# Ketone Derivatives of Poly(Methylphenylphosphazene): Incorporation of an Electrophilic Site into Poly(Alkyl/Arylphosphazenes)

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## Introduction

Poly(phosphazenes) are a diverse family of polymers that have a broad range of properties that reflect the nature of the side groups on the backbone phosphorus atom.[1] The side groups have generally been varied by nucleophilic substitution of poly(dichlorophosphazene), $[Cl_2PN]_n$.[1] Poly(alkyl/arylphosphazenes) such as poly-(methylphenylphosphazene), $[Me(Ph)PN]_n$, **1**, however, are directly prepared by condensation polymerization of *N*-silylphosphoranimines, $Me_3SiN{=}P(OR)(Me)Ph$ where $R = CH_2CF_3$ or Ph.[2] The physical and chemical properties of these simple polymers can be further modified by reactions at either the methyl groups, the phenyl groups, or the backbone nitrogen atom.[3] Of these, deprotonation-substitution reactions have proven to be the most fruitful and have allowed for attachment of organofunctional groups that include alcohols,[4] carboxylic acids,[5] esters,[6] amide, amine,[7] ferrocene,[4] a variety of substituted silyl groups,[8] and grafted organic polymer side chains.[9] Incorporation of simple ketone side groups that could potentially serve as reactive electrophilic sites on these polymers, has, however, been problematic. The most direct route was investigated in our labs several years ago. Not surprisingly, uncharacterized, insoluble materials resulted when the polymer anion intermediate was treated with acid chlorides where both reactive C−Cl bonds and carbonyl carbon atoms are present. Even if the C−Cl bond reacts in the most straightforward manner, the resulting ketone may also be attacked by other anion sites along the polymer backbone, thus facilitating cross-linking. In this paper we discuss our investigation of several methods to circumvent these problems.

## Results and Discussion

A number of polyphosphazenes with pendant alcohol groups, $[Me(Ph)PN]_x\{[RR'C(OH)CH_2](Ph)PN]_y$, have been prepared by reaction of aldehydes or ketones with $[Me(Ph)PN]_x\{[Li^+CH_2^-](Ph)PN]_y$, **2**, the polymeric anion formed by deprotonation of $[Me(Ph)PN]_n$.[4] Initial attempts to prepare ketone derivatives of polyphosphazenes involved oxidation of a ferrocenyl alcohol polymer, $[Me(Ph)PN]_x[FcC(H)(OH)CH_2](Ph)PN]_y$. When this polymer was treated with the oxidant dimethyl sulfoxide (DMSO) in the presence of trifluoroacetic anhydride, monitoring by IR spectroscopy showed no evidence of ketone formation even after overnight stirring at room temperature. A stronger oxidant, e.g., pyridinium chlorochromate (PCC), resulted in oxidation of the ferrocene moiety and was accompanied by apparent decreases in molecular weight as determined by GPC, even in a sodium acetate buffer solution.

Copper salts have often been used to enhance reaction site selectivity. This is demonstrated by the clean formation of ketones from the reactions of organolithium compounds with acid halides in the presence of copper(I) halides.[10] On the basis of this well-known reaction, the polymeric organolithium reagent, polymer anion **2**, (eq 1) was treated with CuI with subsequent coupling of the copper salt intermediate with acid chlorides (eq 2). Both IR ($\nu_{C=O}$ at 1695−1735 cm$^{-1}$) and NMR spectroscopic analysis indicated that the ketone substituted copolymers, **3**, were formed. These materials were soluble in THF and chlorinated hydrocarbon solvents, but purification by precipitation from these solvents into hexanes, aqueous ammonia solution, and water failed to remove the green color indicating that copper ion remained coordinated to the backbone. This is consistent with the facile coordination of metals to the basic nitrogen sites in the polymer backbone.[11]
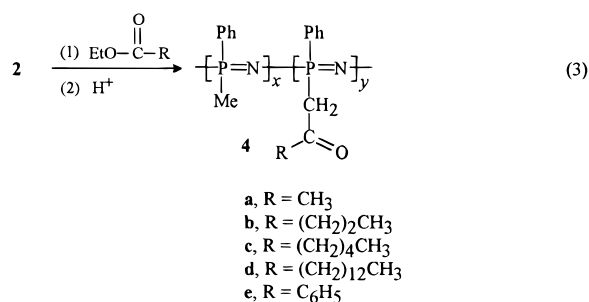
$$(1)$$

$$(2)$$
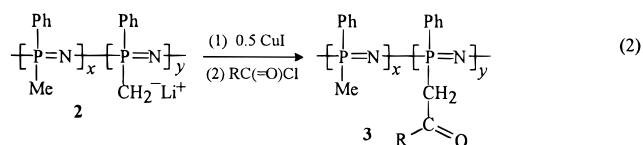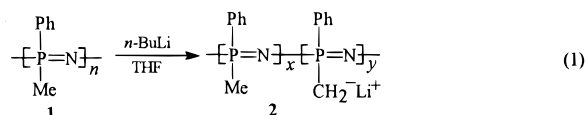
Preparation of ketone derivatives via the reaction of the polymer anion **2** with ethyl esters proved to be the most straightforward method (eq 3). After a mixture of **2** and $RC(=O)OCH_2CH_3$ was stirred overnight, the reaction was quenched with water. The new ketone-substituted copolymers were purified by several precipitations from THF solutions into hexane and water. The infrared spectra of the alkyl ketones **4a**−**d** each contained the expected carbonyl stretching frequency at ca. 1696 cm$^{-1}$ while the carbonyl signal was observed at 1666 cm$^{-1}$ for the aryl ketone **4e**. These are all below the range for carbonyl groups in both the ester starting materials and the carboxylic acids that might have formed from hydrolysis of the esters. The NMR spectra were also consistent with the formation of **4a**−**e**. The $^{31}P$ NMR spectra of each contained two major broad signals at ca. −5 and 2 ppm with significant shoulders on each in most cases as expected for random substitution. Broad signals were observed in both the aliphatic region (0.8−3.0 ppm) and the aromatic region (7.0 and 7.5 ppm) of the $^{1}H$ NMR spectra. The aliphatic signals in **4a**−**d** consisted of the $CH_2C=O$ signal at ca. 2.0 ppm, $PCH_2$ signals at ca. 3 ppm, and multiple, broad signals for the other $CH_2$ groups. Integration of these distinct regions was used to determine the degree or percent $\{[y/(x + y)] \times 100\%\}$ substitution.[12] With the exception of **4d**, these substitutions were generally between 35 and 40% and were verified by elemental analysis (Table 1). Isolated yields were generally at least 75%. It is likely that the steric effects of the long $(CH_2)_{12}CH_3$ group hindered attack of the polymer anion sites on the ester carbonyl group in ethyl myristate, thus resulting in only 10% substitution in **4d**. Moreover, the presence of this group in copolymer **4d** is the probable cause of difficult

**Table 1. Analytical, Size-Exclusion Chromatography (SEC), and Thermal (DSC) Data for Polymers 4a−e**

| polymer | yield (%) | elem anal[a] % C | % N | %H | substitution (%) | $M_w$ | $T_g$ (°C) |
|---|---|---|---|---|---|---|---|
| **4a** | 90 | 60.32 (60.82) | 9.05 (8.98) | 5.67 (5.75) | 40 | 117 000 | 59 |
| **4b** | 87 | 62.18 (62.44) | 8.67 (8.63) | 6.25 (6.31) | 36 | 47 600 | 46 |
| **4c** | 74 | 63.61 (63.85) | 8.15 (8.08) | 6.69 (6.80) | 37 | 65 000 | 30 |
| **4d** | 50 | | | | 10 | 120 000 | 50 |
| **4e** | 75 | 65.35 (65.85) | 7.98 (7.84) | 5.43 (5.41) | 40 | 119 000 | 71 |

[a] Calculated values are in parentheses.

purification since the long alkyl chain greatly enhanced the copolymer's solubility in hexane.



$$
\textbf{2} \xrightarrow[\text{(2) H}^+]{\text{(1) EtO}-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{R}} \quad \textbf{4} \qquad (3)
$$

**a**, R = CH$_3$
**b**, R = (CH$_2$)$_2$CH$_3$
**c**, R = (CH$_2$)$_4$CH$_3$
**d**, R = (CH$_2$)$_{12}$CH$_3$
**e**, R = C$_6$H$_5$

The molecular weights are in the same range as the molecular weights of the parent polymers ($M_w = 90\,000−200\,000$) as determined by size exclusion chromatography. This is consistent with prior deprotonation-substitution reactions which indicated that no significant degradation of the polymer backbone occurred. The glass transition temperatures also follow the expected trend (Table 1). The attachment of the more polar ketone group resulted in $T_g$s that were higher than that of the parent polymer **1** ($T_g = 37$ °C) for the shorter alkyl groups (**4a** and **4b**), but this was offset by the increased free volume afforded by longer alkyl groups (e.g., $T_g$ is 30 °C for **4c** and 46 °C for **4b**).[13] Tangling of the long alkyl chain and the steric effects of the phenyl group account for the higher $T_g$s for **4d** and **4e**.

In summary, ketone functional groups are readily attached to poly(phosphazenes) through deprotonation-substitution reactions using esters as electrophiles. The carbonyl groups should serve as reactive electrophilic sites that facilitate attachment of new types of side groups to these polymers.

## Experimental Section

**Materials**. Poly(methylphenylphosphazene), [Ph(Me)-PN]$_n$, was prepared by the published procedure[2] and was dried under vacuum at 50 °C for at least 18 h. Tetrahydrofuran was distilled from Na/benzophenone immediately prior to use. Acetyl chloride, propionyl chloride, butyryl chloride, hexanoyl chloride, decanoyl chloride, copper(I) iodide, ethyl acetate, ethyl caproate, ethyl butyrate, ethyl benzoate, ethyl myristate, and *n*-BuLi (hexane solution) were used as obtained from commercial sources.

**Equipment**. The $^1$H, $^{13}$C, and $^{31}$P NMR spectra were recorded in CDCl$_3$ on a Bruker WP 200 SY FT NMR spectrometer equipped with a Techmag computer interface or on a SGI/Bruker DRX-400 sb spectrometer. Positive $^1$H and $^{13}$C NMR shifts and $^{31}$P NMR shifts are downfield from the external references Me$_4$Si and H$_3$PO$_4$, respectively. Elemental analyses were obtained on a Carlo Erba Strumentazione CHN Elemental Analyzer 1106 or were done by E+R Microanalytical Laboratory, Inc. The SEC measurements and DSC analysis

were performed as described elsewhere.[11] IR spectra were recorded on a Perkin-Elmer 710B infrared spectrometer using thin films prepared by evaporation of a CDCl$_3$ solution onto KBr plates.

**Synthesis of Ketone Derivatives via Copper Salts and Acid Chlorides.** In a typical procedure, a two-necked round-bottom flask equipped with a magnetic stirrer, and nitrogen inlet was charged with 2.0 g (14.6 mmol) of [Ph(Me)PN]$_n$ and ca. 40 mL of dry THF. The solution was cooled to 0 °C, and then *n*-BuLi (5.8 mL, 2.5 M) was added slowly via syringe. The mixture was warmed to room temperature, and stirred for 1 h at this temperature to ensure complete formation of anion **2**. In another two-necked round-bottom flask, CuI (1.39 g, 7.3 mmol) was dried under nitrogen by heating with a heat gun. After the flask with CuI was cooled to −78 °C, the polymer anion solution prepared above was cooled to −78 °C and transferred to this flask via cannula. The reaction mixture was warmed to 0 °C and stirred 5 h to ensure the formation of the cuprate salt. After the reaction was recooled to −78 °C, acetyl chloride (1.03 g, 13.2 mmol) was added. The reaction mixture was warmed to room temperature and stirred overnight. Then 1 mL of saturated NH$_4$Cl solution was added to quench the reaction. After the reaction was stirred for 1 h, water (ca. 200 mL) was added and the organic solvents were removed by rotary evaporator. The copolymer that precipitated from the water was collected and further purified by precipitating from a THF solution into 30% aqueous ammonia solution two times, into water twice, and two times into hexane. The product was dried at 50 °C in a vacuum oven for more than 24 h.

**Synthesis of Ketone Derivatives from Lithium Salts and Ethyl Esters.** A THF solution of anion **2** (14.6 mmol) was prepared as described above. This was cooled to 0 °C and excess ethyl acetate (4.5 mL, 46.1 mmol) was added. The mixture was warmed to room temperature and was stirred overnight prior to addition of water (ca. 2 mL). The product was purified by slow addition of the reaction mixture into hexane. Further purification involved additional reprecipitation from THF into water and into hexane. All polymer products were dried overnight in a vacuum oven at 50 °C.

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