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13. ABSTRACT (Maximum 200 words) The work described in this proposal is a continuation of work which has been in progress in our labs since 1977. The program involves a detailed study of the synthesis, characterization, and reactions of poly(phosphazenes) in which all substituents are attached to the phosphorus-nitrogen backbone by direct P-C bonds. A large variety of homopolymers and copolymers with simple alkyl and aryl substituents, an array of materials with a number of different organic functional groups, and several graft copolymers have been prepared by simple thermolysis of silicon-nitrogen-phosphorus compounds and by subsequent reactions of polymers prepared by this method. Over 100 of these new materials have been prepared in our laboratories and range from semi-crystalline, film-forming thermoplastics to amorphous gums and fluids.					
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**SYNTHESIS AND CHARACTERIZATION
OF NEW POLY(ALKYL/ARYLPHOSPHAZENES)**

FINAL REPORT

Patty Wisian-Neilson and Robert H. Neilson

November 23, 1991

U. S. ARMY RESEARCH OFFICE



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Southern Methodist University

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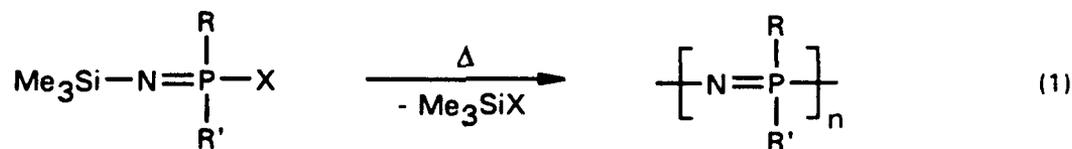
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Statement of the Problem Studied

Since the mid-1960's, one of the most exciting and rapidly expanding areas of polymer science has been the synthesis and characterization of the class of inorganic polymers known as poly(phosphazenes), $[R_2PN]_n$.¹ Because such a large variety of substituents, R, can be attached to the backbone, these polymers, exhibit a very broad spectrum of physical,² biological,³ electrical,⁴ and optical⁵ properties. Thus, there is a vast potential for many practical applications of these unique materials.

Despite the enormous number of poly(phosphazenes) that have been prepared, the synthetic methods for formation of the phosphorus-nitrogen backbone can be grouped into two general categories. The first approach is the ring-opening process developed by Allcock and coworkers. It involves the preparation of poly(dichlorophosphazene), $[Cl_2PN]_n$, by the opening of the cyclic trimer, $[Cl_2PN]_3$. Subsequent substitution of the chlorine atoms along the polymer backbone via nucleophilic displacement reactions affords a large variety of phosphazenes which generally have P-N and/or P-O bonded substituents.¹ In addition to this ring-opening-substitution approach, several significant variations involving certain substituted cyclic phosphazenes have been reported.⁶

The second general approach, which has been under investigation in our laboratories during the last decade, involves the *condensation polymerization* of suitable Si-N-P precursors (eq 1).^{7, 8} This method differs from, and therefore compliments, the ring-opening-substitution approach in two significant respects: (a) *the desired substituents on phosphorus are introduced prior to polymerization*, and (b) *all of the side groups are directly attached to phosphorus via direct P-C bonds*.



R, R' = alkyl, aryl; X = OCH₂CF₃, OPh

In addition to comprising a very interesting new class of poly(phosphazenes) in their own right, these *poly(alkyl/arylphosphazenes)*, e.g., $[\text{Me}(\text{Ph})\text{PN}]_n$, can be further derivatized by

deprotonation-substitution reactions of the pendant P-Me groups. Like the substitution reactions of $[\text{Cl}_2\text{PN}]_n$ and other products of the ring-opening polymerization, these derivatization or substitution reactions of the P-C polymers greatly enhance the diversity of poly(phosphazenes) and allow for the incorporation of an array of functional groups.^{9 - 11} This type of reaction also affords the first general synthetic approach to well-defined poly(phosphazene) graft copolymers.^{12, 13}

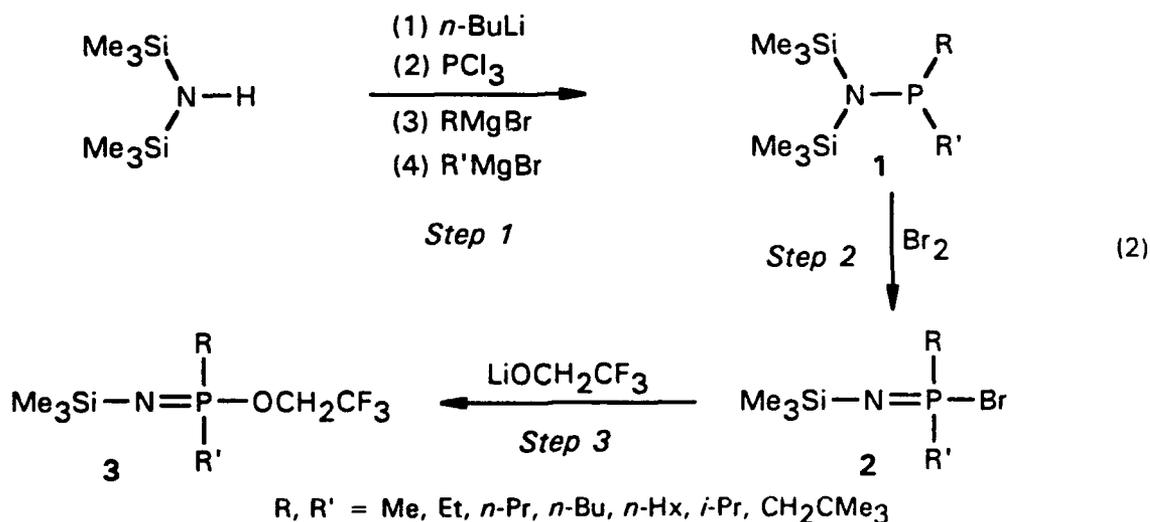
Two recent variations of the condensation polymerization approach to poly(phosphazenes) should also be noted. First, DeJaeger¹⁴ has shown that poly(dichlorophosphazene), $[\text{NPCI}_2]_n$, can be prepared by thermolysis of the phosphoryl substituted phosphoranimine, $\text{Cl}_2\text{P}(=\text{O})-\text{N}=\text{PCl}_3$. Second, and more relevant to this report, is the recent work of Montague and Matyjaszewski¹⁵ involving the fluoride-catalyzed polymerization of certain N-silylphosphoranimines such as $\text{Me}_3\text{SiN}=\text{P}(\text{OCH}_2\text{CF}_3)_3$.

The focus of the work conducted during this contract period has been the expansion of the potential utility of poly(phosphazenes) in which all substituents are attached by direct P-C bonds. The details of the program are discussed in the following section.

Summary of Results

The work under this ARO contract can be conveniently grouped into four areas: (a) small molecule polymer precursors, (b) new polymers from the condensation process, (c) mechanistic and catalytic studies of the process, and (d) new polymers from the derivatization of preformed poly(alkyl/arylphosphazenes). Each of these areas is discussed below.

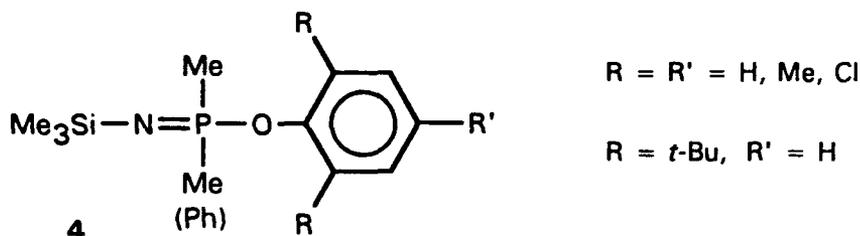
(a) New Phosphazene Precursors and Related Compounds. In order to fully understand the scope of the condensation polymerization (eq 1), we have prepared a much larger series of N-silylphosphoranimines by the general 3-step process (eq 2).¹⁶



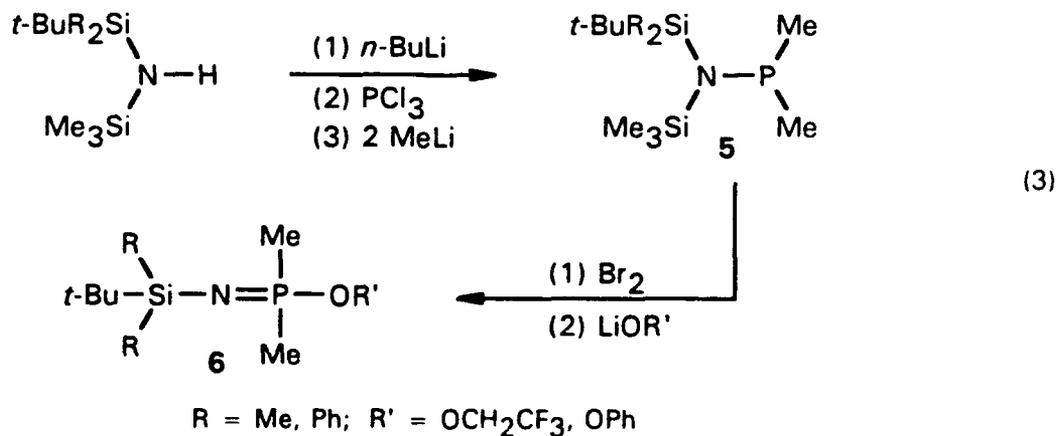
There are a number of variations in this procedure that facilitate attachment of other combinations of alkyl and aryl substituents as well as other potential leaving groups. These include (1) addition of PhPCl₂ instead of PCl₃ in the first step to yield phenyl/alkyl derivatives or addition of two equivalents of the same Grignard reagent (R = R') to afford the symmetrical dialkyl products; (2) use of C₂Cl₆ instead of Br₂ in the second step to give the more thermally stable P-Cl analogs; and (3) substitution of other alkoxide or aryloxy salts for LiOCH₂CF₃ in the third step to incorporate a variety of possible leaving groups.

Using this three-step process, we have prepared and characterized a series of P-aryloxyphosphoranimines, 4, of the type shown below. These derivatives were obtained in

good yields upon treatment of the P-Br precursors, 2, with one equivalent of the appropriate LiOAr reagent.¹⁷ A complete study of the thermolysis reactions of these compounds is still in progress, but we have definitely established that *the simple, P-phenoxy derivatives are excellent precursors to linear poly(phosphazenes)*.

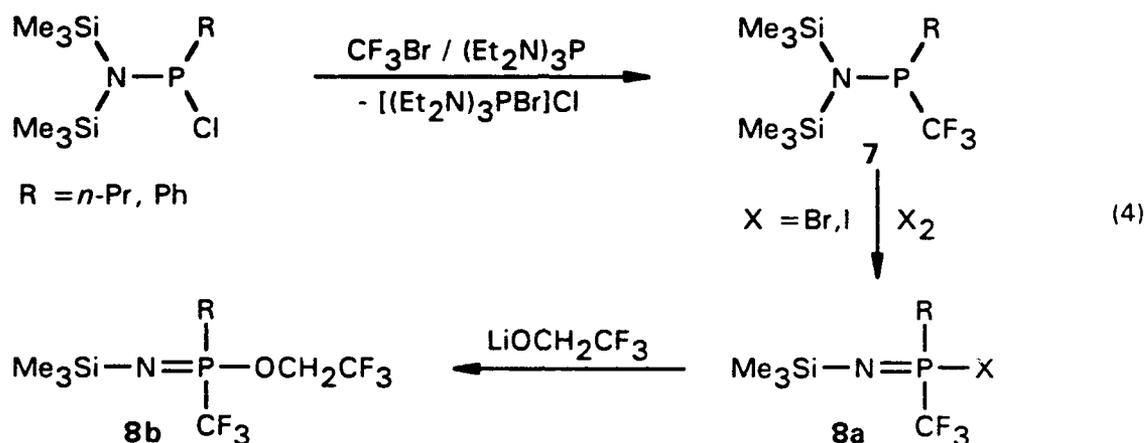


Other important features of the condensation polymerization process that are under investigation include the possibility of controlling the degree of polymerization and/or the chemistry of the polymer's end groups. In one aspect of this effort, we have prepared a series of N-silylphosphoramines, 6, that contain sterically bulky silyl groups (eq 3). Interestingly, some of the compounds that contain the very bulky *t*-butyldiphenyl/silyl moiety are crystalline solids and, to date, both the *dimethylphosphine*, 5, and its P-phenoxy derivative, 6 (R = Ph), have been characterized by single crystal X-ray diffraction. A noteworthy point about this series of compounds is that the *less bulky Me₃Si group is selectively cleaved from nitrogen* during the oxidative bromination reaction.



Another part of our study of the polymer precursors pertains to a new class of poly(alkyl/arylphosphazenes) bearing *perfluoroalkyl groups directly attached to phosphorus*. Due

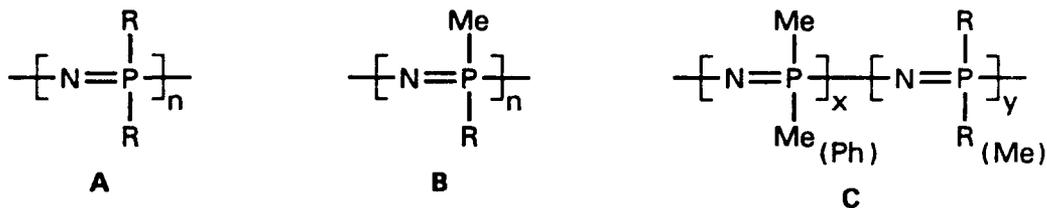
to the instability of reagents like CF_3Li or CF_3MgX , trifluoromethyl substituents cannot be attached to phosphorus as easily as the simple alkyl groups. However, by a modification of the recently reported method of preparing Me_3SiCF_3 and a few simple phosphorus analogs,¹⁸ we were able to obtain the desired CF_3 -substituted (silylamino)phosphines, **7**, (eq 4) in good yields as thermally stable, distillable liquids. Subsequent oxidative halogenation to **8a**, followed by treatment with $\text{LiOCH}_2\text{CF}_3$ cleanly afforded the P-trifluoromethyl-N-silylphosphoranimes, **8b**.



A few preliminary condensation reactions involving these P- CF_3 derivatives have been attempted. In comparison to the related chemistry of the simple P-methyl systems, some significant differences are noted. First, it is immediately apparent that they are much more thermally stable than the methyl analogs as illustrated by the successful *isolation* of even the P-iodophosphoranimes, **8a** ($\text{R} = \text{I}$). Second, the P- OCH_2CF_3 derivatives, **8b**, are recovered unchanged upon heating at 220°C for extended periods of time. Third, while P-Br compounds like $\text{Me}_3\text{SiN}=\text{PMe}_2\text{Br}$ invariably yield only cyclic phosphazenes upon thermolysis, the CF_3 -substituted analogs, $\text{Me}_3\text{SiN}=\text{P}(\text{R})(\text{CF}_3)\text{Br}$, decompose to mixtures of cyclic trimers and linear polymers.

(b) New Polymers via Condensation Polymerization. The thermal condensation reactions of a large series of N-silyl-P,P-dialkyl-P-trifluoroethoxyphosphoranimes, **3**, were studied both individually and in a variety of copolymerizations with the dimethyl or phenylmethyl substituted precursors. These polymerizations (in sealed glass ampules at ca. $180\text{--}200^\circ\text{C}$ for 7-12 days) provide a series of new polymers that can be grouped into three general categories:

symmetrical homopolymers (A), unsymmetrical homopolymers (B), and copolymers (C).



R = Et, *n*-Pr, *n*-Bu, *n*-Hx

Our studies of the physical, solubility, and thermal properties of these materials represent the first systematic analysis of the structure-property relationships among the poly(alkyl/arylphosphazenes). This work indicates that it is now possible to essentially "tailor make" a given alkyl/arylphosphazene polymer with whatever physical characteristics are desired for a particular application. Some of these properties are summarized briefly in the following sections.

Solubility. In general, poly(alkyl/arylphosphazenes) are quite soluble in various organic solvents with the only exceptions found among the symmetrical dialkyl homopolymers (A). Interestingly, while the parent member of this series, poly(dimethylphosphazene), $[\text{Me}_2\text{PN}]_n$, is soluble in CH_2Cl_2 , EtOH, and THF/ H_2O mixtures, all of the other *dialkyl*phosphazenes, $[\text{R}_2\text{PN}]_n$, are insoluble in all common solvents. This insolubility can be attributed to the microcrystalline nature of these symmetrical polymers as confirmed earlier by X-ray diffraction⁸ studies of the dimethyl and diethyl compounds and implied for all of them by intense melt transitions in their DSC traces. It is possible, however, to dissolve any of these materials in organic solvents if a small amount (ca. 1%) of a weak acid such as acetic or benzoic acid is added to partially protonate the polymer backbone. By using these acidified solvents, it is possible to obtain reliable NMR spectroscopic and solution viscosity data for such polymers. The unsymmetrical homopolymers (B) and the copolymers (C) are more amorphous in nature and are very soluble in common organic solvents, especially CH_2Cl_2 and THF, thus facilitating their characterization by size exclusion chromatography (SEC). Notably, the homopolymers with relatively long alkyl chains (B: R = *n*-Bu, *n*-Hx) are also soluble in hexane and other nonpolar hydrocarbons.

Molecular Weights. Except for the dialkyl homologs, $[\text{R}_2\text{PN}]_n$, all of these polymers and

copolymers are soluble in THF. Thus, by employing SEC conditions described elsewhere,⁸ we are able to obtain reliable molecular weight distributions for these polymers. Typically, they have relatively narrow molecular weight distributions ($M_w/M_n \approx 1.4 - 3.5$) and molecular weights (M_w) in the range of 50,000 - 200,000. There are no obvious trends in molecular weight among these polymers and the factors that control the chain length in the condensation polymerization process are still not well understood.

Thermal Transitions. As noted earlier, the polymeric dimethyl- and diethylphosphazenes are microcrystalline powders with melting points of 143 and 217 °C, respectively.⁸ Similar characteristics are observed for the other symmetrical di-*n*-alkyl derivatives although the di-*n*-hexyl polymer is a more wax-like solid that exhibits both a glass transition (-29 °C) and a melt transition (129 °C). On the other hand, the unsymmetrical homopolymers (B) have considerably different physical properties with only the Me/Et derivative being a true solid ($T_m = 80$ °C). With their longer *n*-alkyl chains, the other members of this series are amorphous gums or waxes. All of these Me/alkyl polymers (B) exhibit broad, poorly defined glass transitions around -50 °C as compared to the very distinct T_g at -46 °C observed for $[\text{Me}_2\text{PN}]_n$.⁸ The copolymers (C) exhibit a very broad spectrum of physical properties as would be expected for such a large degree of structural variation of the side groups. These materials vary from microcrystalline solids (e.g., some of the Me_2/R_2 copolymers) to gums (e.g., the Me/Ph-containing copolymers) to viscous fluids (e.g., the dimethyl/methyl-*n*-hexyl copolymers). Accordingly, a wide range of glass transition temperatures from ca. +10 to -70 °C is observed, with the presence of phenyl or *n*-hexyl substituents favoring the higher or lower values, respectively.

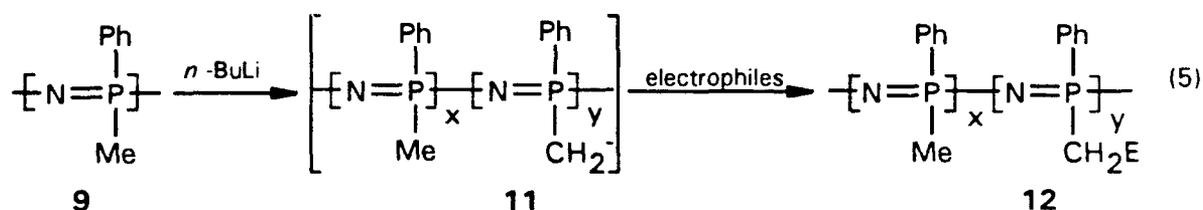
(c) Catalysis of the Polymerization. Since our initial discovery of the condensation polymerization route to poly(alkyl/arylphosphazenes), we have endeavored to improve the overall ease and, ultimately, the cost effectiveness of the method. In this context, the identification and development of simple catalysts for the polymerization process (eq 1) is an important objective. Several years ago in some unpublished work, we found that certain metal oxides (notably PtO_2) did accelerate the reaction, affording complete polymerization in 1 - 2

days at ca. 180 °C. Under similar conditions, solid NaF had no apparent effect. Recently, however, we have conducted a somewhat more systematic study of the F⁻ catalyzed condensation polymerization of Me₃SiN=P(Ph)(Me)OPh in a manner similar to the work of Montague and Matyjaszewski¹⁵ on the catalyzed polymerization of Me₃SiN=P(OCH₂CF₃)₃. Under a wide variety of reaction conditions, using ca. 1 mole percent of (*n*-Bu)₄NF (either neat, as a THF solution, or supported on alumina) at ca. 100 - 180 °C for periods of 12 - 48 hours, the polymerization usually proceeded rapidly to completion. Unfortunately, the molecular weight distributions of the [Ph(Me)PN]_n samples prepared in this manner have a consistently bimodal character (typical peak MW's of ca. 5,000 and 75,000) with the lower MW peak predominating.

In a very exciting recent development, however, we have obtained much better results with NaOPh as the catalyst. In the presence of ca. 1 mole percent of NaOPh at 150 °C, several samples of Me₃SiN=P(Ph)(Me)OPh, the Me₂P analogue, as well as mixtures thereof, have undergone *complete polymerization to yield high molecular weight (ca. 100,000 or more) polymers with narrow MW distributions.* Other potential catalysts are also being studied. For example, in recent, preliminary experiments, we find that addition of 2-3 drops of the simple polar solvent *HMPA, (Me₂N)₃P=O,* to neat samples of the Ph/Me precursor *also catalyzes the polymerization* at ca. 150 °C overnight. Further studies on these very interesting new developments are underway.

(d) Chemistry of Preformed Poly(alkyl/arylphosphazenes). While it is possible to introduce selected functional groups at the carbon attached to phosphorus (e.g., substituted vinyl groups) in the precursor synthesis,¹⁹ many desirable groups are not compatible with the reactive Si-N linkage in the precursors or, in certain cases, may not withstand the thermolysis conditions. Thus, we are investigating methods of introducing a variety of functional groups into the *preformed poly(alkyl/aryl-phosphazenes).* Our primary focus has been the deprotonation-substitution reactions of the methyl substituents on poly(methylphenylphosphazene), [Me(Ph)PN]_n, **9**, and, more recently, on copolymers, [Me(Ph)PN]_x[Me₂PN]_y, **10**.

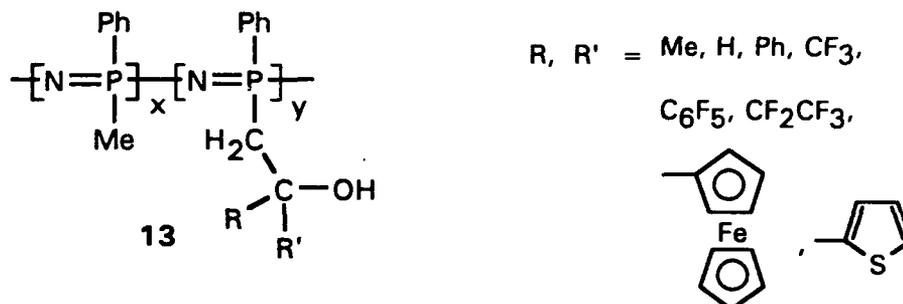
Homopolymer Derivatives. Treatment of a THF solution of the simple homopolymer, **9**, with *n*-BuLi at -78 °C produces a polymer anion intermediate, **11**, which reacts with a number of electrophiles (eq 5) giving new polymers with a variety of functional groups E as discussed below. Both intrinsic viscosity measurements and



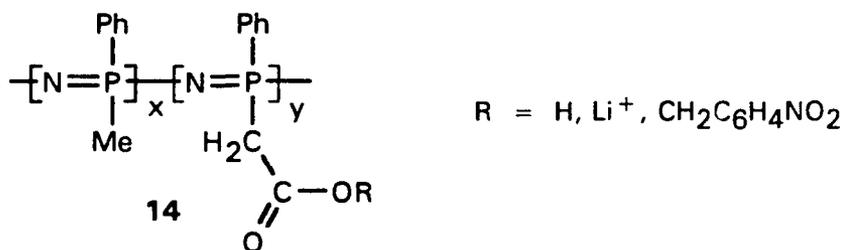
GPC data on a series of silylated polymers, **12**, where E = SiMe₂R [R = H, Me, CH=CH₂, and (CH₂)₃CN] that were prepared in this manner confirmed that treatment with *n*-BuLi does not cause degradation of the polymer chain under these mild conditions.⁹ By analogy to the preparation of the silyl substituted polymers, other poly(phosphazenes) with potentially reactive functional groups (E = PPh₂, Br, CH₂CH=CH₂, Me) have been synthesized by treatment of the anion **11** with some element-halogen (E-X) species.²⁰

Because the polymer anion intermediate behaves as a "typical" organolithium reagent, it can be used for the attachment of a variety of other simple organic functional groups.⁹⁻¹¹ For example, a wide variety of alcohols, **13**,¹⁰ have been prepared simply by treating the anion with aldehydes or ketones, including those with potentially electroactive groups such as ferrocene²¹ and thiophene¹⁰ and surface modifying organofluorine groups.²² The degree of substitution in most of these polymer derivatives is typically about 35% (i.e., x:y = 2:1), but is as high as 45% for the ferrocene and thiophene derivatives. The *T_g* values of the alcohol derivatives show the expected correlation with the size and number of groups R and R' and range from 49 to 102 °C (parent *T_g* = 37 °C). The fluorinated alcohols have *T_g* values very near those of the non-fluorinated analogs and exhibit onsets of decomposition in TGA analysis slightly below that of the simple alcohols. Recent electrochemical studies on one of the ferrocene polymers indicates simple reversible electrochemistry both in solution and as a thin

film on an electrode surface.²³

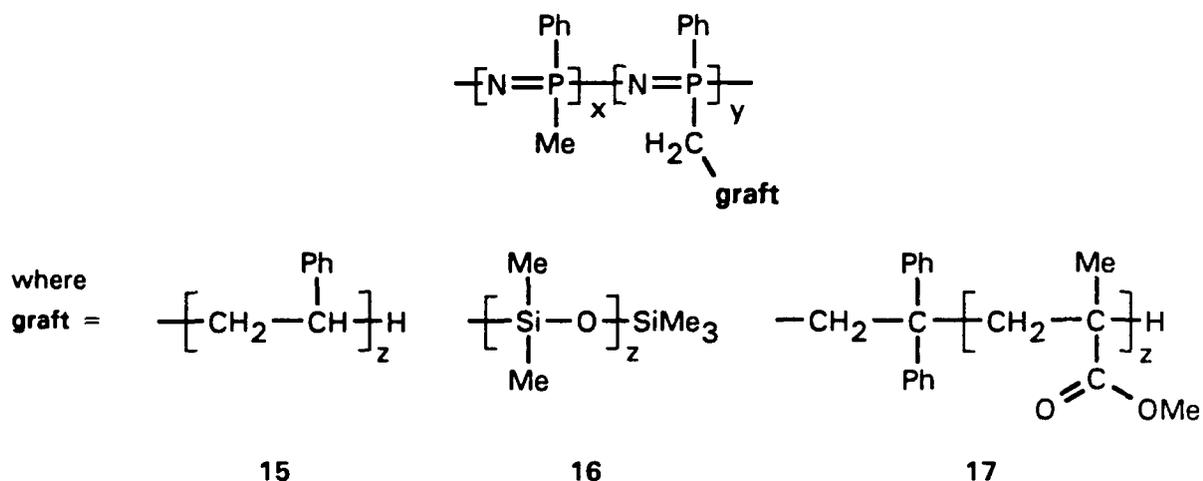


Another interesting class of "organic" poly(phosphazene) derivatives are those with carboxylic acid, salt, and ester groups, 14, which were obtained from the reaction of the anion 9 with CO_2 .¹¹ The 50% substituted salt (where $x = y$, $\text{R} = \text{Li}^+$) is the first water soluble derivative of a poly(alkyl/arylphosphazene). The salts are readily converted to the corresponding carboxylic acids upon protonation or to esters when treated with an activated species such as $4\text{-NO}_2\text{C}_6\text{H}_5\text{CH}_2\text{Br}$. Fluorescence studies of these simple acids indicate that they form a moderately hydrophobic environment in aqueous media.²⁴ The salts and acids are easily crosslinked by addition of divalent metal cations which suggests applications as hydrogels.²⁵ Some preliminary tests have also indicated these may have applications in microlithography.²⁶

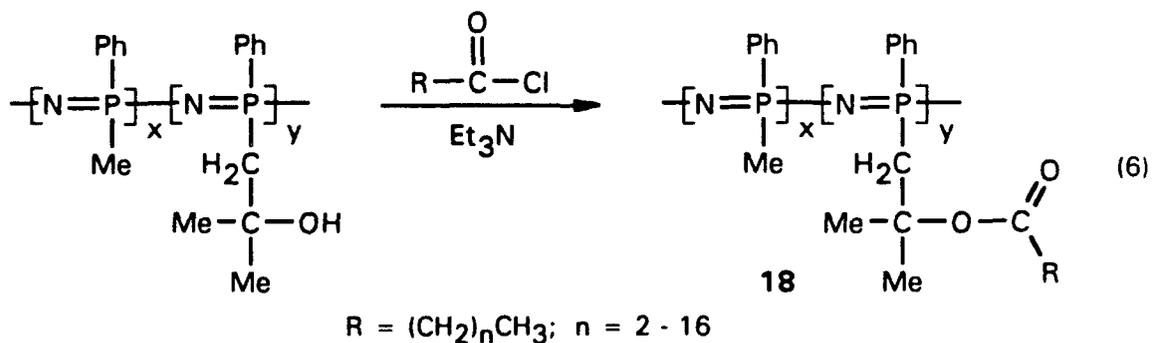


The polymer anion 9 has also been used to initiate anionic polymerization of styrene¹² and hexamethylcyclotrisiloxane¹³ to produce both organic (15) and inorganic (16) graft copolymers of poly(phosphazenes). Grafting has been demonstrated by marked changes in SEC (or GPC) data in terms of higher molecular weights and broadened polydispersity values. More importantly, absolute molecular weight determinations by membrane osmometry confirm the large increases in molecular weight upon grafting. The poly(methyl methacrylate) graft

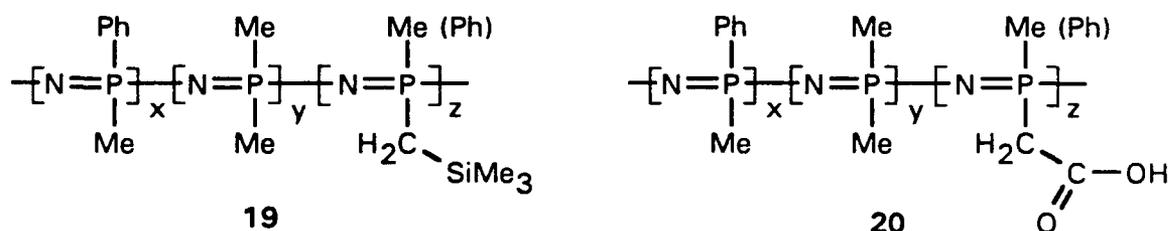
copolymer, 17, has also been made recently by moderating the reactivity of the anion sites with diphenylethylene prior to reaction with methyl methacrylate.



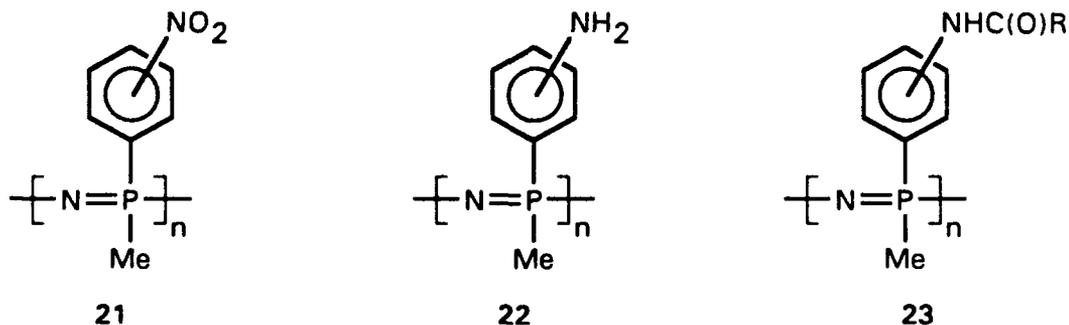
As part of our investigation of the chemistry of the new polymers, we have attempted to prepare both acid chloride derivatives and ester derivatives. The former is complicated by chain degradation which presumably occurs when HCl (or even R_3NHCl) is produced as a byproduct. The chemistry of the alcohol functionality has, however, been more straightforward. As shown in eq 6, the alcohol reacts smoothly with a variety of acid chlorides to give a series of esters, 18.²⁷ While these reactions were initially conducted to test this method for attaching more elaborate groups R, including moieties that might impart liquid crystallinity to the polymers, an interesting trend was observed in the thermal data of these ester derivatized polymers. As the length of the chain is increased from $n = 2 - 6$ the T_g decreases from 37 to 7 °C, but when the length is increased from $n = 10 - 16$, the T_g increases from 14 to ca. 45 °C.



Copolymer Derivatives. As discussed in earlier sections, the properties of the copolymers $[\text{Me}(\text{Ph})\text{PN}]_x[\text{Me}_2\text{PN}]_y$, **10**, are very different from the homopolymers. Thus, the derivatization of the copolymers allows for further variation and control of the ultimate properties of the poly(alkyl/arylphosphazene) derivatives. Indeed, both the silylated, **19**, and carboxylated, **20**, copolymer derivatives have very different solubilities relative to the homopolymer derivatives. For example, the silyl derivatives are partially soluble in hexane and both the 50% substituted acid and the lithium salt of the 25% substituted acid are water soluble.



Derivatives from Electrophilic Aromatic Substitution. Finally, some electrophilic aromatic substitution reactions of the phenyl group in $[\text{Me}(\text{Ph})\text{PN}]_n$ are under investigation. We have found that simple acylation reactions are complicated by chain degradation, presumably due to the production of HCl in many procedures. However, the phenyl group on the polymer can be nitrated by treatment with $\text{HNO}_3/\text{H}_2\text{SO}_4$ (**21**). Subsequent reduction of the nitro group with NaBH_2S_3 affords the amino derivative **22**. Conversion of the amine to an amide (**23**) provides information on the degree of nitration via simple ^1H NMR spectroscopy.



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Scientific Personnel and Degrees Earned

Southern Methodist University	Texas Christian University
Patty Wisian-Neilson (PI) Mary Alice Schaefer (grad. stud.) M. S., 1989 Krishan Raguveer (post-doc.) S. Ganapathaippan (post-doc.) M. Safiqul Islam (post-doc.) LiMing Huang (post-doc.) Tao Wang (grad. stud.) M.S., 1990 M. Quamrul Islam (post-doc.)	Robert H. Neilson (PI) Chris Wood (grad. stud.) anticipated Ph. D. degree date, Spring 1992 David Jinkerson (grad. stud.) Ph. D., 1989 S. Karthikeyen (post-doc.) Remy Samuel (grad. stud.) Kavi Azimi (grad. stud.)

Report of Inventions

R. H. Neilson and C. E. Wood, "New Preparation Methods of Phosphazene Polymers"

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