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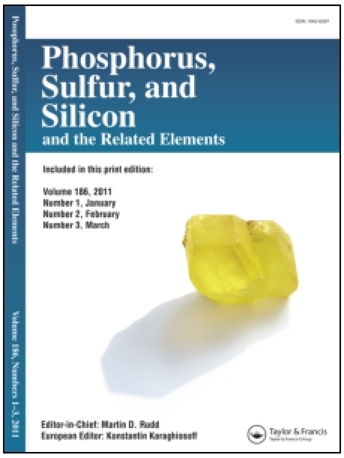

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STUDIES OF POLY(ALKYL/ARYLPHOSPHAZENE) ANIONS

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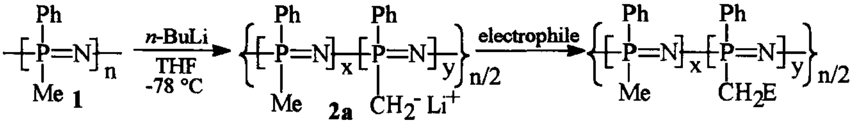
Abstract The deprotonation-substitution reactions of poly(alkyl/arylphosphazenes) such as $[Me(Ph)PN]_n$ have proven to be a simple, one-step method for modification of this class of phosphazene polymers. Recent studies of the anion intermediate produced by deprotonation with *n*-BuLi have shown that complete deprotonation of the methyl groups occurs at room temperature. Subsequent substitution reactions appear to be controlled by the size of the reacting electrophile. These reactions and the preparation of several new polymers with substituted silyl groups that were prepared by this approach are discussed.

INTRODUCTION

Poly(phosphazenes) with simple alkyl and aryl groups attached to the backbone by direct phosphorus-carbon linkages, e.g., $[Me(Ph)P{=}N]_n$, are prepared by the condensation polymerization of appropriate N-silylphosphoranimines such as $Me_3SiN{=}P(OCH_2CF_3)(Me)Ph$.[1] To expand the range of properties and ultimate applications of this class of poly(phosphazenes), we have developed several methods for modifying the alkyl and aryl side-groups once the polymers have been formed. These methods can be grouped into three general categories: (a) electrophilic aromatic substitution at the phenyl groups,[2] (b) deprotonation-substitution reactions of the methyl substituents,[3-7] and (c) Lewis acid coordination to the backbone nitrogen.[8] Deprotonation-substitution reactions, which involve the formation of a polymer anions intermediate, are the most thoroughly studies and successful approach. Small molecule precedent for these polymer reactions include reactions of cyclic alkyl/arylphosphazenes such as conversion of $(Me_2Ph_4P_3N_3)$ to $[(ECH_2)MePh_4P_3N_3]$ where E = Me_3Sn, PhC(O), and Br,[9] formation of $Me_3SiN{=}PMe_2CH_2SiMe_3$ from $Me_3SiN{=}PMe_3$,[10] and preparation of new N-silylphosphoranimine polymer precursors, $Me_3SiN{=}PMe(OCH_2CF_3)(CH_2E)$, from $Me_3SiN{=}PMe_2(OCH_2CF_3)$.[11] Analogous reactions on the preformed polymers are simple, one-step modifications that, as discussed below, have provided access to a wide variety of new poly(phosphazenes).

RESULTS AND DISCUSSION

Although the deprotonation (metallation) and subsequent substitution reactions of N-silylphosphoranimines provide access to potential poly(phosphazene) precursors,[11] it is generally difficult to incorporate many functional groups due to their lack of stability in the presence of silicon-nitrogen or phosphorus-oxygen bonds and instability toward the elevated temperatures and/or catalysts used in the polymerization process. Nonetheless, these reactions have served as models for deprotonation-substitution reactions of preformed poly(alkyl/arylphosphazenes), such as $[Me(Ph)PN]_n$, **1**. Treatment of a THF solution of the simple homopolymer, **1**, with *n*-BuLi at -78 °C produces a polymer anion intermediate, **2a**, which reacts with a variety of electrophiles (eq 1). Mild reaction conditions (-78 °C) were used because of the instability of the corresponding phosphoranimine anion, $Me_3SiN{=}P(OCH_2CF_3)Me(CH_2^-Li^+)$ and to avoid possible chain degradation of the polymer backbone by the organolithium reagent which is known to occur in reactions of RLi with $[Cl_2PN]_n$.[12] The polymeric anion intermediate is essentially an organolithium reagent and thus reacts with electrophiles such as aldehydes and ketones,[4] CO_2,[5] R_2PX, and RMe_2SiCl[3] (eq 1). The anionic sites have also been used to initiate addition polymerization of vinylic monomers such as styrene[6] and ring opening of cyclic siloxanes[7] resulting in controlled synthesis of graft copolymers of poly(phosphazenes).



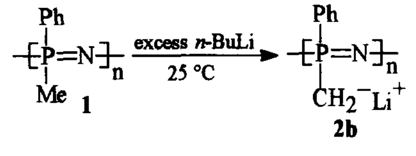
$$\left[\overset{Ph}{\underset{Me}{P}}=N\right]_n \; \mathbf{1} \xrightarrow[\text{THF, -78 °C}]{n\text{-BuLi}} \left\{\left[\overset{Ph}{\underset{Me}{P}}=N\right]_x\left[\overset{Ph}{\underset{CH_2^-\,Li^+}{P}}=N\right]_y\right\}_{n/2} \mathbf{2a} \xrightarrow{\text{electrophile}} \left\{\left[\overset{Ph}{\underset{Me}{P}}=N\right]_x\left[\overset{Ph}{\underset{CH_2E}{P}}=N\right]_y\right\}_{n/2} \qquad (1)$$

$E = SiMe_2R$ [$R = H$, CN, $CH{=}CH_2$, $(CH_2CH_2O)_mCH_2CH_3$], PPh_2, Br, $CH_2CH{=}CH_2$, $C(OH)RR'$ [R, R' = H, Me, ferrocenyl, thiophene, fluoroalkyl], COOR ($R = Li^+$, H, aryl), $[CH_2C(Ph)H]_zH$, $[Si(Me_2)O]_zSiMe_3$

Several features of these reactions are noteworthy. First, the disubstitution of a small number of methyl substituents occurs, producing, for example $[Me(Ph)PN]_x[(Me_3SiCH_2)(Ph)PN]_y\{[(Me_3Si)_2CH)](Ph)PN\}_z$. This is minimized in concentrated solutions and has been verified through sequential substitution reactions.[3] A second feature is that, even when more than an equivalent of *n*-BuLi is used, substitutions do not exceed 50% [i.e., $y/(x + y)\cdot 100 \leq 50$].[3, 5] Until recently, it was unclear whether this indicated that complete deprotonation does not occur or if steric factors inhibited substitution.

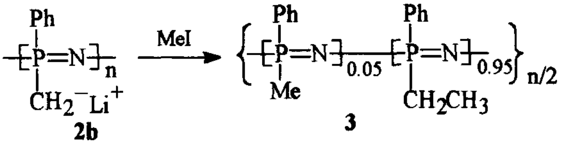
Two experiments in our group suggested that the intermediate anion was sufficiently stable for ^{31}P NMR spectroscopic identification. First, we found that a THF solution of the intermediate anion **2** could be warmed to at least 50 °C without degradation, cross-linking, or reaction with the solvent. Secondly, when **2** was treated with elemental sulfur, it was possible to obtain spectra of the sulfur anion, $\{[Me(Ph)PN]_x[(Ph)(Li^+CH_2S^-)PN]_y\}_{n/2}$. Consequently, ^{31}P NMR spectra of **2**, as prepared from reactions at *room temperature* using both 0.5 and 1.2 equivalents of *n*-

BuLi, were obtained. In the former case, two signals were observed. That at δ 5 was assigned to the unreacted PMe phosphorus, while the downfield signal at δ 34 was assigned to the PCH_2^- phosphorus atom. With a slight excess of *n*-BuLi, however, only a single signal in the downfield region of the spectrum was observed, indicating that deprotonation was complete (eq 2).



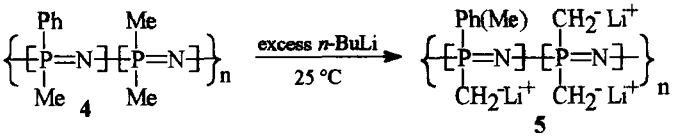
$$\left[\overset{\text{Ph}}{\underset{\text{Me}}{\text{P}}}=\text{N}\right]_n \xrightarrow[25\,^\circ\text{C}]{\text{excess } n\text{-BuLi}} \left[\overset{\text{Ph}}{\underset{\text{CH}_2^-\text{Li}^+}{\text{P}}}=\text{N}\right]_n \qquad (2)$$

Since these results indicated that the lack of high degrees of substitution is a steric effect, the anion was treated with CH_3I, a very small electrophile (eq 3). The ^{31}P NMR and ^1H NMR spectra of the reaction product clearly indicated that almost complete substitution occurred, thus confirming the important role of the size of the electrophile. It should be noted that in quenching of **2b** by either protons or CH_3I, GPC measurements indicated that the deprotonation-substitution occurred without chain degradation, (i.e., $M_w = 72{,}000$, $M_w/M_n = 2.4$ for **3**; $M_w = 80{,}000$, $M_w/M_n = 2.3$ for parent **1**).



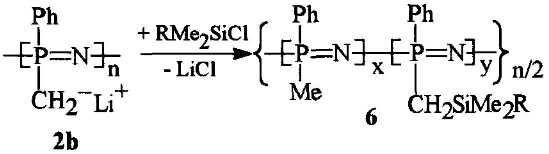
$$\left[\overset{\text{Ph}}{\underset{\text{CH}_2^-\text{Li}^+}{\text{P}}}=\text{N}\right]_n \xrightarrow{\text{MeI}} \left\{\left[\overset{\text{Ph}}{\underset{\text{Me}}{\text{P}}}=\text{N}\right]_{0.05}\left[\overset{\text{Ph}}{\underset{\text{CH}_2\text{CH}_3}{\text{P}}}=\text{N}\right]_{0.95}\right\}_{n/2} \qquad (3)$$

The deprotonation of the copolymer **4** (eq 4) was also investigated by ^{31}P NMR spectroscopy. When a slight excess of *n*-BuLi was used, the spectrum consisted of a very broad peak at δ 32 with a shoulder at the lower end, suggesting that high degrees of deprotonation had occurred. Addition of CH_3I also resulted in the terpolymer $\{[\text{Et(Ph)PN}]_w[\text{Et}_2\text{PN}]_x[\text{Me(Ph)PN}]_y[\text{Me(Et)PN}]_z\}_{n/4}$, where *y* and *z* were very small.



$$\left\{\left[\overset{\text{Ph}}{\underset{\text{Me}}{\text{P}}}=\text{N}\right]\left[\overset{\text{Me}}{\underset{\text{Me}}{\text{P}}}=\text{N}\right]\right\}_n \xrightarrow[25\,^\circ\text{C}]{\text{excess } n\text{-BuLi}} \left\{\left[\overset{\text{Ph(Me)}}{\underset{\text{CH}_2^-\text{Li}^+}{\text{P}}}=\text{N}\right]\left[\overset{\text{CH}_2^-\text{Li}^+}{\underset{\text{CH}_2^-\text{Li}^+}{\text{P}}}=\text{N}\right]\right\}_n \qquad (4)$$

A series of silylated polymers, **6**, with long chain alkyl groups and fluoroalkyl groups were prepared using the fully deprotonated poly(phosphazene) anion intermediate. The new polymers, which were characterized by elemental analysis, gel permeation chromatography, differential scanning calorimetry, and ^1H and ^{31}P NMR spectroscopy, generally decreased as the chain length increased and ranged from -20 to 39 °C. Contact angle measurements made with water showed that the new polymers became more hydrophobic as the length of the alkyl and fluoroalkyl side groups increased and values ranged from 90 to 101° relative to 73° for the parent polymer, 1.



2b

(5)

$R = (CH_2)_mCH_3$, $m = 2, 3, 7, 9, 17$
$R = CH_2CH_2(CF_2)_mCF_3$, $m = 0, 5, 7$

In summary, the complete deprotonation of methyl groups in poly(methylphenylphosphazene) and its copolymers has been demonstrated and can be used to obtain somewhat enhanced degrees of substitution, particularly with small electrophiles.

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