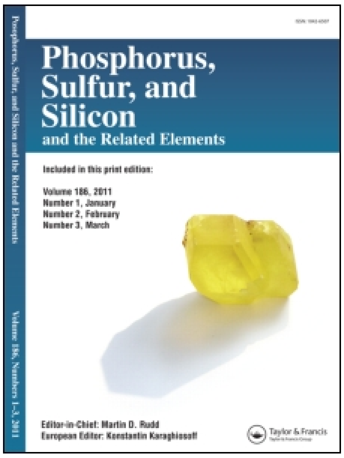

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Derivatives of Poly (alkyl/arylphosphazenes)

Patty Wisian-neilson[a]; Randal Ford[a]
[a] Department of Chemistry, Southern Methodist University, Dallas, Texas, USA

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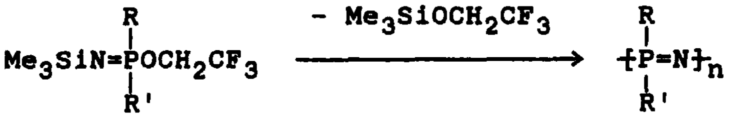
DERIVATIVES OF POLY(ALKYL/ARYLPHOSPHAZENES)

PATTY WISIAN-NEILSON and RANDAL FORD
Department of Chemistry, Southern Methodist
University, Dallas, Texas 75275 USA

Abstract High molecular weight polyphosphazenes $[Ph(Me)P=N]_x[Ph(CH_2Z)P=N]_y$ and their phosphoranimine precursors $Me_3SiN=P(OCH_2CF_3)(CH_2Z)Me$ [Z = RMe_2Si (R = H, Me, $CH=CH_2$, $(CH_2)_3CN$), R_2P (R = Ph, Me_2N), COOH, RR'COH (R,R' = H, Me, Ph, ferrocenyl), Me, $CH_2CH=CH_2$, and CH_2Ph have been prepared by sequential treatment of $[Ph(Me)P=N]_n$ or $Me_3SiN=P(OCH_2CF_3)Me_2$ with n-BuLi and appropriate electrophiles.

A large variety of polyphosphazenes with amino, alkoxy, or aryloxy substituents attached to the backbone phosphorus have been prepared by the substitution method developed by Allcock and coworkers.[1] An additional, complementary route to polyphosphazenes, which further expands this already extremely diverse class of polymers, has also been developed.[2] This process (eq 1), which involves the thermal condensation-polymerization of N-silylphosphoranimines, allows for the attachment of simple alkyl or aryl substituents to the polymer backbone through direct P-C linkages, gives consistently good yields of high molecular weight polymers, and may be used to prepare homopolymers, copolymers, or controllably crosslinked polymers. In addition to our characterization studies of these new materials, one of our major goals is to alter the

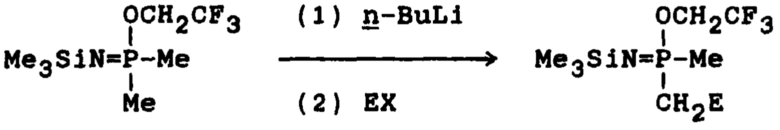


$$Me_3SiN{=}\overset{R}{\underset{R'}{P}}OCH_2CF_3 \xrightarrow{-\,Me_3SiOCH_2CF_3} \left[\overset{R}{\underset{R'}{P}}{=}N\right]_n \qquad (1)$$

substituents at phosphorus. Such changes have been shown to affect factors such as thermal and chemical stability, solubility characteristics, and surface and mechanical properties. The synthetic pathways of major interest are (1) alteration of the substituents at phosphorus in the immediate polymer precursors or (2) alteration of the substituents in preformed polymers such as $[Ph(Me)PN]_n$.

DERIVATIZATION OF POLYMER PRECURSORS

Treatment of an Et_2O solution of $Me_3SiN{=}P(OCH_2CF_3)Me_2$ at -78°C with n-BuLi affords an unstable anionic intermediate. This anion reacts at -78°C with a variety of reactive halogen compounds to form a new series of N-silylphosphoranimines (eq 2), all of which are potential polymer precursors. In general, homopolymerization of these new compounds gives low molecular weight or cyclic phosphazenes, but high polymers can be obtained by cothermolysis of several of the derivatives ($E = R_2P$, Me, CH_2Ph, $CH_2CH{=}CH_2$) with $Me_3SiN{=}P(OCH_2CF_3)Me_2$. In some cases (e.g., $E = Me_3Si$), the phosphoranimines are



$$Me_3SiN{=}\overset{OCH_2CF_3}{\underset{Me}{P}}{-}Me \xrightarrow[(2)\ EX]{(1)\ \underline{n}\text{-BuLi}} Me_3SiN{=}\overset{OCH_2CF_3}{\underset{CH_2E}{P}}{-}Me \qquad (2)$$

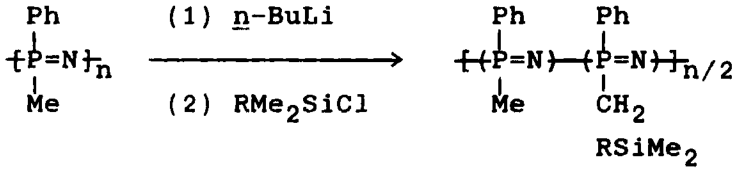
$E = R_2P$ ($R = Me_2N$, Ph), RMe_2Si (R = Me, H, $CH{=}CH_2$, $(CH_2)_3CN$), Me, $CH_2CH{=}CH_2$, CH_2Ph, $Me_3SiN{=}PMe_2$

remarkably thermally stable and fail to eliminate $Me_3SiOCH_2CF_3$ under typical conditions (160-250°C/5-20 days).

DERIVATIZATION OF PREFORMED POLYMERS

Similar reactions can be carried out on the preformed polymer $[Ph(Me)PN]_n$. This approach generally affords a greater degree of substitution, allows the use of quenching agents (e.g., H_2O) which might react with the Si-N or P-O bonds in the precursors, and avoids complicating reactions of the substituents at phosphorus during the thermal polymerizations of the precursor phosphoranimines.

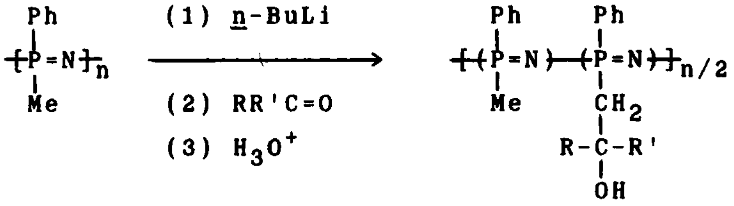
Hence, a series of silylated polyphosphazenes[3] has recently been prepared by sequential treatment of $[Ph(Me)PN]_n$ in THF at -78°C with 0.2 or 0.5 equivalents of *n*-BuLi and RMe_2SiCl (eq 3). Gel permeation chromatography and intrinsic viscosity studies, which



$$\left[\underset{\text{Me}}{\overset{\text{Ph}}{P}}=N\right]_n \xrightarrow[\text{(2) RMe}_2\text{SiCl}]{\text{(1) }n\text{-BuLi}} \left[\left(\underset{\text{Me}}{\overset{\text{Ph}}{P}}=N\right)\left(\underset{\text{CH}_2\text{RSiMe}_2}{\overset{\text{Ph}}{P}}=N\right)\right]_{n/2} \qquad (3)$$

show that the molecular weight distribution of the silylated polymers is essentialy identical to that of the parent polymer, indicate that no chain cleavage has occurred.

Reactive carbonyl compounds have also been used as quenching agents to produce another series of new polymers (eq 4), all of which have molecular weight distributions similar to the parent polymer.



$$\left[\overset{\text{Ph}}{\underset{\text{Me}}{\text{P}}}=\text{N}\right]_n \xrightarrow[\substack{(2)\ RR'C=O \\ (3)\ H_3O^+}]{(1)\ \underline{n}\text{-BuLi}} \left[\left(\overset{\text{Ph}}{\underset{\text{Me}}{\text{P}}}=\text{N}\right)-\left(\overset{\text{Ph}}{\underset{\substack{\text{CH}_2 \\ \text{R}-\text{C}-\text{R}' \\ \text{OH}}}{\text{P}}}=\text{N}\right)\right]_{n/2} \qquad (4)$$

R, R' = H, Me, Ph, ferrocenyl

Similarly, a carboxylic acid derivative $\{[Ph(Me)P=N][Ph(CH_2COOH)P=N]\}_n$ has been prepared from the anionic intermediate and CO_2. Upon treatment with NaOH, the polymer becomes a water soluble carboxylate salt.

Another approach to derivatization of the preformed polymer involves reactions of the phenyl ring rather than the methyl group. Our initial efforts have shown that the ring can be nitrated without chain degradation by simple treatment with nitric and sulfuric acid.

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