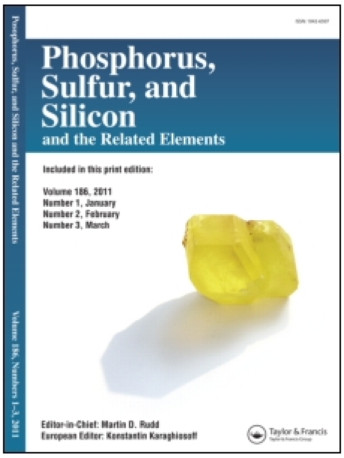

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NEW POLYMERS DERIVED FROM POLY(METHYLPHENYLPHOSPHAZENE)

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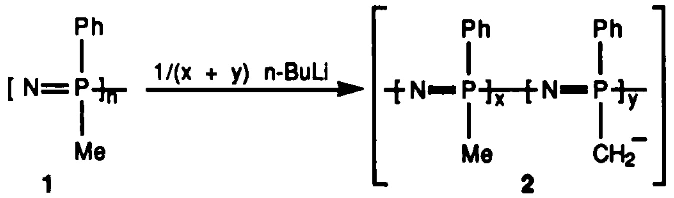
Abstract The sequential treatment of $[Me(Ph)PN]_n$ with *n*-BuLi and electrophiles such as substituted chlorosilanes, aldehydes and ketones, and carbon dioxide results in new functionalized polyphosphazenes. Graft copolymers have also been prepared by using the anionic polymer intermediate to initiate anionic addition polymerization of styrene, $CH_2{=}C(Ph)H$, and ring opening polymerization of hexamethylcyclotrisiloxane, $[Me_2SiO]_3$.

The synthesis of polyphosphazenes, $[R_2P{=}N]_n$, has most generally been accomplished by substitution of poly(halophosphazenes) which are prepared by ring opening of the cyclic halogenated phosphazenes.[1] This ring opening-substitution process has been used to prepare a large variety of alkoxy, aryloxy, and amino substituted polymers. A variation of this involves ring opening of cyclic phosphazenes with both halo and organo substituents.[2] More recently, a condensation polymerization method[3] has been developed which produces poly(alkyl/arylphosphazenes) with all substituents attached to the backbone by direct P-C linkages. The latter process, which involves the thermolysis of appropriate silicon-nitrogen-phosphorus precursors, gives essentially quantitative yields of high molecular weight polymers with simple alkyl and aryl substituents. In order to alter the properties of these poly(alkyl/arylphosphazenes) and to incorporate reactive functional groups into the polymer system, we are investigating the derivatization[4-7] of the preformed polymers.

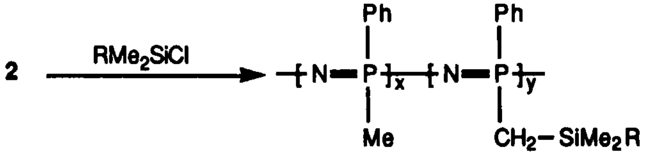
Most of our studies have focused on the derivatization of the methyl group in poly(methylphenylphosphazene), $[Ph(Me)P{=}N]_n$, **1**, which is easily prepared and THF soluble. We have shown that between 10 to 50% of the methyl groups are readily deprotonated, without degradation or molecular weight loss, when treated with *n*-BuLi at -78°C, producing a polymer anion intermediate **2** (eq 1) that reacts with electrophiles (eq 2-6). These deprotonation-substitution reactions resulted in the synthesis of a number of new polyphosphazenes with widely varied properties. The



(1)

new copolymers have been characterized by gel permeation chromatography (GPC); ^{1}H, ^{13}C, ^{31}P, and, where appropriate, ^{29}Si NMR spectroscopy; membrane osmometry; intrinsic viscosity; IR spectroscopy; thermogravimetric analysis; and differential scanning calorimetry.

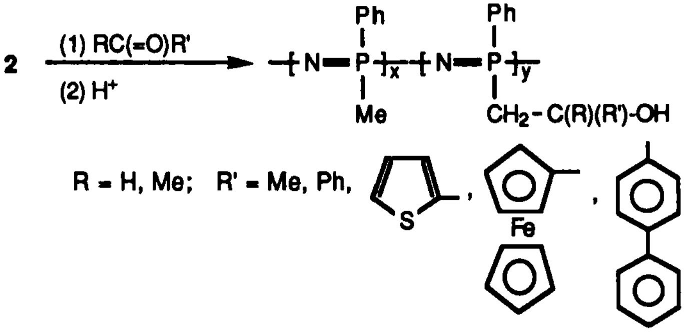
The first type of derivative to be prepared was a series of silylated polymers (eq 2),[5] some of which contained reactive sites for further derivatization or were more thermally stable than the parent polymer $[Ph(Me)PN]_n$.



(2)

R = Me, H, CH=CH$_2$, (CH$_2$)$_3$CN

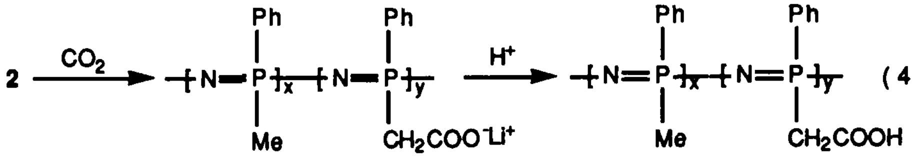
Another series of polymer derivatives which contain the OH functionality were prepared by treatment of 2 with aldehydes and ketones (eq 3). These include poly-



(3)

mers with potentially electroactive thiophenyl and ferrocenyl groups. The ferrocenyl derivatives showed onsets of decomposition of ca. 350 to 380° C, but also retained as much as 50% of the original weight at 800° C. The glass transition temperatures (T_g) of these polymers, which reflect the torsional mobility of the backbone, showed the expected trend of higher T_g with increased bulk and number of substituents. Furthermore, the OH functional group should be easily derivatized and could serve as a crosslinking site.

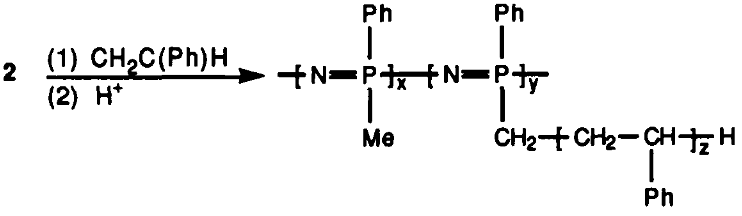
The polymer anion also reacts with carbon dioxide (eq 4) and has been used to prepare polymers with lithium carboxylate, **3**, carboxylic acid, **4**, and ester groups, **5**, the first of which may be considered as ionomers that are potentially of interest, for example, as ionic conducting materials and as membranes. These reactions proceeded cleanly with derivatization of 10, 25, and 50 % of the backbone methyl groups.



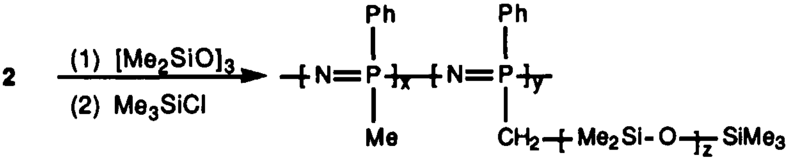
$$\mathbf{2} \xrightarrow{CO_2} \left[N{=}\overset{Ph}{\underset{Me}{P}}\right]_x\left[N{=}\overset{Ph}{\underset{CH_2COO^-Li^+}{P}}\right]_y \xrightarrow{H^+} \left[N{=}\overset{Ph}{\underset{Me}{P}}\right]_x\left[N{=}\overset{Ph}{\underset{CH_2COOH}{P}}\right]_y \qquad (4)$$

3 **4**

The anion sites in **2** have also been used to initiate anionic addition polymerization of selected monomers and certain ring opening polymerizations. Thus far, we have used this approach to prepare two types of graft copolymers, i.e., those with organic polystyrene grafts[6] (eq 5) and those with inorganic silicone grafts.[7] (eq 6) In both cases, a series of soluble, uncrosslinked graft copolymers were



$$\mathbf{2} \xrightarrow[(2)\ H^+]{(1)\ CH_2C(Ph)H} \left[N{=}\overset{Ph}{\underset{Me}{P}}\right]_x\left[N{=}\overset{Ph}{\underset{CH_2\left[CH_2-\underset{Ph}{CH}\right]_zH}{P}}\right]_y \qquad (5)$$



$$\mathbf{2} \xrightarrow[(2)\ Me_3SiCl]{(1)\ [Me_2SiO]_3} \left[N{=}\overset{Ph}{\underset{Me}{P}}\right]_x\left[N{=}\overset{Ph}{\underset{CH_2\left[Me_2Si-O\right]_zSiMe_3}{P}}\right]_y \qquad (6)$$

prepared in which the ratios of the two components were varied by controlling the number (10 to 20% of the phosphazene units were grafted) and the length (ca. 15 to 100 units) of the grafts. Preliminary experiments suggest that it is possible to make many other new inorganic-organic and inorganic-inorganic graft copolymers by related reactions. Although poly(aryloxyphosphazene)-*graft*-polystyrene copolymers have been prepared by a free radical process,[8] these new copolymers are the first examples of graft copolymers of poly(alkyl/arylphosphazenes) and the first examples of anionic grafting reactions on polyphosphazenes.

In summary, the deprotonation-substitution reactions of poly(methylphenylphosphazene) have already resulted in a number of new polyphosphazene polymers, but, more importantly, the diversity of the reaction promises to provide access to a wide range of new polymers in which the properties are controlled by both type and degree of substitution. In view of the many useful properties of polyphosphazenes, which include low temperature flexibility and good thermal, photolytic, and chemical stability, the development of various synthetic approaches to new polyphosphazenes is of practical importance.

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