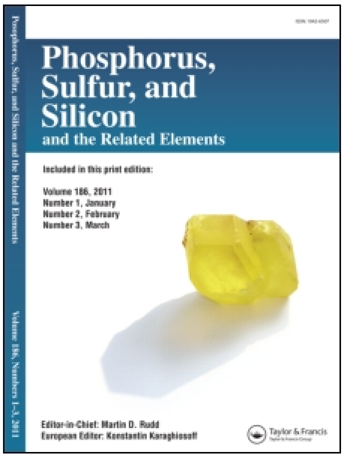

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New Aspects of the Preparation and Polymerization of $C\ell_3PNP(O)C\ell_2$

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The DeJaeger synthesis of poly(dichlorophosphazene), $(NPC\ell_2)_n$ (1) from P-trichloro-N-(dichlorophosphoryl)monophosphazene, $C\ell_3P{=}NP(O)C\ell_2$ (2) represents an attractive alternative to the ring opening polymerization approach to **1**. We have followed the Emsley reaction, i.e. $PC\ell_5$ and $(NH_4)_2SO_4$, under a variety of conditions by ^{31}P NMR spectroscopy. Alternative oxygen atom sources in place of $(NH_4)_2SO_4$were also explored. Model reactions to identify specific pathways potentially operating in the formation of **2** when combined with the NMR studies allow for identification of the most probable sequence of steps leading to **2**. Conversion of **2** to **1** under different conditions was also examined. Molecular weight was monitored as a function of time by GPC with online direct detection of the diphenoxy derivative, $[NP(OC_6H_5)_2]_n$, of **1**. The byproduct of the polymerization of **2** is $POC\ell_3$. After conversion of **2** to $(RO)_3PO$, a one step process has been developed for conversion into $(RO)_3P{=}NSiMe_3$, another class of poly(phosphazene) precursors.

Keywords: poly(dichlorophosphazene); P-trichloro-N-(dichlorophosphoryl)-monophosphazene; poly(phosphazene) synthesis; phosphoranimine synthesis

INTRODUCTION

Linear, high polymeric phosphazenes, $(NPR_2)_n$, are a class of inorganic polymers which have received extensive study at both the fundamental and applied levels.[1-4] A variety of routes to poly(phosphazenes) have been developed. Direct conversion of monomeric phosphoranimines, $R_3P{=}NR'$, in selected cases can provide organo-substituted poly(phosphazenes)[4,5]. This has been a particularly important route to alkyl and aryl derivatives.[4] However, the majority of poly(organophosphazenes) are obtained from substitution reactions of the parent polymer, poly(dichlorophosphazene), $(NPC\ell_2)_n$ (1). Synthesis routes to 1 include ring opening polymerization of hexachlorocyclotriphosphazene, $N_3P_3C\ell_6$ [1-3,6], thermal step polymerization of P-trichloro-N-(dichlorophosphoryl)monophosphazene,

$C\ell_3P{=}NP(O)C\ell_2$ (2), developed by DeJaeger [7,8] and a recently reported process with the characteristics of living polymerization.[9] The ring-opening and thermal step polymerization reactions have both been utilized for commercial production of **1**. The ring opening process has been examined in detail by several groups[6] so we have chosen to focus on further development of the synthesis and polymerization of **2**.

RESULTS AND DISCUSSION

The reaction of $(NH_4)_2SO_4$ and $PC\ell_5$ to yield **2** was reported by Emsley [10] as part of

$$4PC\ell_5 \longrightarrow (NH_2)_2SO_4 \longrightarrow \mathbf{2} + 8HC\ell + SO_2 + C\ell_2$$

a series of papers covering various aspects of linear and cyclophosophazene syntheses. We have investigated various details of the Emsley reaction focusing on both synthetic and mechanistic aspects. Phosphorus-31 NMR spectroscopy was employed to monitor the progress of reactions as well as identify intermediates and products. The synthesis of **2** as described by Emsley, and used in practice, takes place in tetrachloroethane, a common solvent for the preparation of various phosphazenes. We have found that the reaction also occurs in the melt phase of the two reactant in the absence of solvent. The yield of the melt phase reaction is quantitative and the reaction is nearly complete upon the melting of $PC\ell_5$. Conditions for this conversion have been optimized.

A wide range of other reactions involving potential oxygen atom transfer agents in molten $PC\ell_5$ have been explored in order to attempt to suppress certain of the corrosive gaseous byproducts which have been proposed [10] to arise from the Emsley reaction. Ammonium salts included: $(NH_4)SO_3NH_2$, $(NH_4)_2S_2O_8$, $(NH_4)_2C_2O_4$, $(NH_4)CO_2NH_2$,$(NH_4)CO_2H$ and $(NH_2)_2CO$. Variable amounts of **2**, oligomers, **1** and $N_3P_3C\ell_6$ have been observed and quantified. While many of these reactions do give **2**, none compete effectively with the $(NH_4)_2SO_4$reaction in terms of yield. Interestingly, a melt reaction of $PC\ell_5$ and $NH_4C\ell$ goes directly to **1** however cross-linking also occurs.

The next component of the investigation involved a series of model reactions in an attempt to clarify the pathway followed in the preparation of **2**. The first of these involved Na_2SO_4 and $PC\ell_5$ which lead to rapid and high conversion to $POC\ell_3$. Addition of chloride ion suppresses this reaction . Analysis of gaseous byproducts by mass spectrometry was more problematic but SO_2 was observed. The early formation of $POC\ell_3$ was noted in monitoring of the Emsley reaction thus two potential pathways to **2** could be considered. The first involves initial ammonolysis of $PC\ell_5$ by the ammonium ion while in the second the sulfate reaction gives $POC\ell_3$ which could undergo ammonolysis and reaction with $PC\ell_5$. Model reactions of $POC\ell_3/NH_4C\ell$ and $POC\ell_3/PC\ell_5/NH_4C\ell$ give no or trace products respectively. Returning to the first pathway, the reaction of $C\ell_3PNPC\ell_3{}^+PC\ell_6{}^-$, which is the first isolated intermediate in the classical $PC\ell_5$ ammonolysis reactions[11], with Na_2SO_4 provides **2**. Reaction of the phosphazene intermediates with $POC\ell_3$ has previously been shown to also lead to **2**.[11] Based on these observations the major pathway to **2** involves ammonolysis of $PC\ell_5$ followed by oxygen atom transfer from the sulfate anion.

Time vs conversion studies of both the solution and melt phase syntheses of **2** have been conducted. Early detection of $POC\ell_3$ was noted, interestingly $N_3P_3C\ell_6$ forms and eventually disappears, and finally **2**, $C\ell_3PNPC\ell_2NPC\ell_3{}^+PC\ell_6{}^-$ and $POC\ell_3$ reach a constant ratio when the maximum yield of **2** is obtained. The pattern of intermediates and products is identical in the solution and melt phase reactions.

Our major interest in the formation of **2** is the fact that it can be converted to **1** in a thermally driven, step polymerization process. We have established that this reaction can take place in the melt phase in the absence of solvent. Our approach involved conversion to **1** and subsequent derivatization to the diphenoxy derivative $[NP(OC_6H_5)_2]_n$ which was characterizated by gel permeation chromatography with online viscosity detection. Two approaches were examined, one involved polymerization of purified **2** while the other consisted of a one pot process starting from $PC\ell_5$ and $(NH_4)_2SO_4$ and continuing directly onto **1**. The one pot reaction takes place around 50°C lower than the polymerization of pure **2** thus implying a catalytic effect of one or more of the previously identified byproducts of the synthesis of **2**. The molecular weight distributions of $[NP(OPh)_2]_n$ obtained in the polymerization reactions show bimodel behavior for the one pot process and monomodal behavior for the product obtained from pure **2**. In both cases polymerization to **1** can be effected in simple apparatus and leads to products with molecular weights in the 1×10^5 to 1×10^6 range.

In both the formation and polymerization of **2**, $POC\ell_3$ is the principle byproduct obtained. Using well established chemistry, $POC\ell_3$ can be converted to $(RO)_3PO$ (R=alkyl or aryl). We have now shown by ^{31}P NMR spectroscopy that the reaction of $(RO)_3P{=}O$ with $LiN(SiMe_3)_2$ leads exclusively to the phosphoranimine,

$$(RO)_3P{=}O + LiN(SiMe_3)_2 \longrightarrow (RO)_3P{=}NSiMe_3 + LiOSiMe_3$$

$(RO)_3P{=}NSiMe_3$. Isolation methologies are currently under investigation.

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References

- [1] H.R. Allcock, *Phosphorus-Nitrogen Compounds* (Academic Press, New York, 1972).
- [2] H.R. Allcock in *Inorganic Polymers*, J.E. Mark, H.R. Allcock and R. West (Prentice Hall, Englewood Cliffs, New Jersey, 1992), Chap,. 3, pp 61–140.
- [3] R. DeJaeger and M. Gleria, *Progress Polym. Sci.*, **23**, 179 (1998).
- [4] R.H. Neilson and P. Wisian-Neilson, *Chem. Rev.*, **88**, 541 (1988).
- [5] K. Matyjaszewski, M. Cypryk, J. Dauth, R. Montaque and M. White, *Makromol. Chem., Makromol. Symp.*, **54/55**, 13 (1992).
- [6] H.R. Allcock, *Stud. Inorg. Chem.*, **14**, 145 (1992).
- [7] G. D'Helluin, R. DeJaeger, J.P. Chambrette and P. Potin, *Macromolecules*, **25**, 1254 (1992).
- [8] R. DeJaeger and P. Potin, *Phosphorus, Sulfur, Silicon Relat. Elem.*, **76**, 227 (1993).
- [9] H.R. Allcock, C.A. Crane, C.T. Morrissey, J.M. Nelson, S.D. Reeves,, C.IH. Honeyman and I. Manners, *Macromolecules*, **29**, 7740 (1996).
- [10] J. Emsley, J. Moore and P.B. Udy, *J. Chem. Soc. A*, 2863 (1971).
- [11] J. Emsley and P.B. Udy, *J. Chem. Soc. A*, 3025 (1970).