

Poly(ferrocenylsilanes): novel organometallic plastics

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Poly(ferrocenylsilanes) are a novel class of transition metal-containing macromolecules with a backbone that consists of alternating ferrocene and organosilane units. High molecular weight examples of these interesting materials were first prepared several years ago by thermal ring-opening polymerization (ROP) of silicon-bridged [1]ferrocenophanes ([1]silaferrocenophanes). This Feature Article discusses current knowledge of the properties of these readily available and processable organometallic polymers together with recent developments made possible by the discovery of living anionic and transition metal-catalyzed ROP routes. These methodologies have provided ambient temperature access to poly(ferrocenylsilanes) with molecular weight control and also to well defined architectures such as block copolymers. The latter materials self-assemble in the solid state to form ordered arrays of nanoscale redox-active organometallic domains and in solution form well defined supramolecular organometallic polymer aggregates such as spheres, cylinders, and more complex architectures.

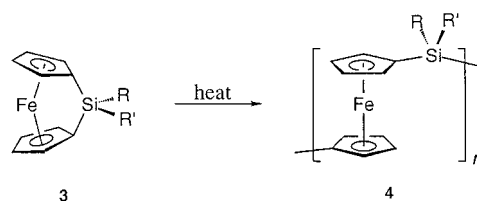
Introduction

Whereas the synthetic scope and technological achievements of organic polymer science are remarkably impressive, the corresponding macromolecular chemistry of inorganic elements is at a much more primitive stage of development.¹ This is particularly the case for transition metal-based polymers which

would be expected to possess a range of interesting and potentially useful physical and/or catalytic properties.^{1,2} Nevertheless, synthetic breakthroughs, which have occurred sporadically over the last 10–15 years and at a more rapid pace recently, have provided access to a range of fascinating new materials.^{1–5} Rigid rod poly(metallaynes) such as **1** and **2** provide an excellent illustration of the potential of this area.⁴ These polymers, of which the first examples were reported at the end of the 1970s, possess novel conjugated backbones, and in several cases interesting physical properties such as lyotropic liquid crystallinity and third-order non-linear optical properties have been established.^{1,4,6}

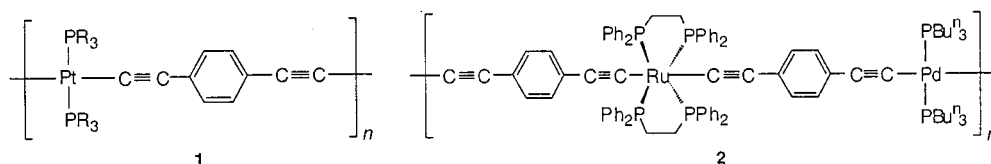
Much of the early pioneering work in transition metal-based polymer science in the 1950s and 1960s targeted poly(metallocenes).⁷ Such efforts were encouraged by the remarkable stability and unusual properties of monomeric and dimeric metallocenes which were discovered by the fundamental, exploratory chemistry conducted during this period.⁸ However, most of the attempted polymer syntheses utilized polycondensation reactions where either the difunctional monomeric precursors were impure or the coupling chemistry was not clean. For such step growth processes this guaranteed the generation of poorly defined, low molecular weight oligomeric materials ($M_n < ca. 3000$) of correspondingly low processability.⁹ In addition, many of the resulting products were insoluble and poorly characterized.⁹

In 1992 our group reported the discovery of a thermal ring-opening polymerization (ROP) route to high molecular weight poly(ferrocenylsilanes) **4**, a novel class of poly(ferrocenes), from strained cyclic, silicon-bridged [1]ferrocenophane ([1]silaferrocenophane) precursors (**3**).¹⁰ This chain growth syn-



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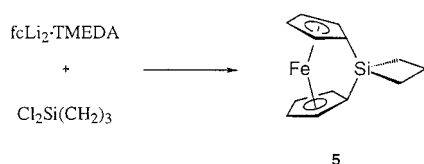
thetic approach permitted access to very high molecular weight polymers with weight average molecular weights (M_w) and number average molecular weights (M_n) of the order of $M_w = 10^5$ – 10^6 and $M_n > 10^5$.^{10–15} We have subsequently expanded this ROP methodology to a range of analogous strained monomers which contain other bridging elements and transition metals or different π -hydrocarbon rings.^{15,16} In this article we



review progress specifically made on poly(ferrocenylsilanes) which have been particularly well studied since the initial ROP discovery. In particular we discuss some new directions arising from the development of more controlled polymerization methods which allow access to block copolymers. These have provided avenues to self-assembled, supramolecular organometallic polymer architectures.

Synthesis and properties of poly(ferrocenylsilanes)

[1]Siliferrocenophane monomers **3** are readily available on a substantial (> 100 g) laboratory scale from the reaction of dilithioferrocene–tetramethylethylenediamine (fcLi₂·TMEDA) with dichloroorganosilanes RR'SiCl₂.¹⁷ The first example of these species, the phenylated derivative **3** (R = R' = Ph), was prepared by Osborn and Whiteley at the University of Exeter in the mid 1970s.¹⁸ The cyclopentadienyl ligands present in [1]siliferrocenophanes are appreciably tilted with respect to one another by 16–21° which is indicative of the presence of appreciable ring strain which has been estimated to be *ca.* 60–80 kJ mol⁻¹.^{16,19} Spirocyclic [1]siliferrocenophanes such as **5** are



also readily accessible.^{18,20} The molecular structures of two typical [1]siliferrocenophanes polymerised in our group are shown in Fig. 1.^{20,21}

Since the initial ROP discovery a wide range of silicon-bridge [1]ferrocenophanes **3** with either symmetrically or unsymmetrically alkyl- or aryl-substituted silicon atoms have been prepared and polymerized to afford high molecular weight poly(ferrocenylsilanes) **4**.¹⁵ Substituents such as hydrogen, chlorine, trifluoropropyl, norbornyl and ferrocenyl groups have also been introduced (Table 1).^{15,22,23} Very recently, we have found a facile route to the first poly(ferrocenylsilanes)

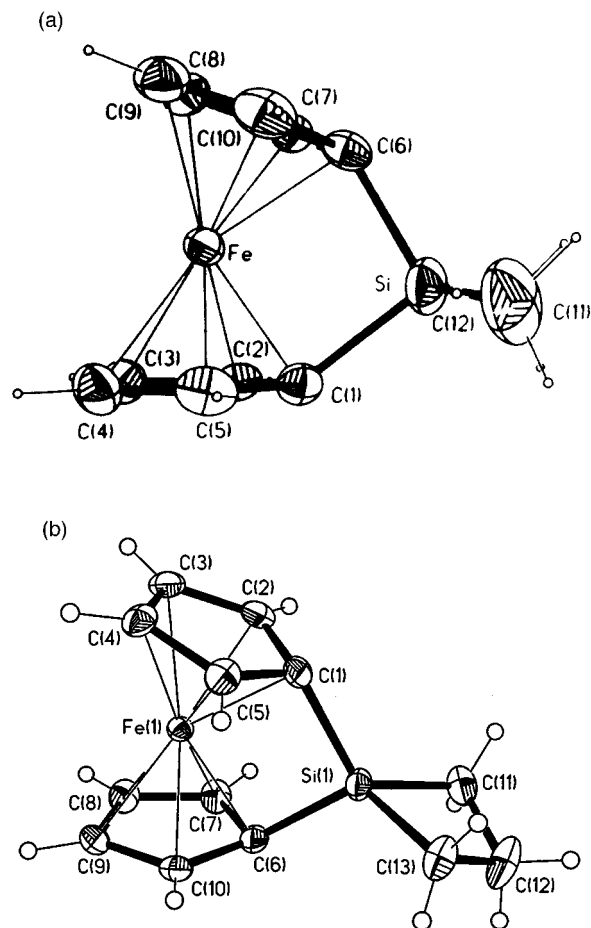


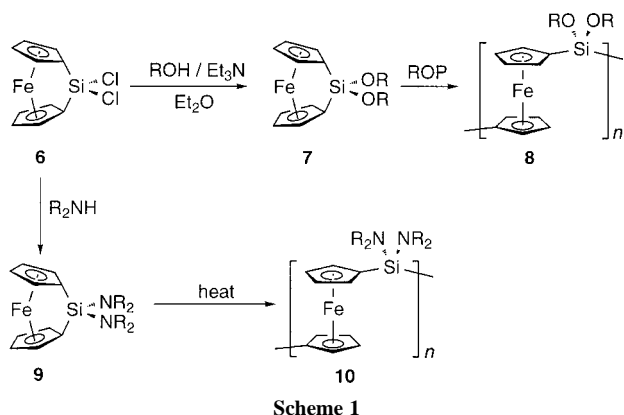
Fig. 1 Molecular structure of (a) silicon-bridged [1]ferrocenophane **3** (R = R' = Me) and (b) spirocyclic [1]siliferrocenophane **5** determined by X-ray diffraction.

with alkoxy, aryloxy, and amino substituents at silicon.²⁴ These stable materials (**8** and **10**, respectively) are accessible *via* the ROP of similarly substituted [1]siliferrocenophane precursors (**7** and **9**) which can be accessed *via* nucleophilic substitution

Table 1 Thermal transition and GPC molecular weight data^a for selected poly(ferrocenylsilanes)^{15,22–24}

Polymer	R/OR	R'/OR	T _g (T _m) ^b /°C	M _n ^a	PDI ^c
4	H	H	16 (165)	— ^e	— ^e
4	Me	Me	33 (122–143)	3.4 × 10 ⁵	1.5
4	Et	Et	22 (108)	4.8 × 10 ⁵	1.6
4	Pr ⁿ	Pr ⁿ	24 (98)	8.5 × 10 ⁴	2.7
4	Bu ⁿ	Bu ⁿ	3 (116, 129)	3.4 × 10 ⁵	2.6
4	<i>n</i> -C ₅ H ₁₁	<i>n</i> -C ₅ H ₁₁	−11 (80–105)	3.0 × 10 ⁵	1.6
4	<i>n</i> -C ₆ H ₁₃	<i>n</i> -C ₆ H ₁₃	−26	7.6 × 10 ⁴	1.5
4	Me	H	9 (87, 102)	4.2 × 10 ⁵	2.0
4	Me	CH ₂ CH ₂ CF ₃	59	8.1 × 10 ⁵	3.3
4	Me	CH=CH ₂	28	7.7 × 10 ⁴	2.1
4	Me	<i>n</i> -C ₁₈ H ₃₇	1 (16)	5.6 × 10 ⁵	2.5
4	Me	Ph	54	1.5 × 10 ⁵	2.0
4	Me	Fc ^d	99	7.1 × 10 ⁴	2.3
4	Me	5-Norbornyl	81	1.1 × 10 ⁵	1.5
8	OMe	OMe	19	1.5 × 10 ⁵	1.9
8	OEt	OEt	0	3.8 × 10 ⁵	2.1
8	OCH ₂ CF ₃	OCH ₂ CF ₃	16	2.2 × 10 ⁵	1.2
8	OBu	OBu	−43	3.9 × 10 ⁵	2.1
8	OC ₆ H ₁₃	OC ₆ H ₁₃	−51	0.9 × 10 ⁵	2.4
8	O(CH ₂) ₁₁ Me	O(CH ₂) ₁₁ Me	(−30)	1.9 × 10 ⁵	2.5
8	O(CH ₂) ₁₇ Me	O(CH ₂) ₁₇ Me	(32)	2.3 × 10 ⁵	2.2
8	OPh	OPh	54	2.3 × 10 ⁵	2.0
8	OC ₆ H ₄ Bu ^t - <i>p</i>	OC ₆ H ₄ Bu ^t - <i>p</i>	89	1.9 × 10 ⁵	1.9
8	OC ₆ H ₄ Ph- <i>p</i>	OC ₆ H ₄ Ph- <i>p</i>	97	5.4 × 10 ⁴	2.4

^a GPC data obtained from the analysis of THF polymer solutions which contained 0.1% [Bu₄N][Br] and molecular weight values are relative to polystyrene standards. Although in this case GPC provides only molecular weight estimates absolute determinations of M_w by static light scattering for several polymers have indicated that GPC underestimates the real values by a factor of two (see ref. 15) ^b DSC data collected at a heating rate of at 10 °C min⁻¹. ^c PDI = M_w/M_n. ^d Fc = (η-C₅H₄)Fe(η-C₅H₅). ^e Insoluble polymer.



reactions on the SiCl_2 -bridged [1]ferrocenophane **6** (Scheme 1). The latter species is easily prepared in high yield *via* the reaction of fcLi_2 -TMEDA with SiCl_4 .

Because of their novel backbone of alternating ferrocene and organosilane units it is interesting to consider how the poly(ferrocenyldimethylsilane) chains pack together in the solid state and the possible chain conformations that might exist.²⁵ Another important feature of these polymers is their glass transition temperature (T_g) which reflects, at least to a certain degree, the conformational flexibility present. Regular packing in the solid state (*i.e.* crystallization) is possible for many symmetrically substituted derivatives.^{15,25} For example, the prototypical poly(ferrocenyldimethylsilane), the dimethyl derivative **4** ($R = R' = \text{Me}$), is an amber, film-forming thermoplastic [Fig. 2(a)] which possesses melt transitions (T_m) in the range 122–143 °C.^{15,25,26} Crystals on the surface of aged polymer films can be observed by atomic force microscopy [Fig. 2(b)].²⁷ This material possesses a T_g at 33 °C, which is remarkably low for a polymer with a bulky unit such as ferrocene in the main chain. The ability of the iron atom in ferrocene to act as a freely rotating ‘molecular ball-bearing’ probably plays a key role in generating the observed conformational flexibility. The manner in which these polymer chains pack in the solid state for this polymer has attracted significant interest and has been examined by detailed conformational calculations and X-ray structural studies of well defined oligomers by O’Hare and coworkers and ourselves, respectively.^{28,29}

Poly(ferrocenyldimethylsilane) [**4** ($R = R' = \text{Me}$)] can be melt-processed into shapes above 150 °C [Fig. 2(c)] and can be used to prepare crystalline, nanoscale fibers (diameter < 1.5 μm) by electrospinning in which an electric potential is used to produce an ejected jet from a solution of the polymer in THF which subsequently stretches, splays, and dries. The nanofibers of different thickness show different colours due to interference effects similar to those in soap bubbles [Fig. 2(d)].³⁰

Like the dimethyl material, other symmetrically substituted poly(ferrocenyldimethylsilanes) with short (C_2 – C_5) alkyl chains at silicon will also crystallize and similar melting behavior is observed (Table 1). In contrast to the poly(ferrocenyldimethylsilanes) with shorter C_2 – C_5 alkyl chains, the *n*-hexyl analogue **4** ($R = R' = n\text{-hexyl}$) is an amber, gummy amorphous material with a T_g of –26 °C. Alkoxy-substituted poly(ferrocenyldimethylsilanes) such as **8** ($\text{OR} = n\text{-hexyloxy}$) are also amorphous and possess T_g values down to –51 °C. Poly(ferrocenyldimethylsilanes) with longer alkoxy side chains [*e.g.* **8** ($\text{OR} = n\text{-octadecyloxy}$)] have been found to crystallize and form lamellar structures with interdigitated side groups.²⁴

In addition to their morphological behavior, considerable effort has also been directed towards investigating and understanding the physical properties of the resulting poly(ferrocenyldimethylsilane) materials the vast majority of which are soluble in organic solvents despite their very high molecular weights. Cyclic voltammetric studies of poly(ferrocenyldimethylsilane) gen-

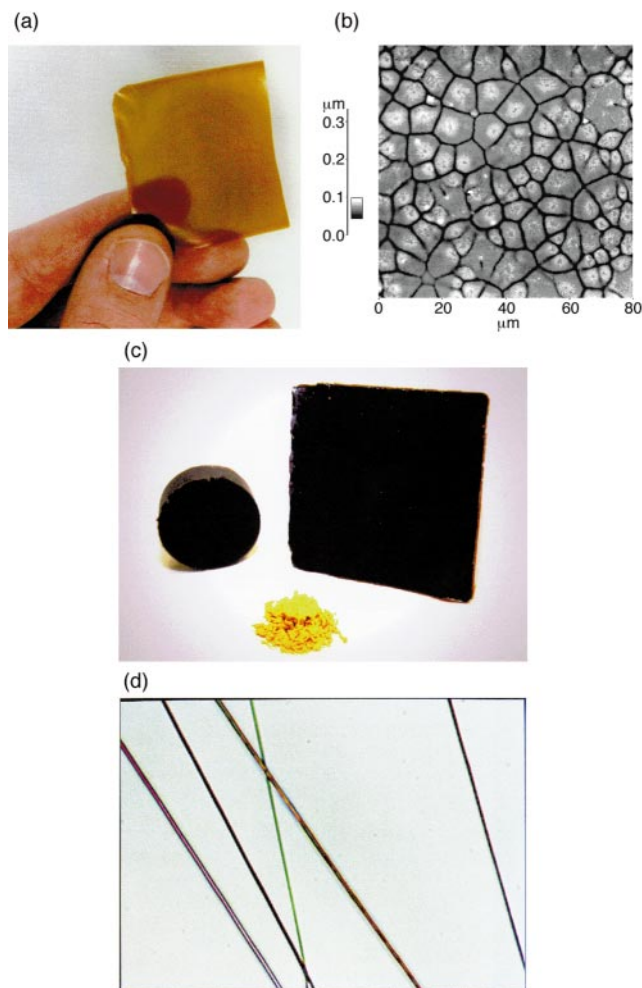
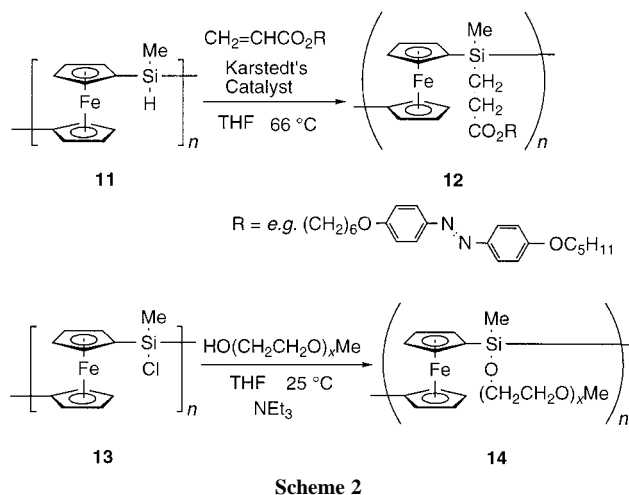


Fig. 2 Poly(ferrocenyldimethylsilane) **4** ($R = R' = \text{Me}$): (a) a solvent-cast film, (b) surface crystals grown on a thin film after 3 months observed by atomic force microscopy, (c) melt-processed fabricated shapes, (d) electrospun fibers. Figures (b) and (d) are courtesy of Nina Sheller and Mark D. Foster and Zhihao Chen, Hao Fong, Darrell H. Reneker, and Mark D. Foster, respectively, of the Institute of Polymer Science at the University of Akron, USA.

erally show the presence of two reversible oxidation waves spaced by *ca.* 0.25 V in a 1 : 1 ratio providing clear evidence for the existence of interactions between the iron atoms.¹⁵ The proposal that initial oxidation occurs at alternating iron sites along the main chain followed by oxidation of those remaining at a higher potential has been supported by recent detailed work on individual members of a series of model oligomers with between two and nine ferrocene units.²⁹ Comparisons of the behavior of poly(ferrocenyldimethylsilanes) with analogous polymers suggest that the metal–metal interactions are mediated by the silicon spacer.³¹ Poly(ferrocenyldimethylsilanes) also possess interesting hole transport properties and partial oxidation leads to a 10^{10} increase in electrical conductivity up to semiconductor values (*ca.* 10^{-3} – 10^{-4} S cm^{-1}).³² Thin films of the polymers are attracting attention as, for example, chemomechanical sensors, electrochromic materials, electrode mediators, and variable refractive-index materials.^{33–36} The polymers also have interesting potential as precursors to ceramic materials. Thus, heating to 500–1000 °C can yield magnetic ceramics containing α -Fe crystallites. In several cases the ceramic yield is >90% and allows the formation of ceramic monoliths with shapes defined by that of the processable polymeric precursor.³⁷ Oxidation of poly(ferrocenyldimethylsilanes) has been reported³⁸ to yield materials which display spin alignment, albeit at low temperatures although other studies have not reproduced these results.³⁹

Very recently, controlled crosslinking of poly(ferrocenylsilanes) has been achieved to yield solvent swellable, redox-active gels. The crosslinking can be controlled by using specific amounts of the spirocyclic [1]ferrocenophane **5** (Fig. 1) in the polymerization mixtures.²⁰

Functionalization of poly(ferrocenylsilanes) has been achieved by several methods (Scheme 2).^{23,40} For example,



Scheme 2

ROP of [1]silaferrocenophane **4** (R = Me, R' = H) with a Si-H functionality affords **11** which undergoes metal-catalyzed hydrosilylation reactions. This methodology has been recently used to prepare thermotropic liquid crystalline poly(ferrocenylsilanes) such as **12**. To illustrate another approach, ROP of **4** (R = Me, R' = Cl) followed by substitution of Si-Cl bonds present in poly(ferrocenylsilane) **13**, permits access to water soluble poly(ferrocenylsilanes) such as **14** ($x \sim 7$).

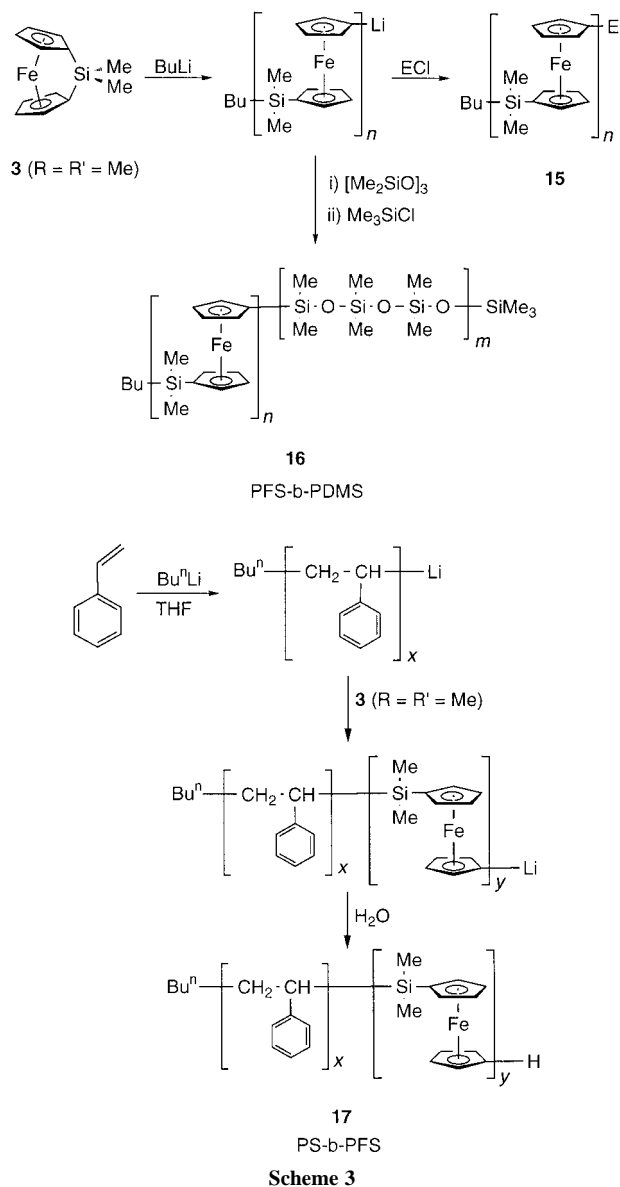
Living anionic ROP of silicon-bridged [1]ferrocenophanes

Thermal copolymerization can be used to prepare random copolymers from mixtures of different silicon-bridged [1]ferrocenophanes and also copolymers of ferrocenophanes with other monomers such as cyclic silanes and silicon-bridged bis(benzene)chromium complexes.^{32,41} However, thermal ROP of metallocenophanes at elevated temperatures leads to virtually no control over molecular weight and the molecular weight distribution is broad with polydispersity indices (PDI = M_w/M_n) of ca. 1.5–2.5. In 1994 we showed that highly purified silicon-bridged [1]ferrocenophanes undergo living anionic ROP at 25 °C using initiators such as BuⁿLi in THF.⁴² This has permitted the synthesis of poly(ferrocenylsilanes) **15** (E = H) with controlled molecular weights and narrow molecular weight distributions (polydispersities < 1.3) and has also allowed the preparation of end-functionalized polymers **15** (E ≠ H) and the first block copolymers (e.g. **16** and **17**) containing skeletal transition metal atoms (Scheme 3).⁴³

Logical further developments of this chemistry include the extension to other organic (and inorganic) monomers to access other poly(ferrocene) multiblock systems. Moreover, the ability to functionalize chain ends should allow the development of end-functionalized, redox-active polymers for surface (e.g. electrode) attachment, *etc.*^{11,43}

Transition metal catalyzed ROP of [1]ferrocenophanes

Transition metal-catalyzed ROP of silicon-bridged [1]ferrocenophanes, which also occurs in solution at room temperature,



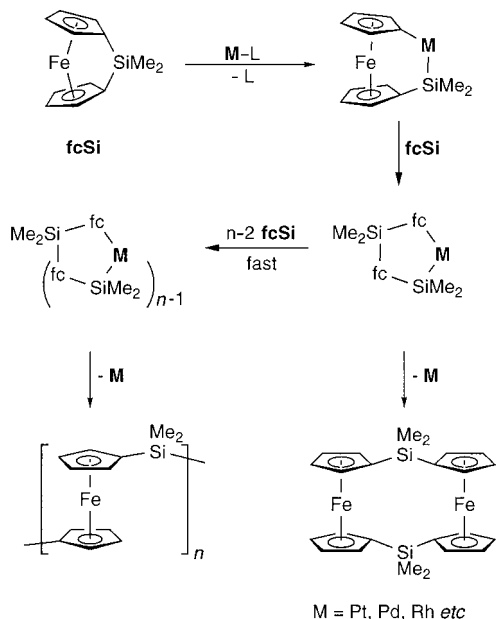
Scheme 3

has also been reported using Pt^{II}, Pt⁰, Rh^I, and Pd^{II} precatalysts.^{44,45} Significant understanding of the mechanism of these transition metal-catalyzed reactions has also been forthcoming and a possible mechanism is shown in Scheme 4.⁹

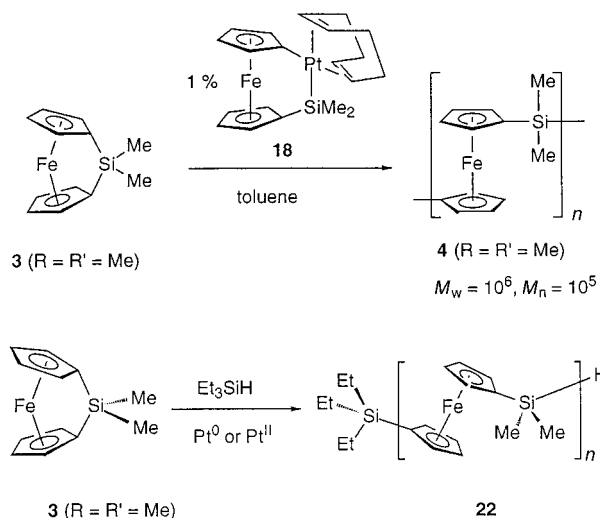
The initial step is believed to be insertion of the transition metal into the strained Cp-Si bond. Indeed, species such as **18** have been prepared from exactly this type of reaction [in the case of **18** from **3** (R = R' = Me) and Pt(1,5-cod)₂] and function as ROP precatalysts.⁴⁶

Transition metal catalyzed ROP is a mild method which does not require monomer with an exceptional degree of purity and has now been developed to the stage where considerable control over poly(metallocene) architectures is possible.^{47,48} For example, [1]silaferrocenophanes with different cyclopentadienyl rings (**19**) undergo transition metal catalyzed ROP to yield the regioregular, crystalline poly(ferrocenylsilane) **20** whereas thermal ROP affords a regiorregular amorphous material **21** (Scheme 5).

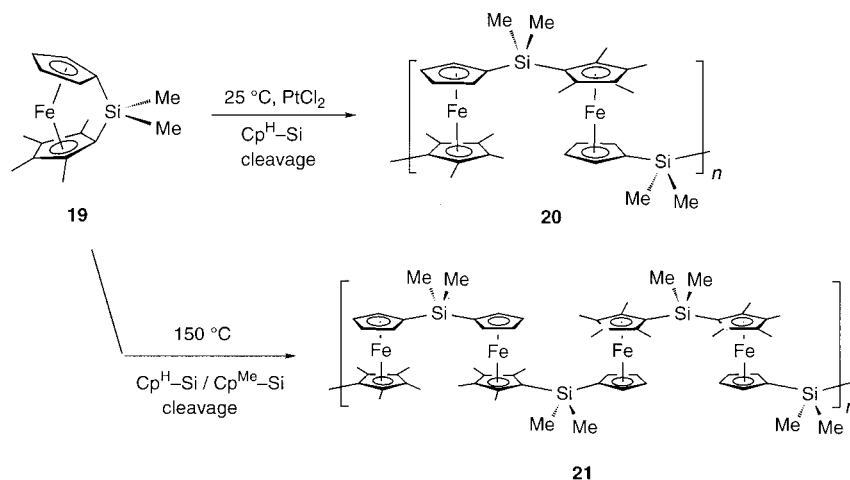
Addition of sources of Si-H bonds such as Et₃SiH to the polymerization mixture allows molecular weight control (Fig. 3). The process is believed to occur *via* competition of the Si-H bond and the strained Si-C bond of the [1]ferrocenophane for oxidative addition at the metal center. Addition of the Si-H bond followed by reductive elimination affords the Et₃Si-fc and Si-H terminated product (**22**).



Scheme 4



If polysiloxanes with Si-H groups as substituents or as termini are used in place of Et_3SiH then graft (**23**) or block (**24**) copolymers can be prepared. Moreover, the use of cyclic tetrasiloxanes as sources of the Si-H functionalities allows the preparation of novel poly(ferrocenes) (**25**) with star archi-



Scheme 5

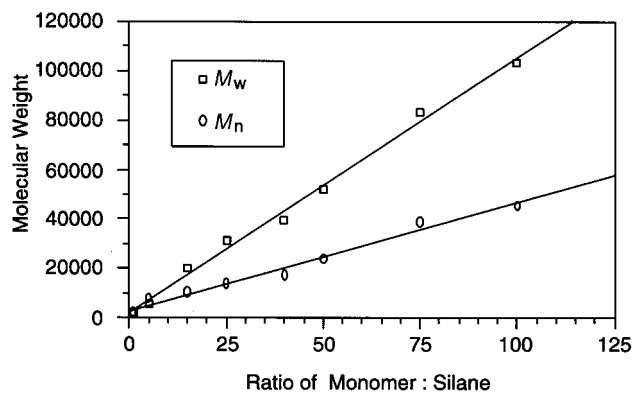


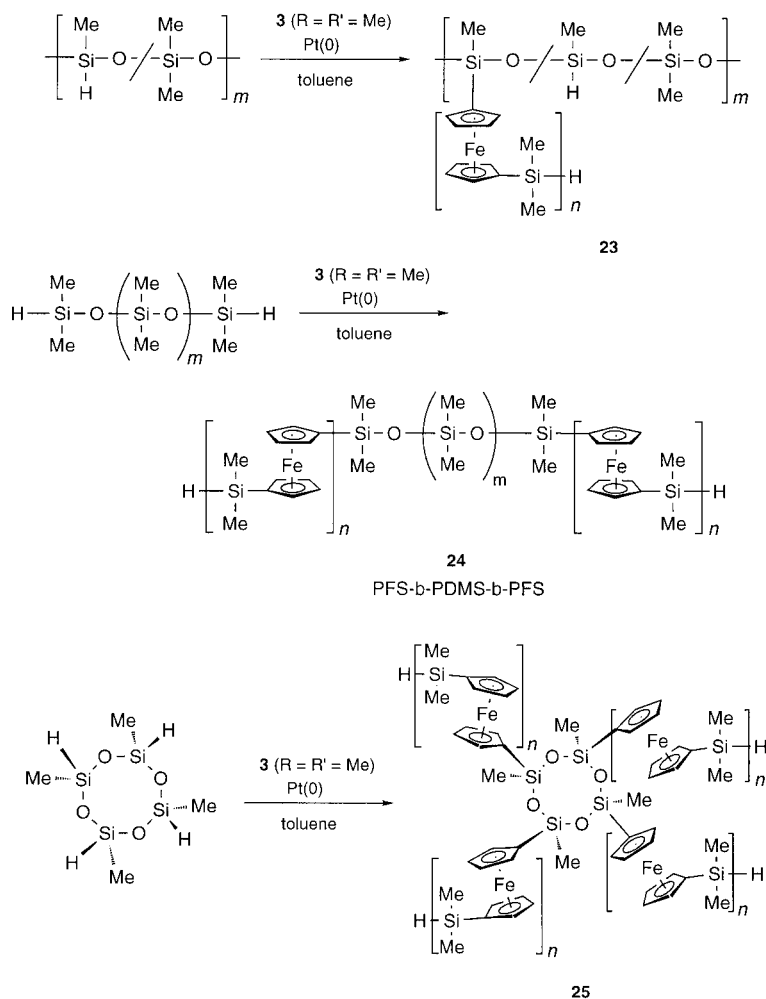
Fig. 3 Plot of M_w and M_n vs. ratio of monomer **3** ($R = R' = \text{Me}$): Et_3SiH demonstrating molecular weight control (using Karstedt's catalyst in toluene).

tures with a cyclosiloxane core (Scheme 6). The remarkable convenience by which complex organometallic polymer architectures can be constructed compensates for the broader polydispersities ($M_w/M_n = 1.4\text{--}1.8$) compared to materials prepared *via* anionic polymerization ($M_w/M_n < 1.3$).

Applications of ring-opened poly(ferrocenes) in the preparation of magnetic nanostructures

As mentioned above, poly(ferrocenylsilanes) function as pre-ceramic polymers and have been shown to yield interesting ferromagnetic ceramic composites at $500\text{--}1000\text{ }^\circ\text{C}$ which contain Fe particles in a SiC/C matrix.³⁷ The use of such involatile but processable polymeric precursors to ceramics is potentially an attractive way of circumventing the difficulty of processing ceramic materials into desired shapes. In collaboration with the group of Ozin at Toronto we have recently explored the pyrolysis of poly(ferrocenylsilanes) within the channels of the mesoporous silica MCM-41 with the aim of accessing nanostructured magnetic ceramic materials (Fig. 4).⁴⁹

The monomer **3** ($R = R' = \text{Me}$) can be sublimed into the hexagonal mesopores at room temperature. The resulting intercalated material was characterized by solid state ^{13}C and ^{29}Si NMR and by X-ray powder diffraction. ROP can then be induced by heating the resulting material at $200\text{ }^\circ\text{C}$, a process that was followed similarly and also by DSC which showed a ROP exotherm. Heating to $900\text{ }^\circ\text{C}$ generates black, nanostructured magnetic ceramic products which can be visualized in the 30 \AA channels by transmission electron microscopy (TEM) (Fig. 5). These materials were also characterized by X-ray diffraction, which showed the presence of small $\alpha\text{-Fe}$ nanoclusters with dimensions $20 \pm 5\text{ \AA}$.⁴⁹ Studies of the



Scheme 6

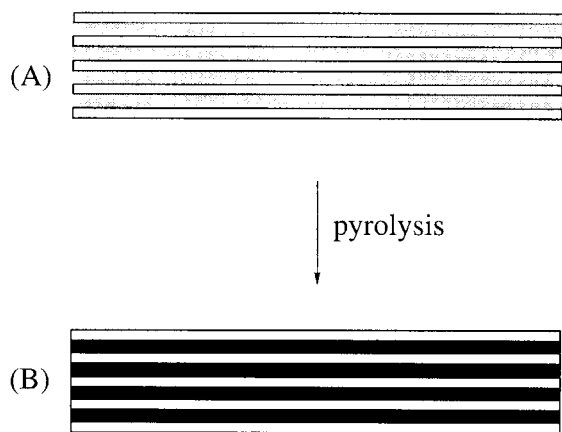


Fig. 4 Formation of nanostructured magnetic composites (B) via the pyrolysis of nanoscale cylinders of a poly(ferrocenylsilane) within the pores of mesoporous silica (MCM-41) (A).

magnetic properties of the composites confirmed that the materials are superparamagnetic rather than ferromagnetic which is consistent with the small sizes of the iron particles and the consequent, facile thermally induced reorientation of the magnetic domains at room temperature.

Self-assembly of poly(ferrocene) block copolymers: supramolecular organometallic polymer chemistry

Poly(ferrocene) block copolymers in which the blocks are immiscible (which is generally the case) would be expected to

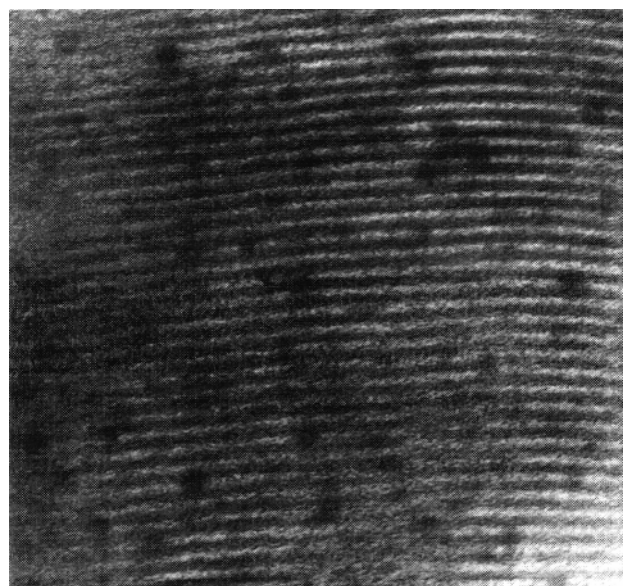


Fig. 5 Transmission electron micrograph perpendicular to the 30 Å channels of MCM-41 showing the incorporation of ceramics derived from the pyrolysis of poly(ferrocenylsilane) 4 (R = R' = Me) in the mesopores at 900 °C.

self-assemble to form phase separated domains in the solid state or to form micellar aggregates in selective solvents for one of the blocks.⁵⁰ This would allow the generation of unique supramolecular organometallic polymer architectures.

Based on the classical behavior of organic block copolymers, in the solid state poly(ferrocene) diblock copolymers should

form domains such as spheres, cylinders (or their anti-structures), double diamonds or gyroids, or lamellae. The preferred domain structure would be expected to be controlled by the ratio of the blocks, their degree of incompatibility (as defined by the Flory–Huggins interaction parameter χ), and the overall molecular weight of the block copolymer.⁵⁰ We reported the first studies in this area using differential scanning calorimetry (DSC) and TEM in 1996.⁴³ In the case of PS-*b*-PFS (**17**) detailed studies confirm that spherical, cylindrical, and lamellar domains are formed by using the expected block ratio variations [see, for example, Fig. 6(a) and (b)]^{27,51} and also indicate that the PS-*b*-PFS materials possess phase behavior

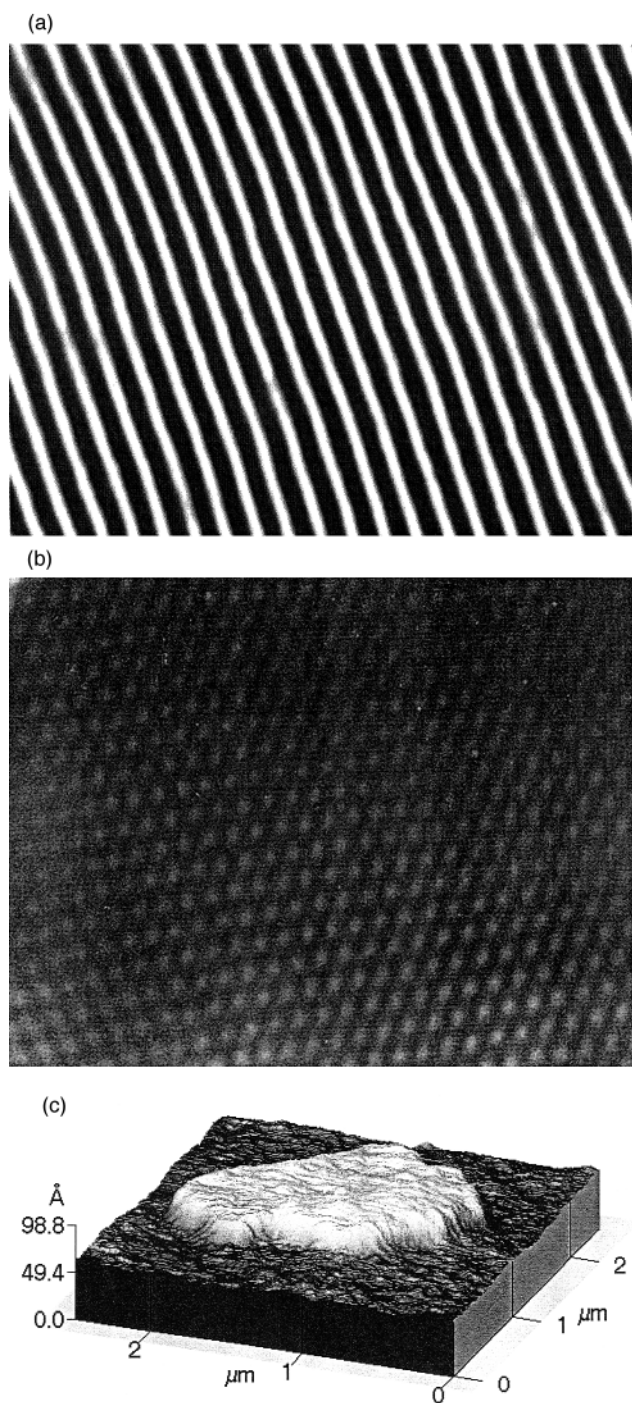


Fig. 6 Transmission electron micrographs of thin films of PS-*b*-PFS showing (a) lamellar morphology formed by a block copolymer with approximately equal block lengths, (b) ordered cylinders (end-on) of PS in a PFS matrix formed by a block copolymer with a 0.74 : 1.00 block ratio, (c) an AFM image showing crystals protruding from the surface of an annealed film. In TEM images (a) and (b) no staining agent was used and the PFS domains are dark and the PS domains light.

which is complicated by the presence of the crystallizable PFS block.^{27,43,51–53} The crystallization is illustrated by the observation of 3D topological features on films of PS-*b*-PFS using atomic force microscopy (AFM) which shows elevated PFS crystallites [Fig. 6(c)].²⁷

The self-assembly of poly(ferrocene) block copolymers in selective solvents for one block would also be anticipated based on studies of organic block copolymers. In the case of organic materials most studies have led to the identification of spherical structures with a core of the more insoluble polymer within a corona formed by the more soluble block. Only comparatively recently have non-spherical structures become more common.⁵⁴

In collaboration with the group of Winnik at Toronto we have studied, for example, PS-*b*-PFS materials with a short PFS block (PS:PFS ratio 9:1). Films of these materials phase separate into spheres of PFS in a PS matrix and, in acetone, which is a selective solvent for low molecular weight PS, spherical micelles with an organometallic PFS core within a PS corona have been characterized.⁵¹

Recently, we have shown that interesting architectures can be generated *via* the solution aggregation of PFS-*b*-PDMS block copolymers (**16**) with long polysiloxane blocks (PFS:PDMS ratio = 1:6). Simply dissolving the amber, tacky block copolymer in warm hexanes leads to the formation of cylindrical, wormlike micelles with a PFS core and a corona of PDMS (Fig. 7).⁵⁵

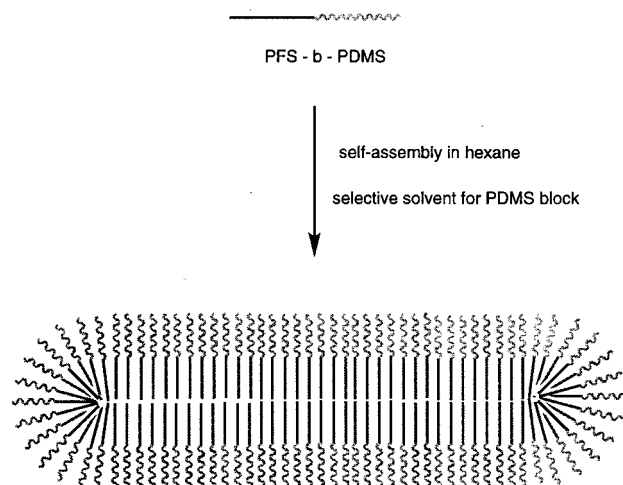


Fig. 7 Self-assembly of PFS-*b*-PDMS into cylindrical micelles in hexane.

These structures maintain their structural integrity in the solid state and the 20 nm iron-rich cores can be readily visualized by TEM which uses electron density differences to obtain contrast [see Fig. 8(a)]. AFM, on the other hand, allows both the core and corona to be imaged. The cylinders show considerable stability in solution and are unchanged in size after heating to 80 °C. However, ultrasonication of samples of the cylindrical micelles leads to a shortening as indicated by light scattering studies and by TEM [Fig. 8(b)].⁵⁵

These cylinders formed in hexane consist of a wire-like core of semiconducting poly(ferrocenylsilane) surrounded by a sheath or corona of insulating poly(dimethylsiloxane) and are of interest as semiconducting nanowires (Fig. 9). Pyrolysis of such structures, particularly if crosslinked, offers the possibility of generating magnetic wire-like structures with a silica coating.

Recently we have prepared amphiphilic poly(ferrocenylsilane) diblock copolymers with *N*-methylated poly(vinylpyridine) (PVP) and poly(ethylene oxide) (PEO) and these materials, PVP-*b*-PFS and PFS-*b*-PEO, are soluble in water as long as the organic block is sufficiently long. Transition metal catalyzed ROP also provides very convenient access to block copolymers. The PFS-*b*-PDMS-*b*-PFS triblock materials (**24**) self-assemble in hexanes to yield a variety of remarkable

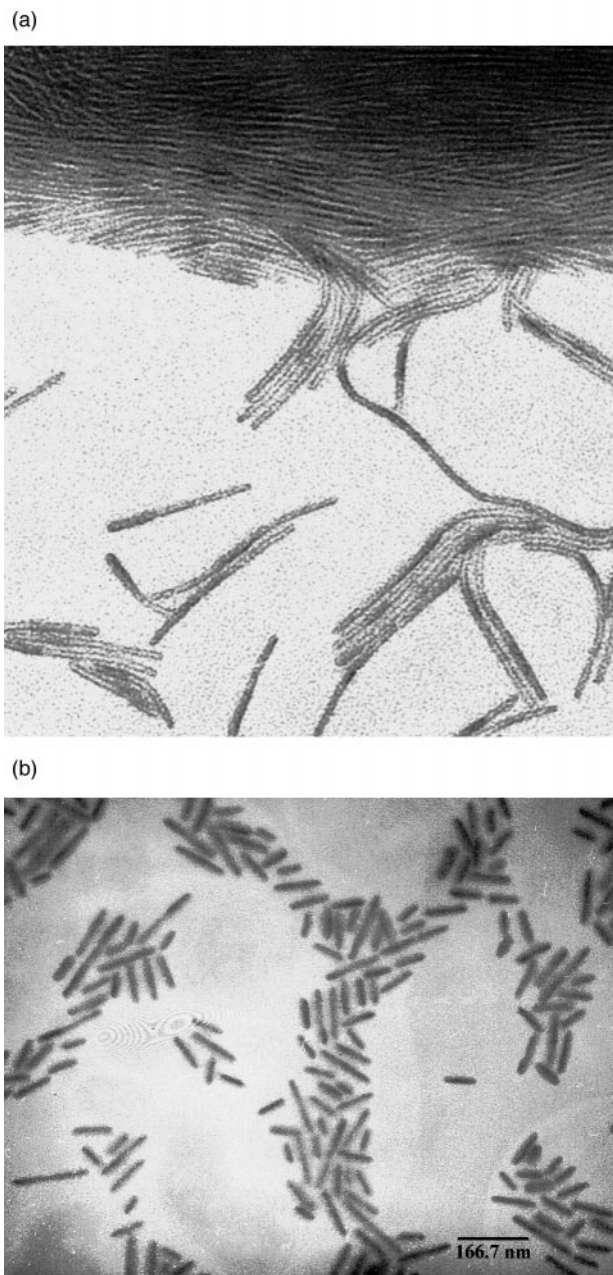


Fig. 8 Transmission electron micrograph of PFS-b-PDMS micelles aerosol-sprayed from a dilute solution in hexanes onto a thin carbon film supported on mica (no staining agent was used); (a) shows a region where the individual cylinders are starting to pack to form a 2D film as well as isolated cylinders; (b) shows the smaller cylinders that are formed after ultrasonication for 2 h (60 W).

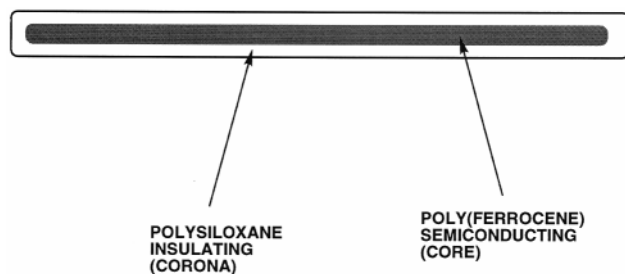


Fig. 9 Structure of cylindrical micelles of PFS-b-PDMS in hexanes.

architectures. In several systems morphologies such as vesicles and compound micelles in addition to spheres and cylinders have been identified.

Future opportunities exist for the generation of highly ordered, periodic structures 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 cylindrical, or lamellar domains (*e.g.* at surfaces) might allow charge transport in certain directions. Of particular interest is an extension of the ideas that have been previously developed (and described above) for the synthesis of magnetic nanostructures *via* the pyrolysis of poly(ferrocene)/MCM-41 composites to ordered, phase-separated block copolymer structures. Thus, nanoscale poly(ferrocene) domains may allow the generation of ordered arrays of magnetic spheres, magnetic multilayers *etc.* *via* oxidation or pyrolysis (*e.g.* using lasers). Selective ablation of blocks (*e.g.* using plasmas) may also provide a methodology for defining patterns.⁵⁶ Research work on many of these ideas and others is ongoing in our group, in many cases in collaboration with other researchers.^{11,43,51}

Summary

ROP of [1]silaferrocenophanes has permitted facile access to poly(ferrocenylsilane) homopolymers, a novel class of processable organometallic materials which have been found to possess a range of interesting physical properties. Living anionic and transition metal catalyzed ROP have allowed the preparation of materials with controlled molecular weights and architectures, *e.g.* block copolymers. Self-assembly of poly(ferrocenylsilane) block copolymers in the solid state or in solution yields well defined supramolecular, nanoscale organometallic architectures. Future work will be directed in particular towards further exploration of the properties of poly(ferrocenylsilane) homopolymers and understanding the self-assembly of block copolymers. In addition, applications in a variety of intriguing areas such as, for example, nanostructured magnetic materials, sensors, and charge-transport materials, and redox-active gels, will also be explored.

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