

Ring-opening polymerization of strained metallocenophanes: a new route to high molecular weight poly(metallocenes)*

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Abstract: Ring-opening polymerization (ROP) of strained ring-tilted metallocenophanes can be achieved thermally, via anionic initiation, or by the use of transition metal catalysts and provides access to a wide range of high molecular weight ($M_w = 10^5$ – 10^6 , $M_n > 10^5$) poly(metallocenes). These materials possess a variety of interesting properties and many are very easy to prepare. This article provides an overview of our work with an emphasis on recent research directions. For example, poly(ferrocene) homopolymers have potential as novel charge dissipation materials. Poly(ferrocene) block copolymers, on the other hand, offer opportunities for the preparation of self-assembled nanoscale micellar aggregates in block selective solvents and applications as anisotropic semiconductors and as nanolithographic patterning materials (e.g. via block selective etching processes) in the solid state.

INTRODUCTION

Polymeric materials are ubiquitous because of their tremendous processing advantages over ceramics and metals. The incorporation of transition metals into a polymer main chain therefore offers unique potential for the preparation of processible materials with properties which differ significantly from those of conventional organic polymers [1,2]. In addition, the diverse range of coordination numbers and geometries which exist for transition elements offer the possibility of accessing polymers with unusual conformational, mechanical, and morphological characteristics. Transition metal-based polymers might also be expected to function as convenient and processible thermal or photochemical precursors to metal-containing ceramic films, fibers, and coatings with high stability and desirable and useful physical properties. However, the development of the area of transition metal-based polymer science has been held up by considerable synthetic difficulties [2]. Much of the early work in the field in the 1950s and 1960s targeted poly(metallocenes) [3]. Such efforts were encouraged by the remarkable stability and fascinating properties of monomeric and dimeric metallocenes which were discovered by the fundamental exploratory chemistry conducted during this period. However, most of the attempted polymer syntheses utilized polycondensation reactions where either the difunctional precursors were impure or the coupling chemistry was not clean. For such step growth processes this guaranteed the generation of low molecular weight materials ($M_n < \approx 3000$) [2]. In addition, the resulting products were often insoluble and poorly characterized.

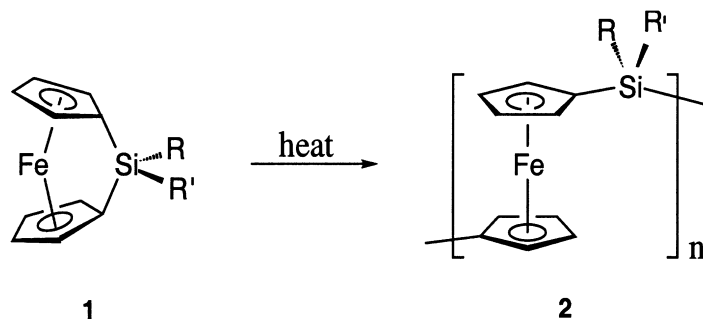
In 1992 we reported the discovery of a ring-opening polymerization (ROP) route to high molecular weight poly(ferrocenylsilanes) from strained [1] silaferrocenophane precursors [4]. The latter species were first prepared in the mid 1970s via the reaction of the dilithioferrocene·tetramethylethylenediamine

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complex($\text{fLi}_2 \cdot \text{TMEDA}$) with organo-dichlorosilanes [5]. ROP processes generally occur via a chain growth route which involve a highly reactive intermediate that reacts rapidly with monomer molecules. This allows the facile formation of long polymer chains making high molecular weight polymers easily accessible [2]. This is vital as high molecular weights ($M_n \approx 10\,000$) are needed in order to realize the chain entanglement needed to access the advantageous properties of macromolecules such as ease of fabrication into films [2].

POLY(FERROCENYLSILANES)

Since 1992, a wide range of silicon-bridged [1] ferrocenophanes **1** with either symmetrically or unsymmetrically alkyl or aryl substituted silicon atoms have been prepared and similarly polymerized to high molecular weight ($M_w = 10^5\text{--}10^6$, $M_n > 10^5$) poly(ferrocenylsilanes) **2** (Eqn 1; Scheme 1). Substituents such as hydrogen, chlorine, trifluoropropyl, norbornenyl and ferrocenyl groups have also been introduced [6,7].



Recently, we have found a facile route to the first poly(ferrocenylsilanes) with alkoxy, aryloxy and amino substituents at silicon. These stable materials are accessible via the ROP of similarly substituted [1] silaferrocenophane precursors which can be accessed via nucleophilic substitution reactions on the SiCl_2 -bridged [1] ferrocenophane **1** ($R = R' = \text{Cl}$) (Scheme 1). The latter species is easily prepared in high yield via the reaction of $\text{fLi}_2 \cdot \text{TMEDA}$ with SiCl_4 .

Considerable effort has also been directed towards investigating and understanding the properties of the resulting poly(ferrocenylsilane) materials, the vast majority of which are soluble in organic solvents despite their very high molecular weights [7]. Cyclic voltammetric studies of the high polymers generally show the presence of two reversible oxidation waves in a 1:1 ratio providing clear evidence for the existence of interactions between the iron atoms [5,6]. The presence of metal–metal interactions has led to studies of the charge transport properties of these materials. Oxidative doping of amorphous samples of poly(ferrocenyldimethylsilane) with I_2 have been shown to yield semiconducting materials ($\sigma \approx 10^{-7} \text{Scm}^{-1}$) but much higher conductivities (up to $\sigma = 2 \times 10^{-4} \text{Scm}^{-1}$) have recently been reported for more crystalline, oriented samples of **2** ($R = R' = \text{Me}$ or $R = R' = n\text{-Bu}$). The latter conductivities represent an order of magnitude increase over the undoped materials which are insulating ($\sigma \approx 10^{-14} \text{Scm}^{-1}$). Charge transport properties such as hole mobility, which are important for xerography and other device applications, have also been measured and are appreciable. Poly(ferrocenes) also function as charge dissipation coatings which provide protection with respect to ionizing radiation such as electrons. The films of poly(ferrocenes) are believed to function in this regard via both radiation scattering and conduction mechanisms [8]. The magnetic properties of oxidized poly(ferrocenes) have also attracted attention [7].

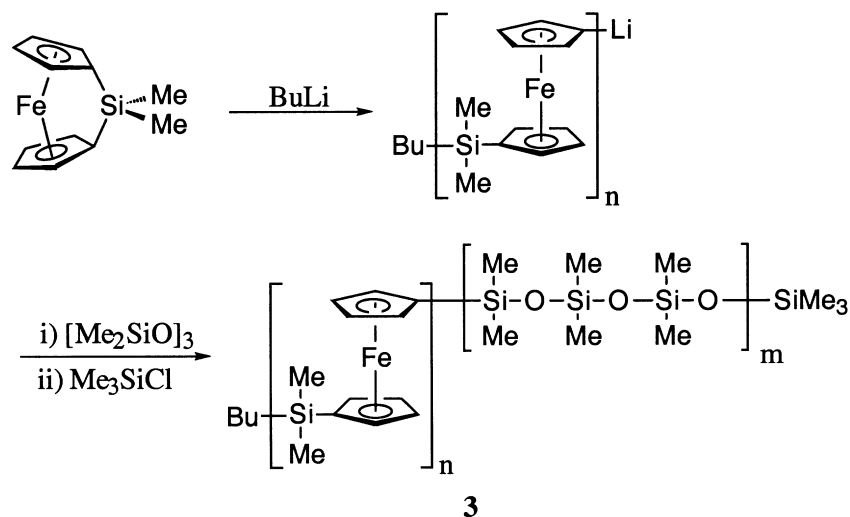
Poly(ferrocenylsilanes) also exhibit interesting morphology and several of the symmetrically substituted derivatives will crystallize. For example, the prototypical poly(ferrocenylsilane), the dimethyl-derivative **2** ($R = R' = \text{Me}$), is an amber, film-forming thermoplastic which possesses melt transitions (T_m) in the range $122\text{--}143^\circ\text{C}$ and a glass transition (T_g) at 33°C . In contrast, the *n*-hexyl analogue **2** ($R = R' = n\text{-hexyl}$) is an amber, gummy amorphous material with a T_g of -26°C . Alkoxy-substituted poly(ferrocenylsilanes) such as **2** ($R = R' = n\text{-hexyloxy}$) possess T_g values down to -51°C , a remarkable testament to the flexibility of poly(ferrocene) chains which probably arises from the freely rotating

'molecular ball bearing' nature of the ferrocene unit. It is remarkable that the incorporation of ferrocene units in the side group structure of organic polymers leads to dramatic T_g increases as the steric rigidity of this organometallic unit dominates and the free rotation is irrelevant. Thus, poly(vinylferrocene) possesses a high T_g of 184 °C [7]. The first liquid crystalline poly(ferrocenylsilanes) have also been prepared recently via hydrosilylation. These materials show a nematic mesophase and the influence of redox state on the liquid crystalline properties is of significant interest.

Many other characteristics of poly(ferrocenylsilanes) have attracted attention. The materials are electrochromic and change color reversibly from amber to dark blue on oxidation [7]. In addition, ferromagnetic products which contain α -Fe crystallites are generated by pyrolysis at temperatures above 500 °C [7]. Very recently, controlled crosslinking of poly(ferrocenylsilanes) has been achieved to yield solvent swellable, redox-active gels [7].

ANIONIC AND TRANSITION METAL CATALYZED ROP

Thermal ROP of metallocenophanes at elevated temperatures leads to virtually no control over molecular weight and the molecular weight distribution is broad. We have shown that silicon-bridged [1] ferrocenophanes undergo living anionic ROP at 25 °C using initiators such as $n\text{BuLi}$ in THF [9,10], This has permitted the synthesis of poly(ferrocenylsilanes) with controlled molecular weights and narrow polydispersities and has also allowed functionalization of polymer chain ends and the preparation of the first block copolymers (e.g. **3**) containing skeletal transition metal atoms (Scheme 2).



Transition metal-catalyzed ROP of silicon-bridged [1] ferrocenophanes, which occurs in solution at room temperature, has also been reported using Pt^{II} , Pt^0 , Rh^{I} , and Pd^{II} catalysts [7]. Molecular weight control can also be achieved and materials with novel architectures such as star and graft polymers are accessible [11]. Moreover, [1] silaferrocenophanes with different cyclopentadienyl rings polymerize to yield a regioregular, crystalline poly(ferrocenylsilane) whereas thermal ROP affords a regiorregular amorphous material [11]. Significant understanding of the mechanism of these transition metal-catalyzed reactions has also been forthcoming [7].

OTHER POLY(METALLOCENES) VIA ROP: CONTROLLING INTERACTIONS BETWEEN METAL CENTERS

The ROP route has also been extended to the synthesis of other polymers from [1] ferrocenophane precursors [12]. Poly(ferrocenylgermanes) were first reported in 1993 and possess similar properties to their silicon analogs [6]. Recently, after unsuccessful earlier attempts in the 1980s, the first tin-bridged [1] ferrocenophane was prepared. This species undergoes thermal ROP to yield a high molecular weight poly(ferrocenylstannane). Interestingly, this ROP reaction also occurs in solution at room temperature.

Studies of this novel ROP process may provide insight into the ROP mechanism for metallocenophanes [12].

We have also shown that poly(ferrocenylphosphines) are also accessible via the thermal ROP of phosphorus-bridged [1] ferrocenophanes [6]. In addition, the latter species has also been shown to undergo living anionic ROP to yield high molecular weight materials including block copolymers [13,14]. Very recently the first chalcogen-bridged [1] ferrocenophanes have been prepared. The sulfur-bridged [1] ferrocenophane is a remarkably strained species with a tilt-angle of 31° . This compound, and the dimethylated analog undergo ROP to yield poly(ferrocenylsulfides). The iron-iron interactions in the resulting polymers are significantly greater than in the analogous poly(ferrocenylsilanes) [12]. The first [1] ferrocenophane containing a first row element (boron) in the bridge has also recently been synthesized in collaboration with the group of Holger Braunschweig at the RWTH Aachen [15]. This highly sensitive species possesses the highest tilt-angle (32°) for an iron group metallocenophane. Attempts to polymerize this and related species to yield soluble polymers are in progress. Boron-bridged [1] ferrocenophanes have been found to possess novel reactivity and insertions of organometallic fragments derived from, e.g. $\text{Co}_2(\text{CO})_8$ into the Fe-Cp bonds are possible [16].

APPLICATIONS OF RING-OPENED POLY(FERROCENES): SELF-ASSEMBLED NANOSTRUCTURES AND NANOLITHOGRAPHY

Poly(ferrocenes) function as preceramic polymers and have been shown to yield interesting ferromagnetic Fe-containing ceramic composites at $500\text{--}1000^\circ\text{C}$ [6,7]. The use of such involatile but processable polymeric precursors to ceramics is potentially attractive way of circumventing the difficulty of processing ceramic materials into desired shapes. In collaboration with the group of Geoff Ozin at Toronto we have recently explored the pyrolysis of poly(ferrocenylsilanes) within the channels of the mesoporous silica MCM-41 [17]. The monomer **1** ($\text{R} = \text{R}' = \text{Me}$) can be sublimed into the hexagonal mesopores at room temperature and ROP can be induced by heating the resulting material at 200°C . Heating to 900°C generates black, nanostructured magnetic ceramic products which can be visualized in the channels by transmission electron microscopy (TEM). The materials are superparamagnetic as the channels restrict the growth of the iron clusters so that they are too small to permit stable magnetization.

Poly(ferrocene) block copolymers also allow access to nanostructured materials. Recently, in collaboration with the group of Mitch Winnik at Toronto we have shown that interesting architectures can be generated via the solution aggregation of poly(ferrocene)-based block copolymers [18–20]. Thus, block copolymers such as poly(ferrocenyldimethylsilane) - b - poly(dimethylsiloxane) **3** ($n:m = 1:6$) with long polysiloxane blocks have been found to afford cylindrical, worm-like micelles in hexanes. These structures maintain their structural integrity in the solid state and can be readily visualized by Atomic Force Microscopy or by TEM. These cylinders consist of a wire-like core of semiconducting poly(ferrocenylsilane) surrounded by a sheath or corona of insulating poly(dimethylsiloxane). Pyrolysis or etching of such structures, particularly if crosslinked, offers the possibility of generating magnetic wire-like structures.

Poly(ferrocene) block copolymers, like organic analogs, also phase separate in the solid state. We reported the first studies of the morphology of such materials in 1996 [10]. TEM was used, for example, to demonstrate that films of poly(ferrocenylsilane)-polystyrene block copolymers generate cylindrical and/or lamellar domain structures in the solid state.

A broad range of exciting opportunities exist for the poly(ferrocene) block copolymers and many of these areas are under investigation in our program in collaboration with other groups.

These include:

- 1 The generation and study of spherical and cylindrical and related self-assembled micellar aggregates as precursors to semiconducting nanostructures by oxidation or magnetic nanostructures by pyrolysis [12,19,20].
- 2 The generation of poly(ferrocene) block copolymer films which contain highly ordered, periodic organometallic nanostructures which could be selectively oxidized (chemically or electrochemically, e.g. by using scanning probe microscope tips) to give materials with interesting properties. For example, the controlled orientation of nanoscale block copolymer spherical, cylindrical, or lamellar

domains might allow charge transport in certain directions or the generation of magnetic nanostructures via oxidation or pyrolysis [12].

- 3 The selective ablation of blocks using reactive ion etching (e.g. O₂, Ar, H₂, etc.) allows the generation of periodic and aperiodic structures of dimensions <100 nm, less than those readily available using conventional lithographic methodologies. Such techniques have been successfully used, for example, by Möller and co-workers where inorganic components in one block allow the etching contrast [21]. Poly(ferrocenes) such as poly(ferrocenylsilanes) possess inorganic Fe and Si components which, in the case of easily ablated organic co-blocks, allows high selective etching contrasts (e.g. via the formation ablation-resistant magnetic ceramic structures using, e.g. oxygen or hydrogen reactive ion etching) [22]. This approach offers opportunities for nanolithography in which periodic and aperiodic structures of dimensions <100 nm are generated [7,22,23]. An interesting extension of these ideas is to use ordered poly(ferrocene) block copolymer films (e.g. spherical and lamellar structures) as photonic crystals in which periodic variations in refractive index are present. These have many potential applications including as, e.g. waveguides. Large dielectric contrast between the blocks is a potential advantage of using poly(ferrocene) materials [24].

SUMMARY

Ring-opening polymerization of metallocenophanes has allowed easy access to a variety of high molecular weight poly(metallocenes). Much has been accomplished in terms of understanding the properties of these novel and interesting materials. Future work will be directed towards investigating the mechanisms of polymerization, developing new polymers with controlled metal–metal interactions, studying the properties of these materials in more detail and exploring applications in a variety of intriguing areas such as, for example, radiation shielding materials, nanostructured in photonic materials and nanolithography, sensors, charge-transport materials, and redox-active gels.

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REFERENCES

- 1 C. U. Pittman Jr, C. E. Carraher, J. R. Reynolds. Organometallic polymers. *Encyclopedia Polymer Sci. Eng.* **10**, 541 (1987).
- 2 I. Manners. *Angew. Chem. Int. Ed. Engl.* **35**, 1602 (1996).
- 3 E. W. Neuse, H. Rosenburg. *J. Macromol. Sci.* **C4**, 110 (1970).
- 4 D. A. Foucher, B. Z. Tang, I. Manners. *J. Am. Chem. Soc.* **114**, 6246 (1992).
- 5 A. G. Osborne, R. H. Whiteley. *J. Organomet. Chem.* **101**, C27 (1975).
- 6 I. Manners. *Adv. Organomet. Chem.* **37**, 131 (1995), and references cited therein.
- 7 I. Manners. *Chem. Commun.* 857 (1999), and references cited therein.
- 8 R. Resendes, A. Berenbaum, G. Stojevic, F. Jäkke, A. Bartole, F. Zamanian, G. Dubois, C. Hersom, K. Balmain, I. Manners. *Adv. Mater.*, submitted.
- 9 Y. Ni, R. Rulkens, I. Manners. *J. Am. Chem. Soc.* **116**, 12121 (1994).
- 10 R. Rulkens, Y. Ni, I. Manners. *J. Am. Chem. Soc.* **118**, 4102 (1996).
- 11 P. Gómez-Elipe, R. Resendes, P. M. Macdonald, I. Manners. *J. Am. Chem. Soc.* **120**, 8348 (1998).
- 12 I. Manners. *Can. J. Chem.* **76**, 371 (1998).
- 13 C. H. Honeyman, T. J. Peckham, J. Massey, I. Manners. *Chem. Commun.* 2589 (1996).

- 14 T. J. Peckham, J. Massey, C. H. Honeyman, I. Manners. *Macromolecules* **32**, 2830 (1999).
- 15 H. Braunschweig, R. Dirk, M. Müller, P. Nguyen, R. Resendes, D. P. Gates, I. Manners. *Angew. Chem. Int. Ed. Engl.* **36**, 2338 (1997).
- 16 H. Braunschweig, R. Dirk, U. Englert, A. Berenbaum, F. Jäkle, A. J. Lough, I. Manners. Unpublished results.
- 17 M. J. MacLachlan, P. Aroca, N. Coombs, I. Manners, G. A. Ozin. *Adv. Mater.* **10**, 144 (1998).
- 18 J. Massey, K. N. Power, I. Manners, M. A. Winnik. *J. Am. Chem. Soc.* **120**, 9533 (1998).
- 19 J. Massey, K. N. Power, M. A. Winnik, I. Manners. *Adv. Mater.* **10**, 1559 (1998).
- 20 R. Resendes, J. Massey, H. Dorn, K. N. Power, M. A. Winnik, I. Manners. *Angew Chem Int. Ed Engl.* **38**, 3321 (1999).
- 21 (a) J. P. Spatz, S. Mößmer, M. Möller, T. Herzog, A. Plettl, P. J. Ziemann. *J. Lumines.* **76/77**, 168 (1998). (b) J. P. Spatz, T. Herzog, S. Mößmer, P. Ziemann, M. Möller. *Adv. Mater.* **11**, 149 (1999).
- 22 J. M. Massey, K. N. Power, L. Cao, M. A. Winnik, I. Manners, J. P. Spatz, M. Möller. Unpublished results.
- 23 H. Ito, E. Reichmanis, O. Nalamasu, T. Ueno, eds. Micro nanopatterning polymers. *ACS Symposium Ser.* 706 (1997).
- 24 S. John. *Phys. Rev. Lett.* **58**, 2486 (1987).