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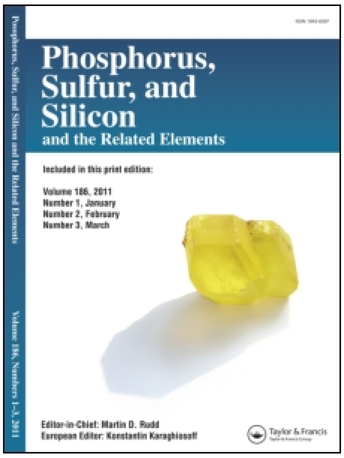

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REACTIONS OF ANIONIC POLY(ALKYL/ARYLPHOSPHAZENES) WITH CYCLIC SILOXANES

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Abstract. Poly(methylphenylphosphazene) is readily derivatized by deprotonation/substitution reactions that involve sequential treatment with *n*-BuLi and electrophiles such as RMe_2SiCl, aldehydes and ketones, CO_2, and styrene. Reactions of the anionic polymer intermediate with the cyclic siloxane, $(Me_2SiO)_3$, are under investigation. The synthesis and characterization of new polyphosphazene-*graft*-polysiloxane copolymers prepared in this manner are reported.

INTRODUCTION

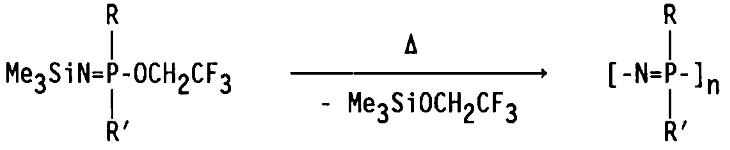
Among inorganic polymers, the isoelectronic polysiloxanes, $(R_2SiO)_n$, and polyphosphazenes, $(R_2PN)_n$, are two of the best known and most studied systems. While the silicones have numerous commercial applications, the polyphosphazenes have unique substituent diversity resulting from a variety of backbone and side-group substitution reactions. The permanent fusion of these two types of polymers through blocking or grafting reactions should provide interesting new materials with the advantages of both systems.

Allcock and coworkers[1,2] have investigated two potential pathways to phosphazene/silicone copolymers. First, the cothermolysis of the phosphazene and silicone rings, $(Cl_2PN)_3$ and $(Me_2SiO)_3$, resulted in several products that included the phosphazene homopolymer, $(Cl_2PN)_n$, higher silicone rings, $(Me_2SiO)_{4\text{-}6}$, and cyclic phosphazenes with chlorosiloxane side groups, $[Cl(Me_2SiO)_m]_nCl_{6\text{-}n}P_3N_3$ where n = 1 or 2. In the later stages of this process P-O-P crosslinked phosphazenes and chlorine terminated siloxane oligomers were also formed.[1] In the second study,[2] the thermal polymerization of cyclic phosphazene trimers joined to tetrameric siloxane rings through CH_2 spacer groups produced linear polyphosphazenes with cyclic siloxane substituents, $\{(Cl_2PN)_2Me[CH_2(Me_2SiO)_4]PN\}_n$. However, subsequent substitution reactions to replace the hydrolytically unstable chloro groups on the backbone resulted in significant cleavage of the PCH_2-Si bonds with loss of most of the silicone side-groups. Polyphosphazenes with the simpler Me_3SiCH_2 group on phosphorus were prepared in a similar manner without analogous difficulties.

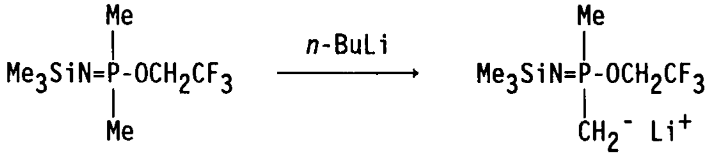
Silicon containing polyphosphazenes have also been prepared in our laboratories by another method that involves deprotonation/substitution reactions on preformed poly(methylphenylphosphazene), $[Me(Ph)PN]_n$.[3] In this paper we will present recent results from our continuing study of derivatization reactions on poly(alkyl/arylphosphazenes) as related to the preparation of new polyphosphazene-*graft*-polysiloxane copolymers.

RESULTS AND DISCUSSION

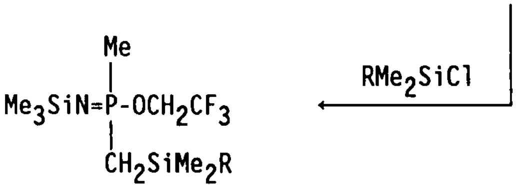
Poly(alkyl/arylphosphazenes) are prepared by a condensation polymerization method that involves thermolysis of suitable Si-N-P compounds (eq 1).[4,5] This process allows for the incorporation of simple alkyl and aryl groups at the precursor stage. Some variation of the substituents at phosphorus in the phosphoranimine precursors is possible through derivatization reactions involving deprotonation of the alkyl groups (eq 2).[6] In particular, simple silyl groups, RMe_2Si, are readily attached in this manner (eq 3).[7] These silyl substituted compounds, however, are remarkably stable, and do not undergo thermal polymerization even upon heating for extended periods at ca. 250°C.



$$Me_3SiN{=}\overset{\displaystyle R}{\underset{\displaystyle R'}{P}}{-}OCH_2CF_3 \xrightarrow[-\ Me_3SiOCH_2CF_3]{\Delta} [-N{=}\overset{\displaystyle R}{\underset{\displaystyle R'}{P}}{-}]_n \qquad (1)$$



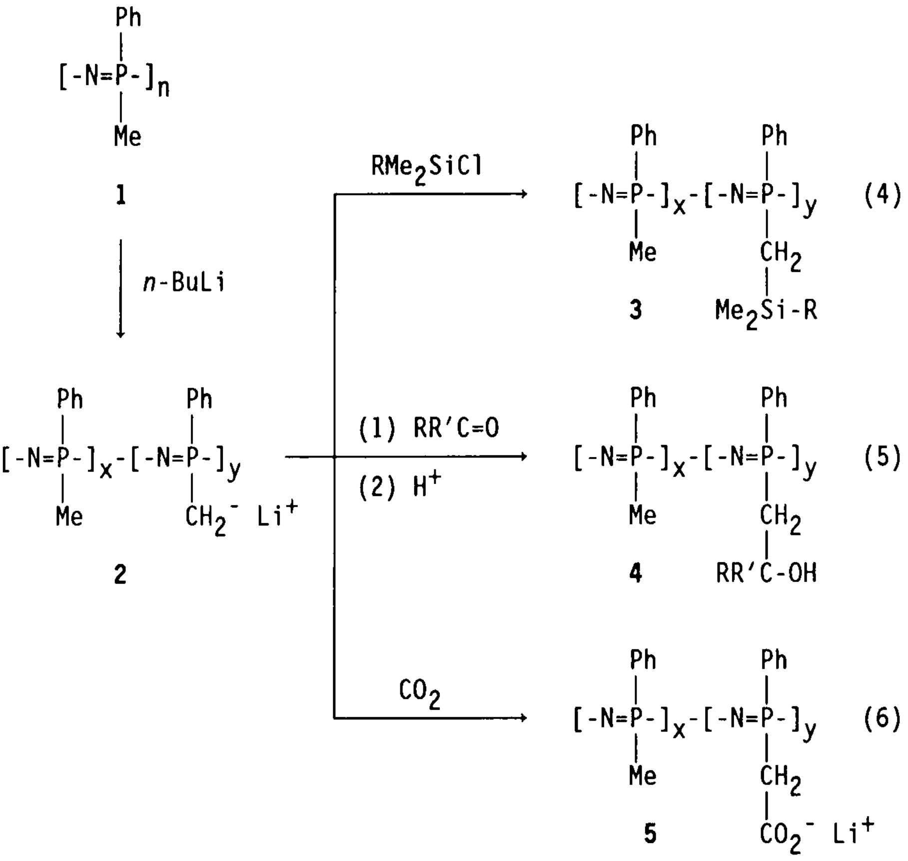
$$Me_3SiN{=}\overset{\displaystyle Me}{\underset{\displaystyle Me}{P}}{-}OCH_2CF_3 \xrightarrow{n\text{-BuLi}} Me_3SiN{=}\overset{\displaystyle Me}{\underset{\displaystyle CH_2^-\ Li^+}{P}}{-}OCH_2CF_3 \qquad (2)$$



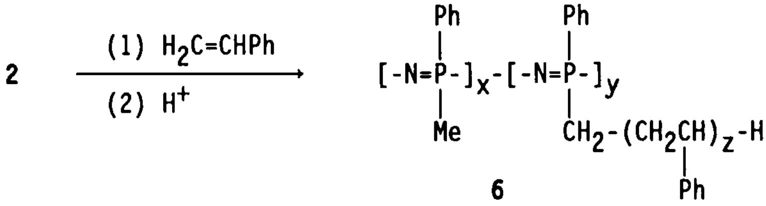
$$Me_3SiN{=}\overset{\displaystyle Me}{\underset{\displaystyle CH_2SiMe_2R}{P}}{-}OCH_2CF_3 \xleftarrow{RMe_2SiCl} \qquad (3)$$

Alternatively, simple silyl substituted polyphosphazenes are accessible through analogous deprotonation/substitution reactions that are carried out on the preformed polymer $[Me(Ph)PN]_n$ (**1**).[3] The sequential treatment of the polymer **1** with *n*-BuLi and various chlorosilanes was used to prepare silylated phosphazenes **3** (eq 4) with 20 and 50% of the backbone units containing the RMe_2SiCH_2 moiety. More importantly, this study revealed that the deprotonations occur with no degradation of the phosphazene backbone.

The successful formation of the anionic polymer intermediate **2** also provides access to a wide variety of other derivatized poly(alkyl/arylphosphazenes). For example, a series of alcohol substituted polymers **4** have been prepared by reactions of the intermediate **2** with aldehydes and ketones (eq 5),[8] and polymers with carboxylic acid, lithium carboxylate, and ester functionalities have been made by quenching the polymer anions with CO_2 (eq 6) followed by aqueous acid or activated alkyl halides.[9] The polymers from the CO_2 reactions have 10, 20, and 50% of the monomer units functionalized.



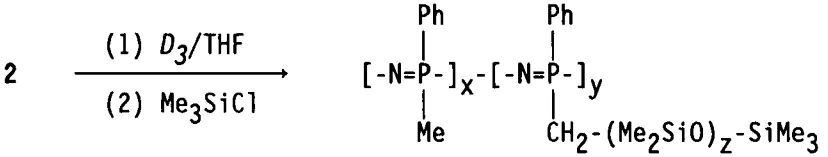
The ease and control of deprotonation of methyl groups in $[Me(Ph)PN]_n$ suggested that the resulting anions along the backbone would be good sites for grafting various polymer systems to the phosphazene backbone. Recently, a series of polyphosphazene-*graft*-polystyrene copolymers **6** was prepared by using the anionic intermediate **2** to initiate the polymerization of styrene (eq 7).[10]



$$2 \xrightarrow[\text{(2) H}^+]{\text{(1) H}_2\text{C=CHPh}} [-N=\overset{\text{Ph}}{\underset{\text{Me}}{P}}-]_x-[-N=\overset{\text{Ph}}{\underset{\text{CH}_2-(\text{CH}_2\underset{\text{Ph}}{\text{CH}})_z-\text{H}}{P}}-]_y \qquad (7)$$

6

The anionic ring opening of cyclic siloxanes is a well-known process and has been used, for example, to make polysiloxane-*block*-polystyrene copolymers via ring opening of $(Me_2OSi)_3$ (i.e., D_3) by "living" polystyrene anions.[11] The successful grafting of polystyrene (eq 7) suggested that the polyphosphazene anion sites in **2** would also successfully ring open D_3. Thus far, graft copolymers **7** have been prepared with ca. 10 and 20% of the phosphazene monomer units having silicone grafts of ca. 3, 15, 30 and 90 Me_2SiO monomer units in length (eq 8).



$$2 \xrightarrow[\text{(2) Me}_3\text{SiCl}]{\text{(1) } D_3\text{/THF}} [-N=\overset{\text{Ph}}{\underset{\text{Me}}{P}}-]_x-[-N=\overset{\text{Ph}}{\underset{\text{CH}_2-(\text{Me}_2\text{SiO})_z-\text{SiMe}_3}{P}}-]_y \qquad (8)$$

7

Typically, a THF solution of $[Me(Ph)PN]_n$ (**1**) was treated with 0.1 or 0.2 equivalents of *n*-BuLi at -78°C and stirred for 1.5 hours. Then a THF solution of D_3 (0.1 to 0.5 equiv) was added and the solution was allowed to stir at room temperature overnight. Gelling of the mixture occurred after several hours, but readily disappeared upon quenching the reaction with Me_3SiCl. After precipitation of the mixture into a 10% aqueous solution of NH_4Cl, reprecipitation of the polymer from CH_2Cl_2 into MeOH afforded the silicone grafted copolymers. Unlike the parent polymer, the grafts are somewhat soluble in hexane. The ^1H NMR spectra of the grafts give the expected integration of the phenyl and MeSi signals and the elemental analyses are consistent with the appropriate number and length of grafted side chains.

By size exclusion chromatography (SEC or GPC), the graft copolymers have higher molecular weights (M_n ca. 44,000 to 130,000) than the parent polymer and the molecular weight distributions are significantly broadened with some bimodal character (Figure 1). Differential scanning calorimetry data also support successful grafting since the strong melting transition of the silicone component was observed along with a broad, weak glass transition (T_g = 37°C) for the polyphosphazene. The weak T_g for the silicone was not observed, presumably because of broadening of the transition as a result of grafting.[12] Further characterization of these new graft copolymers is in progress.

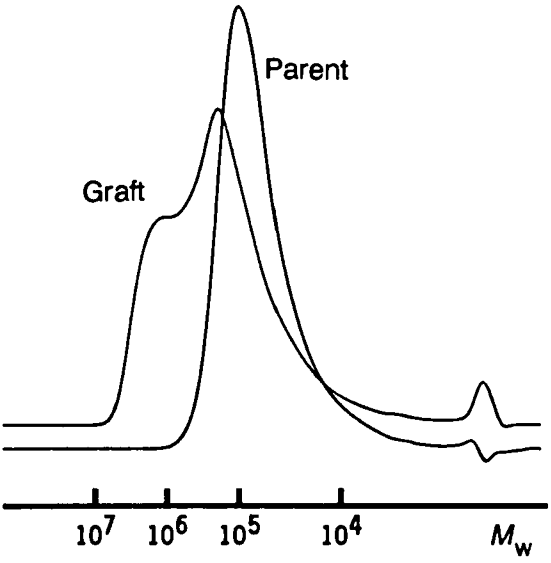


FIGURE 1. SEC molecular weight distribution for parent polymer $[Me(Ph)PN]_n$ (**1**) and silicone graft copolymer **7**.

In summary, the deprotonation/substitution reactions on methyl groups in $[Me(Ph)PN]_n$ provide access to a variety of new polyphosphazenes in which all substituents are attached to the polymer backbone by direct P-C linkages. In addition to polymers with functional groups (e.g., -OH and -COO$^-$) that are potential sites for further derivatization reactions, new phosphazene graft copolymers with both organic and inorganic side chains can readily be prepared.

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