Ambient Temperature Synthesis of Poly(dichlorophosphazene) with Molecular Weight Control

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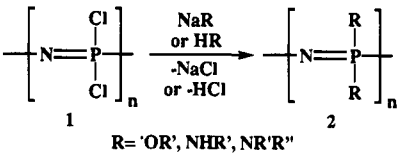
We wish to report a new method for the synthesis of poly(dichlorophosphazene), which is an essential intermediate for the preparation of most organophosphazene high polymers. The new method allows the synthesis of poly(dichlorophosphazene) at room temperature, in the bulk state or in solution, provides an opportunity for control over the polymer molecular weight and structure, and allows access to polyphosphazenes with narrow polydispersities.

Macromolecular substitution reactions carried out on poly(dichlorophosphazene) produce a wide range of inorganic–organic polymers (Scheme 1). These polymers comprise a large class of macromolecules with a variety of well-established and useful properties, which are determined largely by the side groups linked to the polymer backbone. Thus, polyphosphazenes which are hydrophobic or hydrophilic, amorphous or microcrystalline, or which possess liquid crystalline, photochromic, nonlinear optical, or useful biomedical properties have been prepared.[1] However, the currently available ring-opening polymerization and condensation routes to poly(dichlorophosphazene) all involve the use of elevated temperatures, and the molten state ring-opening polymerization route provides little or no control over the molecular weight.[2] Given the substantial number of polymers accessible by the macromolecular substitution route, the development of improved methods for the synthesis of poly(dichlorophosphazene) is extremely important from both academic and industrial viewpoints.[3] Furthermore, a predictable control of the molecular weight of poly(dichlorophosphazene) is a key requirement for the further development of this field.[4] We report here a controllable, reliable, and simple synthetic pathway to poly(dichlorophosphazene) via the PCl_5-initiated polymerization of trichloro(trimethylsilyl)phosphoranimine ($Cl_3P{=}NSiMe_3$, **3**).[5]

The reaction of $Cl_3P{=}NSiMe_3$ with transition metal halides has been shown to proceed with the elimination of Me_3SiCl and the formation of phosphoranimato complexes.[5a] When a single equivalent of $Cl_3P{=}NSiMe_3$ was allowed to react with 2 equiv of PCl_5, elimination of Me_3SiCl was also detected, together with a single phosphorus-containing product. The ^{31}P NMR spectrum of this species consisted of two singlets with chemical shifts consistent with the literature values for $[Cl_3P{=}N{=}PCl_3]^+[PCl_6]^-$.[6] Significantly, it was found that further equivalents of $Cl_3P{=}NSiMe_3$ react with the salt $[Cl_3P{=}N{=}PCl_3]^+[PCl_6]^-$ in CH_2Cl_2 to produce longer cationic P—N chains. The products, identified by ^{31}P NMR spectroscopy, form from the successive additions of 1 and 2 equiv of $Cl_3P{=}NSiMe_3$ and are the cations $[Cl_3P(NPCl_2)_x{-}NPCl_3]^+[PCl_6]^-$, with $x = 2$ and 3, respectively.[7] The elimination of Me_3SiCl is as facile as in the initial reaction of $Cl_3P{=}NSiMe_3$ with PCl_5.

Therefore, it was postulated that the treatment of $Cl_3P{=}NSiMe_3$ with trace quantities of PCl_5 might afford high molecular weight poly(dichlorophosphazene) (**1**) and that control over the ratio of the phosphoranimine to PCl_5 might allow for the control of the molecular weight of the polymer produced. The addition of a trace of PCl_5 (~10 mg) to pure $Cl_3P{=}NSiMe_3$ (1.0 g) at room temperature led, within 24 h, to the formation of a two-phase mixture (Scheme 2). Both phases were clear and colorless, but the upper, more fluid layer was found, by ^1H NMR spectroscopy, to consist mainly of Me_3SiCl. A ^{31}P NMR spectrum of the entire tube contents showed predominantly a sharp singlet characteristic of **1**.[8] Thus, the conversion of $Cl_3P{=}NSiMe_3$ to linear polymer was essentially quantitative. The poly(dichlorophosphazene) product was treated with an excess of $NaOCH_2CF_3$, and the resultant polymer yielded a ^{31}P NMR signal characteristic of the well-known polymer, $[N{=}P(OCH_2CF_3)_2]_n$ (**4**).[8] Analysis of **4** by gel permeation chromatography (GPC) indicated that it possessed only a high molecular weight fraction, having $M_w = 2.1 \times 10^5$ and a polydispersity index (PDI = M_w/M_n) of 1.8 versus polystyrene standards. However, in subsequent attempts to obtain lower molecular weight poly(dichlorophosphazene) by increasing the ratio of PCl_5 to monomer, with the same solvent-free conditions, the initiator and initial cationic products remained primarily insoluble. The molecular weight values of the polymers produced were lower than in the above experiment, but the GPC trace was multimodal. These results suggested a lack of molecular weight control in the solvent-free system due to the heterogeneous nature of the process. However, the reaction of the $Cl_3P{=}NSiMe_3$ with traces of PCl_5 *in methylene chloride* resulted in a quantitative conversion to poly(dichlorophosphazene) (as estimated by ^{31}P NMR spectroscopy and GPC analysis of the trifluoroethoxy derivatives $[NP(OCH_2CF_3)]_n$), accompanied by very narrow polydispersities. An increase in the ratio of phosphoranimine to PCl_5 in solution resulted in an increase in the molecular weight, while still retaining narrow PDI values (see Table 1).

Scheme 1



Scheme 2

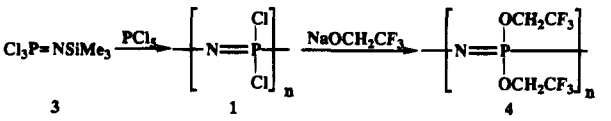


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Table 1. Monomer/Initiator Ratio and Molecular Weight Data

phase[a]	monomer/initiator (mol/mol)	M_w[b]	polydispersity index
bulk	108	210 000	1.8
bulk	15.5	41 000	c
solution	5.4	7 000	1.20
solution	10.8	11 000	1.04
solution	22.6	14 000	1.04

[a] All glassware was pretreated with 5% Me_3SiCl in hexanes and dried under vacuum. PCl_5 was sublimed and stored under nitrogen. Polymerization experiments were on 0.5–2.0 g scale. [b] 0.1% $^nBu_4NBr$ (w/w) in THF eluent. Estimated versus polystyrene standards. [c] Multimodal GPC trace.

The analogous reaction between a trace of PCl_5 and $PhCl_2P{=}NSiMe_3$[5a] in the bulk state at room temperature also yielded a polymeric product. In this case, the polymerization resulted in the formation of poly[aryl(chloro)phosphazene], $[N{=}P(Ph)Cl]_n$, which was converted to the known macromolecule $[N{=}P(Ph)(OCH_2CF_3)]_n$, with $M_n = 8.0 \times 10^4$, $M_w = 1.1 \times 10^5$, and PDI = 1.4.[9]

In preliminary experiments, the activity of the growing polymer chains was also investigated. A solution of poly(dichlorophosphazene) in CH_2Cl_2 was prepared in which all the phosphoranimine had been converted to polymer, as determined by ^{31}P NMR spectroscopy. A portion of this sample was subjected to halogen replacement as described above to yield a trifluoroethoxy-substituted polymer with $M_w = 1.1 \times 10^4$ and PDI = 1.04. Further addition of phosphoranimine to the remainder of the original (unsubstituted) solution resulted in the continued conversion of $Cl_3P{=}NSiMe_3$ to polymer over 48 h. The GPC trace of the trifluoroethoxy-derivatized polymer from this solution showed the presence of polymer with $M_w = 9.2 \times 10^5$ and PDI = 1.71. Thus, it appears that the active chain ends can resume chain growth following the addition of more monomer. This opens up many possibilities for control over the chain length and coupling of the chain ends to other monomers or polymers.

The route described here for the preparation of poly(dichlorophosphazene) and its organic-substituted counterparts is less complicated than the alternatives currently available. The monomer is available in one step from commercially available starting materials. Moreover, the initiated polymerizations allow for fine control over the chain length. Other related initiators, such as $TaCl_5$ and $[Cl_3PNPCl_3]^+[PCl_6]^-$, also appear to initiate the ambient temperature polymerization of phosphoranimine compounds. The access to low-temperature polymerization conditions also opens a route to the direct synthesis of organophosphazenes well below their ceiling temperatures.

From economic and environmental viewpoints, the process also has many advantages. The monomer is prepared from PCl_5 (or $PPhCl_4$) and commercially available $LiN(SiMe_3)_2$ (itself prepared from $NH(SiMe_3)_2$ and butyllithium), and the product from the polymerization (Me_3SiCl) can be recycled into the monomer synthesis. Moreover, the use of room temperature or other moderate temperature conditions compares favorably with the 120–300 °C temperature required for alternative polymerization methods. This, too, offers favorable prospects for the new method to be used for the large scale synthesis of poly(organophosphazenes).

Experimental Details. For the preparation in the bulk phase, a mixture of freshly distilled $Cl_3P{=}NSiMe_3$ (1.94 g, 8.6 mmol) and a trace amount of PCl_5 (~10 mg) was placed in a Pyrex tube, which was then evacuated (0.01 mmHg) and sealed. The resulting mixture was a clear, colorless solution with a very small amount of solid present. This was then allowed to stand at room temperature (22–24 °C). Within 24 h, the mixture had separated into two phases, and the reaction appeared to be complete. After an additional 4 days, to ensure complete reaction, a ^{31}P NMR spectrum (in CH_2Cl_2) of this solution consisted of a singlet resonance at δ −17.5 ppm, which is consistent with the formation of poly(dichlorophosphazene), together with a significantly smaller singlet resonance at δ 20.7 ppm, characteristic of $N_3P_3Cl_6$ (60:1). Isolation resulted in a colorless solid which weighed 1.0 g (100% conversion). A control tube, without the initiator PCl_5, showed no polymerization behavior.

For the preparation in the solution phase, a solution of PCl_5 (100 mg, 0.5 mmol) in CH_2Cl_2 (10 mL) was added to a stirred solution of $Cl_3P{=}NSiMe_3$ (1.0 g, 4.4 mmol) in CH_2Cl_2 (35 mL) under nitrogen. The reaction mixture was stirred for 24 h. A ^{31}P NMR spectrum (in CH_2Cl_2) of this solution yielded a singlet resonance at δ −17.5 ppm, which is consistent with the formation of poly(dichlorophosphazene).

In order to estimate the molecular weight distribution of the polymeric product, it was converted to the well-known trifluoroethoxy derivative $[NP(OCH_2CF_3)_2]_n$. All volatile species were removed. An excess of sodium trifluoroethoxide (1.2 M in dioxane) was added to a solution of poly(dichlorophosphazene) in dioxane (30 mL). The reaction mixture was heated to reflux for 2 h and stirred at room temperature overnight. The mixture was concentrated under reduced pressure, and the resultant viscous liquid was washed with water. The isolated solids were then redissolved in a minimum of THF and precipitated by the addition of water. ^{31}P NMR (THF): δ −6.9 ppm. A GPC trace of a sample of this product showed that only high polymer and no oligomeric material was present.

$[N{=}P(Ph)Cl]_n$ was prepared in the same manner as described for poly(dichlorophosphazene). Treatment of this polymer with sodium trifluoroethoxide gave a polymer identical to that reported in the literature and prepared by an alternative method.[9]

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