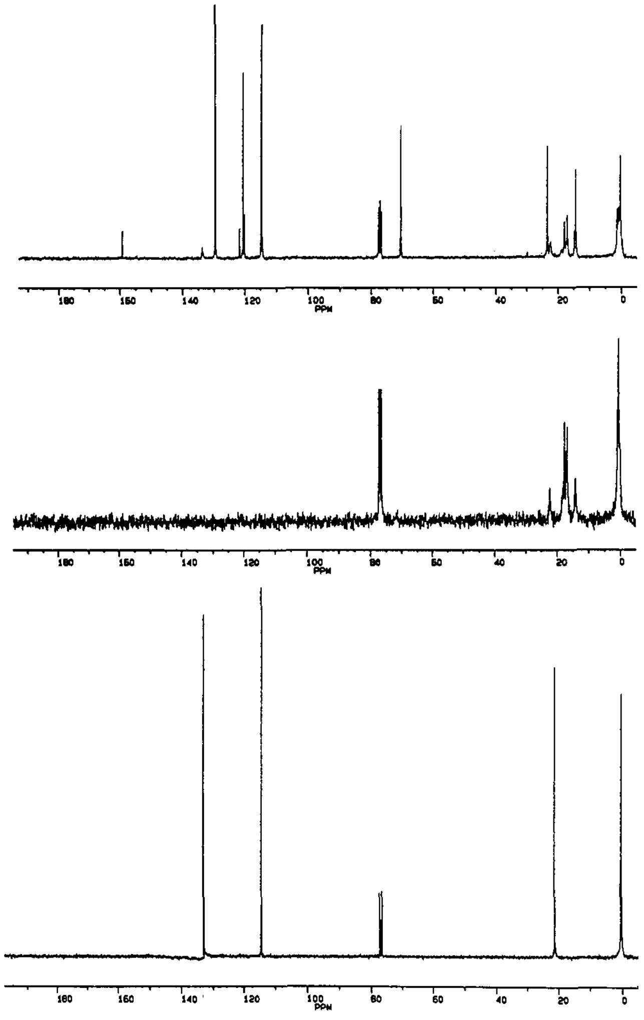
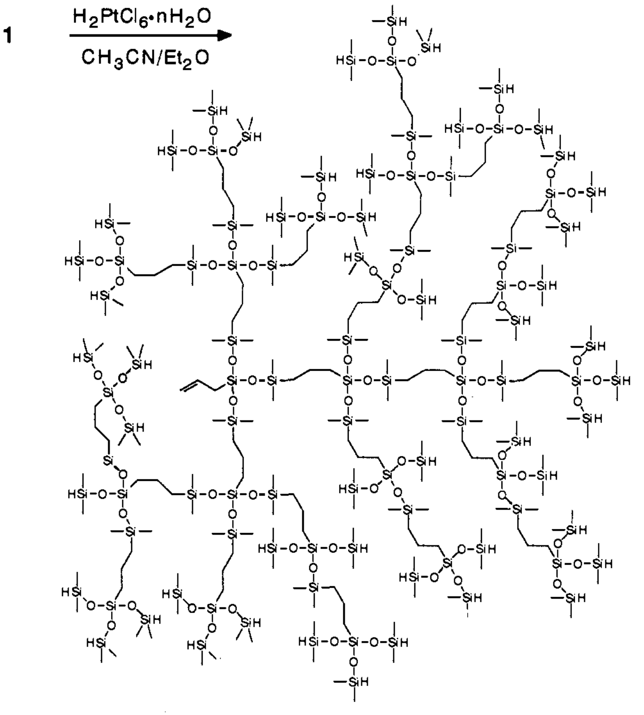


Figure 1. ^{13}C NMR spectra (in $CDCl_3$) of monomer **1** (bottom trace), polymer **2** (middle trace), and end-capped polymer **3** (top trace).



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2 gradually became insoluble due to coupling of Si–H bonds through Si–O–Si formation.[9] Reaction of fresh **2** with allyl phenyl ether as end capper[10] gave polymer **3**. ^{13}C NMR spectra ($CDCl_3$) of **1**, **2**, and **3** confirm polymer formation (disappearance of alkenes) and end capping (appearance of aromatic and CH_2–O peaks without associated allyl ether peaks) (Figure 1). Alternative addition of an allyl-terminated oligomer of oxyethylene gave material with a hydrophobic core and hydrophilic exterior.

The one-pot polymerization and end-group reaction have been repeated several times to confirm facility of formation of terminally derivatized hyperbranched polymers. This approach makes available single-molecule structures with tailored interior and exterior functionality.

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Poly(thionylphosphazenes): A New Class of Inorganic Polymers with Skeletal Phosphorus, Nitrogen, and Sulfur(VI) Atoms

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The synthesis of new inorganic and organometallic polymers is attracting considerable current attention because these macromolecules often provide access to physical, chemical, preceramic, or biomedical properties that are difficult or impossible to achieve with conventional organic systems.[1] In principle, the ring-opening polymerization of cyclic inorganic compounds offers an attractive route to new macromolecular species. However, to date, relatively few examples of the successful use of this approach have been reported.

Cycloheterophosphazenes are an interesting class of inorganic species which are formally derived from the well-studied, polymerizable cyclic phosphazenes by the replacement of a skeletal phosphorus atom by an atom of a heteroelement.[2] Many examples of these small-molecule compounds are now known, and in the last two years the successful polymerization of species with skeletal carbon, molybdenum, or tungsten atoms to yield stable macromolecular products has been described.[3,4] Most recently, the ring-opening polymerization of a cyclic thiophosphazene (**1**) which contains a skeletal sulfur(IV) atom was reported.[5] However, in

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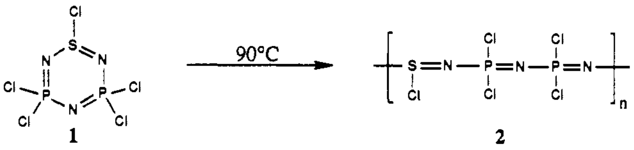
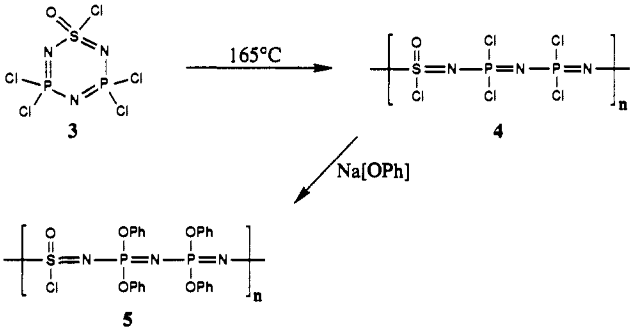


this case, the sulfur–nitrogen bonds present in the poly(thiophosphazene) backbone appear to possess intrinsic hydrolytic sensitivity, and to date, reasonably stable polymers have only been isolated when very bulky side-group substituents are present.[5] We report here our preliminary studies of the polymerization behavior of the cyclic thionylphosphazene **3** which contains a skeletal, high oxidation state sulfur(VI) atom. Cyclic species such as **3** have been known for over 15 years, but to our knowledge, no polymerization studies have been reported.[6] Furthermore, from literature reports, many cyclothionylphosphazenes appear to show much greater stability toward hydrolysis compared to their sulfur(IV) analogues.[6]



When the white, crystalline cyclothionylphosphazene **3**[7] was heated at 165 °C for 4 h in an evacuated Pyrex tube, a marked increase in viscosity was noted. Analysis by ^{31}P NMR showed the products to consist of unreacted **3** (ca. 20%) and the poly(thionylphosphazene) **4** (ca. 80%).[8] The ^{31}P NMR spectrum of **4** (in CH_2Cl_2) comprised a singlet resonance at −10.0 ppm which is significantly shifted to higher field compared to that of **3** (δ = 26.5 ppm). Similar high-field shifts of the ^{31}P NMR resonance are observed for the polymerization of other heterophosphazenes and also classical cyclic phosphazenes.[5] Polymer **4** can be isolated as a pale yellow, hydrolytically sensitive, elastomeric material by precipitation from CH_2Cl_2 into dry hexanes. Additional characterization of **4** was achieved by elemental analysis, which was consistent with the assigned structure, and infrared spectroscopy, which showed strong absorptions characteristic of S=O, P=N, and S=N vibrations.[9]

Because of the sensitivity of **4** to moisture, we have attempted to replace the chlorine substituents by aryloxy side groups. This strategy leads to stable polymers in the case of both poly(carbophosphazenes) and classical poly(phosphazenes).[3,10] Reaction of **4** with excess sodium phenoxide (dioxane, 25 °C, 6 h) afforded a new polymeric product **5**, which was isolated as a colorless, elastomeric material by precipitation into water (twice) and hexanes (once). Polymer **5** was characterized by ^{31}P, ^{13}C, and ^{1}H NMR spectroscopy, infrared spectroscopy, elemental analysis, and gel permeation chromatography (GPC).[11] The ^{31}P NMR spectrum of **5** (in dioxane) showed a single, singlet resonance at −21.5 ppm which is significantly shifted from that of **4** (δ = −10.0 ppm) and is consistent with the complete replacement of the chlorine atoms at phosphorus and, possibly, also at sulfur. The situation was clarified by the ^{13}C NMR spectrum of **5**, which showed only one set of resonances for the phenoxy groups, which indicated that no substitution of the chlorine atoms at sulfur had taken place. By contrast, poly[(aryloxy)carbophosphazenes] which possess aryloxy substituents at both phosphorus and carbon show two sets of ^{13}C NMR aryloxy group resonances.[3] Further evidence for the assigned structure of **5** involving phenoxy substituents at phosphorus and an unsubstituted chlorine atom at sulfur was provided by elemental analysis.[11] Gel permeation chromatography confirmed the polymeric nature of **5** and indicated a weight-average molecular weight (M_w) of 30 500 and a number-average molecular weight (M_n) of 16 030.[12] Polymer **5**, which appears to be indefinitely stable to atmospheric moisture, represents the most stable example of a macromolecule with a sulfur–nitrogen–phosphorus main chain reported to date.[13] This suggests that the sulfur–chlorine bond present in **5** possesses a reactivity similar to that observed for carbon–halogen bonds in, for example, poly(vinyl chloride).

Remarkably, the regiospecific nucleophilic substitution detected for **4** involving the replacement of the chlorine atoms bonded to phosphorus rather than those at sulfur is in stark contrast to the behavior of the sulfur(IV) analogue, the poly(thiophosphazene) **2**, where nucleophilic substitution takes place preferentially at sulfur.[5] This indicates that changing the oxidation state of a skeletal heteroatom (sulfur) in an inorganic macromolecular intermediate can reverse the observed regiospecificity with respect to nucleophilic substitution reactions. The higher reactivity of the phosphorus–chlorine bonds of cyclothionylphosphazenes toward certain nucleophiles has been previously noted[6] and was confirmed in our studies of the reactions of the small molecule **3** with sodium aryloxides. For example, reaction of **3** with excess sodium phenoxide at room temperature (dioxane, 24 h) yielded mainly $NSOCl\{NP(OPh)_2\}_2$ (**6**), and the complete formation of the fully substituted species $NSO(OPh)\{NP(OPh)_2\}_2$ (**7**) was only achieved at elevated temperatures (dioxane, 60 °C, 24 h).[14,15]

The stability of **5** to hydrolysis and the observed regiospecific substitution of polymer **4** represent highly encouraging results in the development of this new inorganic polymer system. Further studies directed at the synthesis and properties of poly(thionylphosphazenes) are in progress.

Acknowledgment. We thank the University of Toronto for financial support.

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(7) Compound **3**, can be prepared in a number of ways (see ref 6). In this preliminary work, a low-yield, two-step procedure involving the reaction of PCl_5 with NH_4Cl to give $[Cl_3P{=}N{=}PCl_3][PCl_6]$ followed by a (3 + 3) cyclocondensation with $H_2NSO_2NH_2$ was used (see: Klingebiel, U.; Glemser, O. *Z. Naturforsch.* **1972**, *27b*, 467). As a result of our successful polymerization of **1**, more convenient routes to this compound are under active investigation in our laboratory.

(8) When heated for extended periods at 165 °C, polymer **4** will cross-link and become insoluble. Similar behavior is observed with poly(dichlorophosphazene) at 250 °C.

(9) For polymer **4**: IR (film) 1307 (vs, ν(S=O)), 1193 (vs, br, ν(P=N)), 1136 (vs, br, ν(S=O)), 733 cm^{-1} (s, ν(S=N)). Anal. Calcd: N, 12.76; Cl, 53.83. Found: N, 12.56; Cl, 56.95. We attribute the significant error in the elemental analysis to the fact that this hydrolytically sensitive, adhesive, elastomeric material is extremely difficult to handle and purify. The elemental analysis of the hydrolytically stable polymer **5** (footnote 11) is probably more accurate as this polymer could be repeatedly precipitated into water and hexanes to remove both polar and nonpolar impurities.

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(11) For polymer **5**: yield 45%; ^{31}P NMR (in dioxane) δ = −21.5 ppm; ^{13}C NMR (in $CDCl_3$) δ = 150.6 (ipso-C), 121.1 (o-C), 129.5 (m-C), 125.2 ppm (p-C); ^{1}H NMR (in $CDCl_3$) δ = 6.98 ppm, br, (OPh); IR (film) (selected peaks) 1300 (s, ν(S=O)), 1194 (vs, br, ν(P=N)), 1161 (vs, ν(CO)), 1137 (sh, ν(S=O)), 952 cm^{-1} (vs, ν(PO)). Anal. Calcd: C, 51.48; H, 3.60; N, 7.50; Cl, 6.33. Found: C, 51.70; H, 3.61; N, 7.46; Cl, 5.68. GPC: M_w = 30 500, M_n = 16 030, polydispersity = 1.90. All NMR chemical shifts are relative to 85% H_3PO_4 (^{31}P), $CDCl_3$ (^{13}C), or TMS (^{1}H).

(12) GPC data were recorded in THF relative to polystyrene standards and are therefore considered estimates.

(13) Polymer **5** shows no sign of decomposition by ^{31}P NMR or GPC after several months of exposure to the atmosphere in the solid state or after 1 month in a 10% solution of water in dioxane at room temperature.

(14) For **6**: ^{31}P NMR (dioxane) δ = 3.5 ppm; MS theory 559, found 559. For **7**: ^{31}P NMR (dioxane) δ = 4.8 ppm; MS theory 617, found 617. Small amounts of **7** are formed in addition to **6** in the room temperature reaction.

(15) Preliminary attempts to substitute the chlorine atom at sulfur in polymer **5** by reaction with aryloxide nucleophiles at elevated temperatures (65 °C in dioxane) appear to lead to degradation of the polymer backbone according to ^{31}P NMR and GPC measurements.