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## Phosphorus, Sulfur, and Silicon and the Related Elements

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## Poly(Alkyl/Arylphosphazenes) and their Derivatives

PATTY WISIAN-NEILSON, CUIPING ZHANG, KARL A. KOCH and  
JEFFREY A. GRUNEICH

*Department of Chemistry, Southern Methodist University, Dallas, TX 75275*

The chemical modification of poly(methylphenylphosphazene),  $[\text{Me(Ph)PN}]_n$ , has been used to prepare a variety of new polymers and facilitates studies of structure-property relationships. Recent work that will be discussed includes (a) the preparation of new ketone derivatives of  $[\text{Me(Ph)PN}]_n$ , (b) related reactions of poly(dialkylphosphazenes),  $[\text{Me(R)PN}]_n$  ( $\text{R} = n\text{-Bu}$  and  $n\text{-Hex}$ ), (c) the chemistry of a poly(phospholenazene), a special type of polyphosphazene in which the backbone phosphorus is part of a heterocyclic ring formed by the polymer substituents, and (d) preparation of phospholenazene spirocyclic materials.

**Keywords:** phosphazene; polymer; phospholenazene; phosphoranimine; spirocyclic

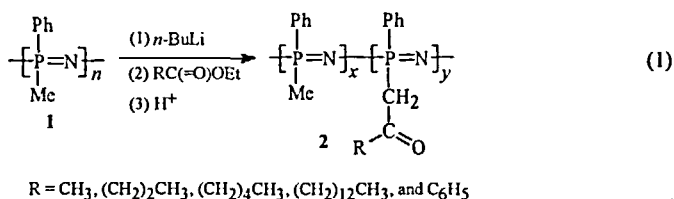
### INTRODUCTION

Poly(alkyl/arylphosphazenes),  $[\text{RR'PN}]_n$ , are a special class of phosphazene polymers<sup>[1]</sup> in which all the substituents along the polymer backbone are attached by direct P-C bonds. These fully substituted polymers have thus far been prepared by the condensation polymerization of N-silylphosphoranimines,  $\text{Me}_3\text{SiN}=\text{P(OR'')RR'}$  [ $\text{R}'' = \text{OPh}$ ,  $\text{OCH}_2\text{CF}_3$ ] that have simple alkyl and/or aryl substituents ( $\text{R}$  and  $\text{R'}$ ) attached to the phosphorus.<sup>[2]</sup> Although a large number of alkyl groups have been attached by this direct process, the diversity of P-C bonded polyphosphazenes has been greatly expanded by chemical modification of the alkyl or aryl substituents along the backbone.<sup>[3 - 8]</sup> In the best studied system, poly(methylphenylphosphazene),  $[\text{Me(Ph)PN}]_n$ , (1) there are three reactive sites that have been exploited: (a) the aryl group which is susceptible to electrophilic aromatic substitution,<sup>[3]</sup> (b) the lone pair of electrons on the backbone nitrogen atom which coordinates readily to many Lewis acids,<sup>[4]</sup> and (c) the methyl group which undergoes deprotonation-substitution reactions.<sup>[5 - 9]</sup> It is this latter type of chemistry that has provided the largest variety of new poly(phosphazenes), including those with alcohol,<sup>[5]</sup> carboxylic acid,<sup>[6]</sup> substituted silyl,<sup>[7]</sup> ferrocene,<sup>[5]</sup> and grafted organic and inorganic polymer side groups.<sup>[8]</sup> The varied nature of the side-groups attached by this process significantly affects properties such as glass transition temperature ( $T_g$ ), surface hydrophobicity, gas permeability,

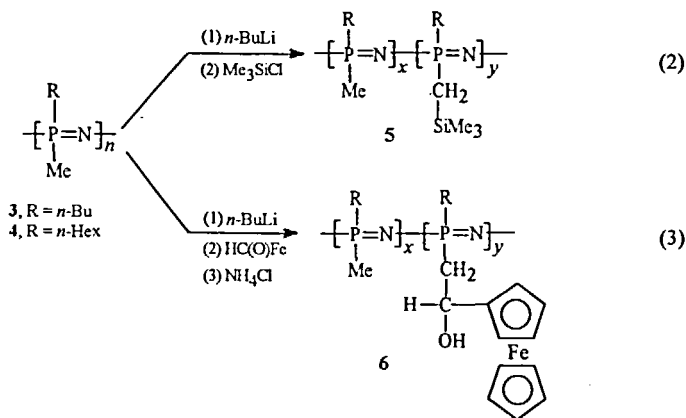
solubility, and refractive index. Structure-property relationships in several other polyphosphazenes are discussed in this paper.

## RESULTS and DISCUSSION

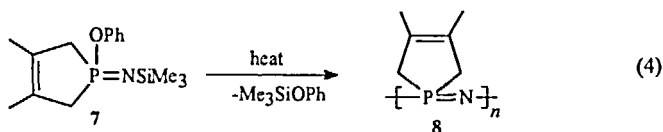
The deprotonation-substitution of methyl groups has produced a number of new derivatives of poly(methylphenylphosphazene), but the incorporation of an electrophilic ketone group has not been straightforward. These problems were circumvented by treatment of the anion sites formed when methyl groups are deprotonated by *n*-BuLi, with ethyl esters (eq 1).<sup>[9]</sup> These new polymers were fully characterized by NMR spectroscopy and elemental analyses. Molecular weights determined by gel permeation chromatography (GPC) were comparable to that of the parent polymer 1. The  $T_g$ s, which reflect the ease of torsional movement of the backbone, varied in the expected manner with longer side chains generally having lower  $T_g$ s (30 °C for R = pentyl, and 46 °C for R = propyl) as a result of larger free volumes generated by these groups.<sup>[10]</sup> This is overcome by chain tangling where R = (CH<sub>2</sub>)<sub>12</sub>CH<sub>3</sub> ( $T_g$  = 50 °C). The large phenyl group, which typically hinders backbone mobility, resulted in a significantly higher value of 71 °C.



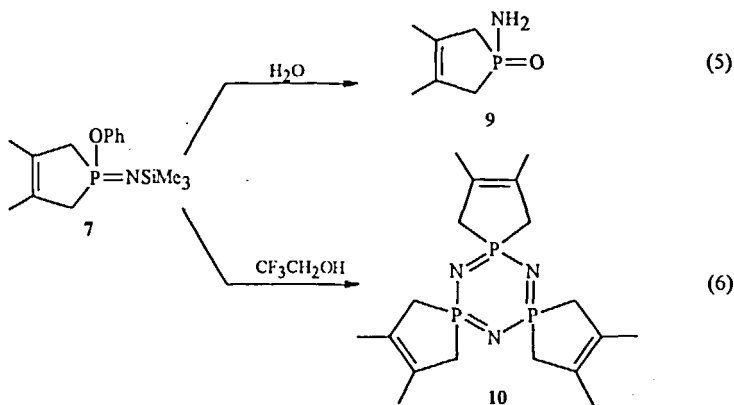
Although [Me(Ph)PN]<sub>n</sub> can be significantly altered through derivatization of the methyl groups, the presence of the phenyl group always has a significant effect on the properties of the resulting system. Generally this group affords greater hydrophobicity, enhanced solubility in organic solvents, and higher glass transition temperatures. Thus, the poly(*dialkyl*)phosphazenes offered potentially greater property flexibility. To correlate the relationship between these structural features and properties, poly(*alkyl*)methylphosphazenes with *n*-butyl and *n*-hexyl groups were subjected to deprotonation-substitution reactions (eq 2 and 3).<sup>[10]</sup> The preferred site of deprotonation in these systems was the P-Me group. This was confirmed by model studies on the corresponding N-silylphosphoranimines, Me<sub>3</sub>SiN=P(OPh)(Me)(alkyl). The new polymers were characterized as above and molecular weights were usually slightly larger than the parent polymers 3 and 4. The  $T_g$ s were higher than the parent, but significantly lower than the corresponding silyl and ferrocenyl derivatives of the [Me(Ph)PN]<sub>n</sub>. The hydrophobicity of the derivatives was also much greater than the starting polymers. This was demonstrated by measurement of Young's contact angles ( $\theta_Y$ ) for 5 and 6 (ca. 85 to 92 °) relative to values of less than 25 ° for 4 and 5.



A related polyphosphazene in which the substituents at phosphorus are part of a heterocyclic ring was also recently reported. The condensation of a Si-N-P compound (eq 4) was used to prepare this new polyphospholenazene.<sup>[11]</sup> The initial formation of the phospholene ring at phosphorus was accomplished using the McCormick reaction.<sup>[12]</sup> The polymer is a semicrystalline material that is soluble only in chlorinated hydrocarbons. Its molecular weight as determined by GPC was ca. 50,000.



Recent studies have shown that reactions of the double bond in the phospholene ring of 8 are generally extremely slow and/or very complex. Reactions on the ring of the polymer precursor 7 are further complicated by the reactive Si-N and P-O bonds. However, the reactivity of these latter bonds produced two unusual phosphorus-nitrogen compounds (eqs 5 and 6). Simple hydrolysis of 7 produced the phospholene oxide 9 with a simple NH<sub>2</sub> group. X-ray crystallographic analysis clearly shows that the reaction byproduct phenol is hydrogen bonded to oxygen of the P=O bond in 9. Treatment of 7 with CF<sub>3</sub>CH<sub>2</sub>OH produced an even more novel spirocyclic phosphazene, one of the first in which the exocyclic rings are attached by P-C bonds.<sup>[13]</sup> Once again, phenol was part of the crystal lattice with attachment via hydrogen bonding to the ring nitrogen atoms. Phenol was removed by treatment with NaOH and the phenol-free spirocyclic was also fully characterized. The structures of the phenol-containing and phenol-free spirocyclics showed different configurations of the exocyclic phospholene rings.



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