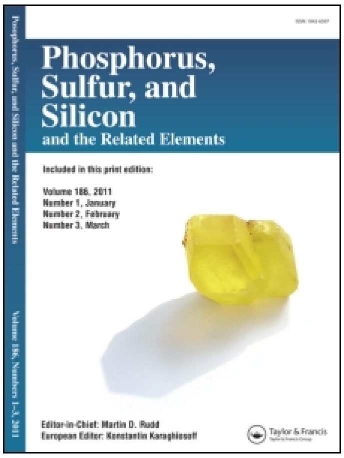

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Manners, Ian(1994) 'Ring-Opening Polymerization (ROP) as a Route to Polymers with Skeletal Transition Metal Atoms', Phosphorus, Sulfur, and Silicon and the Related Elements, 93: 1, 143 — 151
To link to this Article: DOI: 10.1080/10426509408021806
URL: http://dx.doi.org/10.1080/10426509408021806

Phosphorus, Sulfur, and Silicon, 1994, Vol. 93–94, pp. 143–151
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RING-OPENING POLYMERIZATION (ROP) AS A ROUTE TO POLYMERS WITH SKELETAL TRANSITION METAL ATOMS

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Abstract Until recently, most polymers with transition metal atoms in the main chain described in the literature were either of low molecular weight, insoluble, or only poorly characterized. In the last few years the synthesis of examples of these materials which do not suffer from these defects has attracted considerable attention as a result of their potentially novel physical and chemical properties. In this article recent progress on the use of ring-opening polymerization (ROP) as a new route to high molecular weight polymers with ferrocene groups in the polymer main chain is reviewed.

INTRODUCTION

As a result of their excellent mechanical properties and processability, synthetic polymers have become a part of everyday life with a diverse and ever growing range of uses as structural materials. Over the past two decades an exciting new direction in polymer research has emerged which involves the preparation and study of organic macromolecules with novel electronic and optical properties and the potential for advanced, device-oriented applications.[1] For example, electroluminescent polymers such as poly(phenylenevinylene) (PPV) have been prepared and light emitting diodes (LEDs) successfully fabricated.[1b] The development of polymers with transition metals in the main chain structure would be expected to provide access to processable, speciality materials with novel electronic and optical properties and which would also be of interest as pyrolytic precursors to metal-containing ceramics.[2-5] However, apart from several, mainly very recent exceptions, most transition metal-based polymers reported to date are either of low molecular weight, insoluble, or of poorly defined structure. This is partly a consequence of the synthetic routes used to date to prepare these polymers which generally involve condensation polymerizations.[5] These occur by a step growth mechanism and the ratio of difunctional monomers must be close to 1:1 and conversions close to 100 % for high molecular weights to be formed. This is often very difficult to achieve for difunctional organometallic monomers (eg dilithioferrocene) as these species are often difficult to synthesize, extremely reactive, and difficult to obtain a high state of purity.

To help facilitate the development of transition metal-based polymer science we have investigated the synthesis of high molecular weight, well-defined transition metal-based polymers using ring-opening polymerization (ROP) techniques. In contrast to condensation polymerizations, ROP processes generally occur by a chain-growth mechanism which leads more naturally to higher molecular weight products. ROP represents a powerful route to organic polymers and the ROP of cyclic compounds with skeletons containing atoms of main group elements is of growing importance. In contrast, reports of the use of ROP to prepare polymers with transition elements in the main chain are extremely rare.[3b] This article focusses on recent research which has demonstrated that [n]metallocenophanes, species which contain a metallocene group with a bridge containing n contiguous atoms between the cyclopentadienyl ligands, function as precursors to a variety of well-defined high molecular weight macromolecules via ROP processes. A detailed review of work in this area which covers the literature up to the Spring of 1994 will be published in the near future.[5]

THERMAL ROP OF SILICON-BRIDGED [1]FERROCENOPHANES: SYNTHESIS AND PROPERTIES OF POLY(FERROCENYLSILANES)

Previous work on [1]ferrocenophanes **1** with a single silicon atom in the bridge has shown that they possess strained structures in which the planes of the cyclopentadienyl ligands are significantly tilted with respect to one another. In addition, these species have been shown to undergo stoichiometric ring-opening reactions. The strained, ring-tilted structure characteristic of [1]silaferrocenophanes is illustrated for **1** (R = R' = Me) in Figure 1, where the angle between the planes of the cyclopentadienyl ligands is 20.8(5)°. In contrast, ferrocene itself possesses cyclopentadienyl ligands which are parallel. In 1992 we reported the discovery that when [1]silaferrocenophanes **1** are heated in the melt thermally induced ROP occurs to yield high molecular weight poly(ferrocenylsilanes) **2** in quantitative yield.[4]

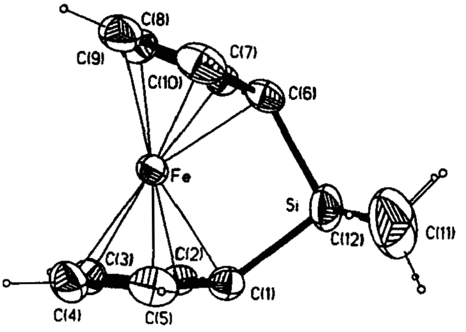
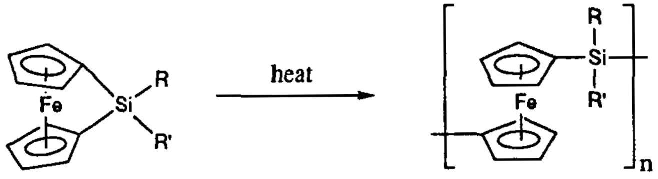


Figure 1 The Molecular Structure of **1** (R = R' = Me).

The strain energy of [1]silaferrocenophane monomers, which has been shown to be high by thermochemical measurements (ca 80 kJmol^{-1} for **1** (R = R' = Me)), provides the driving force for the ROP process. Furthermore, because the strain energy is large, even [1]silaferrocenophanes **1** with bulky substituents such as ferrocenyl, phenyl, and norbornyl at silicon undergo ROP to yield high molecular weight products. This provides a route to a large selection of poly(ferrocenylsilanes). Detailed studies of polymers which have been symmetrically[6] or unsymmetrically[7] substituted at silicon have been published.



1 **2**

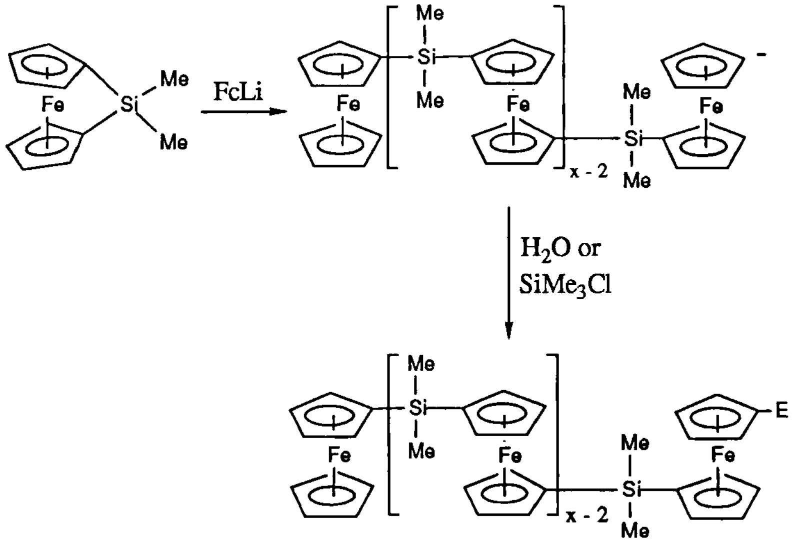
Poly(ferrocenylsilanes) can be glassy, thermoplastic, or elastomeric depending on the side groups present. If long flexible side groups are present (eg $C_{18}H_{37}$) these can also crystallize.[5-7]

Because the poly(ferrocenylsilane) main chain contains transition metal atoms held in fairly close proximity, the electrical properties of poly(ferrocenylsilanes) are of considerable interest and have therefore been studied in some detail. In polymers such as poly(vinylferrocene), which possess electroactive ferrocenyl side groups, the iron centers are essentially non-interacting and a single reversible oxidation wave is detected by cyclic voltammetry. In contrast, poly(ferrocenylsilanes) **2** possess two reversible oxidation waves which has been attributed to interactions between the iron centers present.[3b,4,8,11b]

Poly(ferrocenylsilanes) have also been shown to function as precursors to interesting metal-containing ceramic products. In this area we have found that poly(ferrocenylsilanes) yield interesting, ferromagnetic iron silicon carbide materials when pyrolyzed at 500°C and also novel oligomeric depolymerization products.[9]

ANIONIC ROP OF SILICON-BRIDGED [1]FERROCENOPHANES

The ROP of silicon-bridged [1]ferrocenophanes can also be initiated in solution using anionic initiators such as alkyllithium reagents. Polymer molecular weights (M_w) up to ca 75,000 can be achieved by using this method by using small quantities of initiator. In addition, the polymerization is living which allows, for example, the control of the end groups by termination with eg $SiMe_3Cl$ or H_2O to give Me_3Si-capped or H-capped polymers, respectively (Scheme 1).



3 E = H or $SiMe_3$ x = 2 - 200

Scheme 1

SYNTHESIS, CHARACTERIZATION, AND PROPERTIES OF LINEAR OLIGO(FERROCENYLSILANES): SHORT-CHAIN MODELS FOR POLY(FERROCENYLSILANES)

Studies of short-chain oligomers would be expected to provide additional understanding of the electrical, morphological, and conformational properties of ferrocenylsilane high polymers but such species are often difficult to prepare and even more difficult to crystallize for X-ray diffraction studies. Recently we have shown that the reaction of FcLi with **1** (R = R' = Me) (mole ratio ca 0.5 - 1 : 1) in THF over 10 min at 0°C followed by warming to room temperature and a hydrolytic workup yields a mixture of proton-terminated oligomeric products **3** (x = 2 - 8) which were successfully separated by column chromatography.[10] These species were isolated as amber powders and were characterized by ^{29}Si and ^{1}H NMR and by mass spectrometry. In addition, several of these species have been successfully crystallized and their structures determined by single-crystal X-ray diffraction.[10] The molecular structures of the linear trimer **3** (x = 3) and pentamer **3** (x = 5) are shown in Figures 2 and 3, respectively. The molecular structure of **3** (x = 5) possesses a sufficient number of repeat units to provide intriguing insight into the probable conformations of polymer chains in ordered samples of the high molecular weight poly(ferrocenysilane) **2** (R = Me). The interior ferrocenylsilane repeat units possess a trans planar, zig-zag conformation with the adjacent ferrocenyl groups oriented at ca 110° relative to one another. Interestingly, the ferrocenyl end groups are twisted in opposite directions perpendicular to the plane of the interior. The sets of two methyl groups at silicon on adjacent repeat units are oriented in opposite directions (ca 180°) from one another whereas the iron atoms in the interior repeat units are approximately colinear and are separated by a relatively large distance of 6.913(5) Å. This indicates that the interactions between the iron centers detected in the electrochemistry of these polymers (see below) are more likely to be transmitted via the silicon bridge than by direct, through space interactions. Further evidence for this is provided by the observation that no interactions between iron atoms of ferrocene moieties have been detected by cyclic voltammetry in macrocyclic species with a smaller distance between the iron centers (5.9 Å).[12] The oligo(ferrocenylsilanes) **3** (x = 2 - 8) also provide excellent models for the high polymer **2** (R = Me) with respect to electrochemical properties.[10a] The electrochemistry of the oligomers **3** (x = 2 - 8) is fully consistent with this picture involving initial oxidation at alternating iron sites.

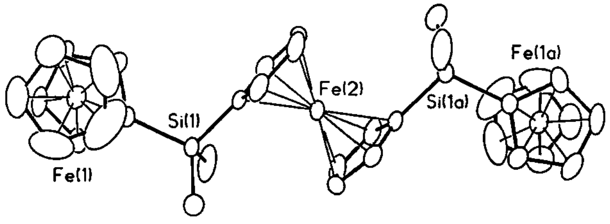


Figure 2 The Molecular Structure of 3 (x = 3)

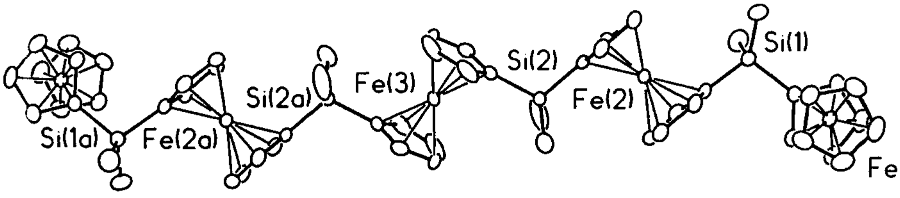
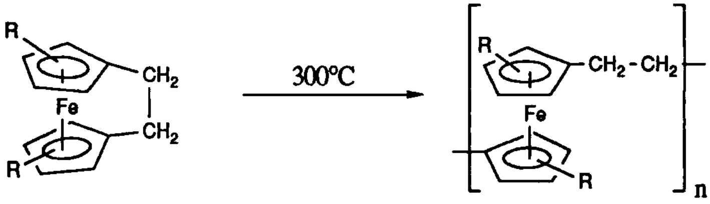


Figure 3 The Molecular Structure of 3 (x = 5)

THERMAL ROP OF OTHER [1] AND [2]METALLOCENOPHANES

The discovery of the facile thermal ring-opening polymerization of silicon-bridged [1]ferrocenophanes suggested that related species with other elements in the bridge might also polymerize.[4] We have found that [1]ferrocenophanes with either germanium or phosphorus in the bridge also undergo ROP and that cooperative interactions between the iron centers in the resulting polymers similar to those detected for their silicon analogues appear to exist.[8,11]

Although [1]ferrocenophanes with a single silicon, germanium, or phosphorus atom were found to readily polymerize, to date, our attempts to extend the ROP methodology to [2]ferrocenophanes which possess *two* silicon atoms in the bridge using either thermal or catalytic initiation have been unsuccessful. The reduced propensity for such species to polymerize has been attributed to the lower degree of ring strain present which is reflected by the very small cyclopentadienyl ring tilt-angle of only ca 4°. However, [2]ferrocenophanes with a hydrocarbon bridge 4 are significantly more strained than their disilane-bridged analogues because of the smaller size of carbon relative to silicon and these compounds can possess ring tilt-angles of ca 21°. We have found that the hydrocarbon bridged species 4 will undergo thermally-induced ROP which provided access to the first examples of well-characterized poly(ferrocenylethylenes) 5.[13] These polymers possess backbones consisting of alternating ferrocene groups and aliphatic C_2 units and are insoluble if R = H but are readily soluble in solvents such as THF if R is an organic group such as methyl.



4 **5**

Poly(ferrocenylethylenes) 5 possess ferrocene units which are separated by a longer and more insulating bridge compared to polymers derived from Si, Ge, or P-bridged [1]ferrocenophanes such as the poly(ferrocenylsilanes) 2.[8] As mentioned above, electrochemical evidence for the latter polymers is indicative of the presence of substantial cooperative interactions between the iron centres. In contrast, studies of the electrochemistry of 5 (R = Me) showed the presence of only a single reversible oxidation wave which indicated that the ferrocene groups interact to much less significant extent. Even more strained [2]metallocenophanes have been prepared by the incorporation larger ruthenium atom in the place of iron.[14] For example, we have recently prepared the first examples of [2]ruthenocenophanes and the ruthenium analogue of 3 (R = H) possesses a tilt angle of 29.6(5)°, which is the largest known to date for neutral iron group metallocenophanes. In addition, we have found that such species with hydrocarbon bridges undergo ROP more readily than their iron analogues to yield poly(ruthenocenylethylenes). In contrast, the analogous disilane-bridged [2]ruthenocenophane is resistant to polymerization. We are therefore attempting to prepare species that are more strained and we have, very recently, obtained preliminary evidence for the first [1]ruthenocenophanes.[15]

Although siloxane-bridged [3]metallocenophanes appear to be resistant to ROP, presumably as a consequence of their essentially unstrained nature, Rauchfuss et al have reported a novel atom-abstraction induced ring-opening polymerization route to poly(ferrocenylene persulfides) from [3]trithiaferrocenophanes using phosphines such as PBu_3 as desulfurization agents.[5,16]

SUMMARY

Since the first report in 1992,[4] thermal ROP has been developed as versatile route to a variety of high molecular weight transition metal-based polymers. We are now attempting to extend the ROP route still further to both related and unrelated systems whilst concentrating on detailed studies of the properties of the polymers prepared to date and mechanisms of the polymerization reactions.

ACKNOWLEDGEMENTS

Our work on the ring-opening polymerization of strained organometallic rings has been supported by the Ontario Center of Materials Research (OCMR), the ACS Petroleum Research Fund (PRF), the Institute of Chemical Science and Technology (ICST), and the Natural Sciences and Engineering Research Council of Canada (NSERC). I would also like to acknowledge and thank my very talented and enthusiastic coworkers who have carried out this research and their names are found in the references. I am also grateful to the Alfred P. Sloan Foundation for a Research Fellowship (1994-96).

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