenols[148,149], which are distinguished by a high rate even at comparatively low temperatures. Thus the reaction of HCP with the diphenoxide of 2,2-di-(4-hydroxyphenyl)propane dispersed in dioxan or ethyl methyl ketone ends after 2–4 h and leads to the formation of soluble and insoluble resins of type A (p. 67). When HCP reacts with an excess of diphenoxide in a medium which is a solvent for both the initial components (in alcohols) then polymers of type (B) are formed[149] (M = Na or K):

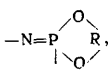


(B)

After the replacement of the phenoxide groups in these products by OH groups resins analogous to those of the phenol formaldehyde type are formed. The reaction of cyclochlorophosphazenes with diphenoxides is accelerated in the presence of pyridine or NaI.[174]

The resins of type (B) and also of type (A) readily harden when heated substances which are donors of formaldehyde; they are also convenient materials for modification or for preparing other polymers based upon them. Thus resin of type (A)[146] is used for the modification of butadiene–acrylonitrile copolymer[175] and resin (B) with phenoxide groups is readily epoxidised with epihalogenohydrins and forms epoxide phosphazene resins[176]. The latter were also obtained by the epoxidation of hexahydroxyarylene-hydroxycyclophosphazotrienes[177,178] (which are synthesised from the monophenoxides of dihydric phenols and HCP[179]) or on using the glycidyl ester of HCP;[180] nevertheless the attempt to obtain such esters by the epoxidation of allylhydroxyphosphazenes with peracetic acid was unsuccessful[181].

In the reaction of cyclochlorophosphazenes with dihydroxy-compounds (especially with glycols), in addition to the polymeric products, substances with a spirane structure are formed with a phosphorus atom in the alcoholic groups:



and partial dehydration of the glycols also takes place[182]. Thus in the reaction of *o*-diphenols (particularly pyrocatechol) with HCP or OCP in tetrahydrofuran in the presence of $(C_2H_5)_3N$[183] or in pyridine[184] a certain proportion of tris- or tetrakis-(*o*-phenylenedioxy)cyclophosphazenes is formed. It is interesting that these substances are capable of forming inclusion compounds with the molecules of various substances[185].

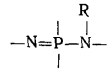
Other cyclic esters were synthesised from HCP and OCP with diphenols such as 2,2-dihydroxybiphenyl, toluene-2,3-dithiol, and 2,3-dihydroxynaphthalene[117].

The ability to form rings is much greater in the reaction of cyclochlorophosphazenes with glycols and other polyfunctional aliphatic compounds[186,187]. An increase in the [chain length of the] aliphatic radical between the OH-groups of glycol decreases the probability of the formation of spirane structures. This is especially noticeable in polyalkylene glycols[188–191]; when these are used polymeric products which can be employed in the production of polyurethane foams are formed[189–191]. This same effect is obtained when part of the chlorine in the initial cyclochlorophosphazenes is replaced by phenoxy-groups[192] or by perfluoroalkylphenol residues[193]. When glycols or amino-alcohols are used ring closure can proceed at different phosphorus atoms of the cyclophosphazene[194].

Phosphazene polymers based on aromatic polyhydroxy-compounds exhibit high thermal stability and fire resistance: they withstand long heating in air at 300°C[195] and can be heated to 500° for a short time[171]; in several instances destruction begins with breakdown of the phosphazene cyclic structures[164]; these polymers are also stable to attack by various chemical agents[145].

2. Heteropolyphosphazenes with –N=P(–)–N Bonds in the Main Chain

Polymers with



bonds in the main chain of the macromolecules (R = H or an organic radical) are obtained from chlorophosphazenes and ammonia or organic amines. The simplest representative of this class of polyphosphazenes—phospham—was first obtained by passing ammonia over molten HCP or by heating HCP with NH_4Cl.[196]

In investigating the ammonolysis of chlorophosphazenes Moureu and Rocquet[197] showed that on heating the prepared aminophosphazenes the irreversible loss of ammonia takes place and a polymeric product is formed—phospham:

$$[PNCl_2]_n + 4n\ NH_3 \xrightarrow[-2n\,HCl]{} [PN(NH_2)_2]_n \xrightarrow[2n\,NH_3]{} [PNNH]_n.$$

Phospham is an infusible powder which in the early stages of its formation can be dissolved in water; it is thermally stable up to 550–600°C and is converted into $(PN)_x$ on heating above 800°C. To accelerate the formation of phospham pyrolysis of aminophosphazenes is effected in the presence of NH_4Cl with passage of dry HCl.[198]

Audrieth and Sowerby[199,200] studied the formation of phospham from cycloaminophosphazenes by a thermogravimetric method. They found that the phosphams which are formed cannot be characterised by starting from the size of the phosphazene ring from which they were obtained. X-Ray structural investigations showed that the phosphams are amorphous substances and Steger[201] was unable to determine by infrared spectroscopy whether the size of the phosphazene rings was unchanged. He concluded that the phosphams are constructed from a disordered array of phosphazo-groups connected by –N= and –NH–structural elements.

The more detailed investigations of Miller and Shaw[202] showed that the formation of phospham in the pyrolysis of pure $P_3N_3(NH_2)_6$ and $P_4N_4(NH_2)_8$ in an atmosphere of nitrogen occurs at ~ 300°C; this was shown by the loss in weight and the composition of the residue. The loss in weight was measured during the heating of phospham to 1000°C; however, the formation of phosphorus nitrides $(P_3N_5)_y$ and $(PN)_x$ was not observed, a difference from previous reports[203]. Often the material of the crucible in which the pyrolysis of the aminophosphazenes was carried out reacted with the reaction mixture[204]. The retention of the phosphazene ring in the formation of phospham from aminocyclophosphazenes is proved by the fact that the phospham obtained from $P_3N_3(NH_2)_6$ has a lower density than the product made from $P_4N_4(NH_2)_8$.[202]. The preparation of a foam based on phospham has also been described[205].

Deammonolysis has been used to obtain organo-substituted phosphams; thus polymers stable above 300°C were obtained by the pyrolysis of compounds of the general formula $P_3N_3R_x(NH_2)_{6-x}$, where R is an organic radical which can be fluorinated and $x \geqslant 3$.[206,207] Polymers with greater thermal stability were obtained by heating phenylaminocyclophosphazenes[208-210] above 300°C with a residual pressure of 10^{-3}–10^{-4} mmHg.

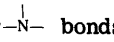
Organo-substituted phosphams were also synthesised by the reaction of chlorophosphazenes with amines. Aniline and HCP or OCP were used most frequently for this; in pyrolysis of the anilidocyclophosphazenes formed by the reaction of these substances aniline is released and phenylphosphams are formed[211]. The latter can again be converted into the original cyclic structures by heating with aniline which is impossible with unsubstituted phospham[202]. Phenylphospham is also formed on heating anilidochlorophosphazenes, obtainable in the non-polar replacement of chlorine in the initial chlorophosphazenes by aniline residues[212]. The formation of polymers from chlorophosphazenes and butylamine has also been reported[213].

Thermostable and fire-resistant polymers are obtained by the reaction of a mixture of crystalline chlorophosphazenes and acetaldehyde[102,214,215]. The process is accompanied by the liberation of HCl and CH_3COCl and, as has been shown[102], proceeds through the formation of cyclic products $(PNNC_6H_5)_n$ with their subsequent thermal polymerisation into a linear polymer. Similar polymers are formed in the reaction of chlorophosphazenes with diphenylurea and other amides[102]. It should be noted that an attempt to prepare the same polymers by ammonolysis of trichlorophosphazo-compounds $RN{=}PCl_3$ was unsuccessful[216]; instead polymers of the



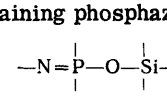
type were obtained; these decompose above 200°C with the formation of anilinium chloride.

The preparation of phosphazene polymers based on chlorophosphazenes and organic diamines has been described[164,217,218]. For this it is usual to employ a mixture of crystalline chlorophosphazenes in which some of the chlorine atoms can be replaced by inert organic radicals. But here the formation of cyclic spirane structures is also possible especially if the initial diamine contains an alkylene radical with 2–4 carbon atoms between the amino-groups[219-220].

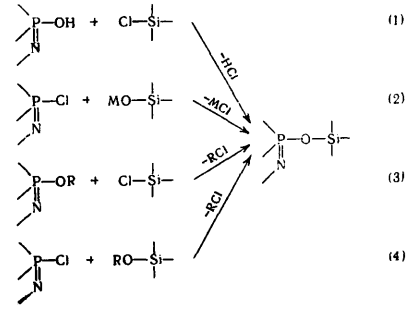
Water-soluble polymers with  bonds in the main chain are evidently also formed when linear chlorophosphazenes are treated with methanol and ammonia simultaneously[221,222].

3. Polyelementophosphazenes

In recent years there have been reports of the synthesis of heteropolyphosphazenes containing silicon, boron, germanium, and other elements. Many of the investigations relate to silicon-containing phosphazenes with



bonds in the main chain. There are four methods for making such polymers:



where M is an alkali metal or hydrogen, R = alkyl, and X is halogen.

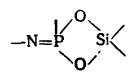
The first syntheses of silicon-containing polyphosphazenes by reaction (1) were effected in 1958–59. Dumont[223-225], who used the reaction of triphenyldihydroxychlorocyclotriphosphazotriene with diorganodichlorosilanes. The high thermal and hydrolytic stability of the polymers obtained was noted. Instead of the dihydroxyphosphazene derivative the tri-functional monomer $P_3N_3(OC_6H_5)_3(OH)_3$ can also be used[226]; this leads to the production of three-dimensional polymers or those capable of hardening.

To obtain siloxyphosphazene polymers of similar type by reaction (2), diphenylsilanediol and linear or cyclic chlorophosphazenes were used[227-229]. With the more reactive linear chlorophosphazenes the reaction takes place under milder conditions and leads to the formation of thermostable polymers[227], which can be used for preparing asbestosplastics[228]. However, in every instance the condensation of diphenylsilanediol with chlorophosphazenes is accompanied by side-reactions of homocondensation of dihydroxysilane and hydrolysis of chlorophosphazenes or of the semiproducts with water liberated in the condensation of dihydroxysilane. Therefore the polymers obtainable by reaction (2) contain a P–OH bond and also considerable amounts of water-soluble polymetaphosphimic acids[229]. The fraction of such side-reactions does not decrease on using acceptors (for example, quinoline). This is evidently due to the fact that the chlorophosphazene–tertiary amine systems are strong dehydrating agents[8].

It was therefore desirable to replace diphenylsilanediol by its siloxane, which is incapable of homocondensation, and thus exclude the appearance of water in the reaction mixture. However, it was shown[230] for monosiloxides and monosilanols that their reaction with hexachlorocyclotriphosphazotriene proceeds by scheme (2) but is considerably more complex and leads to the opening of the phosphazene ring and the formation of a mixture of low-molecular weight products, including disiloxanes. It was suggested that under certain conditions the polysiloxanes can react with the chlorophosphazenes with breaking of the Si–O–Si bond[230]. Thus, by heating hexaethyldisiloxane and HCP at 240°C in an ampoule for 6 h an oligomeric liquid and a solid insoluble polymer containing silicon and phosphorus were obtained[231].

A method for obtaining organosiloxyphosphazene polymers which is new in principle consists in the interaction of cyclic or linear alkoxyphosphazenes with organohalogenosilanes[232]. Its advantages are the high rate of reaction under comparatively mild conditions for carrying it out and the absence of side-reactions.

An investigation of the kinetics of this reaction in the case of hexabutoxycyclotriphosphazotriene and triorganohalogenosilanes[233] suggested that the process proceeds with heterolysis of the silicon–halogen bond and attack by the silicone cation at the oxygen atom of the alkoxyphosphazene. Under our conditions the formation of the organosiloxyphosphazene polymers on the basis of diphenyldichlorosilane and phenyltrichlorosilane[226] a marked decrease in the molecular weight of the polymeric products was noted owing to the partial formation of cyclic spirane structures of the type[226,234]:

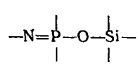


[226, 234].

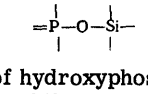
The formation of the latter can be prevented by starting from triphenoxytrialkoxycyclotriphosphazotrienes in which the phenoxy-groups do not react with chlorosilanes: it was then possible to obtain polymers which are three-dimensional or capable of subsequent hardening. Siloxyphosphazene polymers are also obtained by the reaction of cyclochlorophosphazenes with organoethoxysilanes[235].

It was found by differential thermal analysis and isothermal heating that the organosiloxyphosphazene polymers obtainable by reaction (3) start to decompose appreciably at 200°C as a result of the splitting off of the residual alkoxy-groups, whereas the thermal destruction of the main chain begins above 300°C.

Dumont's report[223,224] of the high hydrolytic stability of the phosphazene polymers with



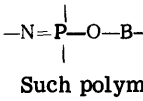
bonds was subsequently not confirmed. An investigation of the hydrolytic stability of the oligomeric and hardened organosiloxyphosphazene polymers showed that they are rather readily decomposed by water at the



bonds with formation of hydroxyphosphazenes and hydroxysilanes or the products of their homocondensation[226,234].

Silicon-containing phosphazene polymers of greater stability to hydrolysis can be obtained by the reaction of alkoxyphosphazenes with halogenoalkylsilanes[236].

Boron-containing phosphazene polymers of various types[237-239] and in particular with



bonds are interesting. Such polymers are obtained by the reaction of boric and organoboric acids with HCP and its alkoxy-derivatives[237] or by the condensation of boric acid (and other inorganic acids) with cyclic acids of alkoxyphosphazenes of the general formula

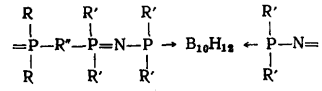
$$[PN(OR)_x(OH)_{2-x}]_n,$$

where $n = 3$ or 4 and $x \leqslant 2$.[238] On using the normal[237] and acid[238] alkoxyphosphazenes the proton-catalysed semiire-esterification of them by the boric and organoboric acids takes place accompanied by the loss of the corresponding alcohol.

In the direct reaction of HCP and boric acids the reaction takes place only in the presence of tertiary amines and leads to the formation in 50–70% yield of an infusible and insoluble polymeric product which is distinguished, according to differential thermal analysis, by high thermal stability (the loss in weight at 600°C is less than 20%) but by ready hydrolysis with boiling water.

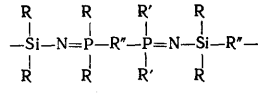
Hydrolytically stable boron-containing phosphazene polymers with a high softening point are obtained by the reaction of bis(azidodiarylphosphino)decaborane with such diphosphines as bis(diphenylphosphino)ethane, 1,4-bis(diphenylphosphino)benzene, etc.[239]

A process which can be effected by heating the initial substances in inert solvents and is accompanied by the liberation of nitrogen leads to the formation of polymers constructed from alternating units of the type



(where R and R′ are aryl and R″ is alkylene or arylene). Organoelemental polymers of the same type are synthesised by the reaction of the sodium derivative of decaborane with $P_3N_3Br_6$.[240]

The basis of a method for making an extensive class of heterochain element-containing phosphazene polymers is the reaction of phosphines with organoelemental azides[241]. In the reaction of the corresponding diphosphites and organoelemental diazides liquid phosphazene polymers of the type



are obtained, where R and R′ are alkyl or aryl and R″ is alkylene or arylene. These polymers are of interest as hydraulic liquids and lubricants or modifying additives for these materials[242-244].

4. Other Heteropolyphosphazenes

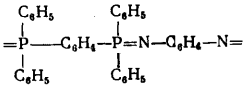
Many polyphosphazenes are known the macromolecules of which contain bonds different from those considered above. Thus resins analogous to the melaminoaldehydes are synthesised by the reaction of aminocyclophosphazenes and aldehydes at 60–80°C and pH 7–11.[245] Phosphazene-containing ureas and polyureas obtained by the reaction of aminocyclophosphazenes and aldehydes at 60°–80° and pH 7–11.[245] Phosphazene-containing ureas and polyureas are obtained by the reaction of $P_3N_3Cl_4(NH_2)_2$ with polyisocyanates[246]; however, this process is much more complex than the simple interaction of H_2N groups with isocyanato-groups[247]. $P_3N_3[N(CH_3)_2]_4(NH_2)_2$ is more reactive with isocyanates; this compound readily forms a urea derivative but in reaction with 2,4-toluene di-isocyanate in any ratio only two molecules of diaminocyclophosphazene are added to one molecule of di-isocyanate and products of higher molecular weight are not formed[247]. Urea derivatives can also be obtained from isocyanatocyclophosphazenes and amines[248]; when glycols are used phosphazene-containing polyurethanes are obtained[249].

Polyphosphazene products are also made by the reaction of HCP with guanidine urea, guanylurea, and other amides[250]. Phosphazene analogues of polycarbonates, formed in the phosgenation of hydroxycyclophosphazenes have been described[251] although the phosgenation products may have a more complex structure, since the reaction of

chlorocyclophosphazenes with organic acids and their salts leads to the breaking of the phosphazene rings[68].

Phosphazene polymers with P–O–P bonds in the main chain are obtained by heating a mixture of $P_3N_3R_4Cl_2$ and $P_3N_3R_4(OC_2H_5)_2$ (R = C_6H_5 or OC_6H_5); the process is accompanied by the release of ethyl chloride and the formation of thermostable products[252-254]. Polyphosphazenes with such bonds are formed in the heat treatment of alkoxyphosphazenes at 150–350°C [255] and also in the condensation of chlorocyclophosphazenes with alkyl phosphates, which is accompanied by the release of an alkyl halide and the formation of polymers stable to 500°C.[256]

A polymer with the structural units



and which softens at 150–200°C is obtained by the reaction of 1,4-bis(diphenylphosphino)benzene and 1,4-diazobenzene[257].

V. POLYMERS WITH PHOSPHAZENE GROUPS IN THE SIDE-CHAIN

Dishon[258] was the first to report the polymerisation of the allyl ester of cyclotriphosphazene into a viscous oil. Later[259] emulsions were obtained from unsaturated ethers of cyclophosphazenes. Infusible and insoluble polymers are formed in the polymerisation of dimethylamino- and phenylallyloxycyclotriphosphazatrienes in the presence of benzoyl peroxide[260]. In several studies it was found that triallyloxy-derivatives of phosphazenes are not polymerised at room temperature for 2 years and the ability to be sublimed in a vacuum up to 160°C is retained[261]. The polymerisation of butoxy- and phenoxy-allyloxycyclophosphazenes and also their copolymerisation with methyl methacrylate were investigated. The copolymers obtained did not exhibit high thermal stability[181]. Allyloxycyclophosphazenes and styrene were copolymerised at 70°C in the presence of benzoyl peroxide and the dinitrile of azoisobutyric acid. The determination of the copolymerisation constants allowed a conclusion to be drawn about the high activity of styrene; however, allyloxycyclophosphazene is more active than other allyl compounds[262]. Thermoplastic polymers and copolymers were obtained based on allylaminocyclophosphazenes. These polymers form stable films with good adhesion and, according to the thermogravimetric analysis, their loss in weight in air at 1000°C is 65%.[263,264]

VI. USES OF POLYPHOSPHAZENES

In contemporary literature, particularly patents and advertisements, there are two main trends in the practical use of phosphazene polymers: the use of homo- and hetero-polyphosphazenes as a basis for the preparation of stuffing plates [box? (Ed. of Translation)] coated with elastomers, etc., and the use of polyphosphazenes for modifying organic polymers and other materials to improve their thermal stability and fire resistance[265].

Use of polyphosphazenes as thermally stable and fire resistant materials. Comparatively long ago an attempt was made to use the thermal stability and fire resistance of polychlorophosphazene, by increasing its hydrolytic stability by replacing chlorine atoms by other atoms and groups. One of the variants of this exchange is based on the observed capability of polydichlorophosphazenes, during their formation in the thermal polymerisation of cyclochlorophosphazenes, to be bonded chemically with various silicate materials[266,267]. On this basis elastic electrical insulating coatings[268,269] and semiceramic products stable up to 500–600°C were prepared[270].

However, organophosphazene polymers are used most frequently for this purpose. The first attempts in this direction were made by Lipkin[101]. The products of the condensation of cyclochlorophosphazenes with polyhydroxyaromatic compounds have the greatest practical value[144-146,254]. Thus the polyhydroxyaryloxyphosphazenes obtainable by the method described in a patent[144] are recommended for use as adhesives, impregnating compositions, and prepared press articles. The same polymers which can be made in the presence of tertiary amines[146] are used as coatings on glass, ceramics, and metals; these coatings are distinguished by high shock resistance, resistance to solvents, acids, and alkalis. On hardening these polymers by heating at 244°C with 10% hexamethylenetetramine and a pressure of 176 kgf cm^{-2}; pressings are obtained with a tensile strength of 422, a bending strength of 703, and a compressive strength of 3160 kgf cm^{-2}.[145] Asbestoplastics from polyhydroxyaryleneoxyphosphazenes obtainable by a patented method[171] have a bending strength of 1600–1700 kgf cm^{-2} but after treatment at 500°C for 50 h it fell to no more than a half of this[271]. The same phosphazene binding agent is also used in making abrasive materials[272]. The products of the condensation of cyclochlorophosphazenes with polyhydroxyaromatic compounds, which are analogous in structure to phenolic resins but surpass them in thermal stability and also the products of the deammonolysis of phenyl(phenoxy)aminocyclophosphazenes[205-207] are undoubtedly some of the most promising phosphazene polymers in a practical respect.

Use of polyphosphazenes as modifiers of organic plastics. Additions of polyphosphazenes to organic polymers (phenolic, polyester, epoxy, and other resins) are made for the increasing the fire resistance and thermal stability of the latter. Polychlorophosphazenes[273-275] and the products of their amination or alcoholysis[276] are used for this purpose; for modification, polyphosphazenes with –OH, NH–, and other functional groups are more convenient to use. Thus, aminophosphazenes react readily with epoxy resins, forming modified products[277]. Fire-resistant polyurethane foams are obtained by using for the OH-containing component the products of the condensation of chlorocyclophosphazenes with glycols[188-191] and also by the introduction of polyphosphazenes with NHR groups into the mixture of components used for making polyurethanes[278].

Aziridinyl derivatives of polyphosphazenes are used as modifying hardeners for polyester compositions[279] and the products of the condensation of chlorocyclophosphanes and diphenols are modified with butadieneacrylonitrile copolymers[175]. Studies of the use of chlorophosphazene oligomers as catalysts for the polymerisation of organocyclosiloxanes have been described[280,281]. Copolymers of polychlorophosphazene with styrene and acrylonitrile have been obtained[282].

Alkoxypolyphosphazenes have been proposed for use as plasticisers for lacquers and cellulose films[122-123]. Polyphosphazenes of various types are widely used for conferring fire resistance on cellulose and other polymeric materials. Studies have been published[283-287] on the conferment of fire resistance on viscose silk, cotton, cotton fabrics, and on the improvement of the water and oil-resistance

of textile articles[288]. Hydroxymethylphosphazenes[285], water-soluble phosphams[289,290], condensation products of chlorophosphazenes with urea and chloroaniline[286], and the products from treating linear chlorophosphazenes with ammonia and methanol[222] are usually employed for this purpose. Polymethoxyphosphazenes[291] and lattices obtainable by the polymerisation of unsaturated bromo-containing alkoxycyclophosphazenes[259] are also used for improving the fire resistance of textiles.

Ion-exchange resins based on polychlorophosphazene[292], copolymers of unsaturated phosphazene derivatives with vinyl monomers[263,264], compositions based on phosphazene oligomers and polyacrylonitrile[293] and copolymers of acrylonitrile with HCP[294] have been synthesised.

Polychlorophosphazenes are used as activators for the hardening of polysiloxanes[295,296] and catalysts of the polymerisation of tetrahydrofuran[297]. Organo-substituted polyphosphazenes can be used for obtaining films, fibres, coatings, etc.[298]

Undoubtedly, in the near future many more possibilities for using polyphosphazenes of various types will appear; this is facilitated to no small extent by both the high thermal stability and other valuable properties of the polyphosphazenes and also their availability.

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