Mass Spectrometrically Induced Polymerization of Hexaphenoxycyclo(triphosphazene)

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The polymerization of hexaphenoxycyclo(triphosphazene), carried out in the ion source of a mass spectrometer, leads to phenoxy-phosphazene polymers, with a polymerization degree of $n = 12$.

Polyorganophosphazenes are organic–inorganic polymers, prepared by the ring-opening polymerization of low molecular weight cyclic halogenated trimers, followed by the nucleophilic replacement of the halogen atoms in the polymer with suitable substituent groups.[1]

In spite of the fact that fluoro-, chloro-, bromo- and isothiocyano-cyclo(triphosphazenes) readily polymerize to give linear high molecular weight phosphazene polymers when heated (at temperatures ranging between 150 and 350 °C),[1] the polymerization of fully substituted cyclophosphazenes has never been reported.[2] This communication deals with the first example of this type of polymerization.

In close analogy with the mass spectrometrically induced polymerization of hexachlorocyclo(triphosphazene) $(NPCl_2)_3$ to poly(dichlorophosphazene) $(NPCl_2)_n$ recently reported,[3] hexaphenoxycyclo(triphosphazene) $[NP(OPh)_2]_3$ (**1**) has been polymerized in the ion chamber of a VG ZAB 2F mass spectrometer in chemical ionisation mode with a sample vapour pressure of 1.5×10^{-1} Torr and at a temperature of 200 °C.

It has been found, in fact, that the main fragmentation process observed for (**1**) under electron impact conditions is the primary loss of a $PhO^{\bullet}$ radical and formation of the $\{[NP(OPh)_2]_3 - PhO^{\bullet}\}^+$ cation (**2**) (*m/z* 600), reaction (1).

This process may be considered as the initiation step of the polymerization of (**1**).

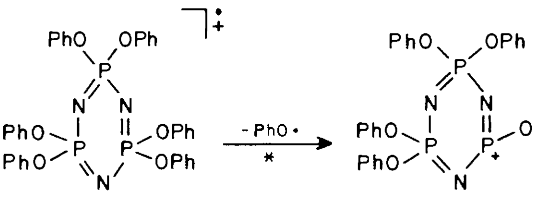
The structure of the species (**2**) has been elucidated *via* mass analysed ion kinetic energy (MIKE) spectra, which demonstrated that the phosphonitrilic ring of (**1**) is preserved in (**2**) even after the loss of the phenoxy group.

On increasing the pressure of (**1**) in the ion source to 1.5×10^{-1} Torr, the polymerization takes place through an electrophilic attack of (**2**) on a nitrogen atom of another phenoxyphosphazene molecule (propagation step), which leads to the formation of a hexameric species $\{[NP(OPh)_2]_6 - PhO^{\bullet}\}^+$ (**3**) (*m/z* 1293), reaction (2).

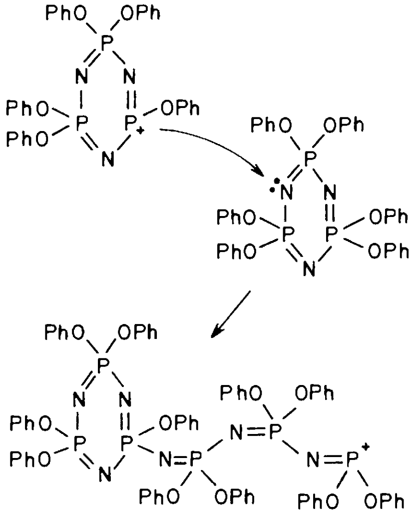
The MIKE spectrum of (**3**) provides evidence for the successive loss of three monomeric units $NP(OPh)_2$ (peaks at *m/z* 1062, 831, and 600 respectively) which suggests that the product (**3**) is formed as a pentaphenoxycyclo(triphosphazene) moiety (*m/z* 600) linked to a linear phenoxytriphosphazene chain.

On further increase in pressure (5×10^{-1} Torr) in the ion source, phenoxy-phosphazene polymers with a polymerization degree of $n = 9$ and $n = 12$ have been detected, which correspond to the species $\{[NP(OPh)_2]_9 - PhO^{\bullet}\}^+$ (*m/z* 1986) and $\{[NP(OPh)_2]_{12} - PhO^{\bullet}\}^+$ (*m/z* 2769), respectively.

An investigation of the effect of temperature on the poly-



(1) (2) (1)



(3) (2)

merization reaction of (1) shows that neither the hexameric species (3) nor the phenoxy polymers, $n = 9$ and $n = 12$, are formed at temperatures above 220 °C, owing to the onset of thermal decomposition processes.

This fact is in close accordance with the reported thermal behaviour of poly(bisphenoxyphosphazene)[4] and gives evidence that hexaphenoxycyclo(triphosphazene) (**1**) does not polymerize thermally because ionic species, of undetermined structures, are formed as the only products at $T > 350$ °C (as shown by electrical conductance measurements)[5] and at this temperature the phenoxyphosphazene polymer is completely unstable.[4]

Mass spectrometry however provides an easy and simple method to produce the highly reactive species (**2**) at a much lower temperature (200 °C), so allowing the survival of the poly(bisphenoxyphosphazene) formed.

Moreover, other experiments performed using several different aryloxy-substituted cyclophosphazenes, showed that other phosphazene trimers readily polymerize to the corresponding oligomers under these experimental conditions.

For example, the polymerization of hexa(*p*-chlorophenoxy)-cyclo(triphosphazene) takes place in the ion chamber of the mass spectrometer with a polymerization yield very close to that found for $[NP(OPh)_2]_3$. In contrast, it has been observed that the polymerization process is strongly inhibited in the case of cyclophosphazenes substituted with bulky groups [hexa(β-naphthoxy)cyclo(triphosphazene)] or with trimers bearing substituents with strong electron-donating functions [hexa(*p*-methoxyphenoxy)cyclo(triphosphazene)].

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