

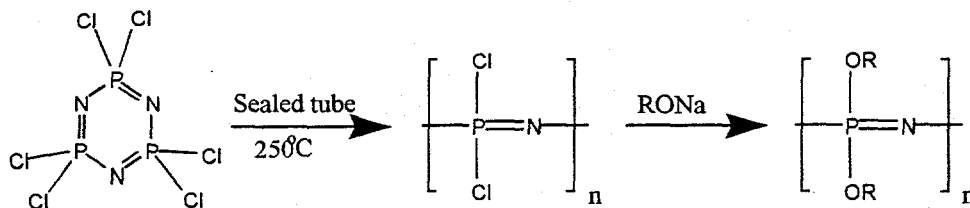
SYNTHESIS AND CHARACTERIZATION OF POLYPHOSPHAZENE COPOLYMERS USING PHOSPHORUS-31 NMR SPECTROSCOPY

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Introduction

Numerous syntheses of polyphosphazenes have been reported^{1,2,3}. These polymers generally are made in a two step process. First, linear poly(dichlorophosphazene) is made using either a ring opening process⁴ from the commercially available phosphonitrilic chloride trimer or is formed in a condensation process⁵. The second step is nucleophilic substitution of the back bone with the appropriate alkoxide or aryloxide^{6,7}. This pathway is unlike common organic polymers or many inorganic polymers such as siloxanes where the monomer is given the desired functionality followed by polymerization. Upon polymerization, phosphazenes are typified by an alternating phosphorus-nitrogen backbone with two halogens occupying the two available sites on the phosphorus. It is important to note that the polymer backbone experiences no electron delocalization, thus these materials are not conductive. In these experiments, the initially formed polymer is poly(dichlorophosphazene). The chlorines are highly susceptible to nucleophilic attack, thus the polymer is hydrolytically unstable. The most common method to stabilize the backbone involves treatment of the polymer with a nucleophile such as alkoxide or aryloxide.



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This two step synthetic approach affords phosphazenes unparalleled versatility with respect to physical and chemical characteristics. Uses for polyorganophosphazenes include membranes for the selective removal of organics from water⁸, organics from other organics⁹, and gas separations¹⁰. In addition, these materials have the potential to be used as flame retardants¹¹, medical devices¹² and ionic conductors¹³. The utility of these materials is dictated by the choice of pendant group.

Experimental

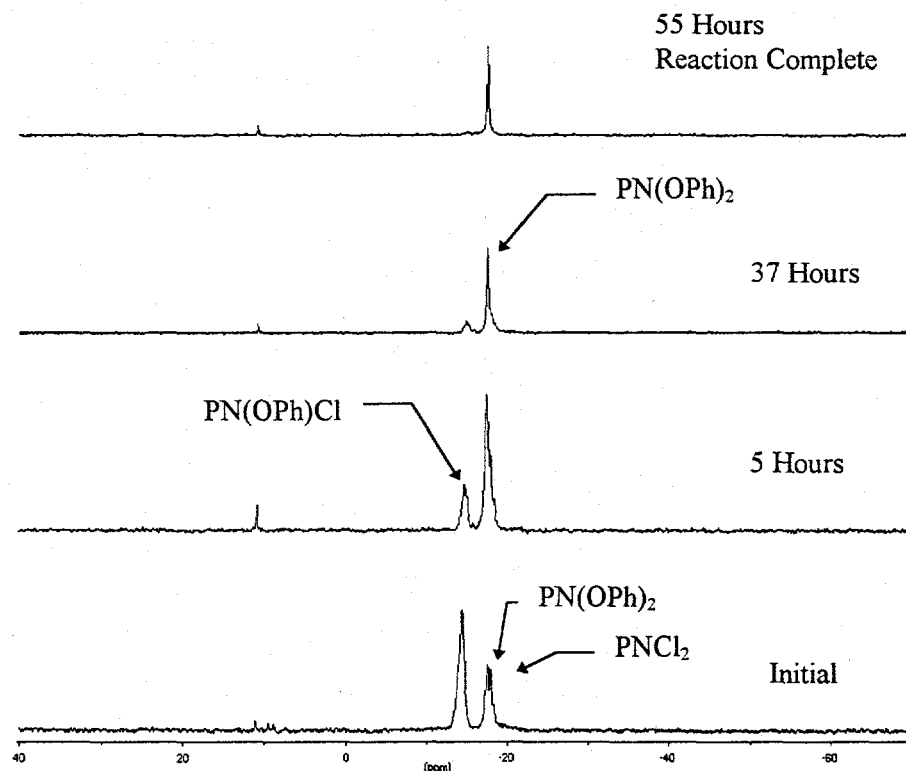
All NMR spectra were acquired using a Bruker AC300P spectrometer operating at 300 MHz (¹H) and 121.5 MHz (³¹P). All ³¹P and ¹H spectra were referenced to an external H₃PO₄ and TMS, respectively.

Poly[bis-(phenoxy)phosphazene] and the mixed substituent polymers were prepared using a modified literature procedure⁴. The general method employed was deprotonation of the appropriate phenol/alcohol using sodium hydride in anhydrous THF contained in a 1 liter 3 neck round bottom flask equipped with a mechanical stirrer. Upon completion of the deprotonation, poly(dichlorophosphazene) in anhydrous toluene was entered into the flask. To this mixture, anhydrous diglyme was added followed by heating. Removal of THF was afforded by a Dean-Stark apparatus and a constant reflux was attained at 115°C. Heating times varied for individual polymer compositions and ranged from 17 to 59 hours. Completion of the reaction was determined using phosphorus-31 NMR spectroscopy. Upon completion, the solution was allowed to cool to room temperature and was poured into methanol where the product

precipitated. This material was collected, dried, and dissolved into THF. This precipitation procedure was repeated using water and hexane to obtain white or off-white solid polymer. Yields are generally between 30 and 70 percent.

Results and Discussion

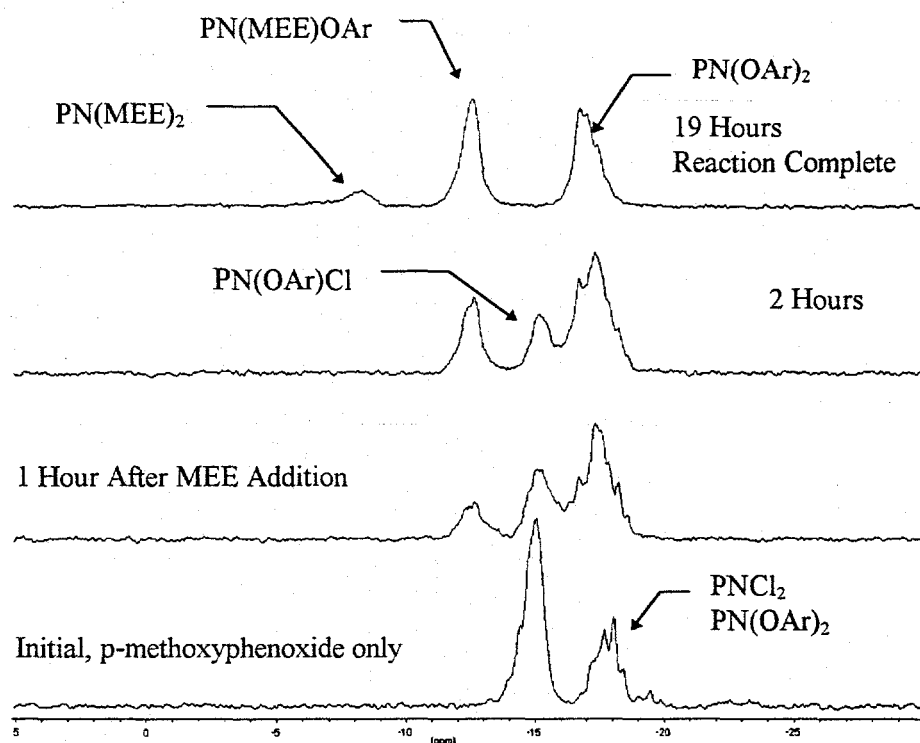
Poly[bis-(phenoxy)phosphazene] is a well characterized material and available commercially, so it was believed that this polymer would make a suitable model for studying the nucleophilic substitution process of phosphazenes by ^{31}P NMR spectroscopy. The progress of the reaction was determined by the removal of small aliquots and diluting them approximately one to one with a deuterated solvent, most commonly deuterated chloroform. The progress of the reaction is shown below.



Upon addition of the poly(dichlorophosphazene) in toluene to the phenoxide solution, the initial ^{31}P NMR spectrum yielded two envelopes that contain the three possible phosphorus species, PNCI_2 , PN(OPh)Cl , and PN(OPh)_2 . At approximately -16 ppm is a broad resonance that has been assigned to PN(OPh)Cl that appears initially and then disappears with increasing heating time. An initial ^{31}P NMR spectrum of poly(dichlorophosphazene) gave a narrow singlet at -17.8 ppm and this peak, as well as the peak assigned to poly[bis-(phenoxy)phosphazene] at -17.5 ppm form the second envelope. Upon heating, the envelope at -17.5 ppm narrows to a singlet corresponding to the conversion of the polymer to poly[bis-phenoxy)phosphazene] and the loss of bis-chlorinated phosphorus species. Smaller peaks observed at approximately 10 ppm are remaining phosphonitrilic chloride trimer substituted with phenoxide.

It is generally accepted that the physical characteristics of phosphazenes vary with the organic substitution onto the backbone. The formation of copolymers offers a higher level of physical and chemical control since the relative effects of each substituent may be balanced by stoichiometry. In this study, methoxyethoxyethanol (MEE) and p-methoxyphenol were employed as substituents. Stoichiometry was controlled during the nucleophilic substitution process. Observed ^{31}P NMR spectroscopic data are shown below.

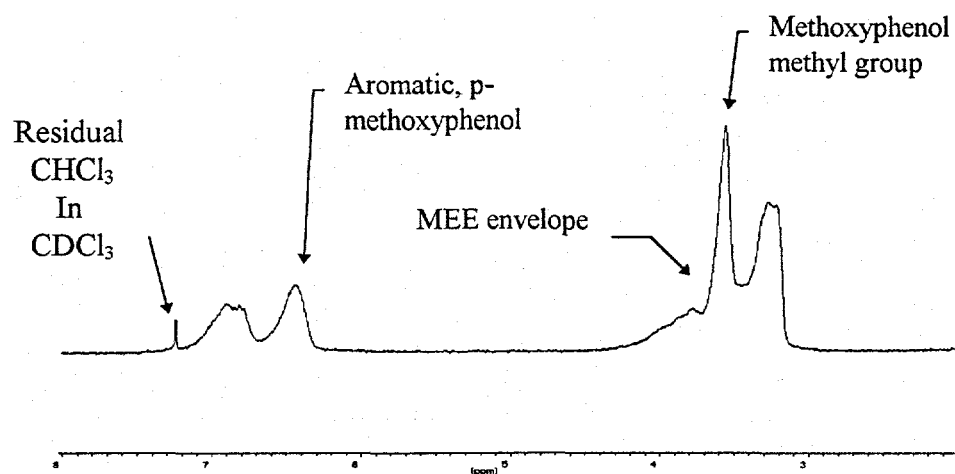
This synthesis was conducted with sequential addition of polymer and ligand. The poly(dichlorophosphazene) in toluene was initially added to an anhydrous THF solution of sodium p-methoxyphenoxide. The resulting ^{31}P NMR spectrum gave two major signals. The broad peak at -15 ppm has been assigned to PN(OAr)Cl , where $\text{Ar} = \text{p-methoxyphenol}$, while the envelope from -17 to -19 ppm has been assigned to PN(OAr)_2 and PNCI_2 . Subsequent addition of MEE salt in anhydrous THF followed by heating gave additional peaks at -8.3 and -12.6 ppm. The -12.6 ppm peak has been assigned to PN(MEE)OAr . The peak at -8.3 ppm has been assigned to PN(MEE)_2 in agreement with literature values.



An additional experiment was performed where the order of addition was reversed, the MEE was exposed to poly(dichlorophosphazene) prior to the sodium p-methoxyphenoxide. The chemical shift for the expected $\text{PN}(\text{MEE})\text{Cl}$ species falls at -12.0 ppm and is obscured in this experiment by $\text{PN}(\text{MEE})\text{OAr}$.

Distributions of ligands on the backbone can be determined using integratable NMR methods. Curve fitting (Lorentzian) deconvolutions of the ^{31}P spectrum obtained at 19 hours suggests that 31% of the backbone sites are substituted with MEE with the remaining 69% being p-methoxyphenol. This data agrees favorably with data obtained from the corresponding ^1H NMR spectrum, see below.

^{31}P NMR spectroscopy allows not only the relative ratios of pendant groups to be determined but speciation of phosphorus as well. This is of particular advantage when comparing synthetic methods. Relative nucleophilicities of the pendant aryl/alkyl oxides may be assessed. Two separate experiments in addition to the synthesis outlined here were conducted and are detailed in the tables below. A preference was evident in all of the experiments for the formation of bis-aryloxy phosphorus centers, contrary to what would be expected from the slightly more sterically bulky phenoxide as compared to MEE.



Phosphorus Speciation as Determined by ^{31}P NMR Spectroscopy

<i>Synthesis method</i>	$\% \text{PN}(\text{MEE})_2$	$\% \text{PN}(\text{OAr})\text{MEE}$	$\% \text{PN}(\text{OAr})_2$
OAr followed by MEE	11	41	48
MEE followed by OAr	21	40	39
$(\text{PNCl}_2)_n$ added to mixed nucleophiles	13	25	62

Percent Organic Substitution on the Polymer Backbone

<i>Synthesis method</i>	<i>% MEE</i>	<i>% OAr</i>
OAr followed by MEE	31	69
MEE followed by OAr	41	59
(PNCl ₂) _n added to mixed nucleophiles	26	74

The percent ligand data suggest a predominance of the first nucleophile added in the two sequential additions. These syntheses were conducted with a 10% excess of each nucleophile so variance in the percentages are reasonable.

In conclusion, it has been observed that competitive nucleophilic addition processes may be observed by ³¹P NMR spectroscopy. In this instance, MEE and p-methoxyphenol readily substitute for chlorine onto phosphorus and the relative rates are generally comparable to each other. Sterically, the phenol presents is slightly larger than MEE but this does not appear to effect substitution judging by the observed PN(OAr)₂ NMR signal. Further study of these processes is on-going and will be reported on in a later report.

Acknowledgements

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