Synthesis of Poly(dichlorophosphazene) by the Melt Phase Polymerization of P-Trichloro-N-(dichlorophosphoryl)monophosphazene

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Abstract A major barrier to commercialization of the myriad exciting applications of the poly(phosphazenes) has been the cost and ease of preparation of the most widely utilized starting polymer, poly(dichlorophosphazene) $(NPCl_2)_n$ (**1**). One attractive route is the thermal polycondnesation reaction of P-trichloro-N-(dichlorophosphoryl)monophosphazene, $Cl_2P(O){=}NPCl_3$(**2**). We are reporting a modified bulk polymerization of **2** which represents a convenient route to laboratory scale amounts of $(NPCl_2)_n$ with moderate molecular weights and polydispersity. GPC characterization data was obtained on the corresponding phenoxy derivatives, $[NP(OPh)_2]_n$. We also have developed a one pot synthesis of **1** from ammonium sulfate and phosphorus pentachloride which are the starting materials for the synthesis of 2 and examined the major variables, time and temperature, for this process. The resulting poly(phosphazene) exhibits more branching than the product of bulk polymerization of **2**.

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1 Introduction

The poly(phosphazene) system of materials has, arguably, the highest application potential of all of the inorganic and organometallic polymers[1]. This is due to a backbone structure which is structurally similar to and isoelectronic with the commercially viable poly(siloxanes) and the extraordinary wide range of derivatives which are conveniently available [1]. While poly(organophosphazenes) with direct phosphorus-carbon bonds are most effectively prepared from the thermolysis of N-silylphosphoranimines[2], most of the remaining derivatives arise via nucleophilic substitution reactions of the parent poly(dichlorophosphazene), $(NPCl_2)_n$ (**1**) [1]. The synthesis of **1** has attracted attention since it was originally reported by Stokes in 1897. The Stokes method was based on the thermal ring opening polymerization of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$. The approach has been carefully studied, refined and transformed into a reliable synthesis method by Allcock [1,3] and still represents the most widely utilized route to **1.** It gives good yields with high molecular weights of uncrosslinked materials with moderate polydispersity. It does require well purified $N_3P_3Cl_6$ which in turn must be prepared and purified by a multistep process. Numerous approaches to catalyzed polymerization of $N_3P_3Cl_6$ in solution have been reported [1,4,5]. An elegant living cationic polymerization process of a cholorphosphoranimine, $Me_3SiN{=}PCl_3$, leads to well defined, low polydispersity samples of **1** with lower molecular weights [1,6,7]. A direct route to **1** from the precursors to $Me_3SiN{=}PCl_3$ [8] and to $N_3P_3Cl_6$ [9] has been reported. A major alternative route to **1** involving the thermal elimination of $P(0)Cl_3$ from P-trichloro-N-(dichlorophosphoryl)monophosphazene, $Cl_2P(O){=}NPCl_3$(**2**), has been developed by De Jaeger [4,10-12]. There are several advantages to this methodology including the ease of preparation, purification and handling of **2**. We have published preliminary reports [13,14] on modifications of the De Jaeger synthesis and have disclosed a patent on our approach [15]. In this communication, we present a more detailed study of the solvent free synthesis of **1** based on our method.

2 Experimental

2.1 Materials

The preparation of P-trichloro-N-(dichlorophosphoryl)monophosphazene, $Cl_2P(O){=}NPCl_3$(**2**) was accomplish by both the traditional Emsley method[16] and our melt phase process[15]. Sample purity was routinely checked by ^{31}P NMR spectroscopy. Standard commercial sources were used for the acquisition of PCl_5, $(NH_4)_2SO_4$ and all other reagents and solvents. Sodium hydride was stored and handled in a nitrogen filled glove box. THF was dried over sodium benzophenone ketyl and was distilled under an atmosphere of dry nitrogen before use.

2.2 Measurements

NMR spectra were recorded on a Bruker ARX-500 spectrometer. ^{31}P NMR (202 MHz) spectra were obtained in CDCl3 with 85 % H_3PO_4 as the external reference. Gel permeation chromatography (GPC) was performed on a Polymer Laboratories Pgel 20 lm MIXED-B column using a 0.1 % weight/volume solution of tetrabutylammonium bromide in THF and an online Viscotek TriSEC system (Dual 250/RALLS detectors). Polystyrene standards were used for calibration.

2.3 Syntheses

2.3.1 *Preparation of poly(dichlorophosphazene) from purified P-trichloro-N-(dichlorophosphoryl)monophosphazene, $Cl_2P(O)=NPCl_3$(**2**).*

In a glovebox, a 50.00g (0.1857mol) of freshly distilled **2** was placed in a 100mL Schlenk flask fitted with a gas inlet and a stirring bar. A flow of N_2 was initiated and a short path distillation condenser equipped with a 50 mL round bottom flask was attached. The Schlenk flask was place in an oil bath which was preheated to 235 ^{0}C. Within 30 min, $P(O)Cl_3$ began to distill off and increased over an additional an 30 min . The rate of distillation dropped slowly during the next 90 min and the temperature was raised to 255-26o ^{0}C. Over an additional 30 min period the reaction liquid increased in viscosity until the stirring bar was held in place and the reaction was stopped at this point. The resulting polymer was placed under vacuum overnight at 120^0 to remove and remaining monomer and $P(O)Cl_3$. Nearly quantitative yields were obtained.

2.3.2 *Preparation of poly(diphenoxyphosphazene)*

The conversion of poly(dicholorophosphazene) to poly(diphenoxyphosphazene) follows established procures[1].

2.3.3 *Preparation of poly(dichlorophosphazene) directly from phosphorus pentachloride and ammonium sulfate*

Under a dry nitrogen atmosphere, 100g(0.48mol) of PCl_5 was mixed with 14.12g(0.107 mol) of $(NH_4)_2SO_4$ in a 1L round bottomed flask equipped with a spin bar, a gas inlet and a reflux condenser attached to a water bubbler. The reaction vessel was placed in an oil bath pre-heated to 165^0 C at which point the solid mixture started to liquefy and the gas inlet was turned off. This occurred concurrently with intense gas evolution as noted in the water bubbler. Within 20 min the all of the solid reactants liquefied and the water bubbler was disconnected and the nitrogen atmosphere reestablished. The condenser was replaced with a distillation head and the temperature was gradually raised to 225^0 C. The pale yellow product was stirred at this temperature for forty minutes and the phosphorus oxychloride distilled off into a 100mL Schlenk flask leaving a viscous, virtually colorless liquid which was identified as poly(dichlorophosphazene)(**1**) by ^{31}P NMR. The yield was 24.78g (100% of theoretical based on $(NH_4)_2SO_4$. The product was then converted to poly(diphenoxyphosphazene) by the procedure described above(2.3.2) for GPC analysis.

3 Results and Discussion

The facile conversion of P-trichloro-N-(dichlorophosphoryl)monophosphazene, $Cl_2P(0)=NPCl_3$(**2**), to polydichlorophosphazene(**1**) was accomplished by simple thermolysis with results similar to those reported by De Jaeger and Potin [12]. The basic structure was confirmed by ^{31}P NMR spectroscopy. A balance between conversion (and hence molecular weight) and crosslinking is maintained by limiting the time for which the polymerization is allowed to proceed. Monomer purity is also a significant factor since it has been shown [10-12] that typical impurities in **2** will enhance the degree of crosslinking. On the other hand, trace amounts of added PCl_5 will suppress crosslinking [11, 12, 17] There are several features of **2** and **1** which are important considerations in this polymerization. Since both functionalities (-Cl and-$P(O)Cl_2$) required for the condensation reaction in this step polymerization process are present in the monomer(**2**) , issues with stoichiometric imbalance of monomers limiting the molecular weight are avoided However, it is also important to note that two potentially reactive phosphorus chlorine units are available in each monomer unit thus there are numerous opportunities for branching and ultimately crosslinking (Scheme 1). It is reasonable to suppose that the terminal phosphorus-chlorine unit in the growing chain is more reactive than the internal phosphorus-chlorine units based on the ease of approach of **2** and the probable higher formal charge on the terminal phosphorus atom. This will favor linear chain growth. However, as the degree of polymerization increases there are more internal sites available thus there is a greater chance for branching and ultimately crosslinking. In kinetic terms, k'[internal] can become competitive with k[terminal] due to the relative concentration terms even if k is much larger than k'. The reaction of any growing chain with a branch containing a phosphorus chlorine unit (internal or terminal) in another chain will lead to crosslinking and thus become more probable as the reaction progresses. GPC data were collected on the phenoxy derivative of **1**, $[NP(OPh)_2]_n$ (**3**), due to the moisture sensitivity of **1**. A representative GPC trace and derived molecular data are shown in Figure 1 and Table 1 respectively. The data show that the sample of **1** obtained by this method exhibits a moderate molecular weight (M_n 549,000) and polydispersity(6.76) which are in the range for many applications such as membranes[14]. In order to obtain significantly higher molecular weights the reaction would need to be carried out in a high boiling(typically chlorinated aromatics) solvents[10-12], or the classical ring opening polymerization of $N_3P_3Cl_6$ [1,3] be employed. However, the method here reported uses only routine laboratory apparatus

-Insert Scheme 1-

- Insert Figure 1-
- Insert Table 1-

and is an easy way to prepare laboratory scale samples of **1**. It is also important to note that this method allows for a convenient route to the fully ^{15}N labeled polyphosphazenes by using $(^{15}NH_4)_2SO_4$[18]. The isotopic substitution allows for additional spectroscopic probes (NMR, vibrational) in the physiochemical characterization of polyphosphazenes [19].

The conversion of ammonium sulfate and phosphorus pentachloride to **2** is essentially quantitative [15, 16] and the polymerization of **2** occurs at a higher temperature than its preparation. These observations prompted us to explore the direct conversion of the aforementioned starting materials to **1** in a one pot reaction**.** It was found that a stoichiometric mixture of ammonium sulfate and phosphorus pentachloride was converted quickly to **2** in a simple round bottled flask immersed in an oil bath at 165^0. Once the gas evolution, the reflux condenser was replaced by a distillation head and the temperature was raised at which distillation of phosphorus oxychloride commenced. The reaction was allowed to continue until a viscous product, **1**, was obtained which in turn was converted to **3** for GPC analysis. Various combinations of time and temperature for the polymerization phase were explored in order to obtain a good balance between molecular weight and a reasonable polydispersity. These data are reported in Table 1. The polydispersity increase is presumably due to increased branching and crosslinking below the gel point. The one pot process shows increase sensitivity to increased time/temperature effects compared to the polymerization of purified **2** (Table 1). This is not unexpected given the established role of impurities in **2** in promoting branching and crosslinking [10- 12]. A GPC trace for the one pot process is shown in Figure 1. The refractive index detector trace shows a single distribution but the viscosity detector trace show two closely spaced distributions representing the linear and branched fractions. It is crucial to note however that these are all soluble materials which don't undergo significant fractionation and hence the resulting polymers will be suitable for selected applications. This is an important observation because this route represents an economically viable route to the polyphosphazene system in that it starts with two common articles of commerce which are inexpensive relative to $N_3P_3Cl_6$, does not require solvents (thus eliminating disposal issues and environmental problems associated with halogenated solvents and the major byproduct, phosphorus oxychloride, is also a commercially used material.

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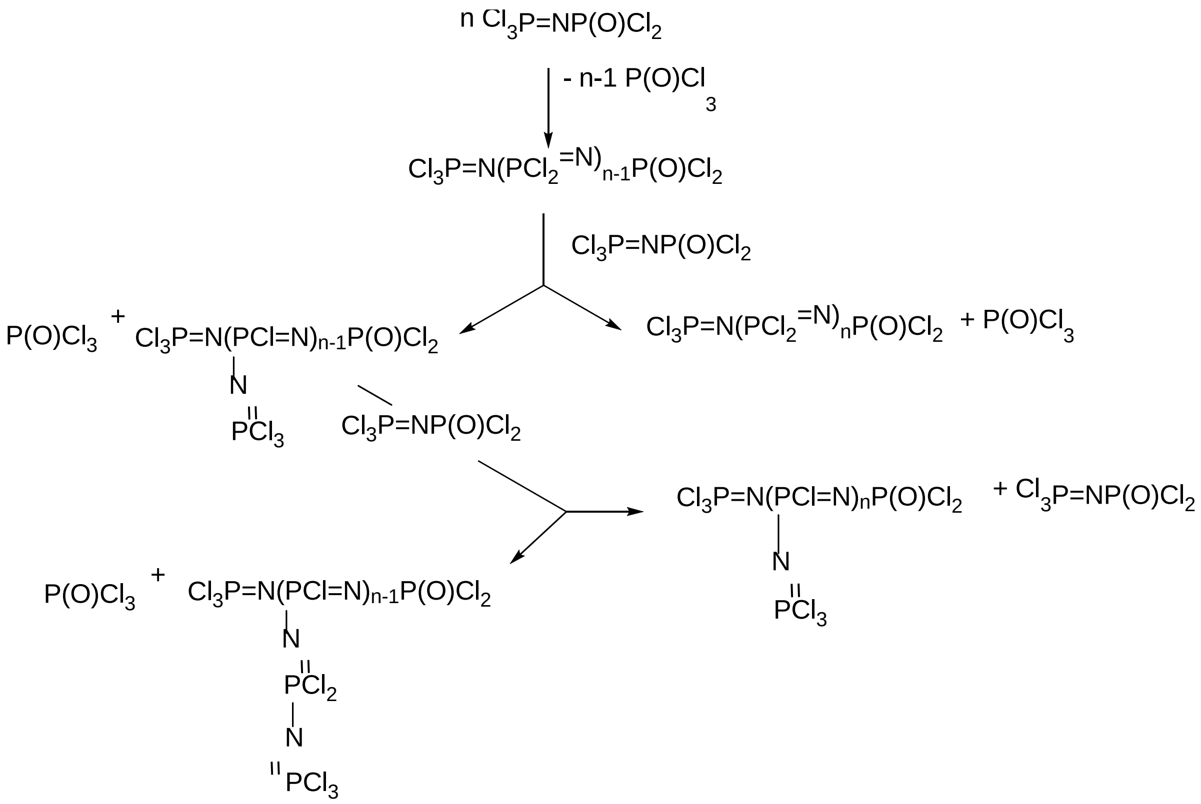

Scheme 1. Polymerization Pathways

Table I. GPC Data for the Poly(diphenoxyphosphazenes) Derivatives

Conditions for preparation of $[Cl_2P=N]_2$	M_n	M_w	Polydispersity
40 min @ 200^0 C [a]	66,900	430,200	6.43
60 min @ 200^0 C[a]	408,600	21,680,000	50.06
20 min @ 225^0 C[a]	136,300	718,000	5.27
40 min @ 225^0 C[a]	205,100	2,098,000	10.23
90 min @ 255^0 C[b]	549,000	3,714,000	6.76

[a] From direct polymerization of the $PCl_5/(NH_4)_2SO_4$ melt.
[b] From polymerization of purified $Cl_2P(O)=NPCl_3$.

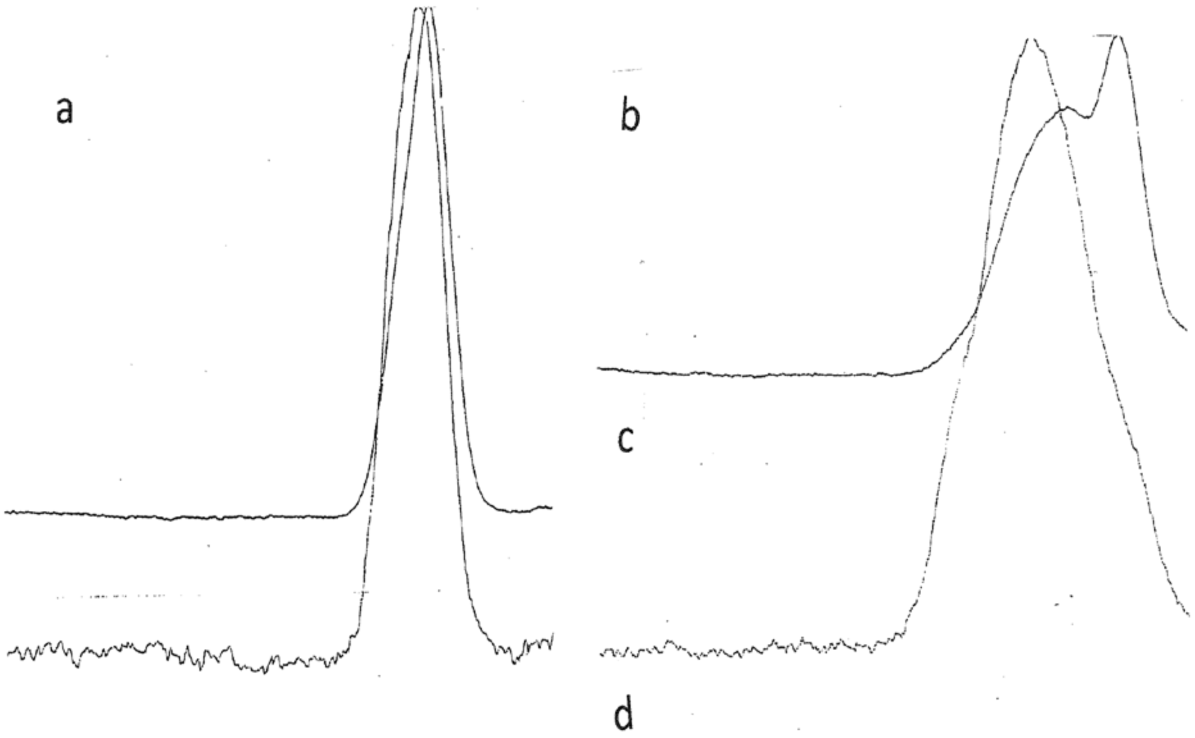

Fig. 1 GPC traces of $[(PhO)_2PN]_n$ derived from $[Cl_2PN]_n$ **;** **a** from pure $Cl_3P{=}NP(O)Cl_2$, **b** from $PCl_5/(NH_4)_2SO_4$ melt, **c** detector, **d** detector.