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Formation of $[(Li^+CH_2^-)(Ph)PN]_n$ at Room Temperature

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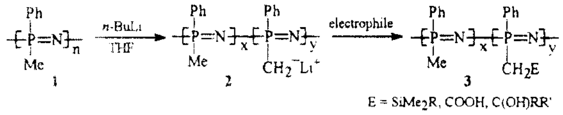
Introduction

The derivative chemistry of poly(methylphenylphosphazene), $[Me(Ph)PN]_n$, which is prepared by condensation polymerization of Si−N−P compounds that contain the *P*-methyl and *P*-phenyl groups,[1−3] has been under active investigation in our laboratory for almost a decade. Most of these reactions have focused on the deprotonation or metal−hydrogen exchange at the methyl substituents and subsequent substitution reactions.[4] This has provided access to polyphosphazenes with a variety of functional groups (eq 1) including silyl,[5] alcohol,[6,7] and carboxylate[8] moieties and to graft copolymers.[9,10] Thus far, however, the degree of deprotonation−substitution has typically not been greater than 50% even when excess quantities of the deprotonating base *n*-BuLi were used. This suggests that either (a) steric size of the electrophile was preventing higher degrees of substitution or (b) electronic limitations associated with increased negative charge prevented complete deprotonation. In this paper we report (a) the first ^{31}P NMR spectroscopic evidence showing complete deprotonation of the methyl groups and (b) greater than 90% substitution of the methyl groups in $[Me(Ph)PN]_n$.



$$\underset{1}{\left[P(Ph)(Me){=}N\right]_n} \xrightarrow[\text{THF}]{n\text{-BuLi}} \underset{2}{\left[P(Ph)(Me){=}N\right]_x\left[P(Ph)(CH_2^-Li^+){=}N\right]_y} \xrightarrow{\text{electrophile}} \underset{3}{\left[P(Ph)(Me){=}N\right]_x\left[P(Ph)(CH_2E){=}N\right]_y} \quad (1)$$

E = SiMe$_2$R, COOH, C(OH)RR′

Results and Discussion

Typically the deprotonation reactions of $[Me(Ph)PN]_n$ have involved very mild conditions consisting of treatment of THF solutions of the polymer with *n*-BuLi at −78 °C. One reason for the use of such mild conditions is the fact that the reactions of poly(dihalophosphazenes) with organolithium and Grignard reagents occur with chain degradation, especially when reaction temperatures are increased to facilitate better substitution.[11] A second reason is that the corresponding anions, e.g., $[Me_3SiN{=}P(Me)(OCH_2CF_3)CH_2^-Li^+]$, of the *N*-silylphosphoranimine precursors to poly(alkyl/arylphosphazenes) such as $[Me(Ph)PN]_n$ have been shown to be unstable above ca. −50 °C.[12] However, we found that when the polymer anion **2** was warmed to 50 °C for ca. 1 h and quenched with Me_3SiCl, essentially no chain degradation occurred as demonstrated by GPC measurements.[13] Furthermore, we have also recently obtained ^{31}P NMR spectroscopic data for a related anion, $[Me(Ph)PN]_x[Ph(Li^+CH_2S^-)PN]_y$, a species obtained from the reaction of **2** with elemental sulfur.[14] The stability of these polymer anion intermediates at and above room temperature indicated that we should also be able to obtain spectroscopic data for polymer anion **2**.

The ^{31}P NMR spectrum of the parent polymer, $[Me(Ph)PN]_n$ (**1**), in THF contains a single resonance at ca. δ 1 (Figure 1). After addition of 0.5 equiv of *n*-BuLi to a THF solution of **1** at room temperature, the ^{31}P NMR spectrum (Figure 1) clearly shows two broad resonances of approximately equal intensity at δ 34 and 5 which can be assigned to the PCH_2^- and PMe phosphorus atoms in polymer anion **2**, respectively. The broadness of the signals as well as the slightly downfield shift of the PMe resonance can be attributed to the random distribution of neighboring PMe and PCH_2^- groups. It is interesting to note that the spectra of this anion remained unchanged when the solution was stored in a septum-sealed NMR tube for several days.

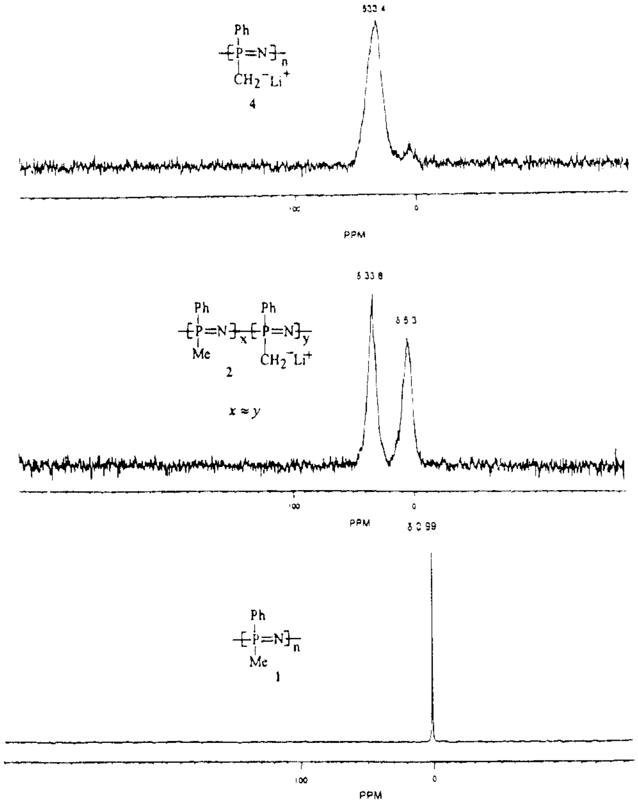
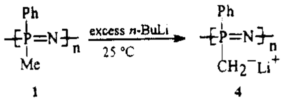


Figure 1. ^{31}P NMR spectra of the parent polymer, $[Me(Ph)PN]_n$, and anions 2 and 4 in THF.

When slightly more than 1 equiv of *n*-BuLi was added to a THF solution of **1**, a broad resonance at δ 33 was observed (Figure 1) along with a very small signal at ca. 5 ppm in the ^{31}P NMR spectrum. The smaller signal completely disappeared when a larger excess of *n*-BuLi was added, clearly demonstrating the complete deprotonation and formation of polymer anion **4** (eq 2).



$$\underset{1}{\left[P(Ph)(Me){=}N\right]_n} \xrightarrow[25\ ^\circ\text{C}]{\text{excess } n\text{-BuLi}} \underset{4}{\left[P(Ph)(CH_2^-Li^+){=}N\right]_n} \quad (2)$$

When anions **2** and **4** were treated with H_2O, the parent polymers were recovered unchanged as demonstrated by ^1H and ^{31}P NMR spectra. More importantly, the GPC traces of the recovered polymers ($M_w = 57\ 000$, $M_w/M_n = 3.1$; parent $M_w = 60\ 000$, $M_w/M_n = 2.7$) were similar to those of the starting material, confirming that no chain cleavage occurred.

In earlier experiments, quenching of the polymer anion formed at low temperatures using an equivalent or more of *n*-BuLi with electrophiles such as Me_3SiCl or CO_2 failed to produce polymers in which more than approximately half of the methyl groups were substituted. Since the spectral data obtained here demon-

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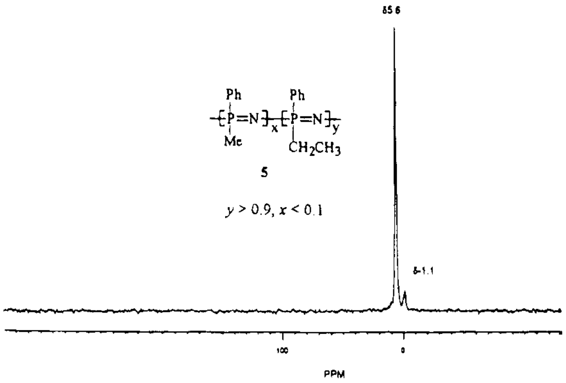
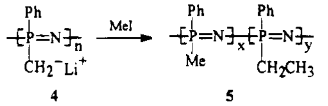


Figure 2. ^{31}P NMR spectrum of $[Me(Ph)PN]_x[Et(Ph)PN]_y$ where $y > 0.9$ and $x < 0.1$.

strate that complete deprotonation does indeed occur, we chose to quench **4** with iodomethane, a significantly smaller electrophile (eq 3). This resulted in the formation of polymer **5** in which nearly complete substitution of the methyl groups had occurred (i.e., $y > 0.9, x < 0.1$). The ^{31}P NMR spectrum of **5** (Figure 2) clearly shows a major signal at δ 5.6 as reported for poly(ethylphenylphosphazene).[1] The proportions of x and y were confirmed by integration of the ^{1}H NMR spectra. This represents the highest degree of substitution achieved thus far for a poly(alkyl/arylphosphazene) and suggests that the steric size of the electrophile plays an important role in the modification of these polymers by deprotonation–substitution chemistry.[15] GPC also indicated that this deprotonation-substitution occurred without chain degradation (i.e., $M_w = 72\,000$, $M_w/M_n = 2.4$ for **5**; $M_w = 80\,000$, $M_w/M_n = 2.3$ for parent **1**).



$$\left[\overset{Ph}{\underset{CH_2^-Li^+}{P}}=N\right]_n \xrightarrow{MeI} \left[\overset{Ph}{\underset{Me}{P}}=N\right]_x\left[\overset{Ph}{\underset{CH_2CH_3}{P}}=N\right]_y \quad (3)$$

4 **5**

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of nitrogen. The parent polymer $[Me(Ph)PN]_n$ was prepared by published procedures.[1,2] THF was distilled from sodium–benzophenone under nitrogen prior to use. Iodomethane and n-BuLi (2.5 M in hexane) were purchased from commercial sources and used as received.

The ^{1}H and ^{31}P NMR spectra were recorded on an IBM WP-200SY FT NMR spectrometer in $CDCl_3$ and THF, respectively. A D_2O insert was used with the THF solutions of the polymer anion. Positive ^{1}H and ^{31}P NMR chemical shifts are downfield from Me_4Si and H_3PO_4, respectively. The size-exclusion (gel permeation) chromatography measurements were performed as reported elsewhere.[16]

Preparation and NMR Study of the Polymer Anions. In a typical experiment, the parent polymer $[Me(Ph)PN]_n$ (1.0 g, 7.2 mmol) was placed in a two-neck, round-bottom flask and dried in a vacuum oven at 50 °C for at least 24 h. The flask was then cooled under vacuum, filled with nitrogen, and equipped with a rubber septum, a nitrogen inlet adapter, and a magnetic stir bar. THF (ca. 10 mL) was added via a syringe, and the mixture was stirred until the polymer had completely dissolved. Then either 0.5 or 1.1 equiv of n-BuLi (2.5 M in hexane) was added slowly to the solution while stirring at room temperature. A portion of the solution was then transferred to an NMR tube equipped with a rubber septum using a syringe. The NMR tube was purged with nitrogen during this transfer.

In a similar fashion, after 0.5 equiv of n-BuLi was added to a solution of the parent polymer, an aliquot was removed for ^{31}P NMR. Then an additional 0.3 equiv of n-BuLi was added, and the ^{31}P NMR spectrum showed a corresponding increase in the signal at δ 34 and a decrease of the signal at δ 5, thus demonstrating sequential deprotonation of the methyl groups.

Reaction of the Polymer Anion with Iodomethane. The anion was formed as described above using 0.5 g (3.6 mmol) of $[Me(Ph)PN]_n$ and n-BuLi (6.0 mmol) and stirred for ca. 20 min. Then iodomethane (0.41 mL, 6.6 mmol) was added via a syringe. After stirring for 15 min, Et_3N (ca. 5 mL) was added to prevent chain degradation by excess MeI[16] and the mixture was stirred for ca. 3 h. The polymer was then collected and purified by precipitation from THF into water and then from THF into hexane. ^{31}P NMR: Figure 2. ^{1}H NMR: δ 7.8, 7.0 (5 H), 1.8, 0.8 (4.7 H).

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References and Notes

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(13) When the anion was formed as described above using 0.5 equiv of n-BuLi, heated slowly to 50 °C over 1 h, and quenched with 0.5 equiv of Me_3SiCl, the resulting silylated polymer[5] had $M_w = 155\,000$, $M_w/M_n = 2.4$ (parent: $M_w = 139\,000$, $M_w/M_n = 2.3$). Islam, M. Q.; Wisian-Neilson, P., unpublished results.
(14) Claypool, C. L.; Wisian-Neilson, P., unpublished results.
(15) As part of a study of the modification of poly(methylphenylphosphazene) to increase hydrophobicity, anion **4** was treated with a series of chlorosilanes, RMe_2SiCl, under the same conditions as the MeI reaction. Degrees of substitution were 70% at best. Wisian-Neilson, P.; Bailey, L.; Bahadur, M. *Macromolecules*, in press.
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