Ambient temperature ring-opening polymerisation (ROP) of cyclic chlorophosphazene trimer $[N_3P_3Cl_6]$ catalyzed by silylium ions

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The temperature required for ring-opening polymerisation of *cyclo*-$N_3P_3Cl_6$ can be dramatically lowered by employing trialkylsilylium carboranes $[R_3Si(CHB_{11}X_{11}]$ as catalysts.

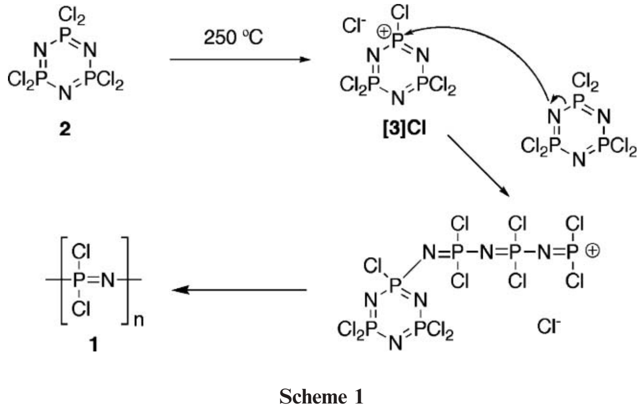
The chemistry of poly(dichlorophosphazene) $[–PCl_2=N–]_n$ (**1**) has played an integral role in the development of inorganic polymer science over the past four decades, due to the inherent tunability of the polymer's properties *via* substitution of chloride by oxygen and nitrogen nucleophiles at the phosphorus centre.[1] The carbon-free backbone of these inorganic polymers provides a versatile scaffold for widespread materials applications, in areas such as high performance elastomers,[2] polymer electrolytes[3] and biomedical membranes.[4]

Due to substituent versatility, a wide variety of synthetic routes to polyphosphazenes have been explored. For example, an ambient temperature, living, cationic chain-growth polycondensation approach to **1** has been developed in recent years.[5] It involves the PCl_5-catalyzed polymerisation of the *N*-silylphosphoranimine monomer $Cl_3P=NSiMe_3$, and gives high yields of **1** with moderately high molecular weight and narrow molecular weight distributions. Substantial molecular weight control is possible by adjustment of the catalyst (PCl_5) to monomer ratio. Nevertheless, the polyphosphazene field remains heavily reliant on the synthesis of **1** *via* classical[6] thermal ring-opening polymerization (ROP) of the cyclic phosphazene trimer $[N_3P_3Cl_6]$ (**2**) in a melt at *ca.* 250 °C.[7] Although the thermal ROP of **2** provides access to many derivatives of high molecular weight polyphosphazenes, this route suffers from a number of drawbacks. High costs are associated with the synthesis of **2**, a high level of monomer purity is required to achieve reproducible polymerization and a high temperature is required to induce ROP. In the melt, only moderate yields of soluble polymer can be obtained (*ca.* 40%) before crosslinking reactions take place. Even when ROP is performed in solution, no appreciable molecular weight control is possible because high temperatures remain necessary. Broad molecular weight distributions are typical.[8]

The ROP of **2** can be catalysed by certain Lewis acids, such as BCl_3[9] and $AlCl_3$,[10] but the reduction in process temperature is modest (to *ca.* 200 °C) and there are reproducibility issues. The lack of generality to a wide range of Lewis acids lends uncertainty to the mechanism of catalysis, but the generally accepted pathway for the ROP of **2** involves initial formation of the cationic intermediate $[N_3P_3Cl_5]^+$ (**[3]**$^+$) *via* a thermally-induced or Lewis acid-assisted loss of chloride ion, followed by electrophilic attack of **[3]**$^+$ on **2** (Scheme 1).[1] There is no direct evidence for the existence of the proposed coordinatively-unsaturated cationic intermediate **[3]**$^+$, although a related cation has been implicated in the PCl_5-catalyzed polymerisation of $Cl_3P=NSiMe_3$.[5]

Reasoning that better routes to coordinatively-unsaturated cation **[3]**$^+$ would lead to better ROP catalysis of **2**, we explored the reaction of **2** with various strong Lewis and Brønsted acids that were potentially capable of producing cations *via* chloride ion abstraction.[11] However, consistent with studies involving neutral Lewis acids,[12] cationic electrophiles such as H^+, Ag^+, CH_3^+ and R_3Si^+ formed adducts with an N atom of **2** rather than abstracting a chloride ion from P, regardless of how weakly coordinating is the accompanying anion.[11,13–15] Nevertheless, H^+, CH_3^+ and R_3Si^+ adducts of **2** with carborane anions were newly isolated and characterized chlorophosphazene cations,[11] so we decided to investigate their behaviour as ROP catalysts. Specifically, we explored the catalytic potential of six salts, **4–9**, shown in Fig. 1. An important feature of these salts is the exceptional inertness of their carborane anions.[16] Without weakly coordinating counter-ions, these cations cannot be prepared because of the low Lewis and Brønsted basicity of **2** (pK_a = −6 in nitrobenzene).[17]

Treatment of **2** with 10 mol% of either the N-protonated phosphazene **4** or the N-methylated phosphazene **5** in 1,2-dichlorobenzene did not trigger ROP at either room temperature or when heated at 160 °C for 7 d. However, when **2** was treated with 10 mol% of the N-silylated derivatives **6–9** (prepared *in situ*) in 1,2-dichlorobenzene at 25 °C,† complete conversion of $[N_3P_3Cl_6]$ (**2**) [$\delta(^{31}P) = 20$][7] to polydichlorophosphazene $[NPCl_2]_n$ (**1**) [$\delta(^{31}P) = -18$][7] was achieved at room temperature, as indicated



Scheme 1

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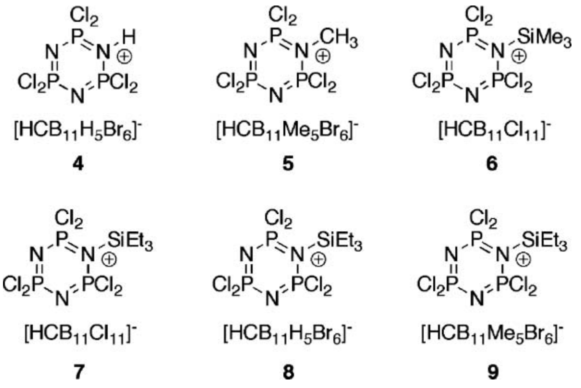


Fig. 1 The protonated, methylated and four silylated phosphazene cations, together with the carborane counterions used in this study.

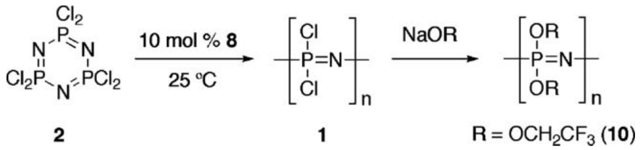
by ^{31}P{^{1}H} NMR spectroscopy. A summary of the polymerisation conditions surveyed in this study is shown in Table 1.

Of the four silyl derivatives **6**–**9**, compound **8** was the easiest to prepare. Catalysts with hexabromo carborane anions (**8** and **9**) were more active than those with the undecachloro carborane anion (**6** and **7**), even though the latter is considered less coordinating. Treatment of a 2 M 1,2-dichlorobenzene solution of **2** with 10 mol% of **8** resulted in the complete conversion to polymer **1** in just 90 min. Shorter reaction times were observed with higher catalyst loadings. Higher concentrations of **2** led to the formation of gels. Lower concentrations of **2** curtailed ROP, probably in part because of the sensitivity of **6**–**9** to moisture and errant nucleophiles in the solvent, and part because of the thermodynamics of ROP. Collectively, these observations are consistent with the energetics of ROP as recently deduced for the cyclic thionylphosphazene [NSOCl(NPCl$_2$)$_2$][18], and are characteristic of the ROP of cyclic monomers with low degrees of ring strain. A weakly coordinating anion is crucial for successful catalysis. The presence of triflate anion quenches catalysis by **8**, presumably *via* desilylation of **6**–**9** to form R$_3$Si(OTf) (trialkylsilyl triflates do not silylate **2**).

In order to determine the molecular weight of a representative polymer obtained from an ambient temperature ROP reaction, a standard P–Cl bond substitution reaction was carried out. Treatment of a sample of polymer **1**, obtained from a 1 M 1,2-dichlorobenzene solution of monomer **2** and 10 mol% catalyst **8**, with sodium trifluoroethoxide in dioxane gave the hydrolytically stable poly(bistrifluoroethoxy)phosphazene [NP(OCH$_2$CF$_3$)$_2$]$_n$ (**10**) as a white fibrous solid in 86% re-precipitated yield (Scheme 2). Gel permeation chromatography indicated a weight average molecular weight (M_w) of 1.12×10^5 g mol^{-1} and a polydispersity index (PDI) of 1.83 *vs.* polystyrene standards. The M_w value is encouragingly high and the polydispersity value promisingly narrow.

Table 1 Conditions of polymerisation

Conc. of **2** in 1,2-dichlorobenzene/M	Catalyst	Mol% of Catalyst	Reaction time/h
0.3	**8**	10	36
0.5	**8**	10	5
1.0	**8**	10	2.5
1.5	**8**	10	2
2.0	**8**	10	1.5
1.0	**8**	5	48
1.0	**8**	20	<1
1.0	**8**	33	<1
1.0	**7**	10	48
1.0	**7**	2	144
1.0	**9**	10	2
1.0	**9**	5	24
1.0	**6**	10	72



Scheme 2

The finding that cations **6**$^+$–**9**$^+$ are potent catalysts for the polymerization of **2** refocuses attention on the mechanism of ROP. It is possible that trialkylsilylation on an N atom provides an unexpectedly low energy pathway for the generation of the key coordinatively-unsaturated intermediate **[3]**$^+$ *via* an *intramolecular* elimination reaction of R$_3$SiCl. Indeed, Et$_3$SiCl is a major byproduct of the thermal decomposition of **8** in the solid state and in solution. An alternative ROP mechanism worthy of consideration involves an electrophilically-assisted associative chain propagation step. With soluble components and ambient temperature catalysis, kinetic experiments to distinguish between the different possible ROP mechanisms are now feasible. In addition, the energetics of alternate mechanisms can be explored computionally. A deeper insight into the ROP mechanism of phosphazenes can be anticipated from the present findings, as well as better control over polymer properties.

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Notes and references

† *Typical ROP reaction of [N$_3$P$_3$Cl$_6$]* (**2**). In an inert atmosphere glovebox, Et$_3$Si(CHB$_{11}$H$_5$Br$_6$) (149 mg, 0.20 mmol) was combined with [N$_3$P$_3$Cl$_6$] (702 mg, 2.0 mmol) and then charged with 2.04 mL of dry 1,2-dichlorobenzene at room temperature (1 M solution). The solution was stirred magnetically and the formation of polymer **1** monitored by ^{31}P{^{1}H} NMR spectroscopy at 122 MHz ($\delta = -17.7$) after 2 (0% conversion), 30 (3% conversion), 60 (35% conversion), 90 (75% conversion), 120 (95% conversion) and 150 (100% conversion) minutes.

Preparation of [NP(OCH$_2$CF$_3$)$_2$]$_n$ (**10**). In a typical experiment, the polymerization mixture was diluted with 50 mL of dioxane and cooled to 12 °C. An excess of NaOCH$_2$CF$_3$ (freshly prepared from Na and CF$_3$CH$_2$OH in dioxane) was added dropwise to the cooled polymer solution. The resulting white suspension was stirred at 100 °C for 2 h, and then at room temperature overnight. The volatiles were removed from the reaction mixture, which was then cooled to 0 °C and quenched with copious amounts of water. The crude polymer was filtered off, dried, redissolved in a minimal amount of dioxane and reprecipitated with hexane in 84% yield. ^{31}P{^{1}H} NMR (122 MHz, δ, CD$_3$CN, 25 °C): −6.9 (s). GPC: M_n = 61 000, M_w = 112 000, PDI = 1.83.

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