Mass Spectrometric Studies on Cyclo- and Poly-phosphazenes. Part 2.† Oligomerization of Hexa(aryloxy)cyclotriphosphazatrienes

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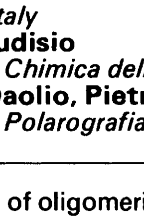
A method of oligomerizing hexa(aryloxy)cyclotriphosphazatrienes to the corresponding oligomers is reported. The oligomerization has been carried out in the ion source of a mass spectrometer, at high vapour pressure of the trimers, and at a temperature of 200 °C. The effects on the oligomerization reaction of experimental parameters, such as temperature, nucleophilicity, electrophilicity, and bulkiness of substituent groups on the trimers, and the presence of acidic species, have been investigated. High reaction temperatures inhibit the oligomerization reaction, leading to the formation of pyrolysis products.

In recent years, research on inorganic macromolecules as possible substitute materials for natural rubbers or traditional carbon-backboned polymers has dramatically increased.[1] Apart from silicon-containing polymers, whose practical utilization has been reviewed,[2] the only other class of inorganic macromolecules emerging from this research and open to technological applications are poly(organophosphazenes) (pop).[3] The general structure ascribed to the latter indicates the

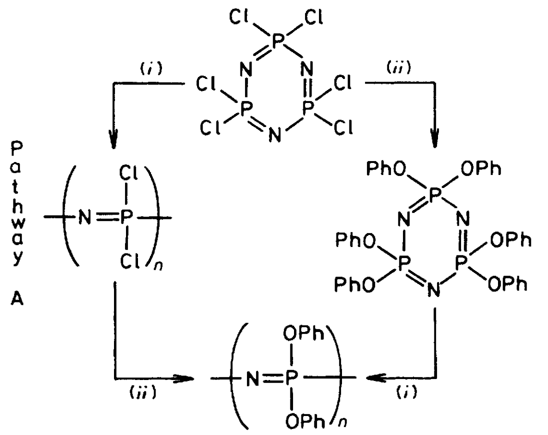

$$\left(-N=\overset{X}{\underset{X}{P}}-\right)_n$$

n = 10 000 - 15 000

inorganic nature of the phosphazene backbone and the presence of two substituent groups X linked to the phosphorus atoms of the polymer chain.

Both from a scientific and technological point of view, the most intriguing feature of phosphazene polymers lies in the method of their preparation.[4] The thermal bulk polymerization at 250 °C of hexachlorocyclotriphosphazene, $(NPCl_2)_3$ (**1**), induces opening of the phosphazene ring and provides poly(dichlorophosphazene), $(NPCl_2)_n$ (**2**), the reagent from which all other phosphazene polymers are prepared by nucleophilic replacement of the chlorine atoms by suitable nucleophilic reagents (Scheme 1, pathway A). This substitution approach to the synthesis of pop is almost unique in polymer chemistry and allows the preparation of many different phosphazene polymers, given the large number of reagents suitable for these syntheses.[5]

Two main disadvantages however have been recognized: (1) the irreproducibility of the thermal polymerization process of $(NPCl_2)_3$ (**1**);[6] and (2) the difficulty of obtaining fully substituted pop without residual, unreacted PCl units, even when forcing reaction conditions (*i.e.* high temperatures and large excess of the substituent) are used.[7] We have already discussed[8] the first point in detail in the context of the mechanism of polymerization of compound (**1**), together with factors which have been found to be of importance in catalysing or inhibiting this reaction. By contrast, the second point still needs consideration, since residual PCl bonds in pop have been invoked to act as possible 'weak points' from which both thermal[9] and photochemical[10] degradation of these polymers may start.



Scheme 1. (*i*) Polymerization; (*ii*) substitution

The synthesis of pop free from such 'weak points' may be considered therefore one of the major objectives in phosphazene polymer chemistry. In order to prepare pop absolutely free from residual chlorine atoms, an alternative method is in principle possible, which involves the polymerization of already fully substituted cyclotriphosphazatrienes (Scheme 1, pathway B). Unfortunately, reactions of this type have been successful only in the polymerization of $[NP(OCH_2CF_3)_2]_3$,[11] catalysed by BCl_3, whilst numerous unsuccessful attempts, using trimers like $[NP(OCH_3)_2]_3$,[12] $[NP(OPh)_2]_3$,[13] $[NP(OCH_2CF_3)_2]_3$,[14] and $(NPPh_2)_3$,[15] have been reported. The failure of the uncatalysed polymerization of these trimers has been rationalized both in terms of general thermodynamic considerations on a ring–chain equilibration process,[16] and/or of steric effects of bulky substituents on the trimers.[17]

This paper describes another method of polymerizing (aryloxy)cyclotriphosphazatrienes by using, as a chemical reactor, the

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Non-S.I. units employed: eV ≈ 1.60 × 10^{-19} J; Torr = (101 325/760) Pa.

ion source of a mass spectrometer. Possible factors which may influence the course of this reaction are also investigated.

Experimental

Mass Spectrometric Measurements.—All measurements were performed with a VG ZAB-2F mass spectrometer.[18] The electron-impact (e.i.) spectra were obtained at 70 eV (200 μA). Chemical ionization (c.i.) data were obtained with the source operating in the c.i. mode (100 eV, 2 mA), using CH_4 as reagent gas.

Polymerization reactions were performed in the c.i. configuration,[19] without any reagent gas, the pressure increase up to 5×10^{-1} Torr being obtained by introduction, under controlled conditions, of pure trimers. In particular, the pressure of the phosphazene trimers in the chamber was detected by a Pirani gauge directly mounted on an insertion port of the ion source,[20] whilst the temperature of the ion chamber was 200 °C, as measured by a thermocouple mounted on it. The sample was introduced under direct electron-impact (d.e.i) conditions,[21] *i.e.* by a soft evaporation technique.

It should be emphasized that all hexasubstituted phosphazene trimers used in this work are strong poisoning agents as regards the ion source, and also severely limit the filament life. Therefore particular care has to be adopted in order to maintain good focusing conditions of the ion source and to achieve good reproducibility of the experiments.

Sample Preparation.—All solvents used were C. Erba analytical grade and were dried by standard methods. Phenols were dried by dissolution in benzene, followed by successive distillations of the water–benzene azeotrope, the residual benzene, and anhydrous phenols, in this order. β-Naphthol was purified by sublimation at 140 °C under reduced pressure.

All the reported preparations were performed under strictly anhydrous conditions according to the following standard procedure. Hexachlorocyclotriphosphazatriene, $(NPCl_2)_3$ (**1**) (5 g, 0.014 37 mol) was dissolved in tetrahydrofuran (thf) (75 cm^3) and treated with a 50% oil dispersion of NaH (8 g, 0.1667 mol). To this mixture, the appropriate phenol (0.1437 mol) in thf (150 cm^3) was added dropwise, over 1 h. Hydrogen was evolved during the addition. The suspension thus obtained was refluxed for 48 h with stirring and finally cooled to room temperature. The resulting NaCl and the unreacted NaH were separated from the reaction mixture by centrifugation. The liquid obtained was evaporated in a Rotovap to give a yellowish paste. This product was treated with an excess of methanol to give the phosphazene trimer as a white solid. The crude product was exhaustively washed alternately with water and methanol and finally purified by several recrystallizations from thf–methanol solutions. The average yields for the trimers thus prepared were 60—70% {Found: C, 62.2; H, 4.30; N, 6.00. Calc. for $[NP(OPh)_2]_3$; C, 62.35: H, 4.35; N, 6.05. Found: C, 48.15; H, 2.50; Cl, 23.4; N, 4.50. Calc. for $[NP(OC_6H_4Cl\text{-}p)_2]_3$: C, 48.0; H, 2.65; Cl, 23.65; N, 4.65. Found: C, 57.85; H, 4.60; N, 5.00. Calc. for $[NP(OC_6H_4OMe\text{-}p)_2]_3$: C, 57.75; H, 4.80; N, 4.80. Found: C, 72.6; H, 4.30; N, 4.05. Calc. for $[NP(OC_{10}H_7)_2]_3$: C, 72.5; H, 4.20; N, 4.25%}.

Results and Discussion

Although the thermal bulk polymerization of $[NP(OCH_2CF_3)_2]_3$ catalysed by BCl_3 has recently been investigated,[11] uncatalysed thermal polymerizations of hexasubstituted cyclotriphosphazatrienes have never been reported. It is however well known that some partially substituted phosphazene trimers, like phenyl-,[15] alkyl-,[22,23] 2,2,2-trifluoroethoxy,[14] and carbaboranyl-[24] halogenocyclotriphosphazatrienes, do polymerize to high-molecular-weight species when heated under suitable experimental conditions.

By accurate evaluation of the experimental findings, it has been concluded that the presence in these trimers of some phosphorus–halogen bonds is always needed[4] in order to allow polymerization to occur. This polymerization reaction is probably initiated by heterolytic cleavage, on heating, of a residual phosphorus-halogen bond in the trimers, to produce a cyclotriphosphazene phosphorus cation.[4] From this species, partially substituted phosphazene polymers may result according to a polymerization mechanism which implies a sequence of electrophilic attacks of phosphorus cations on neutral trimer molecules. A similar mechanism has been proven to be operative in the mass-spectrometrically induced polymerization of $(NPCl_2)_3$ (**1**) to $(NPCl_2)_n$ (**2**).[8]

Thermal heterolytic cleavage of a phosphorus–substituent bond in a trimer is normally achieved quite easily in the case of fluoro-, chloro-, and bromo-phosphazene trimers by heating these molecules at reasonably low temperatures. This is due both to the considerable difference in electronegativity between phosphorus and halogen atoms, and to the remarkable leaving-group ability of halogens, which facilitates the formation of cyclotriphosphazene phosphorus cations. By contrast, such a scission is achieved only with great difficulty for fully substituted phosphazene trimers. In the case of hexaphenoxycyclotriphosphazatriene, $[NP(OPh)_2]_3$ (**3**), for instance, irreversible ionizations to unidentified ionic products are observed only when (**3**) is heated to temperatures above 350 °C, as demonstrated by electrical conductance measurements.[13]

Since the formation of cyclotriphosphazene phosphorus cations both in the case of hexachlorocyclotriphosphazatriene (**1**) and of hexasubstituted phosphazene trimers may be regarded as the initiation step of the polymerization reaction of phosphazene trimers, it seems likely that the possibility of polymerizing phosphazene trimers is intimately related to the ability of trimers to form these species thermally by heterolytic breaking of a phosphorus–substituent bond.

A second parameter which should be carefully evaluated in the thermal polymerization process of hexa(aryloxy)cyclotriphosphazatrienes is the thermal stability of the expected final polymer.

Considering for instance the polymerization reaction of $(NPCl_2)_3$ (**1**), the cation $[(NPCl_2)_3 - Cl]^+$ responsible for the initiation step is formed thermally above 220 °C,[8,13] while the corresponding poly(dichlorophosphazene), $(NPCl_2)_n$ (**2**), starts to undergo thermal depolymerization above 350 °C.[16] In this case the gap between these two temperatures is clearly large enough to ensure the thermal stability of polymer (**2**).

A different situation, on the other hand, arises with poly[bis(phenoxy)phosphazene], since thermal breakdown and depolymerization start for this polymer at around 100 °C and become dramatic as the temperature rises to 300 °C,[9] whereas hexaphenoxycyclotriphosphazatriene, $[NP(OPh)_2]_3$ (**3**), ionizes only above 350 °C.[13] In this case, clearly, no thermal polymerization of the phenoxy-trimer is possible due to the overlapping of these two temperatures.

From these facts it may be concluded that compound (**3**) does not polymerize thermally both due to the difficulty of producing the cyclotriphosphazene phosphorus cation necessary to initiate the polymerization reaction at reasonably low temperatures, and to the pronounced thermal instability of the expected polymer, in the temperature range where the trimer undergoes ionization processes. Temperature therefore seems to play a dual role in this kind of polymerization reaction, since it has to be sufficiently high to allow the formation of cyclotriphosphazene phosphorus cations, but must also be low enough in order to ensure stability of the expected polymers.

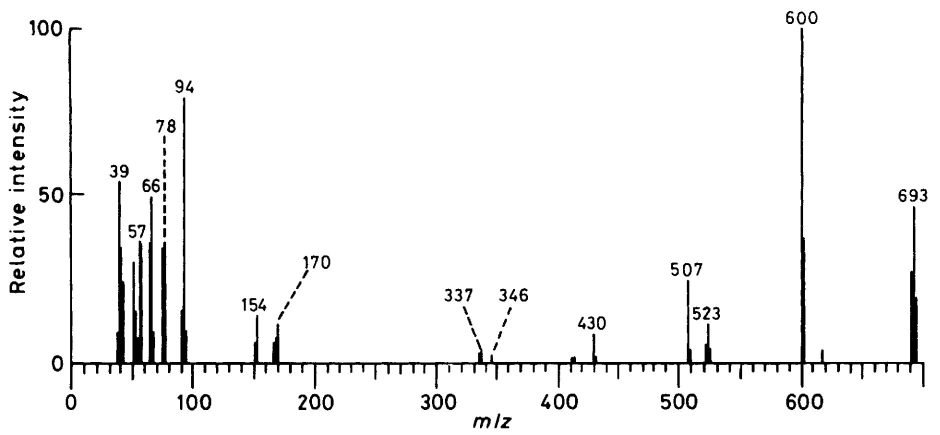
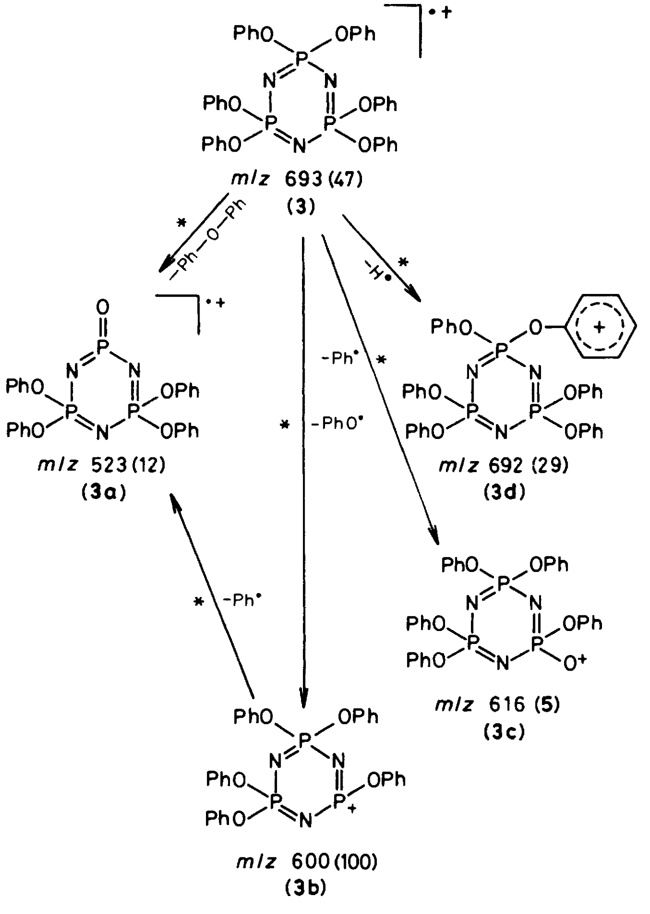


Figure 1. 70-eV e.i. mass spectrum of hexaphenoxycyclotriphosphazatriene (3)



Scheme 2. Relative intensities given in parentheses; * indicates that the fragmentation route has been checked by link scans and supported by metastable transitions

Such a compromise may be considered the key point of the problem of cyclotriphosphazene polymerization.

If it were possible to produce cyclotriphosphazene cations at sufficiently low temperatures to allow the survival of the resulting polymer, then the polymerization reaction of hexasubstituted cyclotriphosphazenes would become feasible. As previously demonstrated for compound (1),[8] mass spectrometry does provide this opportunity, and we used electron impact to induce the heterolytic scission of a phosphorus–phenoxy bond of $[NP(OPh)_2]_3$ (3). The corresponding mass spectrum at 70 eV and at a sample vapour pressure of 1 × 10^{-5} Torr is reported in Figure 1 and the fragmentation pattern, as obtained by linked scans and exact mass measurements, is in Scheme 2.

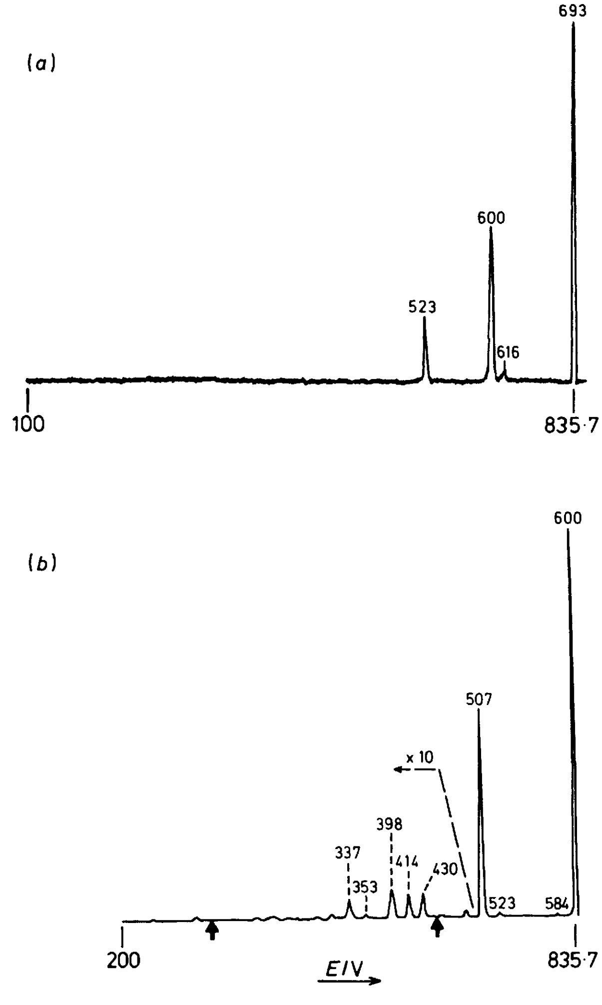


Figure 2. M.i.k.e. spectra of (*a*) M^{+} (*m/z* 693) and (*b*), $[M\text{-PhO}]^{+}$ (*m/z* 600) species of compound (3); the two arrows indicate positions at which $[NP(OPh)_2]^{+}$ (*m/z* 231) and $[NP(OPh)_2]_2{}^{+}$ (*m/z* 462) should appear if the phosphazene ring of (3) is degraded under electron impact

The main fragmentation pathway for species (3) is repre-

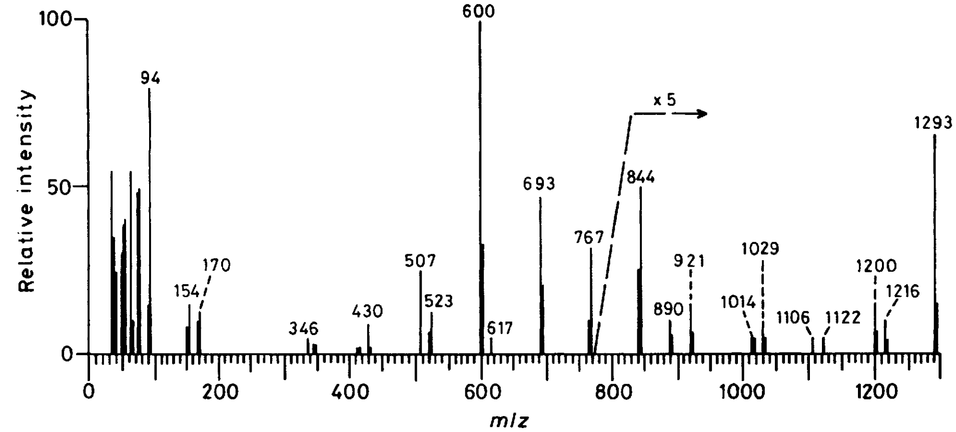


Figure 3. 70-eV e.i. mass spectrum of polymerization products of compound (3) (1.5×10^{-1} Torr)

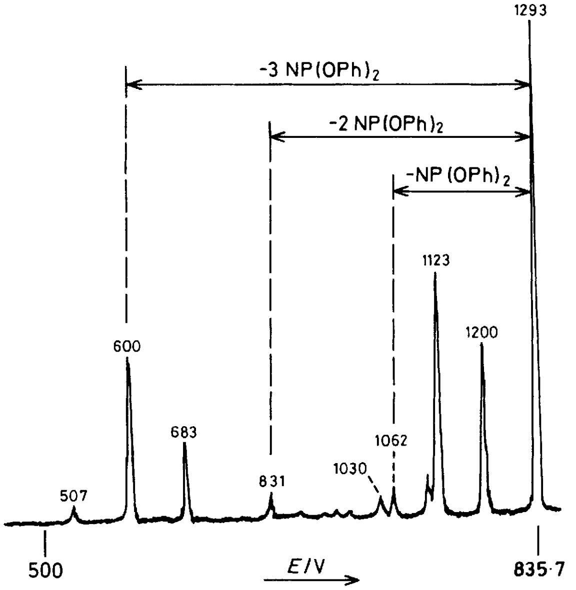
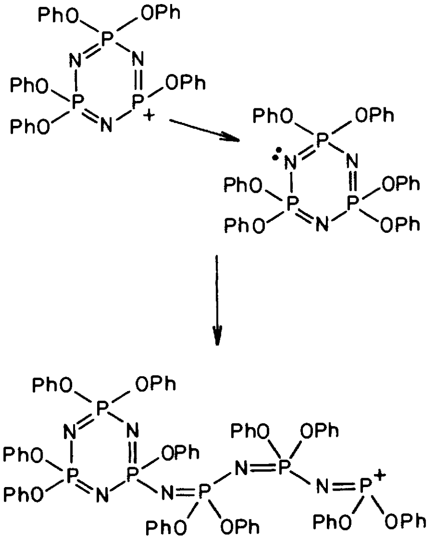


Figure 4. M.i.k.e. spectrum of the ion at *m/z* 1 293 originating from mass spectrometric polymerization of compound (3)



Scheme 3.

sented by the loss of a phenoxy PhO$^\bullet$ radical, with formation of $\{[NP(OPh)_2]_3 - PhO\}^+$ (**3b**) (*m/z* 600). For this ionic species it seems reasonable to assume the structure in Scheme 2, in which the positive charge is largely located on the three-co-ordinate phosphorus atom of the phosphazene ring. The formation of this ion occurs with an abundance ratio, $[M - PhO]^+/M^{+\bullet}$, 2.2:1.

It should be emphasized that no peaks due to $[NP(OPh)_2]^+$ or $[NP(OPh)_2]_2{}^+$ moieties are detectable in the spectrum of Figure 1, which would indicate that the phosphazene ring of compound (3) is completely preserved after the ionization process. The fact is also supported by mass-analysed ion kinetic energy (m.i.k.e.) spectra both of (3) and (**3b**), Figure 2.

Other primary losses of Ph – O – Ph, Ph$^\bullet$, and H$^\bullet$, also illustrated in Scheme 2, lead to the formation of species at *m/z* 523 (**3a**), 616 (**3c**), and 692 (**3d**) respectively, whose structures are also assigned.

In this way we could produce in the ion chamber of the mass spectrometer the ionic species (**3b**), whose structure is very similar to that of the cation $[(NPCl_2)_3 - Cl]^+$ which has been found to be responsible for the initiation step of the polymerization reaction of compound (**1**).[8] The ionic species (**3b**) therefore may be, in principle, able to initiate the polymerization reaction of $[NP(OPh)_2]_3$ (3), and this fact prompted our attempt to induce the oligomerization/polymerization of (3) in the ion source of the mass spectrometer.

This goal was accomplished simply by changing the configuration of the ionization chamber of the mass spectrometer from the e.i. to the c.i. mode,[19] in order to increase the internal pressure of (3) in the chamber to 1.5×10^{-1} Torr: the resulting mass spectrum is shown in Figure 3. Similar to the case of $(NPCl_2)_3$ (**1**),[8] an intense peak at *m/z* 1 293 attributed to a hexameric species, $\{[NP(OPh)_2]_6 - PhO\}^+$ (**4**), is observable, the abundance ratio between this species and $\{[NP(OPh)_2]_3 - PhO\}^+$ being estimated to be around 0.12:1. The structure of these ions may be elucidated from their m.i.k.e. spectra (Figure 4) where the successive loss of three monomeric $NP(OPh)_2$ moieties from the parent ion (peaks at *m/z* 1 062, 831, and 600) suggests the existence in (**4**) of a pentaphenoxycyclotriphosphazene moiety (**3b**) with a linear side chain formed by three $NP(OPh)_2$ monomeric units. Confirmation of this assignment could be obtained only by collisionally activated decomposition experiments using authentic samples; unfortunately none was available.

The formation of this hexameric species can readily be ex-

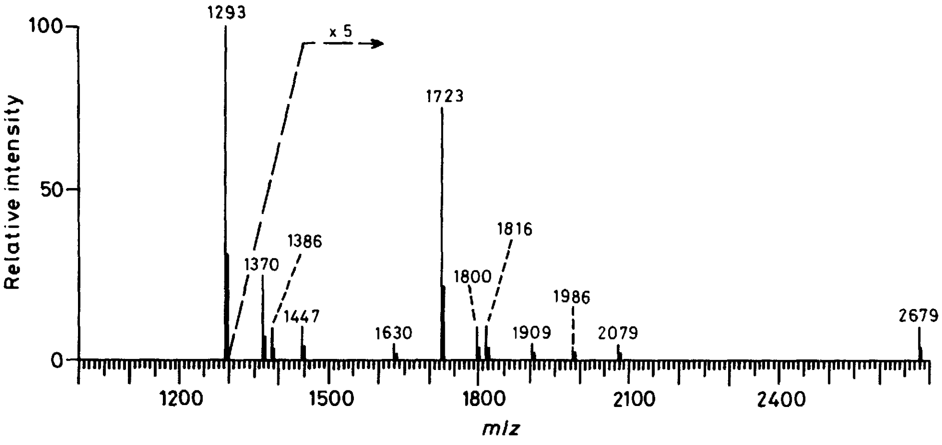


Figure 5. 70-eV e.i. mass spectrum of polymerization products of compound (3) (5×10^{-1} Torr)

plained in terms of an electrophilic attack of compound (**3b**) on a nitrogen atom of (**3**), according to Scheme 3, and may be considered as the propagation step in the oligomerization/polymerization reaction of (**3**).

A further increase of the pressure of compound (**3**) in the ion source to 5×10^{-1} Torr leads to the mass spectrum in Figure 5. In order to increase the mass range of the instrument to obtain this spectrum, the ion acceleration potential of the mass spectrometer has been decreased from 8 to 4 kV, with a consequent decrease in instrument sensitivity. In this spectrum, ions up to m/z 2 679 are detectable; in particular the following are observable: $\{[NP(OPh)_2]_{12} - PhO\}^+$ (m/z 2 679) (**5**); $\{[NP(OPh)_2]_9 - PhO\}^+$ (m/z 1 986) (**6**); $\{[NP(OPh)_2]_6 - PhO\}^+$ (m/z 1 293) (**4**); $[NP(OPh)_2]_9{}^+$ (m/z 2 079); $\{[NP(OPh)_2]_9 - C_{12}H_{10}O\}^+$ (m/z 1 909); $\{[NP(OPh)_2]_9 - C_{18}H_{15}O_2\}^+$ (m/z 1 816); $\{[NP(OPh)_2]_9 - C_{18}H_{15}O_3\}^+$ (m/z 1 800); $\{[NP(OPh)_2]_9 - C_{18}H_{15}O_3 - Ph\}^+$ (m/z 1 723); $\{[NP(OPh)_2]_9 - C_{24}H_{20}O_2\}^+$ (m/z 1 739); and $\{[NP(OPh)_2]_9 - C_{30}H_{25}O_4\}^+$ (m/z 1 630). The observation of products (**4**)—(**6**) unequivocally proves that $[NP(OPh)_2]_3$ (**3**) oligomerizes to oligo[bis(phenoxy)phosphazenes] under our experimental conditions.

Species with a polymerization degree of $n = 12$ have been determined in the mass spectra. Higher homologues, which may be present, could not be detected due to intrinsic restriction of the mass range/sensitivity ratio of our instrument.

Temperature Effect.—The oligomerization/polymerization reaction of $[NP(OPh)_2]_3$ (**3**) has been studied also by varying the temperature of the ion source at low pressures, *i.e.* working with small amounts of sample and with the source in the e.i. configuration. In this case no polymerization of the phosphazene trimer could be observed at 200 °C, and formation of the hexameric species with m/z 1 293 occurs only at 220 °C in a very low abundance ratio, $\{[NP(OPh)_2]_6 - PhO]\}^+$: $\{[NP(OPh)_2]_3 - PhO\}^+ = 3 \times 10^{-4}:1$. Moreover, in the mass spectrum at 220 °C (Figure 6) many ions are detected which are not primary e.i.-induced decomposition products of the hexamer. These may be reasonably formed by secondary thermal decomposition processes and/or by ion–molecule side reactions in the mass spectrometer at this temperature.

Once again it should be stressed that the polymerization temperature is one of the most critical parameters in determining the formation and stability of hexameric and polymeric species. In particular, at temperatures higher than 220 °C no hexameric phosphazene species were detectable.

These results are in good agreement with previous findings [13] and may be taken as further evidence that $[NP(OPh)_2]_3$ (**3**) does not polymerize thermally due to the presence of severe problems both in producing the pentaphenoxycyclotriphosphazene cation and in the thermal stability of the phenoxy-polymeric species.

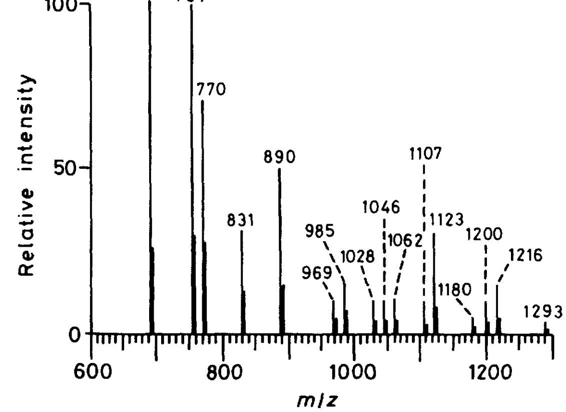


Figure 6. 70-eV e.i. mass spectrum of products obtained by heating compound (3) at 220 °C

Substituent Effect.—With the aim of gaining insight into the mechanism of polymerization of fully substituted trimers, we also investigated the mass spectrometric polymerization of hexakis(*p*-chlorophenoxy)cyclotriphosphazatriene, $[NP(OC_6H_4Cl\text{-}p)_2]_3$ (**7**), and hexakis(*p*-methoxyphenoxy)cyclotriphosphazatriene, $[NP(OC_6H_4OMe\text{-}p)_2]_3$ (**8**). The mass spectra for these compounds are given in Figures 7 and 8 respectively.

By comparison with the mass spectra of compound (**3**) in Figures 1 and 3, new fragmentation processes are observable which are intimately related to the *p*-chloro- and *p*-methoxy-substituents of the phenoxy-rings of these trimers. Moreover, the polymerization process occurs only in the case of the *p*-chlorophenoxy-trimer, as demonstrated by the presence of an ion at m/z 1 667 attributable to $\{[NP(C_6H_4Cl)_2]_6 - OC_6H_4Cl\}^+$ (**9**), whilst in the case of the *p*-methoxyphenoxy-trimer no hexameric or polymeric species were detected. This behaviour can be interpreted on the basis of the electron-withdrawing or -donating ability of the chlorine and methoxy-groups, respectively.

Effect of the Acidity.—A few years ago it was reported [6] that acidic species strongly inhibit the thermal polymerization of

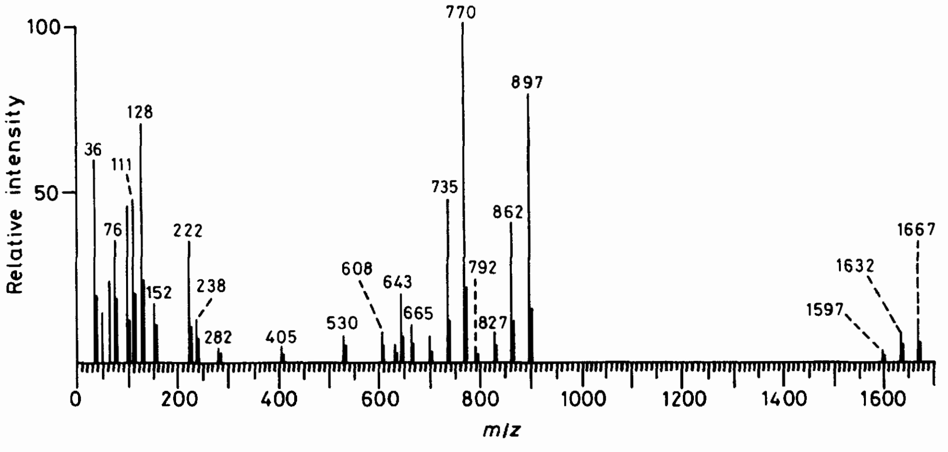


Figure 7. 70-eV e.i. mass spectrum of polymerization products of hexakis(*p*-chlorophenoxy)cyclophosphazene (7) (for clarity, only ions containing the ^{35}Cl iosotope are reported)

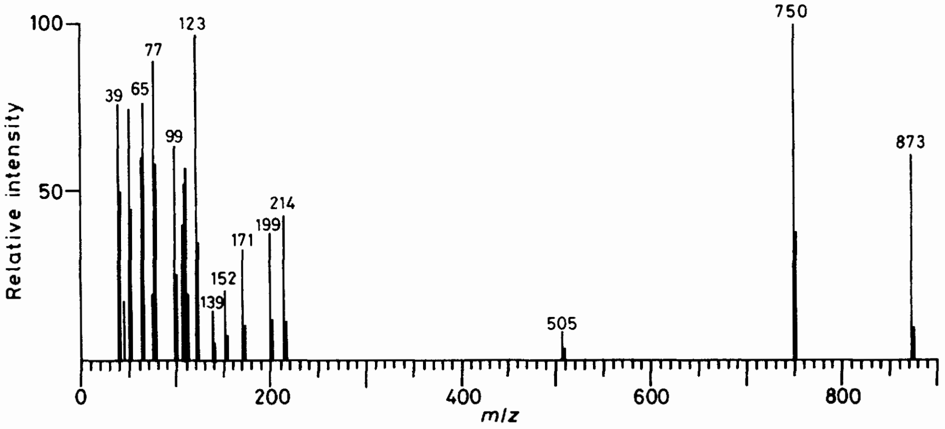


Figure 8. 70-eV e.i. mass spectrum of polymerization products of hexakis(*p*-methoxyphenoxy)cyclophosphazene (8)

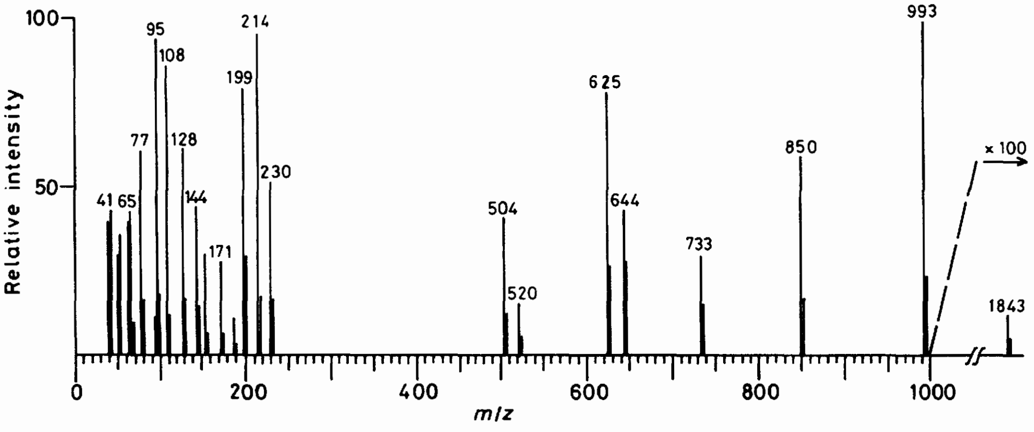


Figure 9. 70-eV e.i. mass spectrum of polymerization products of hexa(β-naphthoxy)cyclophosphazene (10)

$(NPCl_2)_3$ (1) to poly(dichlorophosphazene), $(NPCl_2)_n$ (2). We too have recently demonstrated[8] that the mass-spectrometrically induced polymerization of (1) is completely inhibited in the presence of species like CH_5^+. These inhibition phenomena were always attributed to the protonation of a nitrogen atom of the phosphazene ring, which thus results in withdrawal of electrons from the phosphazene ring and makes protonated molecules of (1) less prone to undergo electrophilic attack by pentachlorophosphazene cations.

The same should in principle be expected for the polymerization reaction of $[NP(OPh)_2]_3$ (3) induced by mass spectrometry. This effect was studied with the ion chamber under c.i. conditions using methane as reagent gas. In the presence of CH_4 the polymerization of compound (3) is strongly suppressed due both to the formation of considerable amounts of protonated phenoxy-trimer, $H[NP(OPh)_2]_3^+$, and to the remarkable decrease in the ion abundance of $\{[NP(OPh)_2]_3 - PhO\}^+$ (**3b**), whose relative abundance ratio, $[M - PhO]^+/[M]^{\cdot +}$, falls to 0.5. At the same time, the hexameric species is formed in very low abundance with respect to the trimeric $\{[NP(OPh)_2]_3 - PhO\}^+$ (abundance ratio 5×10^{-3}) and no higher phenoxy-oligomers could be detected.

Steric Effects.—It has been reported[5,15,16] that the thermodynamic stability of pop is strongly affected by the bulkiness of the side groups bonded to the phosphorus atom of the polymer chain. An increase in the steric bulk of the substituents always results in a decrease in the ceiling temperature (*i.e.*, the temperature above which no high polymer can exist) of the macromolecules. As a consequence, phosphazene polymers bearing bulky groups on phosphorus should show a lower resistance to thermal treatment, whilst degradation and/or depolymerization phenomena should start at considerably lower temperatures.[16]

For these reasons, we investigated the effect of bulky side groups on the polymerization reaction of fully saturated phosphazene trimers induced *via* mass spectrometry, and chose for our study hexa(β-naphthoxy)cyclotriphosphazatriene, $[NP(OC_{10}H_7)_2]_3$ (**10**). We polymerized this trimer under the same experimental conditions used for $[NP(OPh)_2]_3$ (**3**), *i.e.* the ion source in the c.i. mode, at an elevated pressure of the trimer, and 200 °C.

The corresponding mass spectrum, Figure 9, shows that the hexameric species $\{[NP(OC_{10}H_7)_2]_6 - OC_{10}H_7\}^+$ (**11**) is formed in very low abundance with respect to trimeric $\{[NP(OC_{10}H_7)_2]_3 - OC_{10}H_7\}^+$ (abundance ratio 1×10^{-3}), thus confirming that the bulkiness of the β-naphthoxy-group strongly depresses the stability of the oligo[bis(β-naphthoxy)phosphazenes], and inhibits the oligomerization ability of the β-naphthoxy-trimer.

Conclusions

Mass spectrometry has been used to: (1) induce the oligomerization/polymerization of aryloxy-substituted phosphazene trimers; (2) investigate parameters which may influence this reaction, *i.e.* temperature, acidity of the environment, electronic characteristics of the substituent group on the trimer, *etc.*

The results obtained on the gas-phase oligomerization/polymerization of hexa(aryloxy)phosphazene trimers can be explained in terms of ion–molecule reactions between a penta-substituted phosphazene P^+ ion and a neutral molecule of the cyclophosphazene trimer. These findings are in close agreement with the mass spectrometric behaviour of $(NPCl_2)_3$ (**1**) already reported.[8] For this compound, a strict analogy has been found between the mechanism of the thermal bulk and the gas-phase mass spectrometric polymerizations. This similarity suggests that the same may be true also for aryloxyphosphazene trimers.

Although caution has to be used in transferring the results of gas-phase experiments to reactions occurring in the condensed phase, the previously reported results[8] concerning compound (**1**), in our opinion, make this comparison a reasonable one also for (**2**).

Acknowledgements

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