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Synthesis and Characterization of Cyclic and Linear Phosphazenes with Phosphorus-Sulfur Linkages

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INTRODUCTION

Recent research at the INEEL has focused on the versatility inherent in polyphosphazene chemistry to membrane separations involving water transport through polymer materials.¹ Polyphosphazenes, a hybrid organic and inorganic polymer, have been shown to be effective membranes in gas separation² and liquid pervaporation applications.³ These characteristics are due to the inorganic nature of the backbone that provides these materials with remarkable chemical and mechanical stability. Additionally, phosphazene materials can be tailored to specific applications depending on the type of pendant groups that are attached to the phosphorus atoms of the backbone.

Linear polyphosphazenes are generally synthesized by a two-step process: First, linear polydichlorophosphazene is generated either through a thermal ring opening polymerization⁴ of commercially available hexachlorocyclotriphosphazene or via a condensation process.^{5,6} The second step is nucleophilic substitution of the backbone with the appropriate organic nucleophiles (Figure 1).^{4,7,8}

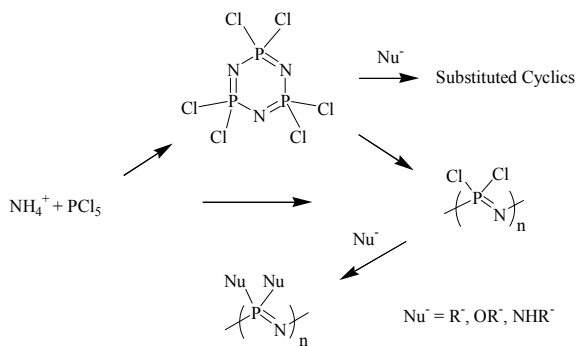


Figure 1. General synthetic route for the formation of substituted polyphosphazenes or cyclic phosphazene trimers.

Hydrophilic pendant groups, such as 2-(2-methoxyethoxy)ethanol, impart this character onto the polymer where hydrophobic pendant groups, such as phenols and perfluorinated alcohols, conversely, make the polymer insoluble in water. The nature of the pendant groups has a dominant effect on the final properties of the polymer. However, the overall solubility characteristics in these polymers are strongly influenced by the inorganic backbone coupled with the P–O linkages of the alkyloxy and aryloxy pendant groups. A logical approach to effectively change the inherent solubility properties of these polymer matrices is by utilizing pendant groups such as thiols, that have sulfur linkages instead of oxygen linkages directly to the backbone phosphorus atoms.

EXPERIMENTAL

General. NMR data were acquired on a Bruker DMX 300WB spectrometer operating at 300.13 MHz (¹H), 121.49 MHz (³¹P), or 75.78 MHz (¹³C) and referenced internally to TMS (¹H and ¹³C) or externally to H₃PO₄ (³¹P). The materials for study by NMR spectroscopy were prepared as dilute solutions using CDCl₃ (Cambridge Isotope Laboratories) as the solvent. Hexachlorocyclotriphosphazene (Strem Chemicals, Inc.) was purified by sublimation prior to use. Tetrahydrofuran (anhydrous, 99.9%) 1-hexanethiol, 4-picoline (Aldrich Chemical Co.), and acetic acid

(Mallinckrodt Baker, Inc.) were used as received. Toluene (Aldrich Chemical Co.) was distilled prior to use.

Thermal Analysis. Glass transition temperatures were determined using a TA Instruments Model 2910 Differential Scanning Calorimeter.

Synthesis of Hexakis(hexanethio)cyclotriphosphazene (1). A flame-dried, three-neck, 1 L round bottom flask, equipped with a water condenser, magnetic stir bar, and a pressure equalizing addition funnel, was charged with hexachlorocyclotriphosphazene (10.0 g, 28.8 mmol) and 1-hexanethiol (30.2 g, 255 mmol). Cyclohexane (200 mL) was added and the mixture was stirred under a flow of nitrogen for 30 minutes. 4-Picoline (35 mL, 360 mmol) was slowly added to the reaction mixture (over 10 min) from the addition funnel. The reaction mixture was then heated at reflux for one week. The 4-picoline was removed by washing the reaction mixture with aqueous acetic acid (75%, 3 x 200 mL). The organic layer was separated and dried *in vacuo* resulting in clear orange oil.

Synthesis of Poly[bis(hexanethio)phosphazene] (2). A flame-dried, three-neck, 2 L round bottom flask, equipped with a water condenser, mechanical stirrer, and a pressure equalizing addition funnel, was charged with polydichlorophosphazene (18.7 g, 161 mmol) and 1-hexanethiol (60.3 g, 511 mmol). Toluene (500 mL) was added and the solution was stirred under a flow of nitrogen for 30 minutes. 4-Picoline (50 mL, 510 mmol) was slowly added to the reaction solution (over 5 min) from the addition funnel. The reaction mixture was then heated at reflux for three days. The 4-picoline was removed by washing the reaction mixture with aqueous acetic acid (80%, 400 mL). The organic layer was separated and dried *in vacuo* resulting in clear orange gum (39.8 g, 88%). DSC *T_g* = –113 °C.

RESULTS AND DISCUSSION

Linear polyphosphazenes containing pendant groups with sulfur linkages to the phosphorus nuclei on the polymer backbone are relatively unknown.^{9,10} To investigate the feasibility of generating the thio-substituted polyphosphazenes, several synthetic methods were first explored for the generation of a hexanethiol-substituted cyclotriphosphazene, hexakis(hexanethio)cyclotriphosphazene (1). The initial route employed elemental sodium as a base, as it is well known in the literature to be effective for nonthio analogues. The sodium metal was used to generate sodium hexanethiolate to react with hexachlorocyclotriphosphazene following well-established procedures.⁷ The ³¹P NMR spectra of the resulting reaction products were indicated a multitude of phosphorus containing products with varying degrees of substitution. Isolation of 1 was not achieved from these reaction mixtures.

Our second route used sodium hydride (NaH) to generate the sodium hexanethiolate and this produced more favorable results. The reaction was quenched by precipitation into water, neutralized, and placed into a separatory funnel. The organic layer was collected and distilled *in vacuo* to separate the phosphorus containing compounds. Separation of the phosphorus compounds through reduced pressure distillation was not successful. However, the isolation and purification of thio-substituted polyphosphazenes is expected to rely on solubility differences and not distillation.

This methodology was then used for the attempted formation of the thio-substituted polyphosphazene, poly(bis-hexanethiophosphazene) (2). Freshly sublimed hexachlorocyclotriphosphazene was heated in a sealed, evacuated glass reaction vessel at 250 °C for approximately 24 hours to generate the polydichlorophosphazene. Upon cooling, the polydichlorophosphazene was dissolved in tetrahydrofuran (THF) and slowly added to a THF solution of sodium hexanethiolate. The ³¹P NMR spectra of the resulting reaction mixture showed several broad resonances indicating complete degradation of the phosphazene material by this synthetic route.

It was now clear that methods established for the synthesis of polyphosphazenes with alkyloxy and aryloxy pendant groups would not work for the thio analogues. Earlier work at the INEEL exploring the generation of polymer precursors reported the syntheses and characterizations of several substituted cyclic trimers and cyclomatrix

materials by a one-step nucleophilic substitution method.¹¹⁻¹³ In these reactions, hexachlorocyclotriphosphazene was reacted with hydroquinone, methyl-, or *tert*-butylhydroquinone in cyclohexane with pyridine or 4-picoline as a base to absorb HCl that was generated during the reaction. Based on this past research synthesizing cyclomatrix materials, an alternate route was explored utilizing this reaction method for the generation of thio-substituted cyclic trimers and polyphosphazenes.

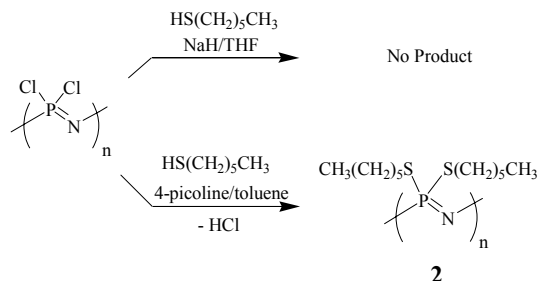


Figure 2. Synthetic routes for the formation of poly[bis(hexanethio)phosphazene] (**2**) from polydichlorophosphazene.

Adapting this procedure to our initial thio-substituted cyclic trimer target species, **1**, 4-picoline was slowly added to a cyclohexane solution of 1-hexanethiol and hexachlorocyclotriphosphazene. The reaction mixture was heated and monitored by ³¹P NMR spectroscopy for a period of seven days. At this point, the reaction mixture was cooled to room temperature and the product was collected in the organic layer after the addition of an aqueous acetic acid solution. The ³¹P NMR spectrum of the product exhibited one major resonance.

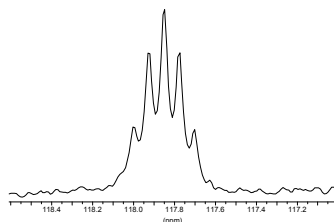


Figure 3. ³¹P NMR spectrum of poly[bis(hexanethio)phosphazene].

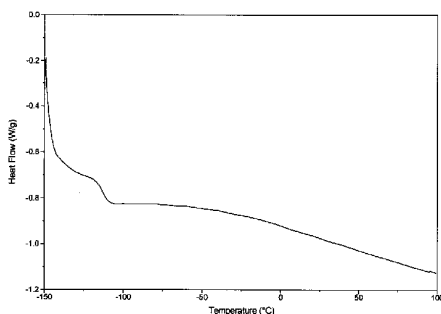


Figure 4. DSC graph of poly[bis(hexanethio)phosphazene] indicating a glass transition temperature (T_g) = -113 °C.

The 4-picoline route was then employed for the generation of **2** (Figure 2). For this reaction, 4-picoline was slowly added to a toluene solution of polydichlorophosphazene and 1-hexanethiol. The reaction was heated at reflux for a period of four days. Aqueous acetic acid was added to the solution and the product was collected by vacuum distillation of the organic layer (88% yield). The ³¹P NMR spectrum exhibited a major resonance (> 90%) with a 3-bond phosphorus-proton coupling of 8.8 Hz (Figure 3). The ³¹P, ¹³C, and ¹H NMR data are

consistent with the structure assignment of the product as poly[bis(hexanethio)phosphazene]. Thermal analysis data of **2** indicate an amorphous material above the glass transition temperature over the temperature range studied (Figure 4).

CONCLUSIONS

Utilizing synthetic methods that were developed for the generation of cyclic trimers and cyclomatrix materials, preliminary research has shown a viable method for synthesizing new thio-substituted polyphosphazenes. The thio-substituted polyphosphazene was unobtainable via well-established synthetic routes for the alkyloxy and aryloxy substituted analogues. Research is ongoing generating new thio-substituted phosphazene materials for the development of membranes for gas separation, liquid pervaporation, and other applications.

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