Development of a One-Pot in Situ Synthesis of Poly(dichlorophosphazene) from PCl_5

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Introduction

Polyphosphazenes are inorganic polymers based on the repeating unit $[N{=}PR_2]_n$, where R can be organic or organometallic groups.[1] These polymers incorporate a large class of macromolecules with a variety of useful properties, which are determined primarily by the side groups attached to the polymer backbone. Several methods have been developed for the synthesis of polyphosphazenes. Ring-opening polymerization of $[N{=}PCl_2]_3$ at 250 °C can afford poly(dichlorophosphazene), $[N{=}PCl_2]_n$.[2] Macromolecular substitution of $[N{=}PCl_2]_n$ with organic groups provides hydrolytically stable poly(organophosphazenes) with alkoxy, aryloxy, or amino side groups.[3] Another general method of polyphosphazene synthesis is through condensation polymerization. Thermal condensation polymerization of preformed alkyl- or aryl-substituted phosphoranimines can produce poly(alkyl arylphosphazenes) which cannot be obtained via the macromolecular substitution route.[4] Other monomers, viz. alkoxy- or aryloxy-substituted phosphoranimines,[5] $O{=}PCl_2{-}N{=}PCl_3$,[6] phosphinoazides,[7] and $Cl_3P{=}NSiMe_3$,[8] have been employed to produce polyphosphazenes via condensation polymerization. Among the methods for preparing poly(organophosphazenes), the most well-developed pathway is the macromolecular substitution of $[N{=}PCl_2]_n$. This route provides access to several hundred kinds of polymers and is commercially used.

Practical, economical methods for the synthesis of $[N{=}PCl_2]_n$ are highly valuable. Some recent progress in synthesis of $[N{=}PCl_2]_n$ particularly focuses on the so-called one-pot method for preferable industrial applications. At molten state, the mixture of PCl_5 and NH_4SO_4 forms $O{=}PCl_2{-}N{=}PCl_3$ at ∼165 °C; continuing heating of this species at ∼225 °C to distill off $OPCl_3$ can lead to the formation of $[N{=}PCl_2]_n$.[9] Precaution has to be taken when heating the mixture at high temperatures so as to avoid cross-linking of $[N{=}PCl_2]_n$,[10] which leads to uncharacterized and useless products. In another development, a 1,2,4-trichlorobenzene solution of PCl_5 and NH_4Cl is heated to reflux (∼214 °C), and high molecular weight $[N{=}PCl_2]_n$ is produced in solution.[11] However, sublimation of PCl_5 at temperatures above 180 °C causes blockage of reaction vessels, thus preventing scale-up attempts of this route. Carriedo et al. have experienced explosion hazards due to this sublimation-caused blockage problem. Also, use of chlorinated solvents can be problematic due to environmental concerns. Therefore, neither of the aforementioned one-pot synthesis methods has been shown to be a potentially satisfactory route for large-scale, industrial applications.

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The living cationic condensation of phosphoranimine $Cl_3P{=}NSiMe_3$ at room temperature can produce $[N{=}PCl_2]_n$ with controlled molecular weight and narrow polydispersities and offers possibilities to synthesize block copolymers.[8] This method (Scheme 1) represents a significant advance over the previous methods to prepare $[N{=}PCl_2]_n$. The scientific and technological importance of the living polymerization from $Cl_3P{=}NSiMe_3$ presents great incentives to enhance the yield of the highly reactive monomer, which was initially produced from the reaction of PCl_5 with either $LiN(SiMe_3)_2$[12a,b] or $N(SiMe_3)_3$.[12c] These methods of making $Cl_3P{=}NSiMe_3$ from PCl_5 give relatively low product yields, and the reason seems to be related to the polymerization mechanism (Scheme 1). PCl_5 is a known initiator for the polymerization of $Cl_3P{=}NSiMe_3$; thus, any product formed in solution would be in immediate contact with PCl_5 and instant, concurrent reaction of the monomer into oligomeric or cyclic phosphazenes would be inevitable. Also, a polymerization inhibitor $ClN(SiMe_3)_2$ is often formed; this species needs to be separated via additional steps from $Cl_3P{=}NSiMe_3$ to afford suitable monomer for polymerization.[8b]

To circumvent this concurrent polymerization dilemma, a new method for synthesizing $Cl_3P{=}NSiMe_3$ avoids the use of PCl_5.[13] Starting from PCl_3, a stable phosphine intermediate $Cl_2P{-}N(SiMe_3)_2$ is prepared in solution and subsequently oxidized by SO_2Cl_2 to afford $Cl_3P{=}NSiMe_3$ (Scheme 2). ^{31}P NMR monitoring is used to ensure that the sequential formations of both $Cl_2P{-}N(SiMe_3)_2$ and $Cl_3P{=}NSiMe_3$ are clean processes. Therefore, by excluding PCl_5 from the reactants, the degree of concurrent polymerization is greatly reduced. Also, this route does not generate $ClN(SiMe_3)_2$[8b] so the additional purification operation is not required. Phosphoranimine has been isolated at high yields (>80%) on large laboratory scales (>0.3 mol).

Because of intriguing recent progress in one-pot synthesis of $[N{=}PCl_2]_n$,[9,11] a more robust preparation method of $[N{=}PCl_2]_n$ from commercially available materials becomes interesting to study. Of particular interest is to study the possibility of combining the two well-established techniques: living cationic polymerization for $[N{=}PCl_2]_n$ and the new method to synthesize $Cl_3P{=}NSiMe_3$. The objective of such an approach is to construct a coherent, one-pot fashion synthesis route, which involves room temperature solution synthesis of $[N{=}PCl_2]_n$ without vacuum distillation isolation of the monomer. Conceptually, this kind of new synthesis method will present great potential for large-scale, industrial polyphosphazene preparations. The experimental details of the method development of such an approach are discussed below.

Results and Discussion

Literature Examination of the $Cl_3P{=}NSiMe_3$ and $[N{=}PCl_2]_n$ Preparation Methods. Recently, a few reports[14] have used $Cl_3P{=}NSiMe_3$ synthesized via the improved, high-yield method[13] as a precursor. However, this highly versatile phosphoranimine is isolated through stepwise, variable temperature vacuum distillation. In a typical experiment, after the LiCl is filtered, the solvent (e.g., Et_2O) and $ClSiMe_3$ are distilled off at 0 °C under ∼20 mmHg. The phosphoranimine is

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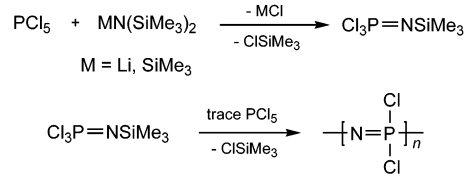
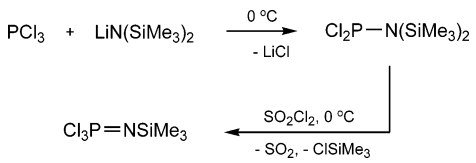
Scheme 1. Living, Cationic Polymerization for $[N{=}PCl_2]_n$ and Preparation of $Cl_3P{=}NSiMe_3$ from PCl_5



Scheme 2. Preparation of $Cl_3P{=}NSiMe_3$ from PCl_3



then collected by distillation at room temperature under ~0.1 mmHg. The isolation step is often the most likely factor for low product yields in laboratory preparations, and it also appears less favored from industrial viewpoints compared to procedures requiring no vacuum distillation. After distillation, a yellow gellike residue is often observed left in the vessel. ^{31}P NMR of this residue has revealed a single peak around −18 ppm, indicating the formation of $[N{=}PCl_2]_n$.

During the preparation of $Cl_3P{=}NSiMe_3$, major byproducts include $ClSiMe_3$, LiCl, and gaseous SO_2 that escapes from the reaction medium.[13] After purification, $Cl_3P{=}NSiMe_3$ can begin condensation polymerization when initiated by a Lewis acid such as PCl_5. Therefore, it is interesting to examine whether $Cl_3P{=}NSiMe_3$ prepared in situ can start polymerization in the presence of *all* of these byproducts in the *same reaction medium*. When the monomer is prepared, low boiling point solvents such as ether and pentane have been chosen to facilitate the distillation process for better monomer yield. In polymerization reactions, CH_2Cl_2, toluene, benzene, and dioxane have been employed.[15] Toluene appears to be the most economical and feasible to handle among the solvents used.

Polymerization of $Cl_3P{=}NSiMe_3$ Prepared in Situ from PCl_3. In toluene, $Cl_2P{-}N(SiMe_3)_2$ was prepared by reacting PCl_3 and $LiN(SiMe_3)_2$ (which can be acquired from commercial sources or prepared from $HN(SiMe_3)_2$ and *n*-BuLi) and confirmed by ^{31}P NMR. This compound was stable in solution and had been stored in the reaction medium for a few days without decomposition. Addition of SO_2Cl_2 to the solution containing $Cl_2P{-}N(SiMe_3)_2$ led to the formation of $Cl_3P{=}NSiMe_3$. The reactivity of this phosphoranimine in the same reaction medium was tested consequently. The mixture, mainly containing $Cl_3P{=}NSiMe_3$, $ClSiMe_3$, and LiCl, was added with a trace amount of PCl_5 or no PCl_5 at all. Stirring overnight at room temperature produced a product that demonstrated one sharp ^{31}P NMR resonance (−17.6 ppm) characteristic of polymer **1** (Scheme 3). From the observations, the multistep conversion of PCl_3 to $[N{=}PCl_2]_n$ was essentially quantitative in one reaction medium. No inhibition of polymerization had been observed. The question of the role of PCl_5 in the in situ polymerization was revealed to some degree through molecular weight measurements (vide infra). In our laboratory, $[N{=}PCl_2]_n$ has been routinely prepared through this one-pot method on scales from a few to a few hundred millimoles. After filtration and solvent removal, $[N{=}PCl_2]_n$ can be subsequently treated to produce other valuable derivatives, stored in bulk in an inert atmosphere, or preserved in a diglyme solution[16] for future modification.

Scheme 3. One-Pot in Situ Synthesis of $[N{=}PCl_2]_n$ from PCl_3

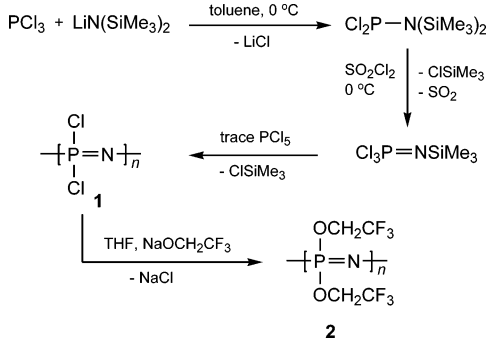


Table 1. Results of the One-Pot Synthesis of $[N{=}PCl_2]_n$ from PCl_3

run	time (before adding PCl_5)	PCl_3, mmol	$LiN(SiMe_3)_2$, mmol	PCl_5, mmol	M_w[b]	PDI[b]
1	N/A	218	220	0	103 300	2.35
					59 600	1.26
2	1 h[a]	10.3	10.3	0.51	49 600	1.24
3	1 h	8.1	8.2	0.17	20 900	1.61
4	6 h	8.3	8.3	0.41	124 000	2.14
5	2 days	80.2	81.3	3.98	245 100	3.95

[a] Stirred at 0 °C. [b] M_w and PDI are for $[N{=}P(OCH_2CF_3)_2]_n$.

Molecular Weight Measurements of the Derivative Polymers $[N{=}P(OCH_2CF_3)_2]_n$ (2). To examine the properties of the $[N{=}PCl_2]_n$ formed through the one-pot method, nucleophilic substitution was performed to afford hydrolytically stable derivatives. Polymers **1** were treated with excess $NaOCH_2CF_3$, and the resultant species yielded a ^{31}P NMR singlet characteristic of the known polymer $[N{=}P(OCH_2CF_3)_2]_n$ (**2**) (Scheme 3). Starting from PCl_3, the yields of $[N{=}P(OCH_2CF_3)_2]_n$ are in the 40−50% range (see Experimental Section). Gel permeation chromatography (GPC) analysis of a few examples of $[N{=}P(OCH_2CF_3)_2]_n$ indicated that all polymers possessed high molecular weight fractions only (Table 1). The initiation of polymerization in the mixture was analyzed. In run 1, the $Cl_3P{=}NSiMe_3$ mixture was left stirring at room temperature overnight to form $[N{=}PCl_2]_n$. The resultant $[N{=}P(OCH_2CF_3)_2]_n$ demonstrated a bimodal distribution. This suggests that there are at least two species in the reaction medium to have initiated polymerization independently. To prevent the spontaneously initiated polymerization by unspecified species, the formed $Cl_3P{=}NSiMe_3$ was kept at 0 °C before addition of PCl_5 (run 2). The derivative $[N{=}P(OCH_2CF_3)_2]_n$ demonstrated a relatively narrow PDI. When the $Cl_3P{=}NSiMe_3$ mixture was left stirring at room temperature for ~1 h (run 3) before addition of PCl_5, the resultant $[N{=}P(OCH_2CF_3)_2]_n$ showed a little wider molecular weight distribution (1.61 vs 1.24 from run 2). When the monomer was left stirring at room temperature for ~6 h (run 4) or left standing for 2 d (run 5) before addition of PCl_5, the resultant $[N{=}P(OCH_2CF_3)_2]_n$ showed a broader molecular weight distribution. In total, we have 22 runs under the reaction conditions outlined above, and all gave similar results. Only a few examples were sent for GPC analysis with the results shown in Table 1. PCl_5 seems to have played a very competitive role among the initiators. Promptly added PCl_5 provides better control over polymer molecular weight distribution. In general, because

of the competition among various initiation species, this route does not provide the same level of control over molecular weight (PDI < 1.1) as evidenced in the living polymerization route starting with purified $Cl_3P{=}NSiMe_3$.[8] However, polyphosphazenes prepared through the traditional ring-opening mechanism, which possess wide molecular weight distribution (~19),[2] have gained significant industrial applications. This new one-pot method has prepared $[N{=}PCl_2]_n$ with narrower molecular weight distribution than that prepared via the ring-opening route. Therefore, the new method could have similar industrial application potentials as the traditional ring-opening technique regarding molecular weight distributions.

Conclusion

We report a new route to $[N{=}PCl_2]_n$ based on a convenient combination of the recently reported improved synthesis of the $Cl_3P{=}NSiMe_3$ monomer and the living cationic polymerization method for this monomer. The new route proves to be a beneficial alternate method to prepare $[N{=}PCl_2]_n$. Starting from PCl_3, this route proceeds through a multistep, quantitative conversion, one-pot fashion under ambient temperature and pressure to synthesize $[N{=}PCl_2]_n$. The yields of the moisture stable derivative polymers $[N{=}P(OCH_2CF_3)_2]_n$ are in 40−50% range starting from PCl_3. The whole process does not require demanding vacuum distillation of the highly reactive monomer and thus can be viewed as a more cost-effective alternate to the living cationic polymerization route using purified monomer. The conditions used in this study are likely to be modified for large-scale, industrial applications; therefore, it possesses distinct advantages over other one-pot synthesis routes, which face acute scale-up problems. This method warrants favorable applications for both industrial and laboratory preparation of polyphosphazenes.

Experimental Section

Materials and Equipment. $LiN(SiMe_3)_2$ (Aldrich, 97%), SO_2Cl_2 (Aldrich, 97%), PCl_3 (Eastman, 98%), PCl_5 (Aldrich, 95%), NaH (Aldrich, 60% dispersion), $HOCH_2CF_3$ (Aldrich, 99%), *n*-BuLi (Acros, 2.5 M in hexanes), and $HN(SiMe_3)_2$ (Avocado Research Chemicals Ltd., 98%) were used as received. THF was distilled over sodium and benzophenone prior to use, and dioxane and toluene were distilled over CaH_2. The reactions were performed using standard Schlenk techniques under an atmosphere of nitrogen (Aeriform). $^{31}P\{^1H\}$ spectra were recorded on a Bruker AC250 NMR spectrometer operated at 101.1 MHz, or on a Bruker EFT90 NMR spectrometer operated at 36.4 MHz, with the chemical shifts externally referenced to 85% phosphoric acid.

Molecular weight estimates were obtained using gel permeation chromatography (GPC) using a Waters Associates 2690 separations module equipped with a column heater, Ultrastyragel columns with pore sizes of 10^3−10^5 Å, in-line degasser, and a differential refractometer. The GPC possesses a triple detection system (refractive index, light scattering, viscosity) such that absolute molecular weights are reported for homopolymers. A flow rate of 1.0 mL/min was used, and the eluent was THF with 0.1% *n*-Bu_4NBr (w/w).

A Typical Procedure for the Synthesis of $[N{=}P(OCH_2CF_3)_2]_n$ from PCl_3. $LiN(SiMe_3)_2$ (1.73 g, 10.3 mmol) was dissolved in 40 mL of toluene, and the solution was cooled to 0 °C. PCl_3 (0.9 mL, 10.3 mmol) was then added dropwise over 10 min. The resulting mixture was stirred for 30 min at the same temperature followed by stirring at room temperature for ~1 h, giving a white suspension. ^{31}P NMR revealed complete conversion of PCl_3 to $Cl_2P{-}N(SiMe_3)_2$ (188.5 ppm, toluene/$CDCl_3$). SO_2Cl_2 (0.85 mL, 10.5 mmol) was then added dropwise over 10 min to this suspension at 0 °C. The reaction was allowed to proceed at 0 °C for ~1 h. $Cl_3P{=}NSiMe_3$ (−54.5 ppm, toluene/$CDCl_3$) was the only product present by ^{31}P NMR. PCl_5 (106 mg, 0.51 mmol) was then added, and the resultant mixture was stirred overnight at room temperature. $[N{=}PCl_2]_n$ was observed from ^{31}P NMR (−17.6 ppm, toluene/$CDCl_3$). The mixture was then filtered through Celite (dried at ~110 °C for >48 h prior to use), which was then washed with toluene (2 × 5 mL). The volatiles from the resulting pale yellow filtrate were removed under reduced pressure to give a yellow gellike solid. THF (~40 mL) was used to dissolve the solid. To this resulting solution, 10 mL of 2.5 M $NaOCH_2CF_3$ (prepared from NaH and $HOCH_2CF_3$ in dioxane) was added, and the mixture was stirred overnight at room temperature and $[N{=}P(OCH_2CF_3)_2]_n$ was the only product according to ^{31}P NMR (−7.2 ppm, THF/$CDCl_3$). The reaction mixture was concentrated by rotary evaporation, and the polymer was purified by multiple precipitations into acidified water (pH ~ 5) and hexanes followed by drying on a vacuum line. Yield = 1.0 g (41%).

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