Synthesis of Poly(dichlorophosphazenes) from $Cl_3P{=}NP(O)Cl_2$. 1. Kinetics and Reaction Mechanism

G. D'Halluin and R. De Jaeger*

Laboratoire de Spectrochimie Infrarouge et Raman (CNRS UPR A 2631 L),
Université des Sciences et Techniques de Lille Flandres Artois, Bât. C.5,
59655 Villeneuve d'Ascq Cedex, France

J. P. Chambrette and Ph. Potin

Atochem (Groupe Elf Aquitaine) Groupement de Recherches de Lacq, BP 34, 64170 Artix,
France

Received October 18, 1990

ABSTRACT: Type $Cl_3P{=}N(PCl_2{=}N)_{n-1}P(O)Cl_2$ poly(dichlorophosphazenes) have been synthesized by solution polycondensation of *P*-trichloro-*N*-(dichlorophosphoryl)monophosphazene, $Cl_3P{=}NP(O)Cl_2$. Monitoring the progress of the reaction using ^{31}P NMR spectroscopy allowed us to determine an order of magnitude of the reactivity ratio for the species $n = 1–4$ and to propose a mechanism. The results obtained enabled us to prepare a range of polymers with an intrinsic viscosity varying in the solvent THF at 30 °C from 10 to 72 mL/g and to establish the Mark–Houwink relationship in the same solvent.

Introduction

There have been many studies on the synthesis of linear poly(dichlorophosphazene) [$(NPCl_2)_n$ or PCPZ] from linear oligomers of low molecular weight.[1]

However, to date, the only procedure which results in a PCPZ with a sufficiently high molecular weight is the thermal polymerization of hexachlorocyclotriphosphazene $(NPCl_2)_3$. This method was described for the first time by Allcock et al. in 1965[2] and has since been optimized for industrial application. A detailed study of this reaction was published in 1981 by Hagnauer,[3] and more recent articles have shown that high molecular weight polymers can be obtained if the polymerization is conducted in solution[4] (for example, in carbon sulfide or 1,2,4-trichlorobenzene). In this case cross-linking reactions can be avoided.

The present work describes a new access route for PCPZ which depends on the polycondensation of *N*-(dichlorophosphoryl)-*P*-trichloromonophosphazene, $Cl_3P{=}NP(O)Cl_2$ (I), in solution.[5] A similar type of polycondensation process was used by Neilson and Wisian-Neilson[6] in 1988 to prepare substituted poly(alkylphosphazenes).

At high temperature I behaves as a difunctional compound bearing two leaving groups: $P(O)Cl_2$ and Cl. The elimination of these two groups as $P(O)Cl_3$ results in the condensation of the phosphazene monomer as indicated by eq 1.[7]

$$n\mathrm{Cl_3P}\underset{\mathrm{I}}{\mathrm{N}}\mathrm{O(O)Cl_2} \rightarrow$$

$$\mathrm{Cl_3P{=}N(\text{-}PCl_2{=}N\text{-})_{\mathit{n}-1}P(O)Cl_2} + (n-1)\mathrm{P(O)Cl_3} \quad (1)$$

Results and Discussion

Bulk Polycondensation. The condensation reaction (eq 1) normally occurs around 200 °C. However, this reaction can be set off at much lower temperatures if the monomer I is not sufficiently pure or in the presence of catalysts. The degree of conversion p can be followed by weighing the $P(O)Cl_3$ released. Generally speaking, the $p = f(\text{time})$ curves comprise three phases (Figure 1).

The first phase is the initiation of the reaction. Its duration depends on the reactivity (and thus on the purity of I) and on the temperature. During the second phase ($15\% < p < 65\%$) the variations of p are linear. The apparent kinetic order is 0.

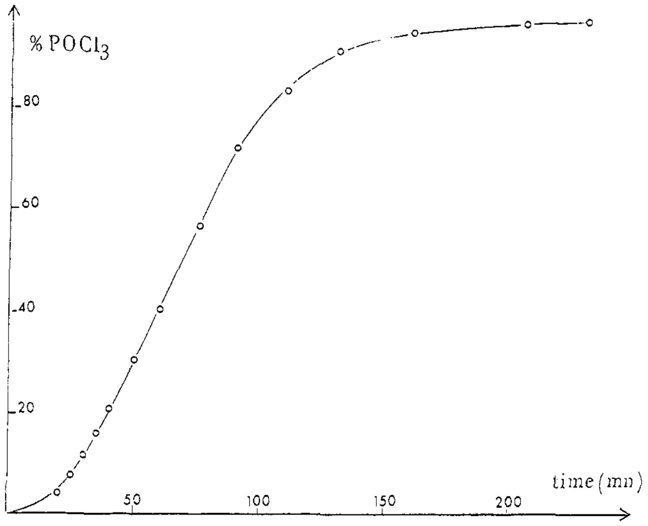


Figure 1. Percentage of released $P(O)Cl_3$ versus time.

Above 65% conversion the $p = f(\text{time})$ curve tends to an asymptote. For this period, during which a significant increase in the viscosity can be noted, the kinetic order is 2. The reaction ceases when the viscosity becomes such that the polycondensate rises up along the stirring rod. At this stage the degree of polycondensation of the polymers is fairly low, between 700 and 1000.

Polycondensation in Solution. The use of a solvent reduces the viscosity of the polycondensate, which can then be stirred throughout the reaction. The choice of the solvent must satisfy a number of criteria. The main requirements are as follows:

(1) It must dissolve the PCPZ at the polycondensation temperature.

(2) It must be chemically inert with respect to phosphochlorinated compounds at the same temperature.

(3) It must be easily separable from the $P(O)Cl_3$ formed during the reaction.

Trichlorodiphenyl, which satisfies these requirements and also provides remarkably stable polycondensate solutions, was used for most of our experiments.

0024-9297/92/2225-1254$03.00/0 © 1992 American Chemical Society

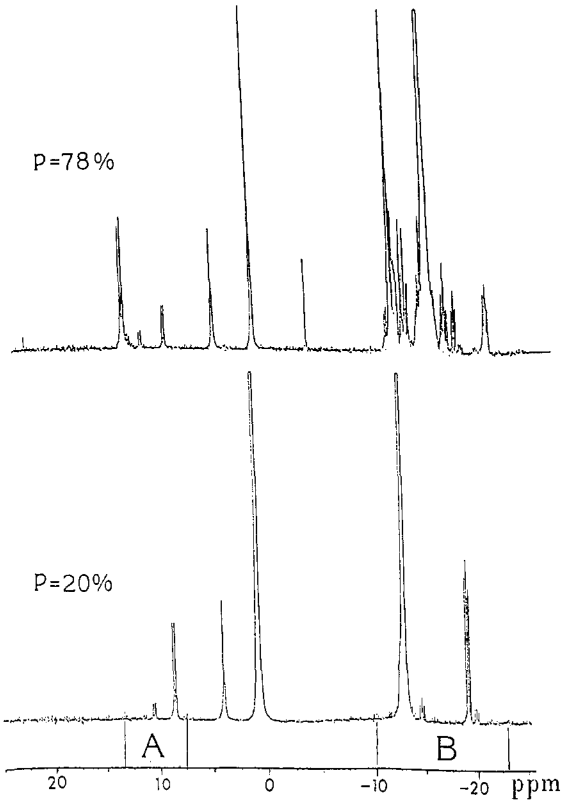


Figure 2. ^{31}P NMR spectra of two samples taken at $p = 20$ and 78%: (●) $Cl_3P{=}N$ end groups in $Cl_3P{=}N(-PCl_2{=}N-)_{n-1}P(O)Cl_2$ oligomers and polymers (spectral zone A); (+) $P(O)Cl_3$; (△) cyclic species $(NPCl_2)_4n$ ($n = 3$ and 4). (Spectral zone B) $P(O)Cl_2$ end groups; $N{=}PCl_2$ units in oligomeric and polymeric chains; cyclic species $(NPCl_2)_n$ ($n > 4$).

^{31}P NMR Control. Kinetic Study. Reaction 1 was followed by ^{31}P NMR analysis of samples taken during a bulk polycondensation at 240 °C. Two spectra recorded during the course of the reaction ($p = 20$ and 78%) show the different species present (Figure 2).

Table I shows the attributions of the measured chemical shifts of the various phosphorus atoms in each of these compounds. The following remarks can be made on examination of Figure 2 and Table I:

(1) Spectral zone A which ranges from $\delta = 13$ to 7 is characteristic of the $Cl_3P{=}N$ end groups in oligomers of type $Cl_3P{=}N(PCl_2{=}N)_{n-1}P(O)Cl_2$ ($n > 1$), for $n = 1$, $\delta = 0.5$. Study of the chemical shift as a function of n shows that it moves toward weak fields as n increases up to the limit ($\delta = 12$) when $n > 4$. The signal can be easily integrated for $n = 1$–3 (for $n = 4$ the measurement gives only an order of magnitude).

Table I
^{31}P NMR Spectroscopic Data[8]

compd	δ,[a] ppm	J, Hz
$Cl_3PNP(O)Cl_2$[b]	P1: 0.5 (d)	16.2
1 2	P2: −12.8 (d)	
$Cl_3PNPCl_2NP(O)Cl_2$[b]	P1: 8.5 (d)	$J_{13} = 30$
1 3 2	P2: −12.4 (d)	$J_{23} = 28.5$
	P3: −19.2 (dd)	
$Cl_3PNPCl_2NPCl_2NP(O)Cl_2$[b]	P1: 10.5 (d)	$J_{13} = 34.5$
1 3 3′ 2	P2: −12.8 (d)	$J_{33'} = 39$
	P3: −14.6 (dd)	$J_{3'2} = 27.7$
	P3′: −19.9 (dd)	
$Cl_3PNPCl_2NPCl_2NPCl_2NP(O)Cl_2$[b]	P1: 11.2 (d)	$J_{13} = 34$
1 3 3″ 3′ 2	P2: −13 (d)	
	P3: −13.6 (dd)	$J_{23'} = 29.4$
	P3′: −21 (dd)	
	P3″: −16.2 (dd)	$J_{3'3''} = 35$
		$J_{33''} = 37.4$
$Cl_3PN(PCl_2N)_{n-1}P(O)Cl_2$, $n > 4$	P1: 12 (d)	
1 3	P3: −16.6 (s)	
$(NPCl_2)_3$	21 (s)	
$(NPCl_2)_4$	−5 (s)	
$(NPCl_2)_5$	−16 (s)	
$P(O)Cl_3$	3.5	

[a] Solvent: C_6D_6. [b] Compounds synthesized for this study.

(2) Spectral zone B ranging from $\delta = -10$ to -23 is representative of phosphorus atoms present in the end groups $P(O)Cl_2$, in the $N{=}PCl_2$ units of the polymeric chains, and in chlorocyclophosphazenes $(NPCl_2)_n$ with $n > 4$.

The disappearance of one $Cl_3P{=}N$ end group in eq 1 results in the formation of a new $N{=}PCl_2$ unit. Therefore the number of phosphorus atoms present in these two groups at any time t is equal to N_0, the initial number of molecules of monomer I.

Each $Cl_3P{=}N$ end group of spectral zone A has a corresponding $=NP(O)Cl_2$ end group in spectral zone B.

Since the proportion of cyclic species is low (as will be shown later in this paper), the molar fraction N_n/N_0 can be deduced from the spectra (where N_n is the number of n-mer molecules at time t).

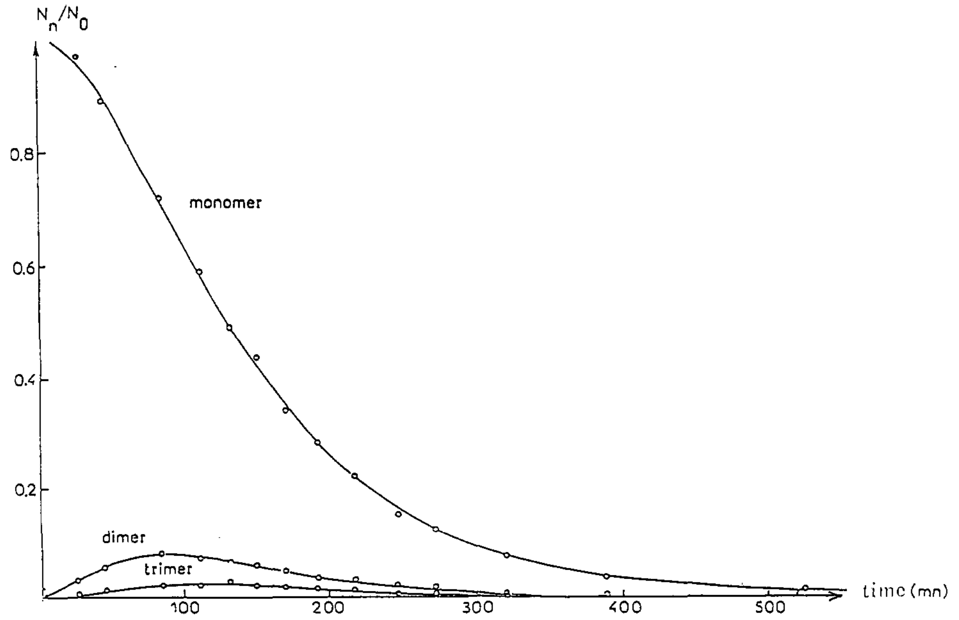


Figure 3. Variations of N_n/N_0 versus time for $n = 1$–3.

This fraction is given by

$$\frac{N_n}{N_0} = \frac{I(\mathrm{Cl_3P{=}N})_n}{I'[(\mathrm{Cl_3P{=}N}) + (\mathrm{N{=}PCl_2})]} = \frac{I(\mathrm{Cl_3P{=}N})_n}{I'[({=}\mathrm{NP(O)Cl_2}) + (\mathrm{N{=}PCl_2})]} = \frac{I(\mathrm{Cl_3P{=}N})_n}{I'(\mathrm{B})}$$

where $I(X)_n$ represents the integration of the X group of an n-mer molecule, $I'(X)$ the integration of all the X groups, and $I'(B)$ the integration of spectral zone B.

Variations of N_n/N_0 as a function of time are represented in Figure 3 for $n = 1$–3. It can be noted that the number of linear oligomers remains low: the maximum values for N_n/N_0 are 8% for $n = 2$ and 2.5% for $n = 3$. (For $n = 4$ it can be estimated to be 0.7%.) Thus these oligomers are more reactive than monomer I. This is confirmed by comparing the experimental variations of N_n/N_0, as a function of the degree of conversion p, with those calculated in the case of a "stepwise" chain growth ($N_1/N_0 = 1 - p$) and also for a "random" chain growth which supposes an equal reactivity of all different species ($N_n/N_0 = (1 - p)^2p^{n-1}$) (Figure 4).

It seems obvious that we are dealing with an intermediary mechanism. If it is assumed that the variations in the chemical shift of the $Cl_3P{=}N$ end groups are due to a reduced electron density on the phosphorus atom, it can be expected that their reactivity should increase from the monomer to the tetramer.

Similarly, as the characteristic signal of the $P(O)Cl_2$ end group does not move, it can be assumed that its reactivity hardly changes from one species to another.

Assuming these hypotheses, all the reactions eq 2 involving the chlorine atom of the $Cl_3P{=}N$ group of an n-mer molecule and the $P(O)Cl_2$ end group of an n'-mer species can be characterized by a single kinetic constant k_n.

$$\mathrm{Cl_2(O)P(\text{-}N{=}PCl_2\text{-})_1Cl + Cl_2(O)P(\text{-}N{=}PCl_2\text{-})_{n'}Cl \xrightarrow{k_1} Cl_2(O)P(\text{-}N{=}PCl_2\text{-})_{n'+1}Cl + P(O)Cl_3}$$

$$\mathrm{Cl_2(O)P(\text{-}N{=}PCl_2\text{-})_2Cl + Cl_2(O)P(\text{-}N{=}PCl_2\text{-})_{n'}Cl \xrightarrow{k_2} Cl_2(O)P(\text{-}N{=}PCl_2\text{-})_{n'+2}Cl + P(O)Cl_3}$$

$$\mathrm{Cl_2(O)P(\text{-}N{=}PCl_2\text{-})_nCl + Cl_2(O)P(\text{-}N{=}PCl_2\text{-})_{n'}Cl \xrightarrow{k_n} Cl_2(O)P(\text{-}N{=}PCl_2\text{-})_{n'+n}Cl + P(O)Cl_3} \quad (2)$$

This leads to the reaction scheme shown in Figure 5, which represents the first stages of the polycondensation. Applying the principle of stationary states to the dimer, trimer, and tetramer species gives the equations

$$k_1(A)^2 = k_1(A)(B) + k_2(B)[(A) + (B) + (C)] - k_3(B)(C)$$

$$(k_1 + k_2)(A')(B') = k_1(A)(C') + k_2(B')(C') + k_3(C')[(A') + (B')]$$

$$(k_1 + k_3)(A'')(C'') + k_2(B'')^2 = (k_1 + k_4)(A'')(D'')$$

in which (X), (X'), and (X'') are the molar fractions of the n-mers ($n = 1$–4) to the experimental maxima of dimer, trimer, and tetramer species.

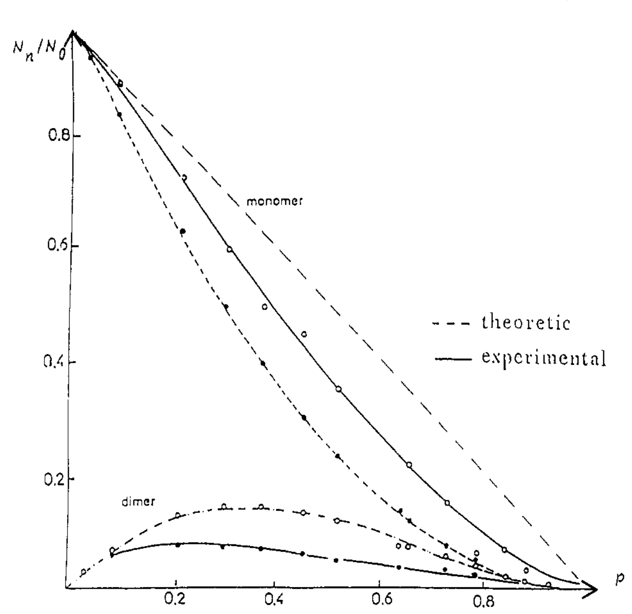


Figure 4. Experimental and calculated variations of N_n/N_0 versus p for $n = 1$ and 2.

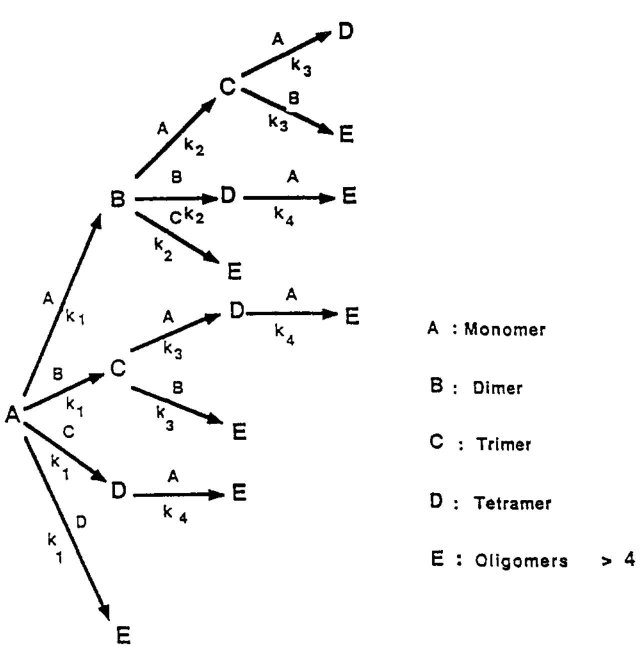


Figure 5. First stages of the polycondensation.

Solving this system of equations allows the kinetic constants to be determined and shows that

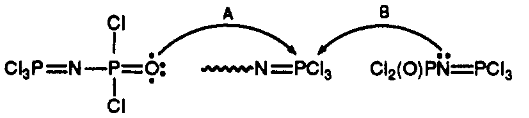
$$k_2 = 7k_1 \qquad k_3 = 16k_1 \qquad k_4 = 32k_1$$

(only an order of magnitude for k_4).

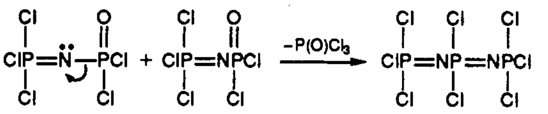
According to these results, the $Cl_3P{=}N$ end group in the trimer is about 16 times more reactive than the same group in monomer I.

This reasoning does not take account of the reversibility of reaction 1. This simplification is justified since the depolycondensation rate is very low compared to that of the polycondensation. Since the presence of 5% $P(O)Cl_3$ by weight in the polycondensate effectively limits the average degree of condensation to a value of about 1000, the ratio between these two rates is approximately 10^4 (the detailed study of this equilibrium will be published at a later date).

Reaction Mechanism. It can be supposed from these results that the driving force for reaction 1 lies in the affinity of the electron-rich N-dichlorophosphoryl group for the phosphorus atom of the electron-poor trichlorophosphazene. The donor capacity of the $=NP(O)Cl_2$ is provided by either the oxygen (A) or by the nitrogen atom (B):

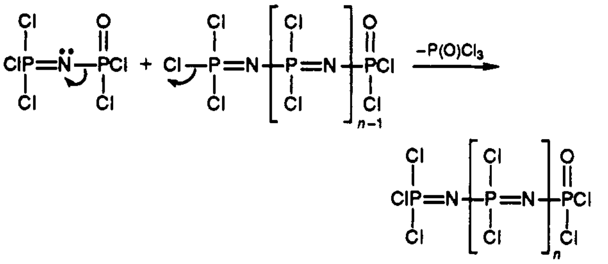


The formation of a P=N-P= bridge requires the phosphoryl bond to be broken for case A, and the less stable P-N bond to be broken for case B. A situation of type A is thus rather unlikely, and the formation of $P(O)Cl_3$ at the beginning of the reaction can only be explained by the nucleophilic attack of the $Cl_3P{=}N$ phosphorus in I by a nitrogen atom of another monomer molecule as shown in eq 3.



$$\underset{Cl}{\overset{Cl}{ClP}}{=}\ddot{N}-\underset{Cl}{\overset{O}{PCl}} + \underset{Cl}{\overset{Cl}{ClP}}{=}N\underset{Cl}{\overset{O}{PCl}} \xrightarrow{-P(O)Cl_3} \underset{Cl}{\overset{Cl}{ClP}}{=}N\underset{Cl}{\overset{Cl}{P}}{=}N\underset{Cl}{\overset{Cl}{PCl}} \quad (3)$$

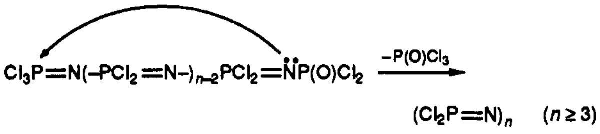
The existence of an induction period as well as the reactivity ratios calculated previously proves that eq 3 is slow in comparison with the reaction of I with oligomers, according to reaction 4, or with interoligomer reactions.



$$\underset{Cl}{\overset{Cl}{ClP}}{=}\ddot{N}-\underset{Cl}{\overset{O}{PCl}} + Cl-\underset{Cl}{\overset{Cl}{P}}{=}N\left[\underset{Cl}{\overset{Cl}{P}}{=}N\right]_{n-1}\underset{Cl}{\overset{O}{PCl}} \xrightarrow{-P(O)Cl_3} \underset{Cl}{\overset{Cl}{ClP}}{=}N\left[\underset{Cl}{\overset{Cl}{P}}{=}N\right]_{n}\underset{Cl}{\overset{O}{PCl}} \quad (4)$$

As n increases, a tendency toward equal reactivity of the end groups can be assumed, and so the oligomers react randomly between each other by a reaction of the type in eq 5. This causes a quicker increase in the degree of condensation and thus in the viscosity. The formation of cyclic species can be explained by intramolecular reactions of the type in eq 6.

$$Cl_3P{=}N(PCl_2{=}N)_{n-1}P(O)Cl_2 + Cl_3P{=}N(PCl_2{=}N)_{m-1}P(O)Cl_2 \xrightarrow{-P(O)Cl_3} Cl_3P{=}N(PCl_2{=}N)_{n+m-1}P(O)Cl_2 \quad (5)$$



$$Cl_3P{=}N(-PCl_2{=}N-)_{n-2}PCl_2{=}\ddot{N}P(O)Cl_2 \xrightarrow{-P(O)Cl_3} (Cl_2P{=}N)_n \quad (n \geq 3) \quad (6)$$

This can be shown by juxtaposing parts a and b of Figure 6, which represent the percentages of phosphorus atoms present both in the $Cl_3P{=}N$ end groups of linear oligomers (n = 2 and 3) and in the cyclic species (n = 3–5). It can be noted that the rings are formed at the beginning of the reaction when the linear homologues are present, their concentration subsequently remains constant (from a conversion rate of about 85%). This proves that their formation is not due to a degradation of the polymer formed. (Measurements were performed during a polycondensation in solution at 240 °C.)

The percentage of phosphorus in these rings is greater when the concentration of I is lower (at 270 °C, this ratio is 2% for a polycondensation in bulk and 10% for a reaction in solution with a I concentration of 50% by weight).

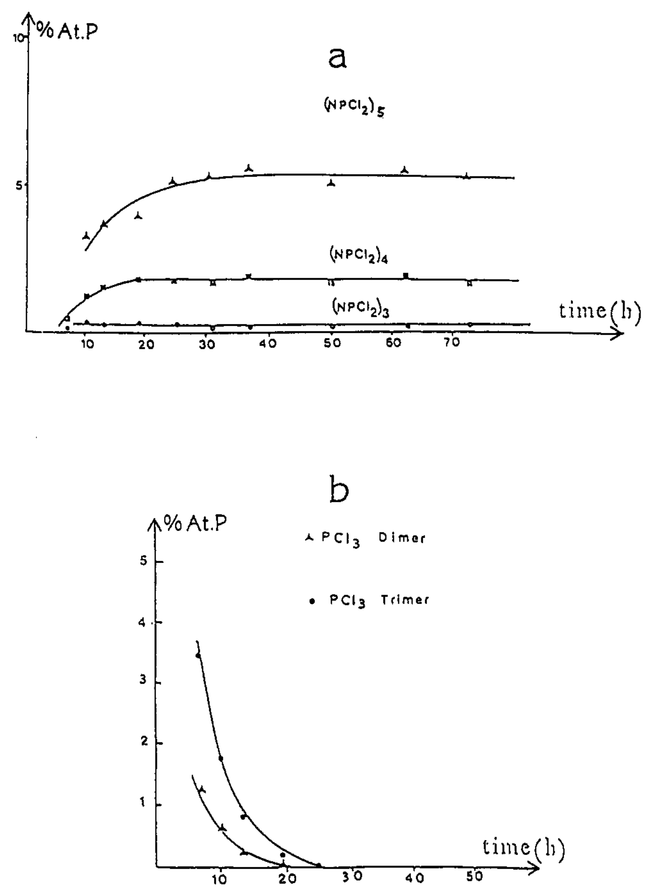
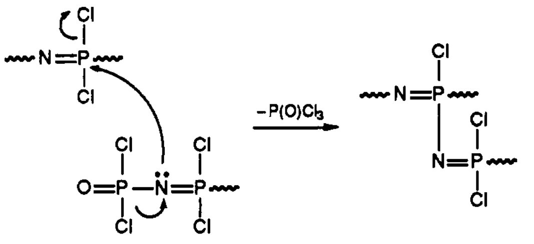


Figure 6. Percentages of phosphorus atoms present in $Cl_3P{=}N$ end groups of oligomers and in cyclic species versus time.

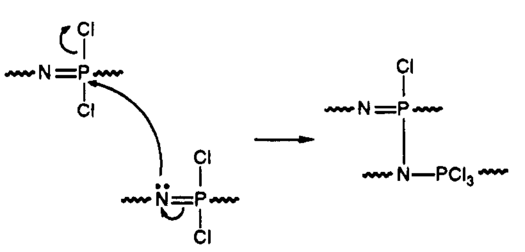
This important result leads us to suggest that, in order to obtain a polymer containing the minimum number of cyclic species, the first stage of reaction 1 must be conducted in bulk and the solvent only introduced after the release of $P(O)Cl_3$ has ceased.

As illustrated by eq 7 branching reactions can occur simultaneously with reactions 3–6.

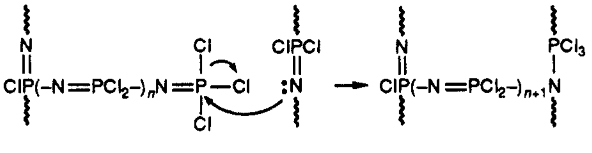


(7)

Cross-linking results either from repetition of eq 7 on the same molecule or from intermolecular reactions of the types in eqs 8 and 9 as noted by Allcock.[9]



(8)



(9)

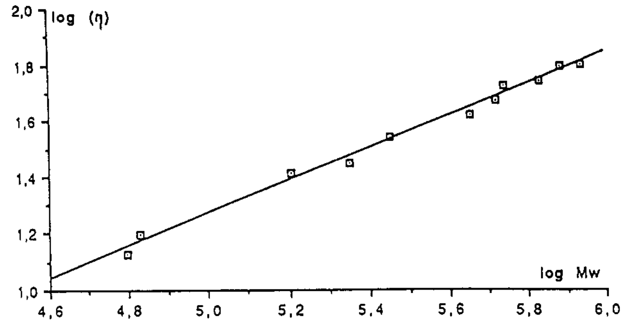


Figure 7. Mark–Houwink law for poly(dichlorophosphazenes) in THF at 30 °C.

For bulk polycondensation, reactions 7–9 become dominant when conversion is high, or in other words when diffusion becomes the limiting factor of the process.

For this reason all the factors which improve the diffusion, such as stirring or reduction of the viscosity, favor reactions 3–5 at the expense of these unwanted reactions. Effectively, the addition of a solvent stabilizes the polycondensate and allows high molecular weights to be obtained.

The thermal stability of PCPZ in trichlorodiphenyl is highlighted by the fact that it is possible to maintain the corresponding solution at 280 °C for 60 h without gel formation.

Associating these results with those of other studies, either completed or in progress, on, for example, the regulation of molecular weight,[10] the control of the ratio of cyclic species,[11] or the purification of PCPZ[12] (studies due for publication shortly) has enabled us to prepare a range of chlorinated polymers with an intrinsic viscosity varying from 10 to 72 mL/g.

The molecular weight of these polymers was determined using a low-angle laser light scattering photometer. From these figures it was possible to establish the Mark–Houwink law (eq 10) (Figure 7). The $\bar{M}_w$'s of the PCPZ polymers prepared cover the range 3×10^4–1×10^6.

$$\eta = 0.02475 M_w^{0.5749} \qquad (T = 30\ ^\circ\mathrm{C};\ \text{solvent, THF};\ \eta \text{ in mL/g}) \quad (10)$$

Conclusion

The contribution of this work to the chemistry of polyphosphazenes lies in the description of a new route to poly(dichlorophosphazene), based on the solution polycondensation of the monomer $Cl_3P{=}NP(O)Cl_2$.

Reactivity ratios between the monomer and $Cl_3P{=}N(PCl_2{=}N)_{n-1}P(O)Cl_2$ oligomers were compared by means of a ^{31}P NMR study of the reaction; a reaction mechanism is proposed.

The essential advantages of this process lie in the simple, high-yield synthesis of high-purity monomer, in the obtention of gel-free polymers, and in the possibility of regulation of the molecular weight.

This process is currently being developed by Atochem.

Experimental Section

Materials and Equipment. The method described by Emsley et al.[13] was used to obtain I. It was purified by distillation under reduced pressure: bp 90 °C (0.1 Torr); yield 94%. Its purity was checked by elemental analysis (Cl, N, P) and ^{31}P NMR.

Trichlorodiphenyl (Atochem) was dried by stirring at 280 °C while being flushed with dry nitrogen. The dried product was then stored before use in polycondensation reactions.

Lithium bromide was from Janssen (99%), and chlorotrimethylsilane was from Fluka (99%).

Tetrahydrofuran (SDS, France, 99.7%) was stabilized with 0.03% of 2,6-di-*tert*-butyl-4-methylphenol and kept on a 4-Å molecular sieve.

^{31}P NMR spectra were made with a Bruker AM 400 WB spectrometer. The reference was 85% H_3PO_4. The convention used was δ positive at low fields.

Viscosimetric and molecular weight measurements were made by taking samples of the poly(dichlorophosphazene) solution in trichlorodiphenyl during polycondensation.

The viscosimetric equipment is described in ref 14. LiBr (1 mol/L) and $(CH_3)_3SiCl$ (2 mol/L) were added to THF: temperature, 30 ± 0.1 °C. The solvent and solutions were filtered on FHLP Millipore filters (0.5 mm).

Weight-average molecular weights M_w were obtained by measuring the diffused light in a Chromatix CMX 100 detector connected to a Waters 150 ALC/GPC chromatographic instrument. The chromatograph was used without a column and calibrated using polystyrene reference NBS706. The solvent was pure THF, the flow rate 1 mL/min, and the temperature 30 °C. $dn/dc = 0.111$ mL/g; the injection was 50 mL of 2 g/L of $NPCl_2$ in THF.

Polycondensation Equipment. The equipment consists of the following: (1) a 2-L three-necked, double-walled glass reactor with an outlet valve at the bottom; (2) a step-by-step stirring motor with an electronic speed variator and an rpm-meter; (3) silicone 710 oil for heating; (4) a reflux condenser supplied with oil at 130 °C, ending in a descending cooling condenser followed by a graduated flask itself connected to an Erlenmeyer flask by means of a Teflon tap. This equipment allows continuous quantification of the eliminated $P(O)Cl_3$ by volumetric measurement or by weighing.

The glassware was washed, carefully dried, and kept under nitrogen pressure.

Experimental Procedure. A total of 1824 g (6.774 mol) of monomer I is introduced into the reactor which has been previously brought to the reaction temperature. This operation is taken as $t = 0$. During the first part of the reaction the temperature is maintained at 245 °C. The flow of $P(O)Cl_3$ ceases after 7.7 h. At this point the conversion rate is 95%.

The polycondensate is then brought to 276 °C, and the reactor is flushed with nitrogen until the elimination of $P(O)Cl_3$ ceases for a second time. After 10.33 h, the conversion rate is 97.8%.

Trichlorodiphenyl (1710.5 g) is then added and the polycondensate maintained at 276 °C. From this point, the evolution of the reaction is controlled by taking samples and measuring their intrinsic viscosity: $t = 12.07$ h, $[\eta] = 28.9$ mL/g; $t = 27.33$ h, $[\eta] = 53.6$ mL/g; $t = 33.06$ h, $[\eta] = 70.8$ mL/g.

References and Notes

(1) See for example: (a) Lund, L. G.; Paddock, N. L.; Proctor, J. E.; Searle, H. T. *J. Chem. Soc.* **1960**, 2542. (b) Moran, E. F. *J. Inorg. Nucl. Chem.* **1968**, *30*, 1405. (c) Allen, G.; Lewis, C. J.; Todd, S. M. *Polymer* **1970**, *11*, 31. (d) Yakubovich, A. Ya.; Shvetsov, N. I.; Lebedeva, I. V.; Yakubovich, V. S. *Russ. J. Inorg. Chem.* **1963**, 8 (No. 8), 953. (e) Li, H. M. U.S. Patent 4,374,875. 1983.
(2) Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216.
(3) Hagnauer, G. L. *J. Macromol. Sci., Chem.* **1981**, *A16* (1), 385.
(4) (a) Scopelianios, A. G.; Allcock, H. R. *Macromolecules* **1987**, *20*, 432. (b) Mujumdar, A. N.; Young, S. G.; Merker, R. L.; Magill, J. H. *Macromolecules* **1990**, *23*, 14.
(5) Nomenclature recommended by: Shaw, R. A.; Fitzsimmons, B. W.; Smith, B. C. *Chem. Rev.* **1962**, *62*, 247.
(6) Neilson, R. H.; Wisian-Neilson, P. *Chem. Rev.* **1988**, *88*, 541.
(7) Helioui, M.; De Jaeger, R.; Puskaric, E.; Heubel, J. *Makromol. Chem.* **1982**, *183*, 1137.
(8) Allcock, H. R.; Tollefson, N. M.; Arcus, R. A.; Whittle, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 5166.
(9) Allcock, H. R. *Phosphorus Nitrogen Chemistry*; Academic Press: New York, 1972.
(10) Pagniez, G.; Passimourt, N.; Potin, Ph. Patent pending (France) 8709406, 1987.
(11) Bordere, S.; Chambrette, J. P.; Pagniez, G.; Potin, Ph. Patent pending (France) 8804085, 1988.
(12) De Jaeger, R.; D'Halluin, G.; Pagniez, G.; Potin, Ph. Patent pending (France) 8913753, 1989.
(13) Emsley, J.; Moore, J.; Udy, P. B. *J. Chem. Soc. A* **1971**, 2863.
(14) De Jaeger, R.; Lecacheux, D.; Potin, Ph. *J. Appl. Polym. Sci.* **1990**, *39*, 1793.