work was supported by a grant from the United States–Israel Binational Scientific Foundation, Jerusalem, which is gratefully acknowledged.

Registry No. S_2-homopolymer, 89908-21-4; (S_2)·(styrene) (copolymer), 89908-22-5; M_2-homopolymer, 57981-89-2; (M_2)·(MMA) (copolymer), 51816-58-1; A_2-homopolymer, 89908-24-7; (A_2)·(MA) (copolymer), 89908-25-8; S_6-homopolymer, 89908-27-0; (S_6)·(styrene) (copolymer), 89908-28-1; M_6-homopolymer, 89908-30-5; S_2-monomer, 89908-20-3; M_2-monomer, 25952-50-5; A_2-monomer, 89908-23-6; S_6-monomer, 89908-26-9; A_6-monomer, 89908-31-6.

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Mass Spectrometric Studies on Cyclo- and Polyphosphazenes. 1. Polymerization of Hexachlorocyclophosphazene

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ABSTRACT: The polymerization of hexachlorocyclophosphazene $[(NPCl_2)_3]$ to poly(dichlorophosphazene) $[(NPCl_2)_n]$ has been carried out in the ionization chamber of a mass spectrometer. The mechanism of the reaction has been studied in detail under different experimental conditions, with the aid of linked scans, mass analyzed ion kinetic energy spectra, collisionally activated decomposition experiments, and energy release measurements. Comparison of the mass spectrometric reaction with the bulk thermal polymerization of $(NPCl_2)_3$ has given substantial evidence of the identity of the two reaction mechanisms.

Introduction

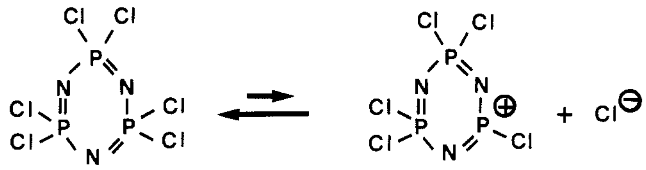
It is well-known[1] that poly(organophosphazenes) (POP) are an unusual class of inorganic polymers whose main chain is based on a sequence of P–N repetitive units.

As far as their synthesis is concerned, they possess a nearly unique characteristic; i.e. they are all prepared by reacting the same parent compound, the highly unstable poly(dichlorophosphazene), $(NPCl_2)_n$ (I), with suitable nucleophilic groups, so obtaining a complete replacement of the chlorine atoms bonded at the phosphorus of the polymer chain. $(NPCl_2)_n$ is in turn prepared by the thermal bulk polymerization of the low molecular weight cyclic trimer, the hexachlorocyclophosphazene, $(NPCl_2)_3$ (II).

In spite of the fact that there has been a great increase of the basic investigations and technical development of POP during the last two decades,[2,3] the mechanism of the reaction which leads hexachlorocyclophosphazene II to poly(dichlorophosphazene) I is not yet fully understood.[4]

The normal experimental procedure for the preparation of I involves a reaction of II at 250 °C for 8–30 h in evacuated, sealed glass tubes, followed by separation of the residual II, for instance by vacuum sublimation.[5]

Scheme I



In the past, several possible reaction mechanisms have been considered[4] for this reaction, in an attempt to obtain a satisfactory explanation of all the reported experimental findings; however, it is now widespread opinion that the polymerization process occurs via the cation mechanism.[6]

The primary initiation step of the reaction is believed to be the heterolytic scission of a P–Cl bond of II, leading to the formation of a P^+Cl^- ion couple (Scheme I).

The propagation step of the polymerization is supposed to be a successive electrophilic attack by P^+ ion on the unpaired electron pair of a nitrogen atom of a second II molecule, followed by the opening of the cyclophosphazene ring. The positive charge on the phosphorus atom is in this way transferred from the P cation on the phosphazene ring to the P atom at the end of the chain, so enabling the

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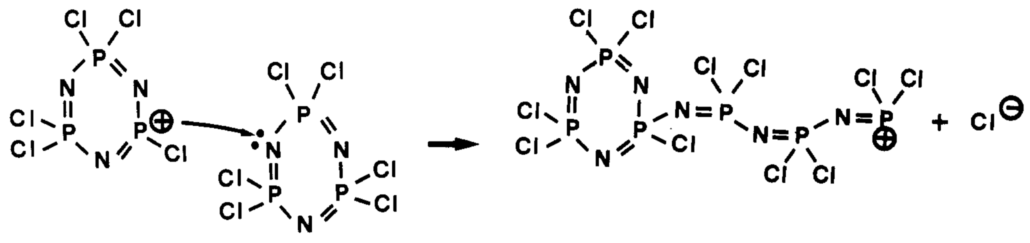
Scheme II



polymer to reach 10 000–15 000 monomeric units (Scheme II).

The polymerization process may be terminated by decreasing the reaction temperature to 25 °C, since in these conditions any further formation of P^+ ions from P–Cl bonds is strongly suppressed.

The overall polymerization process has been found to be irreproducible,[7,8] so much so that equal POP exhibit completely different characteristics and properties, even if prepared from the same batch of II following an identical sequence of experimental steps.

The unpredictable behavior of the polymerization of II, suggests that the mechanism of this reaction may be more complex than previously proposed.[4]

These facts prompted research in the past, in an attempt to elucidate factors which may play a significant role in the polymerization process.

Several kinds of substances like metals, sulfur, alcohols, ethers, ketones, and carboxylic acids[8] have been reported to catalyze the reaction; recently, also the influence of PCl_5, H_2O, and HCl on the polymerization of II have been investigated.[7]

Moreover, it was reported that the glass walls of the reaction vessel may play a certain role in determining the polymerization rate and yield.[9]

Given the above mentioned facts and the promising results obtained by Podda et al., using the ionization chamber of a mass spectrometer as a chemical reactor,[10] we have undertaken the present study, in order to ascertain the possibility of polymerizing II in the ion source, with the aim of gaining insight in the polymerization mechanism of II.

Experimental Section

All measurements were performed with a VG ZAB2F mass spectrometer. The electron impact spectra were obtained at 70 eV (200 μA). Chemical ionization data were obtained with the source operating in the CI mode (100 eV, 2 mA) with NH_3 or CH_4 as reagent gases.

Polymerization reaction was performed in CI configuration, without any reagent gas, the pressure increase being obtained by massive introduction, under controlled conditions, of trimer II.

Collisionally activated decomposition experiments were obtained with 8-keV ions colliding with air in the second field free region. Metastable transitions were detected by B/E and B^2/E linked scans. The sample was introduced in direct electron impact (DEI)[11] conditions.

It should be stressed that II acts as a strong poisoning agent for the ion source, with particular regard to filament life. Therefore special care has been adopted in order to maintain good focalizing conditions of the source and to achieve good reproducibility of the experiments.

Hexachlorocyclophosphazene was purchased from Fluka and purified by precipitation from hexane, followed by several vacuum sublimations.

Results and Discussion

Mass Spectrometry and Polymerization of II. The EI mass spectrum of compound (II) is reported in Figure 1. It may be seen that the most of the total ion current is due to $[(NPCl_2)_3]^{+\cdot}$ (m/z 345) and to $[(NPCl_2)_3 - Cl]^+$ (m/z 310) species, while other less abundant peaks are due to $[NP_2Cl_2]^+$ (m/z 146), $[(NPCl_2)_3 - 3Cl]^+$ (m/z 240), $[NP_2Cl]^{+\cdot}$ (m/z 111), $[PCl_2]^+$ (m/z 101), and $[PCl]^{+\cdot}$ (m/z 66) ions.

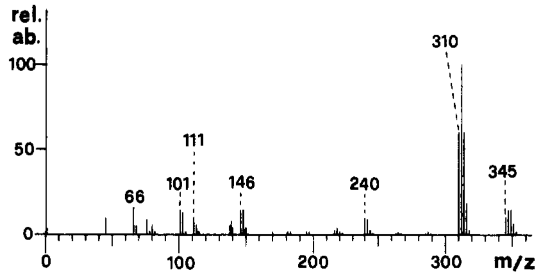


Figure 1. EI (70 eV) mass spectrum of compound II.

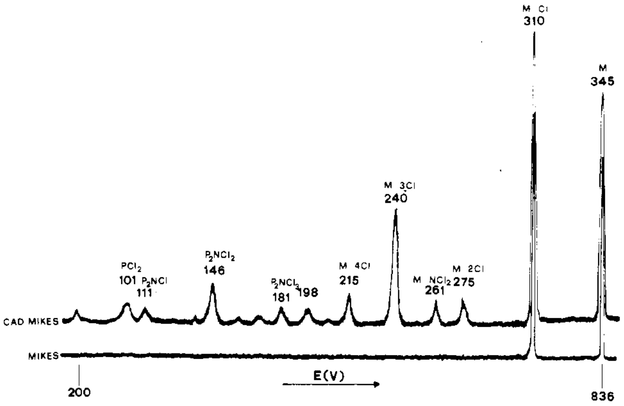


Figure 2. MIKE (bottom) and CAD MIKE (top) spectra of $M^{+\cdot}$ (m/z 345) of compound II.

B/E linked scans as well as MIKE spectra (Figure 2) indicate only a primary chlorine loss for $[(NPCl_2)_3]^{+\cdot}$ and show that the formation of other ionic species is due to secondary EI-induced decompositions.

Collisionally activated decomposition (CAD) experiments on $[(NPCl_2)_3]^{+\cdot}$ (m/z 345) lead to the spectrum shown in Figure 2, in which the ion structure assignment is also reported. It is noteworthy that both in EI and in CAD degradative conditions monomeric ($NPCl_2$) and dimeric $(NPCl_2)_2$ species are absent. Such a behavior supports the cyclic structure of $[(NPCl_2)_3]^{+\cdot}$ as already suggested by Paddock et al.[12] and by Schmulbach et al.[13]

In a similar way, the cation at m/z 310, due to the primary chlorine loss from II, leads to the CAD spectrum reported in Figure 3. In this case, scarcely abundant ions corresponding to $[N_3P_3Cl_5 - NPCl_2]^+$ (m/z 195) and to $[N_3P_3Cl_5 - N_2P_2Cl_4]^+$ (m/z 80) become observable.

The presence of these species might suggest an open, linear structure for the $[(NPCl_2)_3 - Cl]^+$ ion; however, the very large width of the metastable peak (875 meV) corresponding to $[PCl_2]^+$ ion formation observed in the simple MIKE spectrum (see Figure 3) more convincingly suggests a cyclic structure for $[(NPCl_2)_3 - Cl]^+$ (m/z 310) as the more reasonable one.

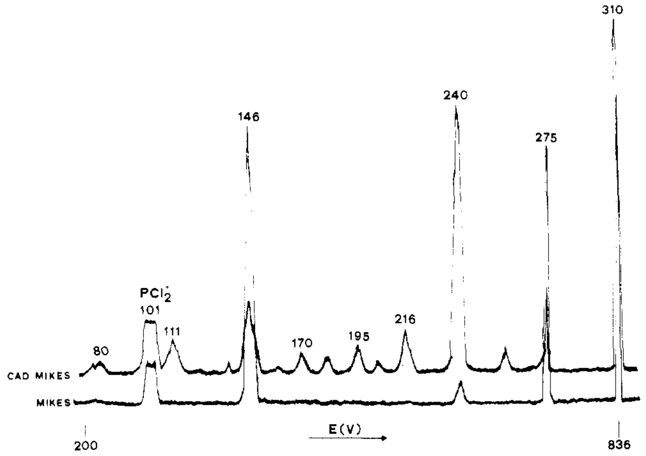


Figure 3. MIKE (bottom) and CAD MIKE (top) spectra of [M − Cl]$^+$ (m/z 310) ions of compound II.

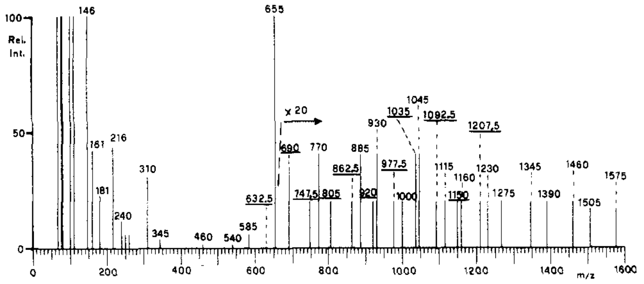


Figure 4. Mass spectrum of polymerization products of compound II (for easier reading, only ions containing ^{35}Cl isotope are reported; the underlined m/z values refer to double-charge ions).

We may therefore conclude that into the mass spectrometer ion source, under EI conditions, the hexachlorocyclophosphazene II preferentially maintains its ring structure, the main modification undergone being the loss of a chlorine atom; in this way, via mass spectrometry, the same species is formed which has been indicated as being responsible for the initiation step of the thermal polymerization (see Introduction).

This fact prompted our attempt to induce the polymerization of the phosphazene cyclic trimer II directly in the ion chamber of the mass spectrometer, in order to have an immediate description (as an in situ analysis) of the reaction products and possibly to get more information about the intimate mechanism of the polymerization reaction of II.

As a matter of fact, simply changing the configuration of the ion source from the EI to the CI mode, so increasing the pressure in the ion chamber (the pressure read at the ion gauge was 5×10^{-5} torr, corresponding to 0.1–1 torr in the ion chamber), and operating at a temperature of 200 °C, the phosphazene cyclic trimer actually polymerizes to poly(dichlorophosphazene) $(NPCl_2)_n$ with $4 \leq n \leq 21$, as evidenced by the presence in the mass spectrum of ions up to 1575 daltons (see Figure 4).

The most abundant species present in this spectrum is $[(NPCl_2)_6 - Cl]^+$ (III) (m/z 655) in agreement with the suggested propagation step of the thermal polymerization (see Introduction) in which is invoked the presence of an hexameric phosphazene intermediate.

A question arises, however, on the molecular structure of the species III produced in the mass spectrometer ion source, since the CAD MIKE spectrum of $[(NPCl_2)_6 - Cl]^+$ ion (Figure 5) shows the more intense peaks at m/z 655, 540, 425, and 310.

The first three peaks of the series correspond respectively to the hexameric parent compound and to species formed by the loss of one or two $NPCl_2$ moieties, which strongly suggest the presence in III of a linear trimeric $NPCl_2$ chain.

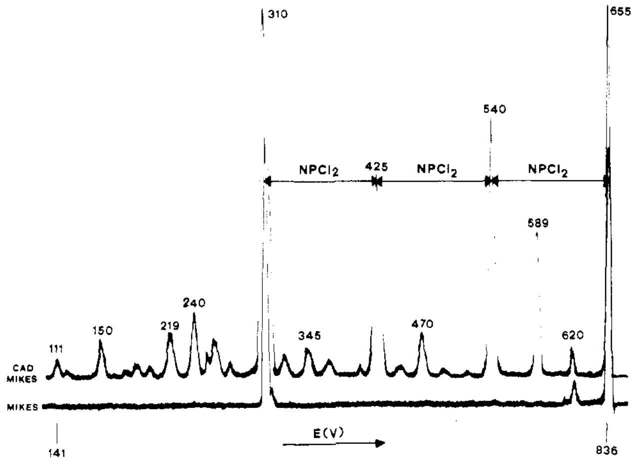


Figure 5. MIKE (bottom) and CAD MIKE (top) of ions at m/z 655 originating from the polymerization of compound II.

The fourth peak at m/z 310 is attributed to the $[(NPCl_2)_3 - Cl]^+$ ion, for which the cyclic structure has been above demonstrated.

No further peaks are present at mass values lower than m/z 310, which may be due to successive losses of $NPCl_2$ moieties (115 daltons).

These facts conclusively prove that the hexameric species III formed in the mass spectrometer ion source has the same structure as that of the molecule indicated as responsible for the propagation step of the thermal polymerization of II (see Scheme II).

In Figure 4, besides the $[(NPCl_2)_6 - Cl]^+$ hexameric ion, another series of species is also present starting from m/z 310 up to m/z 1575, which may be attributed to $[(NPCl_2)_n - Cl]^+$ oligomers of the phosphazene polymer. Quite surprisingly, by accurate B^2/E linked scans, it has been proved that the $[(NPCl_2)_n - Cl]^+$ species at lower molecular weight are not due to unimolecular EI-induced decomposition of ions at higher mass values; they are all genuine products of the polymerization reaction of hexachlorocyclophosphazene.

In the same mass spectrum of Figure 4, in addition to trimeric, hexameric, and oligomeric [phosphazene − Cl]$^+$ ions, also ions due to $[(NPCl_2)_4 - Cl]^+$ (m/z 425) and $[(NPCl_2)_5 - Cl]^+$ (m/z 540) are present in a small amount.

The occurrence in the mass spectrum of these compounds, not present as impurities in the starting phosphazene trimer, may be explained in terms of general thermodynamic considerations involving a thermal equilibration process of II with the tetramer and pentamer rings during heating in the ion source and/or under EI conditions.[14]

Alternatively, according to another possible explanation, they may arise from hexameric phosphazene ions, by successive losses of neutral $NPCl_2$ moieties, not detectable via mass spectrometry. Unfortunately any attempt to elucidate tetramer and pentamer structure via MIKE and CAD MIKE spectra failed, probably due to the scarce abundance of these ions.

However it should be further stressed that the formation of tetrameric and pentameric species is not due to the unimolecular EI-induced decomposition of $[(NPCl_2)_6 - Cl]^+$ through the sequential loss of monomeric units.

Double-Charge Ions. In the mass spectrum of $(NPCl_2)_n$ (Figure 4) double-charge ions of structure $[(NPCl_2)_n]^{2+}$ for $9 \leq n \leq 21$ are detectable, while the

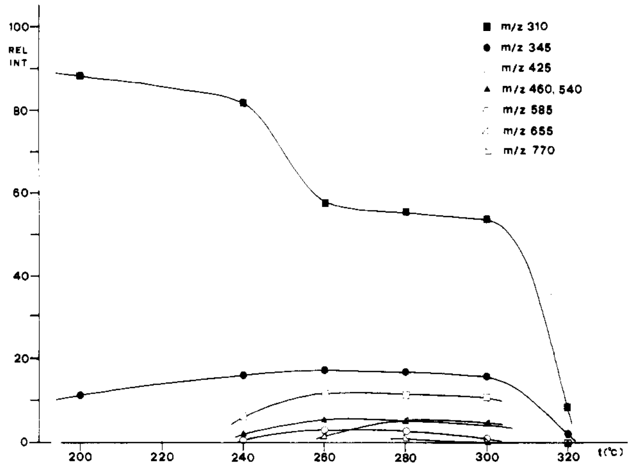


Figure 6. Trends of relative abundance vs. temperature (°C) of the main species originating from thermal polymerization of compound II.

corresponding $[(NPCl_2)_n]^+$ are completely absent.

This behavior may be simply explained on the basis of charge distribution; in fact, the threshold value of $n = 9$ for the occurrence of double charge species is highly indicative that positive charges are better stabilized as a function of the length of the polymer chain.

Polymerization of II at Different Temperatures. The polymerization reaction of II has also been studied at low pressure (2×10^{-6} torr as read on ion gauge) with the mass spectrometer in EI configuration, as a function of the ion source temperature.

The relative abundance of ions at m/z 310, 345, 425, 460, 540, 585, 655, and 770 vs. ion source temperature are reported in Figure 6. It may be observed that oligomeric $(NPCl_2)_n$ species become detectable over 230 °C and disappear over 310 °C, well paralleling the data obtained in the thermal polymerization of II.

It must be stressed that the sharp decrease of the m/z 310 ion abundance at temperature around 250 °C, in close correspondence to the onset of $(NPCl_2)_3$ thermal polymerization, may be considered as convincing evidence of the ion–molecule character of this reaction.

Influence of Acids. Since it is well-known that the thermally induced bulk polymerization of $(NPCl_2)_3$ is inhibited by the presence of acidic species,[7] this influence on the mass spectrometric reaction was also investigated.

In CI (CH_4) conditions, where the proton donor species is CH_5^+, $[(NPCl_2)_6H]^+$ (m/z 691), $[(NPCl_2)_6 - Cl]^+$ (m/z 655), $[(NPCl_2)_3H]^+$ (m/z 346), and $[(NPCl_2)_3 - Cl]^+$ (m/z 310) ionic species are formed in an abundance ratio of 1:10:2:8.

By use of NH_4^+ as protonating agent (ammonia gas instead of methane is introduced in the CI source) the same sequence of ionic species is found but in an abundance ratio of 1:4:5:3. In both cases the formation of higher molecular weight species is completely suppressed.

These experimental results agree very well with earlier investigations on the influence of acidic species on the polymerization of II, in which the presence of strong acids, like HCl, inhibits the formation of $(NPCl_2)_n$ polymer and/or strongly reduces its yield.[7]

In the present case, with both CH_4 and NH_3 CI reagent gases, we observed the formation of $[(NPCl_2)_3H]^+$ and $[(NPCl_2)_3 - Cl]^+$ ions; the latter is the highly reactive intermediate responsible for the polymerization reaction of II, as above reported, while the former one can be attributed to a nitrogen-protonated trimer molecule.[15]

In this context, the electrophilic attack of $[(NPCl_2)_3 - Cl]^+$ species on the protonated phosphazene trimer becomes increasingly difficult due to the presence of a positive charge on the phosphazene ring. All these facts are in good agreement with the general polymerization scheme reported in the Introduction section.

It is interesting to note the difference in yield of hexameric moieties (m/z 655) as a function of the acidity of the protonating species ($CH_5^+ > NH_4^+$): the more acidic the reacting species, the lower is the yield of hexamer production, which also fits very well with the general polymerization mechanism of II.

Conclusions

In this paper mass spectrometry shows an unusual preparative aspect. In fact the use of some new mass spectrometric techniques enables us to: (1) induce the polymerization reaction of hexachlorocyclophosphazene II directly in the ionization chamber of a mass spectrometer; (2) clarify the intimate mechanism of the above reaction; (3) obtain valuable information about the chemical structure of reactive species formed during polymerization; (4) investigate the influence of several parameters (such as the pressure and temperature of the ionization chamber, as well as the acidity of the system) on this polymerization.

The obtained results point to a substantial analogy between the mechanism of the bulk- and gas-phase mass spectrometric polymerization of II.

It should be stressed that a satisfactory knowledge of this mechanism may be considered as a preliminary condition in order to overcome the experimental difficulties inherently due to the irreproducibility of the polymerization process, which would finally lead to a predictable synthesis of POP.

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Registry No. $(NPCl_2)_3$, 940-71-6; $(NPCl_2)_n$, 26085-02-9.

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