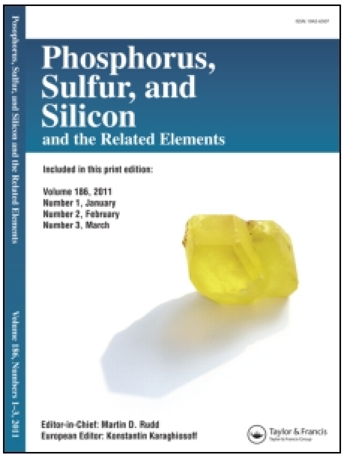

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Polydichlorophosphazene from N-Dichlorophosphoryl- P-Trichloromonophosphazene

R. De Jaeger[a]; Ph. Potin[b]
[a] LASIR, CNRS, UPR A 2631 L, Université des Sciences et Technologies de Lille, Villeneuve d'Ascq, Cedex, France [b] Atochem S. A. (Elf Aquitaine) Groupement de Recherches de Lacq, Artix, France

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POLYDICHLOROPHOSPHAZENE FROM N-DICHLOROPHOSPHORYL-P-TRICHLOROMONOPHOSPHAZENE

R. DE JAEGER*, Ph. POTIN**
*LASIR, CNRS, UPR A 2631 L, Université des Sciences et Technologies de Lille, Bât. C5, 59655 Villeneuve d'Ascq Cedex, France
**ATOCHEM S.A. (ELF AQUITAINE)
Groupement de Recherches de Lacq, BP 34, 64170 Artix, France.

Abstract : Description of an access route for polydichlorophosphazene based on the polycondensation of N-dichlorophosphoryl- P-trichloromonophosphazene.

The present report describes an access route for polydichlorophosphazene based on the polycondensation of N-dichlorophosphoryl-P-trichloromonophosphazene (I)[1]

$Cl_2(O)\,P - N = PCl_3$ (I)

At high temperature, the elimination of the two departing groups $P(O)Cl_2$ and Cl as $P(O)Cl_3$ results in the condensation of the phosphazene monomer according to (1)

$$nCl_3P{=}N{-}P(O)Cl_2 \longrightarrow Cl_3P{=}N\ (PCl_2{=}N)_{n-1}\ P(O)Cl_2 + (n-1)\ P(O)Cl_3 \qquad (1)$$

Monitoring the progress of the reaction with the use of ^{31}P NMR spectroscopy in the case of a bulk polycondensation allowed the variations of molal fraction of monomer (n=1) dimer (n=2) and trimer (n=3), as a function of time and degree of conversion p to be determined (Fig. 1).

The experimental values obtained in this work are compared with those calculated in the case of "stepwise" and "random" chain growth (Fig. 2). It shows that an intermediary mechanism is involved and that the reactivity increases from monomer to oligomers. A study of the chemical shifts of the $Cl_3P{=}N{-}$ and $P(O)Cl_2$ groups as a function of n shows that the former moves toward weak fields as n increase (up to a limit when n > 4), and that the second does not move. Therefore, it can be expected that the reactivity of oligomers is due to the one of the PCl_3 groups.

Assuming this hypothese it can be expected that all the reactions involving the chlorine atom of the PCl_3 group of an n-mer molecule, and the $POCl_2$ group of an n'-mer specie can be characterized by the kinetic constant k_n.

In this case, the application of the principle of stationnary state to dimer and trimer allows the kinetics constants to be determined and shows that $k_2 \neq 7\ k_1$ and $k_3 \neq 16\ k_1$.

This reasoning is a simplification because the reaction is reversible. However the depolycondensation rate is very low compared to that of polycondensation, and this simplification is justified (see next report).

This polycondensation leads also to the formation of cyclic species.

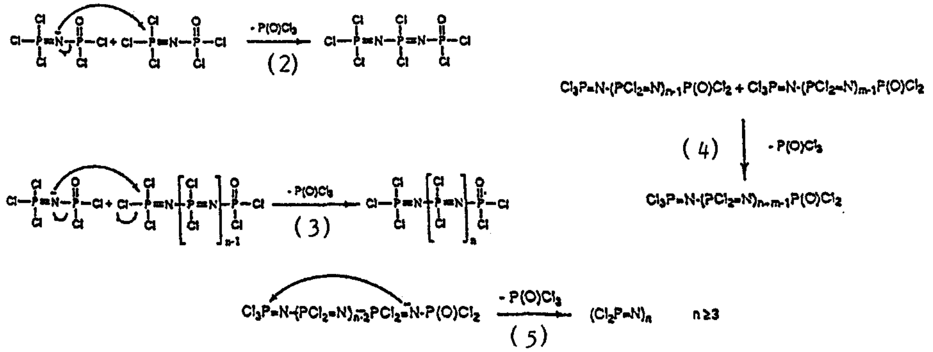
These rings are formed during the first 80 % conversion, when the linear homologues are present. After, their concentration remains constant (Fig. 3).

Thence their formation is not due to a degradation of the polymer but to a linear oligomers cyclisation.

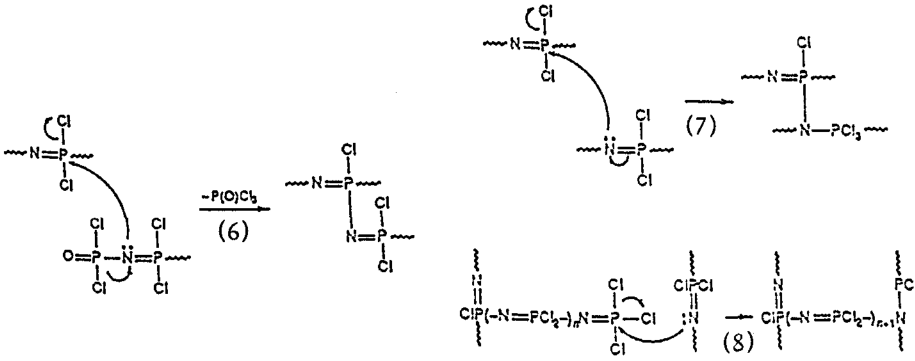
The relative concentration of these rings is greater when the monomer concentration is lower.

This result leads us to suggest that for to obtain a polymer with the minimum of cyclic species, the reaction must be firstly conducted in bulk and the solvent only introduced after the release of $POCl_3$ has ceased.

The reactions (2) to (5) summarize the reaction mechanism. The rate of (2) is low in comparison with (3). When n increase, the PCl_3 end groups have the same reactivity and so the oligomers react randomly according to (4). Intramolecular reactions (5) explain the formation of cyclic species.



Cross linking reactions can be explained by repetition on the same molecule of the reaction (6) or by the intermolecular reactions (7) and (8) as indicated by Allcock[2]. These reactions become dominant in a bulk condensation when conversion is high. The addition of solvent stabilizes the polycondensate and allows high molecular weights to be obtained. It is possible to maintain a solution of Polydichlorophosphazene in trichlorodiphenyl at 280°C for 60 h without gel formation.



Ammonium chloride and bis(dichlorophosphoryl)imide $HN(POCl_2)_2$ which are impurities derived from the monomer synthesis are catalysts for (1) (Fig. 4). Pyrophosphoryl chloride and some tertiary amines have the same catalytic effect.

Inversely PCl_5 and $Cl_3PNPCl_3^+\ PCl_6^-$ are inhibitants

The application of these results, along with those of other studies described in the next report, has enabled us to prepare a range of polymers with a molecular weight varying from 3.10^4 to 10^6 g/mol.

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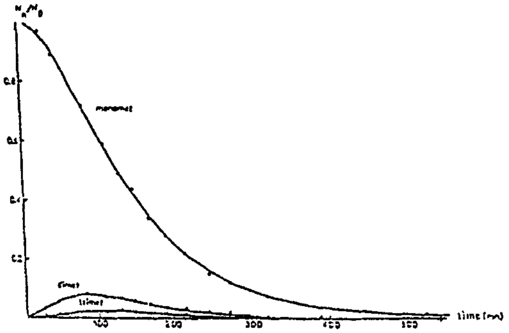

Fig 1: Variations of N_n/N_0 versus time for n=1-3.

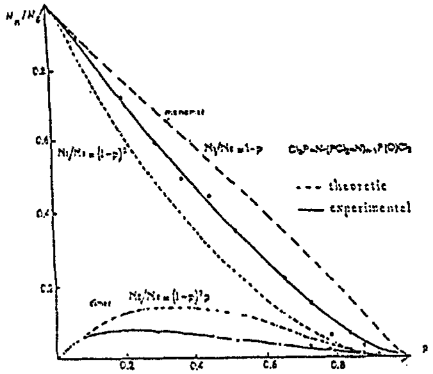

Fig 2: Experimental and calculated variations of N_n/N_0 versus p for n=1 and 2.

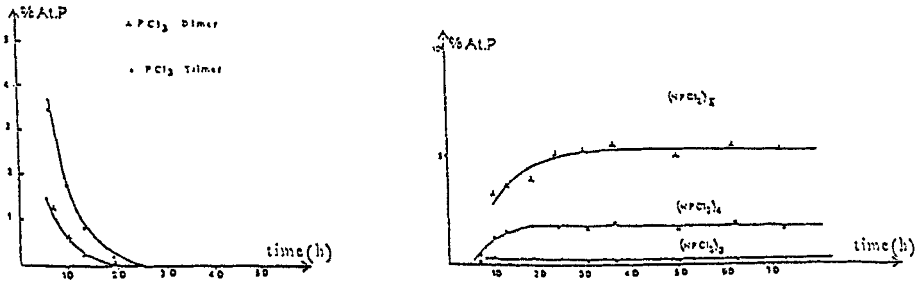

Fig 3: Percentages of phosphorus atoms present in $Cl_3P=N$ end groups of oligomers and in cyclic species versus time.

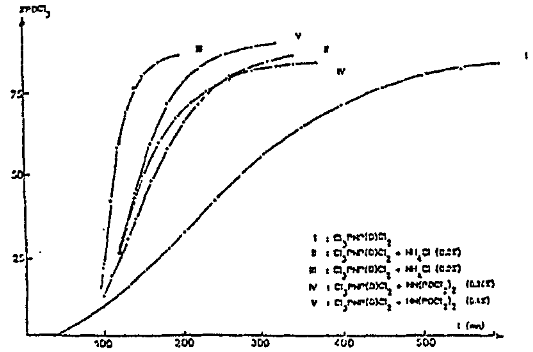

Fig 4 : Catalytic effect of $HN(POCl_2)_2$ and NH_4Cl