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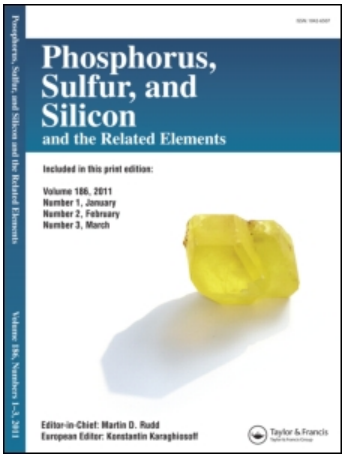

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Polycondensation of Dichlorphosphoryltrichlorophosphazene: Alternatives for Orienting the Reaction

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POLYCONDENSATION OF DICHLOROPHOSPHORYLTRICHLOROPHOSPHAZENE : ALTERNATIVES FOR ORIENTING THE REACTION

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Abstract: The previous presentation illustrated the steps and mechanism of the polycondensation of dichlorophosphoryltrichlorophosphazene (P_2NOCl_5). Here we wish to show the possible ways in which the reaction can be oriented depending on the objectives determined by the final use of the polymer.

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REVERSIBILITY OF THE POLYCONDENSATION

The question of the reversibility of the reaction was merely touched upon in the presentation on the polycondensation mechanism. This aspect of the polycondensation reaction will be expanded here by considering the results of two types of experiment. The first illustrates and the second tries to quantify this phenomenon.

Figure 1 shows an experiment where after a polycondensation to [η]=64 ml/g (Mw =860000) adding of 2.65 molar % of $POCl_3$ decreases [η] to 23 ml/g (Mw= 147000) after 13 h. At this point the re-establishing of the initial polycondensation conditions, allows Mw coming back to a high level ([η]=69 ml/g or Mw=977000).

The second type of experiment (Fig. 2) was designed to establish the relationship between the concentration of dissolved $POCl_3$ in the polycondensate and the degree of polycondensation at equilibrium during polycondensation, then during depolycondensation following additions of $POCl_3$. In this last graph, a considerable difference can be observed between the two curves. This could be explained by the central position of bonds obtained by polycondensation which gives a high evolution of weight average molecular weight and the more frequently breakage due to $POCl_3$ at the edges of coils, producing relatively short chains and giving small evolution of weight average molecular weight.

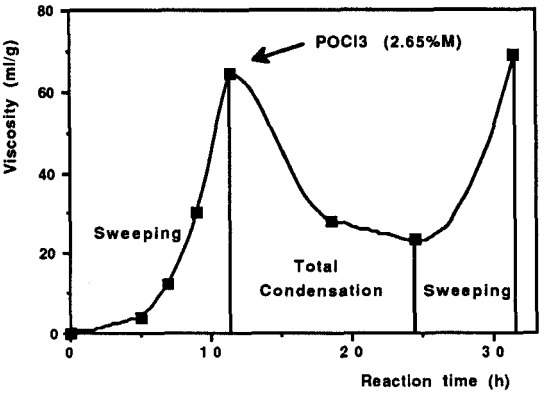

Figure 1

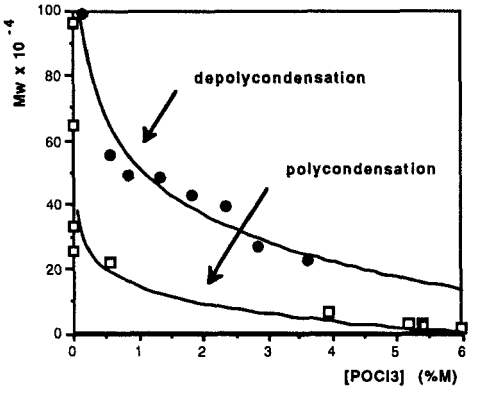

Figure 2

The kinetic equilibrium (1) is highly displaced to polycondensation and quite high Mw can coexist with detectable $POCl_3$ concentration. k_1/k_2 is in order of 10^3.

$$(1)\quad Cl_2P(O)\text{-}(N=PCl_2)_{m+n}\text{-}Cl + POCl_3 \underset{k_1}{\overset{k_2}{\rightleftharpoons}} \begin{cases} Cl_2P(O)\text{-}(N=PCl_2)_m\text{-}Cl \\ Cl_2P(O)\text{-}(N=PCl_2)_n\text{-}Cl \end{cases}$$

THERMAL STABILITY

This last experiment gives a good illustration of the thermal stability of the polycondensate against cross-linking. 30 h for the polycondensation plus 7 times each 24 h for depolycondensation steps leads to a total run of about 200 h at a temperature from 260 to 280°c. At the end, no traces of gel were found.Another experiment of the same type ran 250 h with no more gel. When a polycondensate is maintained near 280° in a closed reactor during a long time, 2 days for example, not only no gel but also no Mw decreasing occurs. These observations show that , when no catalyst is used,polydichlorophosphazene brings up the characteristics of high thermally stable polymer.

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REGULATION OF THE MOLECULAR WEIGHT

One of the main advantages of polycondensations is the relationship existing between the duration of the polycondensation and the molecular weight obtained. In this way it is possible to select the molecular weight of polydichlorophosphazene within a high range, from $5x10^4$ to more than $2x10^6$. Molecular weights can also be controlled within the lower range by changing the reaction time, but in this case the substituted polymer exhibits an higher average polydispersity. The only upper limit comes from the stirring equipment. If by any chance the molecular weight increases too much, it has been shown above that it is easy to reduce it by addition of $POCl_3$. The polycondensation can then be continued.

If polymers of molecular weight < 50 000 are wanted, the molecular weight can be regulated more conveniently by the use of a chain terminator.

The first type of chain terminator should have an active chlorine atom allowing it to react with the end of the chain and $POCl_3$ to be released(2). Compounds containing an active chlorine atom such as diphenylphosphine chloride or triphenylsilane chloride have been shown to have no regulating action. Triphenylmethane chloride leads to cross-linking.

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(2) $RCl + Cl_2P(O) - N \sim \longrightarrow R - N \sim + POCl_3$

(3) $\sim N = P\,Cl_3 + Cl_2P(O) - R \longrightarrow \sim N = PCl_2 - R + POCl_3$

Second type of chain terminator (3) shows a usefull activity with the substituted monomer by phenol (4). The correlation between the weight average molecular weight and the concentration of chain terminator was satisfactory (Fig.3). Additionally, a lower polydispersity was measured for the substituted polymers.

(4) $Cl_2P(O) - N = P(O\Phi)_2Cl$

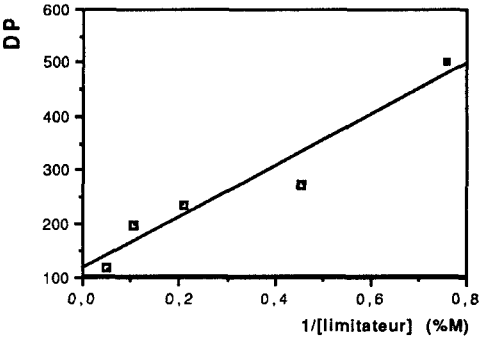

Figure 3

REGULATION OF THE CONCENTRATION OF CYCLIC OLIGOMERS

In the previous presentation, it was shown that cyclic oligomers are formed by cyclisation of their linear homologues. The fact that their concentration remains constant proves that there is no further polymerization of these cyclic species and that they are not formed by degradation of the polymer. Regulating the concentration of cyclic oligomers allows easy and efficient alteration of the rheological properties of the final polymer.

The most important parameter in regulating the quantity of cyclic oligomers is the concentration of monomer at the start of the polycondensation. Figure 4 indicates that this concentration exerts a considerable influence : at 30 wt% (the concentration which is normally used during the second part of the polycondensation) the concentration of trimer + tetramer + pentamer rises to 18%. The very good reproducibility of these results allows the following relationship to be established (5) :

(5) $\log[\text{Oligomers}]\ \% = -1.43\ 10^{-2}\ [P_2NOCl_5] + 1.727$ (at 270°C)

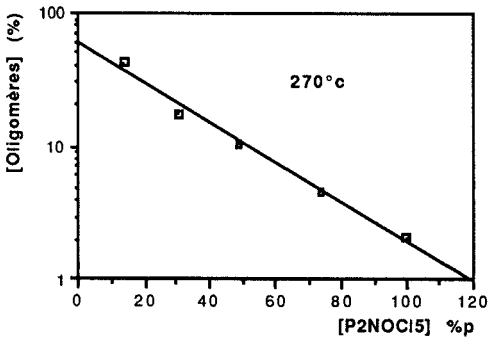

Figure 4

CONCLUSION

These results highlight the considerable flexibility of this process for the synthesis of polydichlorophosphazene, what allows an almost complete regulation of the molecular weight. In addition to that, the regulation of the cyclic oligomers allows different grades of plastified polymer to be produced without incurring any extra cost. Finally this polycondensation represents a decisive progress due to the exceptional thermal stability of the polycondensate : thermal stability against degradation and against cross-linking.

But to obtain these results, mainly to avoid any crosslinking or chains growth blocking by by-products, one condition is essential : the quality of monomer. The improving of the monomer synthesis gave us the key point of this new route.

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