JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

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A Cooperative Role for the Counteranion in the PCl_5-Initiated Living, Cationic Chain Growth Polycondensation of the Phosphoranimine $Cl_3P{=}NSiMe_3$

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Supporting Information

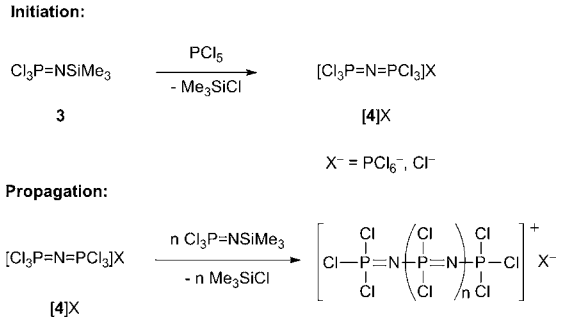
ABSTRACT: The counteranion associated with the cationic initiator $[Cl_3P{=}N{=}PCl_3]^+$ ($[\mathbf{4}]^+$) generated during the PCl_5-initiated living, cationic chain growth polycondensation of the *N*-silylphosphoranimine $Cl_3P{=}NSiMe_3$ (**3**) to give poly(dichlorophosphazene), $[N{=}PCl_2]_n$ (**2**), has been found to have a dramatic effect on the polymerization. When the counteranion of $[\mathbf{4}]^+$ was changed from PCl_6^- or Cl^- to the weakly coordinating anions $[BAr^{*F}{}_4]^-$ and $[BAr^F{}_4]^-$ (Ar^{*F} = 3,5-$\{CF_3\}_2C_6H_3$, Ar^F = C_6F_5) instead of the polymerization of **3** being complete in 4−6 h, no reaction was observed after 24 h. Remarkably, the polymerization of **3** may be initiated by Cl^- anions even in the *absence* of an active cation such as $[\mathbf{4}]^+$. However, in the *presence* of $[\mathbf{4}]^+$, the reaction proceeded significantly faster and allowed for molecular weight control. These results reveal that the currently accepted mechanism for the PCl_5-initiated living polymerization of **3** needs to be revised to reflect the key role of the counteranion present.

Well-defined polymers and block copolymers with inorganic elements as a key component are emerging as an interesting and broad class of easily processed materials with properties and functions that complement those of state-of-the-art organic macromolecular materials.[1] Polyphosphazenes, $[N{=}PR_2]_n$, represent one of the most versatile classes of main-group polymers, and the ability to tune their chemical and physical properties through the choice of the substituents (R) has enabled a broad range of promising applications.[2] The most well-developed route to these materials involves the thermal ring-opening polymerization (ROP) of the cyclic phosphazene trimer $(N{=}PCl_2)_3$ (**1**) at 200−250 °C to yield poly(dichlorophosphazene), $[N{=}PCl_2]_n$ (**2**),[3,4] which offers access to various polyphosphazenes via macromolecular substitution of the P−Cl bonds. Although a range of other synthetic methods affording phosphazene polymers have been developed,[5] including examples that operate at room temperature,[6] all suffer from poor molecular weight control and the formation of broad molecular weight distributions due to the likely presence of a combination of chain transfer, chain termination, and slow initiation events.

In 1995, our group and Allcock and co-workers collaboratively reported the first example of a living polymerization route to polyphosphazenes.[7,8] This process, a rare example of a living chain growth polycondensation,[9] involves the treatment of trichloro(*N*-trimethylsilyl)phosphoranimine, $Cl_3P{=}NSiMe_3$ (**3**),[10] with PCl_5. In contrast to other routes, this method allows the molecular weight of the polymer to be controlled by altering the monomer to initiator ratio to give **2** in high yield with a relatively narrow molecular weight distribution. Furthermore, block copolymers may be prepared via sequential monomer addition to the living chain ends or the use of macroinitiation methods.[11,12] The improvement in the control of the molecular weight and polydispersity enabled access to well-defined materials suitable for self-assembly studies[12] as well as to biodegradable macromolecular anticancer drug carriers.[13]

Although the discovery of the PCl_5-initiated living polymerization route to **2** has permitted a range of synthetic advances, the polymerization mechanism has not been fully elucidated. The proposed mechanism involves initiation by the reaction of monomer **3** with PCl_5 to form the cationic species $[Cl_3P{=}N{=}PCl_3]^+$ ($[\mathbf{4}]^+$) (Scheme 1). The latter reacts with further equivalents of **3** to form a growing polymer chain, $[Cl_3P{=}N{-}(PCl_2{=}N)_n{-}PCl_3]^+$, with concomitant elimination of the condensation byproduct Me_3SiCl.[7,8] According to this mechanistic sequence, the PCl_5-initiated polymerization of **3** may be classified as a cationic chain growth polycondensation process.

Scheme 1. Proposed Reaction Sequence in the PCl_5-Initiated Polymerization of 3



We recently examined the reactivity of the species $[\mathbf{4}]^+$ and $[Cl_3P{=}N{-}PCl_2{=}N{-}PCl_3]^+$ ($[\mathbf{5}]^+$) formed in the initiation step and the first propagation step, respectively, using model

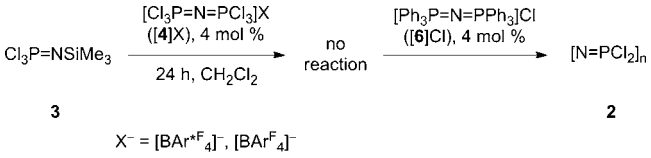
Received: August 3, 2012
Published: September 5, 2012

   dx.doi.org/10.1021/ja307703h | *J. Am. Chem. Soc.* 2012, 134, 15293−15296

compound studies.[14] Although the reactivity detected was consistent with the propagation step in Scheme 1, we also found that PCl_6^-, which might be formed as the counteranion of $[4]^+$ via the reaction of monomer **3** with two molecules of PCl_5,[15] is not innocent as previously assumed but may actually participate in the polymerization of **3**. Thus, stoichiometric reactions between **3** and the salt $[Ph_3P{=}N{=}PPh_3]PCl_6$ ($[\mathbf{6}]PCl_6$), which contains an inert countercation devoid of P−Cl bonds, resulted in the formation of cationic oligomers $[Cl_3P{=}N{-}(PCl_2{=}N)_x{-}PCl_3]^+$ in which the phosphorus center of the PCl_6^- anion was incorporated into the phosphazene chain.[14] To eliminate unwanted effects of "noninnocent" counteranions on the molecular weight distribution of the resulting polyphosphazenes, we explored the potential of salts of $[4]^+$ with inert, weakly coordinating counteranions for use as polymerization initiators. With this strategy, ion pairing effects should also be largely suppressed, which was expected to lead to highly efficient initiation. In this preliminary communication, we present the unexpected results of these studies, which disclose additional fundamental insight into the mechanism of the PCl_5-initiated living polymerization of **3**.

The new potential polymerization initiators $[4][B(3,5\text{-}\{CF_3\}_2C_6H_3)_4]$ (denoted as $[4][BAr^{*F}{}_4]$) and $[4][B(C_6F_5)_4]$ (denoted as $[4][BAr^F{}_4]$) were prepared via the salt metathesis reactions of $[4]Cl$[16] with $Na[BAr^{*F}{}_4]$ and $Na[BAr^F{}_4]$, respectively. Surprisingly, when the polymerization of **3** was attempted using $[4][BAr^{*F}{}_4]$ or $[4][BAr^F{}_4]$ in CH_2Cl_2 at 25 °C (Scheme 2), instead of highly efficient initiation, no reaction

Scheme 2. Attempted Polymerization of 3 Using $[4][BAr^{*F}{}_4]$ or $[4][BAr^F{}_4]$ and Subsequent Addition of [6]Cl



was observed by $^{31}P\{^1H\}$ NMR spectroscopy after 24 h [Figure 1a and Figure S2 in the Supporting Information (SI)]. In striking contrast, the polymerization of **3** initiated by $[4]Cl$ under otherwise identical conditions was complete within 5 h (Figure S1).[17] Moreover, upon subsequent addition of chloride ions to the mixture of **3** and $[4][BAr^{*F}{}_4]$ or $[4][BAr^F{}_4]$ in the form of the salt $[Ph_3P{=}N{=}PPh_3]Cl$ ($[\mathbf{6}]Cl$; 1 equiv with respect to $[4]^+$), which has an inert countercation, rapid polymerization of **3** occurred with quantitative conversion to **2** in less than 6 h (Figure 1b and Figure S3).

Clearly, the Cl^- anion, which might be generated during the PCl_5-initiated polymerization of **3**, is not an innocent spectator but rather plays a crucial role in this process. This result prompted us to investigate the possibility of initiating the polymerization of **3** by Cl^- in the *absence* of an active cation such as $[4]^+$. Indeed, when $[6]Cl$, in which the cation is devoid of P−Cl bonds, was used as an initiator (25:1 ratio) in CH_2Cl_2 at 25 °C, **3** was completely consumed within 3 weeks (Scheme 3).[18] A $^{31}P\{^1H\}$ NMR spectrum showed the presence of the cyclic phosphazene **1** (20.6 ppm; ca. 3%) as well as a resonance characteristic of **2** at −17.4 ppm (97%). Following derivatization of **2** with $NaOCH_2CF_3$ to yield the air- and moisture-stable polymer $[N{=}P(OCH_2CF_3)_2]_n$ (**7**), gel-permeation chromatography (GPC) analysis (UV detection) of the latter showed it to have high molecular weight [number-average molecular weight (M_n) = 64 580 g mol^{-1}; polydispersity index (PDI) = 1.36]. Moreover, after equimolar amounts of **3** and $[6]Cl$ were stirred for 24 h in CH_2Cl_2 at 25 °C, a $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture revealed full consumption of **3** and the formation of the cyclic phosphazene trimer **1** (63%) and the cyclic tetramer $(N{=}PCl_2)_4$ (−5.9 ppm; 15%) as well as polydichlorophosphazene **2** (22%).

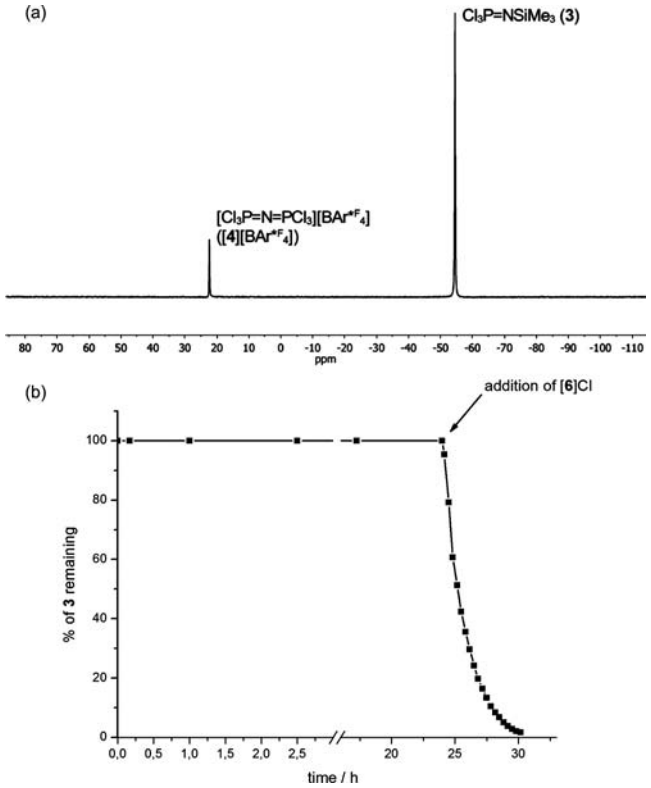
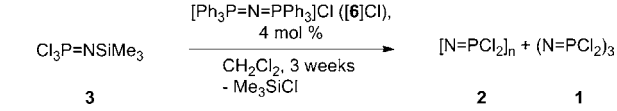


Figure 1. (a) $^{31}P\{^1H\}$ NMR spectrum of a mixture of $[4][BAr^{*F}{}_4]$ and 10 equiv of **3** after 24 h in CH_2Cl_2. (b) Amount of **3** remaining (as determined by $^{31}P\{^1H\}$ NMR signal integration) during the reaction between **3** and $[4][BAr^{*F}{}_4]$ (25:1) before and after the addition of $[6]Cl$ (1 equiv with respect to $[4][BAr^{*F}{}_4]$).

Scheme 3



Although these experiments showed that the Cl^- anion is able to initiate the polymerization of **3**, several features of this reaction indicate that Cl^- alone cannot account for the formation of polymer **2** in the living, PCl_5-initiated process. First, the reaction is much slower than that involving $[4]Cl$, wherein the cation contains reactive terminal P−Cl bonds (reaction time of 3 weeks vs 4−6 h). Second, a significant quantity of cyclic trimer **1** is formed, and broad polydispersities result. To examine a potential *cooperative* role for Cl^- and $[4]^+$, we investigated the effect of their concentrations on the reaction time and the resulting molecular weight distribution in more detail. Specifically, two sets of experiments were conducted: First, to examine the influence of Cl^- concentration, a solution of **3** and $[4][BAr^{*F}{}_4]$ (4 mol %) in CH_2Cl_2 (Scheme 2) was treated with a CH_2Cl_2 solution of $[6]Cl$ in

dx.doi.org/10.1021/ja307703h | J. Am. Chem. Soc. 2012, 134, 15293−15296

varying concentrations. Second, to examine the influence of the active phosphazene cation $[4]^+$, a solution of $[4][BAr^{*F}_4]$ in a range of concentrations in CH_2Cl_2 was added to a solution of **3** and [**6**]Cl (4 mol %) in CH_2Cl_2 (Scheme 2). The reactions were monitored by $^{31}P\{^1H\}$ NMR spectroscopy and stirred at 25 °C until **3** was completely consumed to form **2**. Subsequently, **2** was subjected to halogen replacement to yield the hydrolytically stable polymer **7**, which was analyzed by MALDI−TOF MS and GPC (Tables 1 and 2).[19]

Table 1. Effect of Changing the Amount of [6]Cl on the Polymerization of 3 in the Presence of $[4][BAr^{*F}_4]$ (Scheme 2) to Afford $[N=P(OCH_2CF_3)_2]_n$ (7) after Derivatization of $[N=PCl_2]_n$ (2)

Cl^-:[4][BAr^{*F}_4]:3 molar ratio	time (min)[a]	M_n (g mol^{-1})[b]	PDI[b]
0.17:1:25	380	6350	1.04
0.33:1:25	240	7370	1.04
0.5:1:25	180	7670	1.04
0.72:1:25	140	7020	1.02
1:1:25	100	8220	1.02

[a]Time required for full consumption of **3** to form **2** as observed by $^{31}P\{^1H\}$ NMR spectroscopy (see the SI for details). [b]Determined by MALDI−TOF MS. At lower concentrations of Cl^-, slightly larger amounts of cyclic trimer and tetramer were formed.

Table 2. Effect of Changing the Amount of $[4][BAr^{*F}_4]$ on the Polymerization of 3 in the Presence of [6]Cl (Scheme 2) to afford $[N=P(OCH_2CF_3)_2]_n$ (7) after Derivatization of $[N=PCl_2]_n$ (2)

Cl^-:[4][BAr^{*F}_4]:3 molar ratio	time (min)[a]	M_n (g mol^{-1})	PDI
1:0.17:25	<960	37100[b]	1.03[b]
1:0.33:25	<960	25200[b]	1.07[b]
1:0.5:25	450	20000[b]	1.13[b]
1:0.72:25	360	12970[c]	1.03[c]
1:1:25	100	8430[c]	1.04[c]

[a]Time required for full consumption of **3** to form **2** as observed by $^{31}P\{^1H\}$ NMR spectroscopy (see the SI for details). [b]Determined by GPC (UV detection) vs polystyrene standards (a correction factor was applied for M_n; see ref 19). [c]Determined by MALDI−TOF MS.

This study revealed that an increase in the proportion of the chloride ion led to a significant decrease in the time taken for full consumption of **3** to form **2**. The GPC data showed no appreciable difference in the molecular weight of the prepared polymer with different relative amounts of Cl^- (Table 1). This suggests that Cl^- is not responsible for the molecular weight control observed in the PCl_5-initiated polymerization of **3**. On the other hand, an increase in the relative amount of the active cation $[4]^+$ clearly led to a decrease in the molecular weight of the obtained polymer (Table 2). This indicates that the cation may provide molecular weight control in the PCl_5-initiated polymerization of **3**. No significant change in PDI was observed with changes in the relative amount of either $[4]^+$ or Cl^-.

In summary, our studies have disclosed that the mechanism of the PCl_5-initiated living polymerization of **3** is much more complex than originally proposed.[7,8] The Cl^- anion generated at an early stage is not innocent, as has previously been implied, but in fact plays a key cooperative role with the living cations in the polymerization process in both the initiation and chain propagation steps. Thus, we have shown that Cl^- anions initiate the slow polymerization of **3** even in the *absence* of an active cation, yielding polymers with high molecular weight and moderate polydispersity. Although an active cation such as $[Cl_3P{=}N{=}PCl_3]^+$ ($[4]^+$) is not required for the polymerization of **3** to proceed, its presence dramatically increases the rate of propagation and provides molecular weight control. These preliminary results have led us to reassess the mechanism of the PCl_5-initiated living polymerization of **3**. For example, it is possible that the initiation of the polymerization of **3** requires prior association of Cl^- with the monomer. We are currently working on further detailed mechanistic investigations in order to provide an in-depth understanding of this interesting polymerization reaction with the ultimative aim of broadening the applications of polyphosphazenes in nanoscience.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, GPC traces, and MALDI−TOF and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

V.B. thanks the States of Jersey for a Ph.D. scholarship. S.P. and H.H. thank the Deutscher Akademischer Austauschdienst (DAAD) and the Deutsche Forschungsgemeinschaft (DFG), respectively, for postdoctoral fellowships. A.P.S. thanks the EU for a Marie Curie Fellowship. I.M. thanks the EU for financial support.

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(15) Phosphoranimine **3** undergoes a clean stoichiometric reaction with 2 equiv of PCl_5 to give $[Cl_3P{=}N{=}PCl_3]PCl_6$ ($[\mathbf{4}]PCl_6$). The latter may be used to initiate further oligomerization as well as polymerization of **3** (see refs 7 and 14).
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(17) MALDI–TOF MS analysis of the hydrolytically stable polymer $[N{=}P(OCH_2CF_3)_2]_n$ (**7**) obtained upon derivatization of **2** via macromolecular substitution of Cl in the P–Cl bonds using $NaOCH_2CF_3$ showed it to have M_n = 6260 g mol^{-1} and PDI = 1.10.
(18) In a control reaction in which **3** was stirred alone in CH_2Cl_2 (0.5 M) at 25 °C, no change was detected within 24 h. After 72 h, the formation of a <1% yield of $[N{=}PCl_2]_n$ (**2**) was observed by $^{31}P\{^1H\}$ NMR spectroscopy, and after 1 month, a 20% yield of **2** was detected; its formation may have been initiated by trace impurities in **3**.
(19) MALDI–TOF MS could only be used successfully for molecular weights up to ca. 15 000 g/mol. However, comparison of the molecular weights obtained by MALDI–TOF with those obtained by GPC showed that GPC overestimated the molecular weights of polyphosphazenes under the conditions applied. Thus, from the materials where both types of molecular weight data were available, an average correction factor of 0.75 was calculated and applied to all of the GPC M_n data for the polymers **7** reported here.