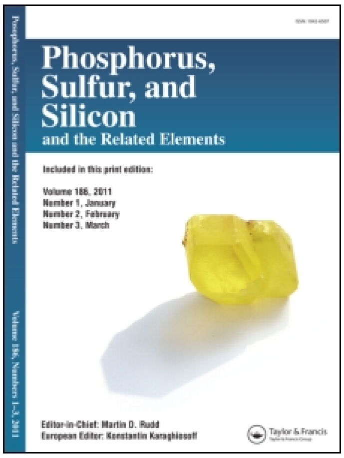

Phosphorus, Sulfur, and Silicon and the Related Elements

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Rings, Polymers, and New Materials Containing Phosphorus and Other Main Group Main Elements or Transition Metals

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RINGS, POLYMERS, AND NEW MATERIALS CONTAINING PHOSPHORUS AND OTHER MAIN GROUP ELEMENTS OR TRANSITION METALS

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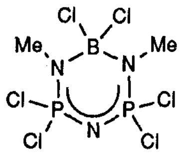
Abstract Polymers which contain inorganic elements are attracting considerable attention because they provide access to materials with interesting, unusual and potentially useful properties. In this paper we emphasize some of our recent work aimed at exploiting ring-opening polymerization as a route to new inorganic and organometallic polymers containing the main group element phosphorus.
For example, attempts to prepare new polymers which also contain boron are reported. In addition, recent results on the ring-opening polymerization of [1]-metallocenophanes such as cyclic ferrocenylsilanes and cyclic ferrocenylphosphines, which possess strained ring-tilted structures, are described. Finally, some recent research on poly(thionylphosphazenes), a novel class of inorganic polymers with sulphur(VI)-nitrogen-phosphorus backbones, is discussed.

INTRODUCTION

Polymers which contain inorganic elements as part of the main chain structure are of considerable interest because of their unusual properties and potential applications.[1] As part of our program aimed at exploring the synthesis, material properties, and applications of new classes of inorganic or organometallic macromolecules we are investigating the preparation of polymers via ring-opening polymerization. In this paper we discuss some of our recent work on polymers containing phosphorus.

POLYMERIZATION BEHAVIOR OF RINGS CONTAINING BORON, NITROGEN, AND PHOSPHORUS ATOMS

One of the exploratory projects in our group involves an investigation of the polymerization behavior of inorganic heterocycles which contain boron atoms. For example, species such as **1** are readily available from the reaction of $[Cl_3P{=}N{=}PCl_3][BCl_4]$ with $[MeNH_3]Cl$.[2] When heated in the melt at elevated temperatures a polymeric material is formed. However, analysis of the reaction products has shown that the polymer is the classical polyphosphazene $[NPCl_2]_n$ and that the boron atom is extruded. The isolated boron containing product is the borazine **2** which was identified by ^{11}B NMR and mass spectrometry. A possible sequence of events which would explain the isolated products involves the elimination of methyl chloride followed by extrusion of the iminoborane $ClB{\equiv}NMe$[3] which subsequently cyclotrimerizes to **2** in the condensed phase.[4] This would generate a $[NPCl_2]_2$ fragment which would almost certainly be expected to polymerize as this cyclic is unknown and would be highly strained. We are investigating the mechanism of this reaction by thermogravimetric analysis-mass spectrometry (TGA-MS) in order to detect reactive intermediates.



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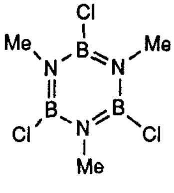
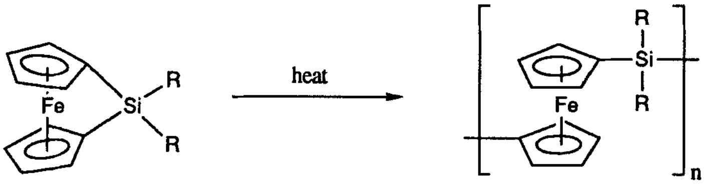


2

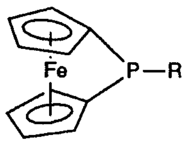
RING-OPENING POLYMERIZATION OF [1]-FERROCENOPHANES

We have recently discovered a novel, ring-opening route to the first examples of high molecular weight poly(ferrocenylsilanes) which possess an unusual main chain comprising ferrocene units and silicon atoms.[5] Thus, cyclic ferrocenylsilanes such as **3** (R = Me) polymerize thermally in the melt at 130 - 200°C to yield soluble polymers **4** which readily form free-standing amber films when cast from solvents such as toluene or THF. Based on the facile polymerization of **3** we have investigated the polymerization behaviour of [1]ferrocenophanes which contain atoms in the bridge other than silicon.



3 **4**

Cyclic ferrocenylphosphines such as **5** are accessible via the reaction of dilithioferrocene.tmeda (tmeda = tetramethylethylenediamine) with dichloroorganophosphines. When heated in the melt compound **5** (R = Ph) rapidly polymerizes to yield the poly(ferrocenylphosphine) **6**. Polymer **6** (R = Ph) has been previously prepared by Seyferth et al by using condensation procedures.[6] We have attempted to generalize our ring-opening route by synthesizing **5** (R = Cl) from dilithioferrocene.tmeda and PCl_3. Preliminary results show that **5** (R = Cl), which has been crystallographically characterized, will react to give a variety of compounds of general structure **5** by chlorine replacement.[7] This general approach to potential cyclic ferrocenylphosphine polymerization monomers avoids the use of malodorous and toxic species of type $RPCl_2$.



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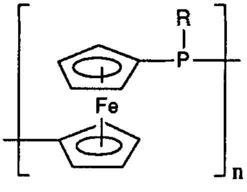
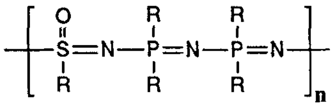


6

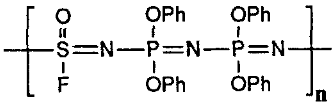
POLY(THIONYLPHOSPHAZENES)

Recently, we reported the synthesis of the first examples of poly(thionylphosphazenes) **7**, which possess backbones of sulfur(VI), nitrogen, and phosphorus atoms.[8] Even though the polymers are at a very early stage of development, unusual and unique features in the chemistry and material properties are already emerging.[8,9] Thus, the ability exists to regiospecifically tune the poly(thionylphosphazene) microstructure for **7** (R = Cl) by exploiting the differential reactivity of the sulfur-halogen and phosphorus-halogen bonds towards substitution reactions. In addition, polymers with halogen substituents directly bound to the sulphur atom in the polymer backbone (eg **8**) are stable to moisture which is very unusual for inorganic polymers as bonds between halogens and inorganic elements are usually highly reactive. Furthermore, recent results indicate that poly(thionylphosphazenes) show significant differences from classical polyphosphazenes[1] in terms of material properties.[9,10]



$$\left[\overset{O}{\underset{R}{S}}=N-\overset{R}{\underset{R}{P}}=N-\overset{R}{\underset{R}{P}}=N \right]_n$$

7



$$\left[\overset{O}{\underset{F}{S}}=N-\overset{OPh}{\underset{OPh}{P}}=N-\overset{OPh}{\underset{OPh}{P}}=N \right]_n$$

8

ACKNOWLEDGEMENTS

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