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Ferrocene polymers: current architectures, syntheses and utility

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Abstract

The discovery of ferrocene and its structural characterisation initiated an explosive rebirth of organometallic chemistry. Today, 50 years after this event, new uses are still being found for this remarkable organometallic moiety. The inclusion of ferrocene units into polymeric arrays has attracted much attention due to the electronic donating ability, reversible redox chemistry, steric properties and ready functionalisation of this stable fragment. This review outlines the current syntheses and architectures available for the construction of ferrocene-containing polymeric systems and examines some of the uses of the emergent metallocene polymers. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ferrocene; Metallocene; Polymer; Ring-opening polymerisation

1. Introduction

In recent years interest in organometallic materials has increased greatly with the recognition that they may be of use in a plethora of different applications. These have included nonlinear optical (NLO) devices [1], light emitting diodes [2], electrochemical sensors [3], molecular magnets [4], thin film transistors [5] and liquid crystals [6] to name but a few. It may be the case that the incorporation of metallocenes into polymeric architectures is a good strategy for the easy processing of these residues and possibly may lead to enhancement of their properties by cooperative mechanisms. Ferrocene has long been recognised as having great potential in this area and it was only shortly after its discovery in 1951 that attempts were made to produce polymeric derivatives of this remarkable compound. In 1955 the first well-characterised polymers bearing ferrocene as a side-chain were obtained by the polymerisation of vinyl ferrocene [7]. However, subsequent attempts to incorporate ferrocene in the main-chain were not particularly successful [8] and it was not until the mid-1970s that well-defined ferrocene-containing polymers were finally being reported [7]. It was to be another 15 years before this area really began to expand with the development of new polymerisation techniques, in particular the discovery of the ring-opening polymerisation (ROP) of strained [1]ferrocenophanes [9].

The two main architectures possible for ferrocene-containing polymers are schematically represented in Fig. 1. These comprise main-chain polymers (**A**), in which there is a 1,1′-substitution pattern of spacers about the ferrocene unit and side-chain polymers (**B**), in which the metallocene is appended in some way to the polymer backbone. Type **B1**, the embedded side-chain polymer, represents a rare subclass of type **B** in which the iron atom forms the point of lateral attachment of the side chain to the main chain. It is the aim of this mini review to give the reader an overview of the current ways in which ferrocene is incorporated into polymeric structures.

2. Main-chain polymers

2.1. The ring-opening polymerisation (ROP) reaction

Ring-opening polymerisation (ROP) (Scheme 1), undoubtedly takes centrestage in the formation of polymeric systems which include ferrocene as a main-chain element. This is due in large part to the enormous

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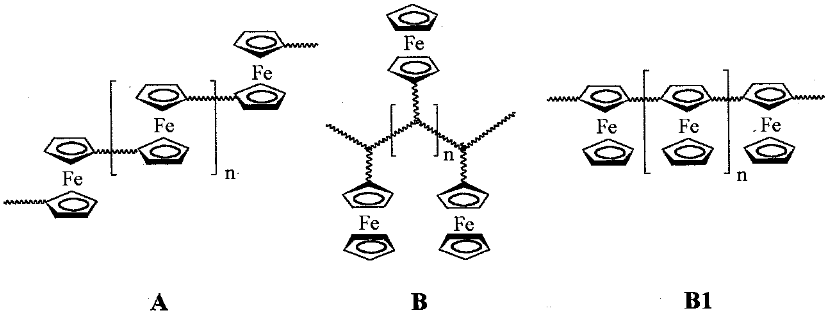
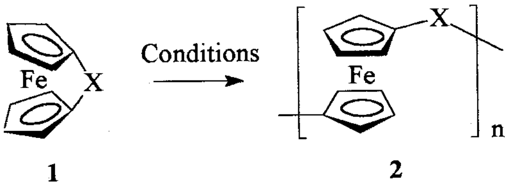


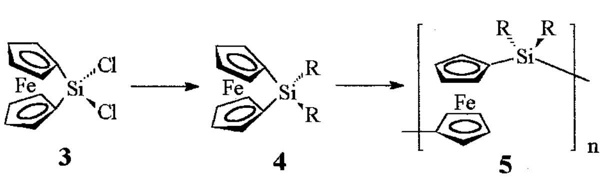
Fig. 1. Structural classes of ferrocene-containing polymers.

efforts of Manners and coworkers over the last decade [10]. This research was initiated by their serendipitous discovery of a thermal ROP route to poly(ferrocenylsilanes) **2** [11] from strained ring-tilted ferrocenophanes **1** (Scheme 1) such as those first reported in 1975 by Osborne et al. [12]. These structures were originally dismissed by Rosenberg as 'impossibly strained' in 1970 [13] and it is perhaps ironic that in their reinvestigation of the Rosenberg synthesis of silyleneferrocenylene polymers [14] in 1997, Pannell and Sharma concluded that strained ferrocenophanes were probably intermediates in these very early preparations of ferrocene-containing polymers [15].

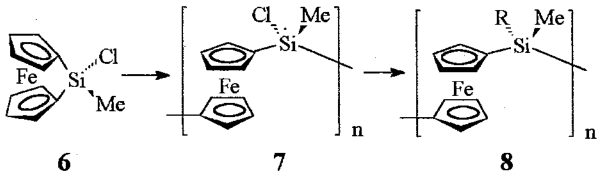
Since that time a wide variety of [1]ferrocenophanes incorporating Group 13 (B) [16], Group 14 (Si, Ge, Sn) [17], Group 15 (P, As) [18], and Group 16 (S, Se) [19], elements have all been shown to undergo ROP reactions.



Scheme 1. Ring-opening polymerisation (ROP).



Direct Substitution Pathway



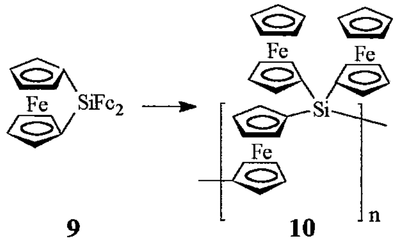
Sequential Substitution Pathway

Scheme 2.

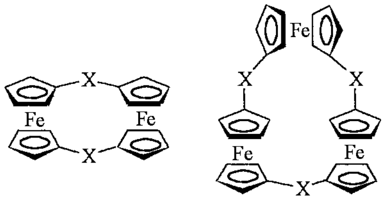
Most of these have afforded soluble materials with enormous molecular weights ($M_n > 10^5$ in the case of silicon-bridged [1]ferrocenophanes) [20]. Much of the work on the ROP reactions of heteroatom-bridged ferrocenes has been thoroughly reviewed [9,10,20,21] and only very recent developments will be discussed here.

Most of the work on the ROP reaction has been conducted on [1]silaferrocenophanes and initially the substituents attached to the silicon atom were limited to aryl and alkyl groups [9] but recently a general route to [1]silaferrocenophanes substituted with amino, alkoxy and aryloxy was reported [22]. This has been further extended to give access to the hydrophilic or water-soluble polymers **5** by the inclusion of polyether or ionic substituents introduced by treatment of the chloride-substituted precursor **3** with a polyether alcohol or ethanolamine in the presence of triethylamine (Scheme 2, direct substitution pathway) [23]. Such substituents had previously been introduced after the ROP step (Scheme 2, sequential substitution pathway) by reaction of **7** with organolithium reagents to afford the products **8** [24] but this new protocol represents a much more convenient synthetic method. The resulting polyethers **5** (R = OX) were readily soluble in water, methanol, THF and benzene. Similarly, after protonation or quaternisation the ammonium polyelectrolytes **5** ($R = N^+X_3$) were water soluble and formed slightly cloudy solutions. Dynamic light scattering studies suggested that the polymers formed aggregates which were easily dissociated by mild sonication. However, within 30 min the majority of the polymer chains recombined to their previously aggregated state. This route has also been employed by Cerveau et al. in order to afford a variety of alkoxy-substituted [1]silaferrocenophanes which have been incorporated into a silica matrix by a non-hydrolytic sol-gel process [25]. Similarly the polymers from thermal ROP reactions of these monomers were found to undergo hydrolytic sol–gel polycondensation to afford solids with conservation of the electrochemical properties of the original polymers [26].

Recently efforts have been made to produce systems containing highly metallised side chains and in an early example the ROP reaction of fcSiMeFc (Fc = (η-C_5H_4)Fe(η-C_5H_5), fc = (η-C_5H_4)$_2$Fe) was shown to give



Scheme 3.



11a X = $SiFc_2$ **12a** X = $SiFc_2$
11b X = PPhS **12b** X = PPhS

Fig. 2.

high molecular weight polymers ($M_n = 7.1 \times 10^4$) under thermal conditions [27]. Evidence for metal–metal interactions between all the ferrocene units was provided by cyclic voltammetry [28]. Indeed two-wave cyclic voltammograms are generally obtained for this class of compounds and have been explained in terms of the stepwise oxidation of alternating iron sites followed by the subsequent oxidation of the intervening iron atoms indicating that the ferrocenes are in communication with one another [11,29]. Recently the sterically encumbered [1]silaferrocenophane **9**, with two ferrocenes on the silicon atom was synthesised and DSC indicated that it undergoes ROP in the solid state between 150 and 230 °C (Scheme 3) [17a]. The polymerisation reaction was examined at various temperatures and at 250 °C insoluble polymeric material **10** was obtained but at lower temperatures (e.g. 200 °C) a soluble ($CHCl_3$) oligomeric mixture was isolated. This was characterised as a 3:1 ratio of the cyclic dimer **11a** and trimer **12a** and represents the first observation of cyclic oligomers from the thermal ROP of a [1]silaferrocenophane (Fig. 2). Similar by-products were obtained by Miyoshi and coworkers on attempted ROP of fcPPh (fc = $(\eta\text{-}C_5H_4)_2Fe$) initiated by UV irradiation [18c]. After sulfurisation with elemental sulfur the polymeric material was separated and analysed by gel permeation chromatography (GPC) to afford a polymer with an estimated $M_w = 1.1 \times 10^4$ and $M_n = 1.9 \times 10^3$. The dimer **11b** and trimer **12b** were also isolated separately as crystalline compounds and examined by X-ray analysis.

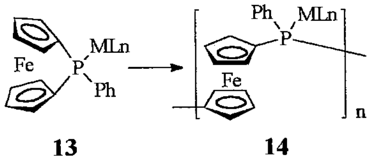
Pannell et al. have investigated the crystal structures of poly(ferrocenylenedimethylsilylene) PFDMS and poly(ferrocenylenedibutylsilylene) PFDBS (obtained by the ROP of the dimethyl and dibutyl [1]silaferrocenophane precursors) by X-ray diffraction [17g]. Both of these materials were crystalline polymers and both appeared to coexist as a mixture of 3D crystalline phases (monoclinic) and mesophases (2D crystals with a hexagonal or tetragonal packing of macromolecules) in non-oriented specimens. When PFDMS was oriented by extrusion, then only the monoclinc cyrstalline phase appeared to be present. This 3D monoclinic phase possessed the planar 2/1 helix conformation of the all-*trans* zig-zagging main chain. The existence of the partially disordered crystalline phases is related to the close energies of their various conformations.

The phosphorus-containing polymers are of particular interest since they offer not only monodentate but multidentate sites for coordination of a metal fragment and thus the possibility of polymer-supported catalytic domains. Phosphorus-bridged metallocenophanes were first reported in the early 1980s [30] and the first thermal ROP reaction of this species was recorded by Manners and coworkers in 1995 [31]. More recently living anionic ROP has provided materials with controlled molecular weights as well as poly(ferrocenylphosphine) block copolymers [32]. Transition metal (TM) catalysed routes to these polymers had been precluded until recently since all known catalysts coordinate to the P(III) centre of such species without leading to ROP. Manners has once again led the way in developing the first phosphonium-bridged [1]ferrocenophane to undergo both thermal and transition metal-catalysed ($PtCl_2$) ROP, affording polymers with over 100 repeat units. The molecular mass of these was determined by comparison of the glass transition temperature to those of a number of known permethylated poly(ferrocenylphosphine) polymers [33]. In an extension of this methodology attempts were made to polymerise borane adducts of fcPPh (fc = $(\eta\text{-}C_5H_4)_2Fe$) (readily formed by the addition of BH_3 or BCl_3) with $PtCl_2$, Karstedt's catalyst (platinum divinyltetramethyldisiloxane complex), $Pt(cod)_2$ (cod = cyclooctadiene) and $[Rh(cod)_2]OTf$ with varying degrees of success [18b]. However the borane adducts do successfully undergo thermal ROP. Miyoshi and coworkers have reported a complementary route to both the thermal and TM-catalysed methods to afford phophorus-bridged polymers by ROP upon UV irradiation [34] and have recently successfully polymerised metal-bearing [1]ferrocenophanes fcPPh[MLn] to afford the highly metallised polymers **14** with $M_w = 2.2 \times 10^4$ and $M_n = 2.2 \times 10^4$ for **14b** (Scheme 4) [18c]. In a related study directed towards the formation of highly metallised [1]silaferrocenophanes, Manners and coworkers have reported the synthesis of $Co(CO)_4$-substituted silicon-bridged monomers and are currently examining their ROP reactions [35].

Brunner et al. have begun to examine the catalytic potential of TM-modified polymers and have reported the first optically active [1]phosphaferrocenophanes obtained from the condensation of both (-)-dichloromenthylphosphine and (−)-bornyldichlorophosphine with 1,1′-dilithioferrocene (TMEDA adduct). Subsequent ROP under thermal conditions afforded oligo(ferrocenediylphosphines) of up to eight repeat units [18a]. Rhodium complexes were formed from these materials and the catalytic hydrogenation of folic acid using the polymers was found to proceed in good yield (> 90%) but only in low diastereomeric excess (de) (2%). This is in contrast to the catalytic species generated from the polymer precursors which gave higher de (> 20%).

2.1.1. Mechanistic studies of the ROP reaction

A good deal of crystallographic data has been collected for the monomeric precursors **1** and the tilt angle α has been identified as a crucial structural indicator of strain (Fig. 3). As might be expected the larger the value of α, the greater the enthalpy of ROP which may be determined by differential scanning calorimetry (DSC) (Table 1). The apparently anomalous value for boron with respect to sulfur has been explained in terms of the differing steric bulk at the bridging moieties. This causes substantial destabilisation of the polymers relative to the monomers leading to decreased polymerisation enthalpies. No substituents are present on the sulfur atom whereas bulky amino substituents have been attached to the boron atom in the cases so far reported. No sterically unencumbered boron-bridged [1]ferrocenophane has yet been synthesised for a realistic comparison of intrinsic ring strain with other [1]ferrocenophanes [16a].



13 **14**

14a MLn = $Mn(C_5H_4Me)(CO)_2$
14b MLn = $Mn(C_5H_5)CO)_2$
14c MLn = $W(CO)_5$

Scheme 4.

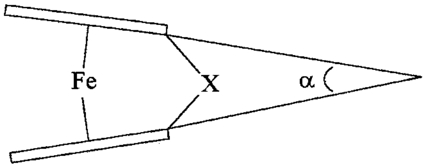


Fig. 3. Tilt angle α, for strained metallocenes.

Table 1
Tilt angles and ROP enthalpies for strained [1]ferrocenophanes

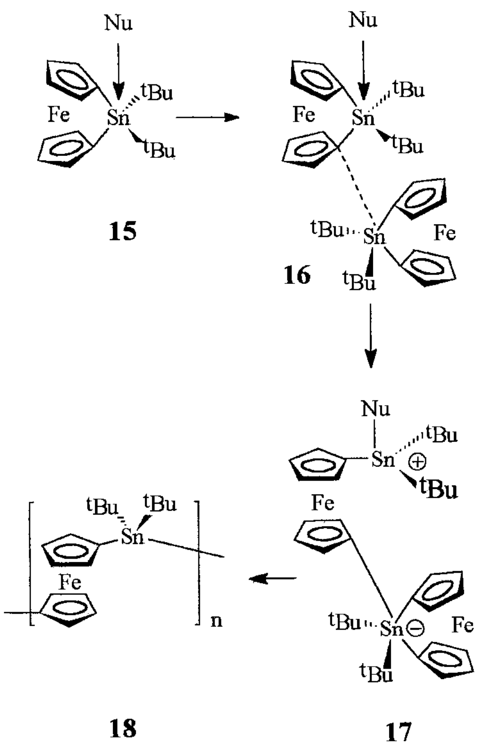
Bridging element X	α [a] (°)	Enthalpy of ring opening [b] ($kJ\ mol^{-1}$)	Reference
Ti, Zr, Hf	6		[36]
Ge, Sn	14–19	36	[17d,f], [41]
Si	16–22	70–80	[17a,b]
P, As	23–27	68–83	[18]
Se	26	110	[19]
S	31	130	[19]
B	31–32.4	95	[16]

[a] Angles determined by X-ray diffraction studies.
[b] Values determined by DSC.

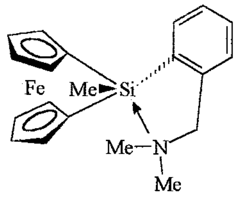
Strained ring-tilted [1]- and [2]metallocenophanes may be polymerised by a number of protocols including thermal ROP [21a], living anionic ROP [37], nucleophilically assisted ROP [38], TM-catalysed ROP [39] and photoinitiated ROP [18c] and the mechanisms of some of these reactions are under scrutiny.

Of these methods the thermally induced ROP is currently the most general synthetic route to high molecular weight polymetallocenes from [1]- and [2]metallocenophanes [21a]. The mechanism for these reactions may involve heterolysis [40], but this has not been established. However a recent mechanistic study of the newly discovered nucleophilically assisted ROP reactions of Group 14 element bridged [1]ferrocenophanes may shed some light on the course of this reaction [38a]. Tin-bridged [1]ferrocenophanes **15** bearing sterically demanding substituents undergo an apparent spontaneous ROP in solution to afford the high molecular weight polyferrocenylstannanes **18** (Scheme 5) [17e]. A radical mechanism was proposed for this process but neither radical traps, radical initiators or irradiation had a substantial effect on the rate of polymerisation. However it was found that addition of amines did lead to increased reaction rates [38a]. The authors invoked a tin-ate complex as an intermediate in the polymerisation and not a free anion as might be expected (Scheme 5). Although examples of amine coordination to tetraorganotin are rare, it has been observed and leads to elongated tin–carbon bonds displaying enhanced chemical reactivity [42].

This new ROP methodology has been extended to germanium and silicon [1]ferrocenophanes. An analogous mechanism must be considered for thermal ROP in the melt since the [1]ferrocenophane substrates are often synthesised in the presence of TMEDA adducts of ferrocene and small amounts of amine impurities may be carried through into the polymerisation. With this in mind a hypercoordinate silicon-bridged [1]ferrocenophane **19**, has been prepared by the reaction of **6** with $Li[2\text{-}C_6H_4CH_2NMe_2]$ [38b]. The single-crystal X-ray structure (Fig. 4) which was obtained of this substance shows an Si–N distance of 2.776(2) Å (which is the shortest reported for a tetraorganosilane)



Scheme 5.



19

Fig. 4. Crystal structure of **19**.

and the silicon environment is substantially distorted towards a trigonal-bipyramidal configuration. This complex may then serve as a structural model for the proposed intermediate in the nucleophilically assisted ROP reaction of these compounds. In related work Manners has shown that silicon-bridged [1]ferrocenophanes (**9** and **20**) may also serve as precursors to solvated Si cations with ferrocenyl substituents [43].

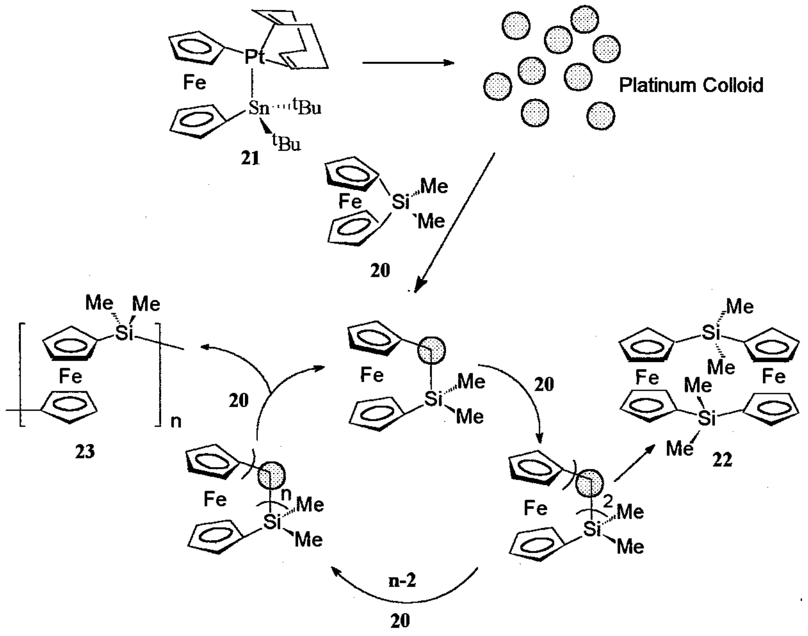
A variety of late transition metal complexes catalyse the ROP of silicon-bridged [1]ferrocenophanes to afford highly controllable molecular weight distributions and access to block copolymers [44]. These include Pt(1,5-cod)$_2$, Karstedt's catalyst (platinum divinyltetramethyldisiloxane complex), PtCl$_2$, PdCl$_2$ and [Rh(coe)$_2$(μ-Cl)]$_2$ and since the discovery of this reaction [39] efforts have been directed at deducing its mechanism. Originally it was proposed that a *homogeneous* pathway was operating [45] in which there is an initial insertion of the metal into the strained Si–C bond followed by consecutive oxidative addition and reductive elimination reactions (or σ-bond metathesis processes) to afford the polymeric materials [46]. However, a very recent study using the precatalyst **21** found that there was no incorporation of the ferrocenophane component of the precatalyst into either the resulting polymer **23** or oligomers (e.g. **22**) isolated from the supernatant [47]. Furthermore, the polymerisation cycle was inhibited by mercury which suggests colloidal platinum may be the major catalytic species and a revised *heterogeneous* mechanism has been proposed (Scheme 6).

2.1.2. Uses of materials derived from the ROP of [1]ferrocenophanes

Reports on the formation of Fe–Si–C ceramics from the pyrolysis of organoiron polymers have recently appeared [48]. In particular the polymers derived from ROP look promising since they may provide highly metallised organosilicon networks that function as 'controlled iron delivery vehicles' for subsequent pyrolysis to form lightweight ceramics with tunable magnetic properties [49]. The thermal ROP of the spirocyclic monomer **24** provides a cross-linked network with three possible Si microenvironments **25**, **26**, **27** and this is consistent with NMR observation (Fig. 5). Pyrolysis under an inert atmosphere below 900 °C provided high ceramic yields ($90 \pm 2\%$) of a material retaining its overall shape and in which the iron nanoclusters were superparamagnetic. At higher temperatures larger ferromagnetic iron clusters embedded in the 'carbosilane–graphite matrix' were obtained [50].

In an elegant attempt to control the size of these magnetic domains the ROP of **20** has been conducted inside the channels of mesoporous silica MCM-41 followed by pyrolysis of the modified material to afford a composite with Fe nanoparticles of ca. 30 Å embedded in the channels [51].

The discovery of the anionic ROP of silicon-bridged [1]ferrocenophanes has allowed the preparation of the first examples of block copolymers with transition metal atoms in the main chain [37] and this methodology has been used for the formation of poly(ferrocenyldimethylsilane-*b*-dimethylsiloxane) (PFDMS-*b*-PDMS) (block ratio 1:6) which unexpectedly formed cylindrical micelles in *n*-hexane [52]. These consist of an organometallic core of PFDMS and a corona of PDMS chains resulting from the immiscibility between the PFDMS blocks and the solvent. The dimensions of these micelles (which also form from the related PFDMS-*b*-polyisoprene) can be varied and their lengths may be controlled from ca. 70 nm to over 10 μm (Fig. 6) [53]. Similar block copolymers have been synthesised by the initiation of the anionic ROP of the phenyl phosphorus-bridged [1]ferrocenophane by living polyisoprene in THF [54]. Very recently the micellisation behaviour of these materials has been studied and



Scheme 6. Possible mechanism for metal-catalysed ring-opening polymerisation.

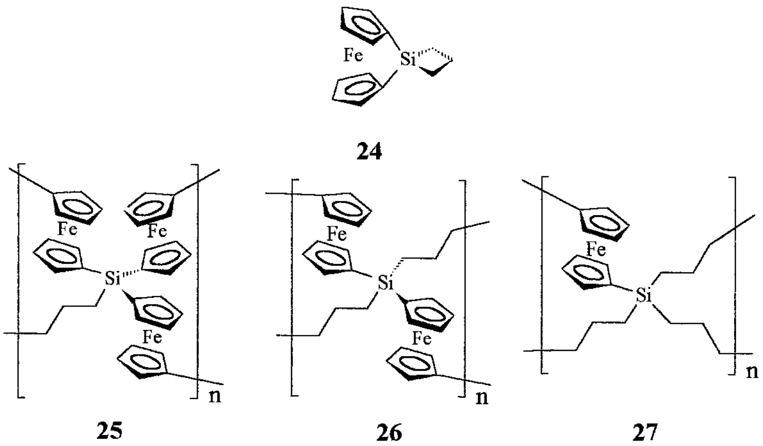


Fig. 5. Possible silicon micro-environments in the polymer derived from **24**.

they have been found to form ‘star like’ spherical micelles in hexane. This class of block copolymer is of twofold interest since the alkenes in the polyisoprene shell were cross-linked by UV irradiation in the presence of AIBN while the phosphorus sites in the backbone of the polymer were coordinated to gold. The modified materials still afforded micelles but with a larger size and broader size distribution [55]. Such self-assembled metal-containing micelles may be of interest for catalytic applications, redox active encapsulants or precursors to magnetic nanostructures such as those discussed below.

These observations have recently been exploited for the formation of oriented nanoscopic ceramic lines [56]. Cylindrical micelles were successfully aligned using capillary forces on semiconducting substrates and were

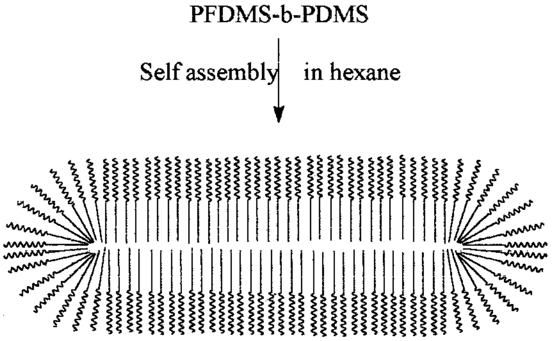
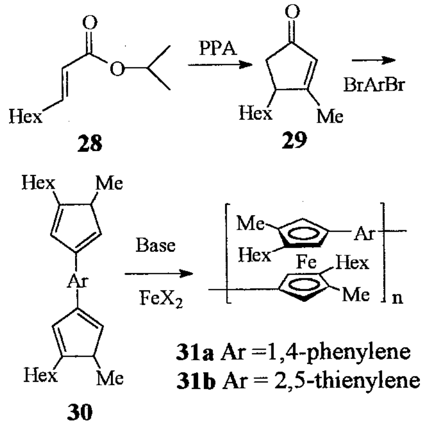


Fig. 6. Cylindrical micelle formation.



Scheme 7.

found to act as resists leaving cylindrical clusters of Fe, Si, O and C after etching with hydrogen plasma for 10 min at 100 W. The authors suggest that this technique may provide access to connected, potentially magnetic nanoscopic ceramic patterns not accessible by conventional lithographic techniques [57].

2.2. Main-chain ferrocenyl polymers not derived from ROP

Of course ROP is not the only method to afford polycondensed ferrocenes. There are numerous ways in which this has been achieved, for example palladium-catalysed methods including Heck [58], Susuki [59], Sonogashira [60] and Negishi [61] have all provided a variety of novel polymer architectures. Condensation methods such as the Knoevenagel condensation [62], the reaction between lithiated bisfulvenes and ferrous halides [63] and substituted cyclopentadienyl salts also with ferrous halides [64] have each proved fruitful. Ring-opening metathesis polymerisation (ROMP) has likewise been successful in this area [65]. Again, much of the work in this area up to mid-1998 was summarised in the excellent reviews by Manners [20], Swager [66] and Rehahn [21b] and the reader is directed towards these articles for a detailed discussion of the literature pre-1999.

2.2.1. Condensation polymerisation

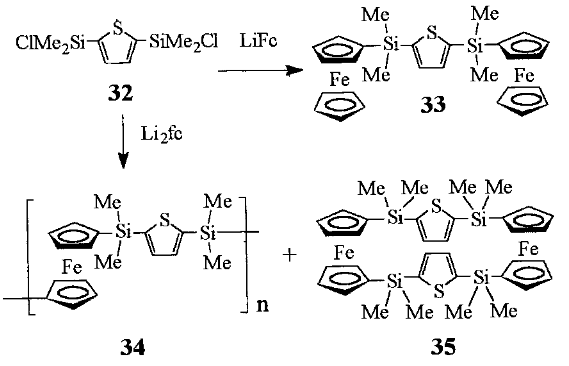
One of the most important goals fuelling the synthesis of metallocene polymers has been the desire to fully understand the electronic and magnetic properties of these novel materials [67]. For example the presence of magnetic ordering of paramagnetic iron centres in partially or fully oxidised oligomers and polymers remains unsettled [17b,68]. Curtis and coworkers have been developing a general route to conjugated ferrocene polymers in order to address this issue and have recently described the synthesis of soluble poly(ferrocenylenearylene)s **31**, from the condensation of bis(alkylcyclopentadienide)arenes **30**, (Ar = 1,4-phenylene and 2,5 thienylene) with ferrous halides (Scheme 7) [69]. In contrast to the materials obtained from ROP these polymers have a conjugated backbone which should enhance communication between the metal centres. The authors suggest that the magnetic and spectroscopic properties may be fine-tuned by the judicious choice of bridging element. In order to improve the solubility of the materials, hexyl and methyl groups were built into the monomers and the inevitable asymmetrically substituted polymers obtained by the step-growth condensation methodology ensured high solubility of the resultant compounds. The polymerisation produced significant amounts of cyclic oligomers but this could be suppressed somewhat by the incremental addition of the iron salt to the reaction mixture over several days and materials with $M_w = 5 \times 10^4$ and $M_n = 4 \times 10^3$ were obtained. CV measurements indicated that the iron centres exhibited significant interactions in the neutral polymers but the mixed valence materials (formed from conproportionation between the fully oxidised polymers and neutral species) appeared to show little electron transfer between metal centres as measured by IR, NIR (near IR) and Mössbauer spectroscopy. Unusual magnetic properties were also observed in some of the oxidised polymers but these were ascribed to effects of the degenerate ground state of the ferrocenium ions and not to any long-range magnetic ordering.

In a related study, Nishihara and coworkers examined the NIR photoconductivity of poly(2,2′-dihexylferrocenylene) doped with varying amounts of TCNE [29b,63,70]. The polymers, which were also solubilised by pendant hexyl groups, were found to exhibit a higher electrical conductivity on photoirradiation with NIR light compared to visible light and this was attributed to the existence of both intervalence-transfer bands and charge-transfer bands in the NIR region. A positive dependence between the NIR photoconductivity and the number of ferrocenylene units in the main chain was also observed. The Mössbauer spectra of the partially oxidised species gave both the singlet due to Fe^{III} and the doublet due to Fe^{II} which indicated that the charge is localised on the Mössbauer time-scale.

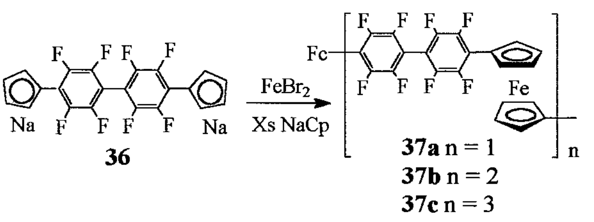
In an alternative approach to the synthesis of thienyl spaced polymers **31b**, which may have extended conjugation in the backbone, Pannell has investigated the step-growth polymerisation of 1,1′-dilithioferrocene with 2,5-bis(chlorodimethylsilyl)thiophene **32** (Scheme 8). This was intended to afford polymers with a Si–thienyl–Si spacer moiety, **34** but as is often the case for this methodology, a series of low molecular weight cyclic oligomers was obtained [71].

The structure of the first of this series **35**, was determined by X-ray crystallography and the Fe–Fe distance was found to be 7.57 Å. The acyclic compound **33** was synthesised for comparison and electrochemical studies indicated that there are two discrete redox processes for the cyclic dimer but only a single wave for **33** (in which the crystallographically determined Fe–Fe distance is 11.28 Å). This suggested that a through space interaction may be operating in the former and that the > 11 Å distance between the iron atoms in the latter precludes such a mechanism. The authors have previously noted that in diferrocenyl oligosilanes Fc(SiMe$_2$)$_n$Fc, when n is equal or greater than 4 then the cooperativity between the iron atoms is also lost [72].

A similar and perhaps more surprising loss of interaction between adjacent iron centres has recently been reported by Deck and coworkers for perfluorinated biphenylene-linked ferrocene oligomers **37** (Scheme 9) [73]. Their original approach to these systems utilised the step-growth oligomerisation of the fluorinated dibasic ligand **36**, prepared from NaCp and decafluorobiphenyl, using carefully controlled reactant ratios in order to isolate the oligomers **37** albeit in low yields. From electrochemical studies no communication was evident between the iron centres of **37a**. Two reversible oxidations were seen for the triferrocenyl system **37b** in which the central metallocene is flanked by two perfluoroaryl groups but the additional potential required to oxidise this moiety is no greater than that predicted on the basis of the extra substituent effect.



Scheme 8.



Scheme 9.

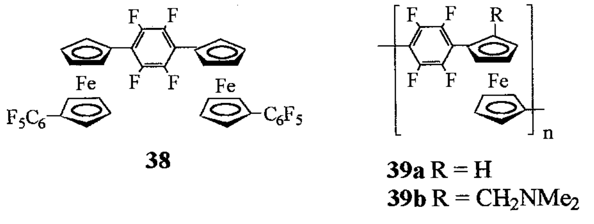


Fig. 7. Perfluorinated phenylene-linked ferrocene polymers.

The authors have since reported a modification in their synthesis of these highly fluorinated systems in which 1,1′-dilithioferrocene was reacted with hexafluorobenzene in order to produce the polymers **39** (Fig. 7) [74]. Unfortunately the poor solubility of **39a** (even in fluorous solvents) and the problems associated with the formation of very pure 1,1′-dilithioferrocene frustrated their efforts to obtain high molecular weight polymers with these reagents and end group analysis of the partially purified materials produced an estimated degree of oligomerisation in the range $10 < D_n < 20$. In an attempt to overcome the solubility problems a CH$_2$NMe$_2$ unit was introduced and more soluble oligomeric fractions **39b**, were obtained corresponding to a molecular weight of about $M_n = 3500 \pm 500$. Electrochemical investigation of **38** in which the ferrocenes are separated by only one 1,4-C$_6$F$_4$ moiety (in contrast to the perfluorobiphenylene linkage in the original study [73]) showed that only a very weak interaction was operating between them and the authors conclude that such complexes 'hold little promise' for applications as 'molecular wires'.

Recently the first examples of azo-bridged polymeric ferrocenes have appeared and were generated by the addition of N$_2$O to 1,1′-dilithioferrocene [75]. The synthesis of well-defined oligomeric materials was also carried out in order to investigate their electrochemical properties [76]. These systems are related to the fluorinated examples above since the azo group is strongly electron withdrawing and a similar pattern is seen for the stepwise oxidation of the trimer. It is interesting to note that two irreversible reduction waves were observed for this species which suggests that electronic communication between the azo groups through the central ferrocene unit was in operation. A detailed study of the partially oxidised materials revealed that the intervalence transfer (IT) band characteristics were highly solvent dependent. In donating solvents a hole transfer mechanism may be at work. Elemental analysis indicated that the polymeric materials obtained were of a mixed nature comprised of azo and directly connected ferrocene units according to the formula $[\text{–(Fc–N=N–Fc)})_{0.6}\text{–(Fc–Fc)}_{0.4}\text{–}]_n$. The molecular weight of the soluble component was $M_w = 8.7 \times 10^4$ and $M_n = 1.3 \times 10^4$. The electrochemical characterisation of this material showed a broad quasi-reversible redox wave which appears between the potentials for the azo-bridged ferrocene oligomers and those for the directly connected ones.

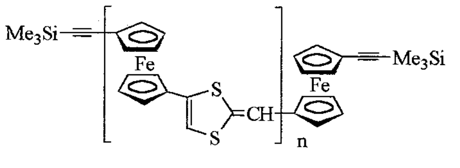


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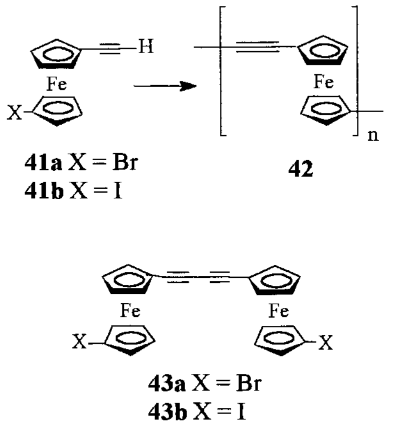
Fig. 8. Dithiafulvene-linked ferrocene polymers

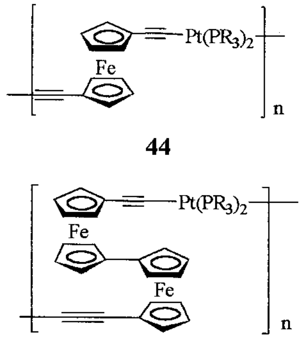


41a X = Br
41b X = I

42

43a X = Br
43b X = I

Scheme 10.



44

45

Fig. 9. Alternating main-chain platinum-ferrocene polymers.

2.2.2. Cycloaddition polymerisation

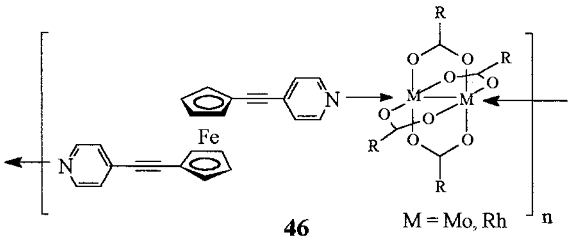
The polymer **40**, composed of alternating ferrocenes and dithiafulvenes has recently been reported, and in contrast to the above it represents a system in which both of the units in the main chain are electron donors (Fig. 8) [77]. The synthesis of this system was accomplished by an elegant cycloaddition polymerisation of ferrocenyl thioketenes to afford the π-conjugated systems and, depending on the reaction conditions, materials up to $M_w = 2570$ and $M_n = 1930$ were obtained. For comparative purposes the authors also synthesised a model compound in which two ferrocenes were linked by one dithiafulvene. The redox properties of this compound were as expected and three reversible oxidation peaks due to the three coupled redox sites were observed (no oxidative dimerisation was seen as is usual for 1,4-dithiafulvenes under these conditions). However, the polymer showed only a single, albeit broad, oxidation peak and the authors have attributed this to effective interaction between the two donors. The polymer was found to readily form a soluble charge transfer complex with TCNQ and could be easily oxidised with iodine.

2.2.3. Metal-catalysed polymerisations

Attempts to prepare polymers containing alkyne linkages have also been investigated and in particular poly-1,1′-ferrocenylacetylene has been much sought after due to its similarity to polyphenylethyne and the close proximity of adjacent redox active sites. However these substances have remained elusive due to difficulty in the synthesis of appropriately substituted bisalkynyl ferrocenes and their sensitive nature. Indeed early attempts involving the use of 1,1′-bisethynylferrocene precursors yielded only the products from intramolecular coupling to afford ferrocenophanes [78]. More recently coupling of diiodoferrocene with 1,4-bis(trimethylstannylalkynyl)benzene was attempted but was frustrated by the sensitivity of the reaction [79]. Poly[1,1′-bis(-diorganosilylethynyl)ferrocene] and its dicobalt hexacarbonyl adducts have also been examined [48b,80]. Lately Butler et al. have published a facile route to 1-iodo- and 1-bromo-1′-ethynylferrocenes **41** which were obtained as low melting yellow oils (Scheme 10) [81]. The authors attempted to polymerise these materials under palladium-catalysed conditions and obtained a mixture which they propose to contain polymeric fractions **42** along with homocoupled **43** and oligomeric products. Although they give no indication of molecular weights this report nonetheless represents an important achievement, if conditions can be found to produce clean polymerisation of the monomers.

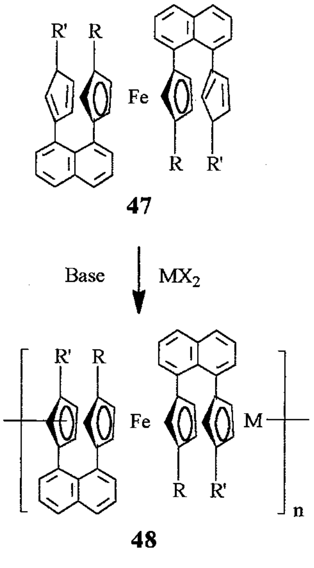
2.2.4. Polymers including both ferrocene and other metals in the main chain

2.2.4.1. Condensation polymerisations. Several routes have been developed for the synthesis of mixed metal species with ferrocenylethyne units which also incorporate nickel and palladium metal centres in the main chain but problems associated with purification have thus far precluded single step polymerisation procedures [82]. However, recently Long et al. have reported a new route to alkynylferrocene and biferrocene ligands and their polymerisation to platinum-containing dimers and oligomers [83]. Trimethylsilyl protected 1,1′-diethynylferrocene was converted to the bistrimethyltin analogue in excellent yield and was found to form oligomers **44**, upon the addition of one equivalent of *trans*-Pt(PR$_3$)Cl$_2$ with catalytic CuI (Fig. 9). The air- and moisture-stable 1,1‴-diethynylbiferrocene was found to react similarly and whilst the former produced oligomers **44**, with molecular weights of $M_w = 4600$ and $M_n = 2800$ (52% yield) the biferrocene derived materials **45**, afforded up to 12 repeat units ($M_w = 11\,800$ and $M_n = 2640$) in much better yield (80%) (Fig. 9). The authors have performed an analysis of the frontier molecular orbitals in order to determine whether the possibility for communication exists between the Fe and Pt atoms and concluded that the HOMO does not provide a good route for conjugation between the metal centres since it is located on the iron atom and there are no contributions from the other centres. The SHOMO does show good π-conjugation between the d_{xz} orbitals of the platinum atoms, the p_x orbitals of the alkyne carbon atoms and the p_x orbital of the linking carbon on the cyclopentadienyl ring but this conjugation is not continued through the Cp–Fe–Cp system suggesting that Pt–Fe–Pt communication cannot be achieved through this molecular orbital. This was validated by the observation that only a single irreversible oxidation was observed by cyclic voltammetry in contrast to the two wave oxidations often seen for polymers in which the ferrocenes are in communication [84].



46 M = Mo, Rh

Fig. 10. Bimetallic coordination polymers of ferrocene.



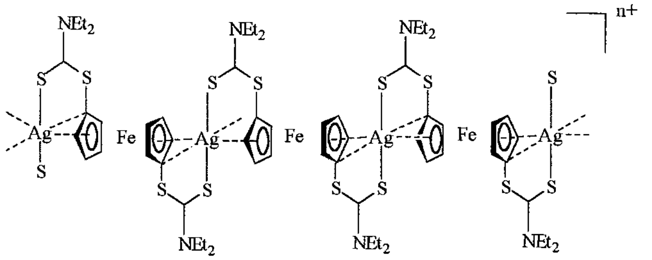
Scheme 11.

2.2.4.2. Coordination polymers. Coordination polymers have also been prepared with ferrocene as a main-chain element. 1,1′-bis(diphenylphosphino)ferrocene was found to form polymeric complexes with gold [85] (see also structure **49**, Section 2.3) and Wagner and coworkers have recently prepared a number of low-dimensional polymers which take advantage of the facile formation of boron–nitrogen adduct bonds. These were prepared from bisborylated ferrocenes by reaction with nitrogen heterocycles. Tris(1-pyrazoyl)borates have been used to form homo- and heterobimetallic structures linked through these 'scorpionate' ligands and the authors make the point that the metal–metal distances in such materials are fixed upon intramolecular motion. Unfortunately the metal centres did not seem to show any indication of electronic communication. Polyferrocenes with 4,4′-bipyridine [86] or pyrazine bridges have also been prepared and these ligands do appear to promote charge transfer along the polymeric rod [87].

Kühn and coworkers have reported the first example of a polymer **46** composed of bimetallic monomers and organometallic spacing groups but despite the apparent conjugated nature of the rigid backbone the ferrocene units appear to be isolated from one another (Fig. 10) [88]. Both rhodium and molybdenum complexes were examined and the number of repeat units was estimated by elemental analysis to be up to 14 $(Rh_2(O_2CCF_3)_4]_n(BPEF)_{n+1}$. The rhodium polymers were insoluble in most common solvents and the molybdenum species was found to decompose in the presence of a coordinating solvent such as THF; nonetheless thermogravimetric analysis indicated that the metal–axial interaction in the oligomers was quite strong.

2.3. Rigid rod main-chain polymers containing ferrocene

Organic rigid rod polymers generally comprise polyaromatic systems with σ-bond or alkyne linkages. However there are very few examples of systems with ferrocene forming part of the inflexible main chain [89] although it has been linked to polyarylacetylenic 'molecular wire' bridges as an end group [90]. Very special architectures must be designed in order to confine the ferrocenes in a one-dimensional array. Indeed the high rotational mobility of the cyclopentadienyl ligands has caused ferrocene to be characterised as a molecular ball bearing [91]. For the purposes of the 'rigid-rod' classification here, this rotational freedom must be restricted to the mainchain axis of the polymer. Most notably Rosenblum et al. have developed a synthetic route to rigid architectures in which the ferrocenes are constrained to lie in a face-to-face arrangement by their *peri*-disposition about a naphthalene spacer **48** (Scheme 11). The initial attempt to construct these systems was via a condensation route



49

Fig. 11. A rigid-rod stacked ferrocene coordination polymer.

involving the palladium cross-coupling of 1,1′-dichlorozinc ferrocenes with 1,8-diiodonapthalene but the high reactivity of the ferrocene reagent along with the low solubility of the rigid polymer frameworks precluded exact stochiometric control and materials of only $M_n = 4000$ were obtained [61b]. This approach was revisited by Jang recently and 4-butyl-1,8-diiodonaphthalene was employed to improve the solubility of the resultant polymers which were shown to contain up to 13 ferrocenes units [61a]. In an alternative approach, monomers **47** were prepared sequentially from 1,8-diiodonaphthalene (Scheme 11). Polymerisation of these monomers with sodium bis(trimethylsilyl)amide and $FeCl_2$ provided higher weight materials **48** $M_n = 18\,000$ particularly when solubilising groups (R = R′ = 2-octyl) were incorporated into the structures [64c,92]. In a related study Jang has used 4-decyl-1,8-diiodonaphthalene to prepare polymers with up to 17 ferrocene residues [64a]. Recently a more expeditious route employing the RCpZnCl reagent has allowed facile access to aryl-substituted cyclopentadienyl monomers **47** (e.g. R = R′ = 4-benzyloxybenzyl) and the all iron and iron/nickel copolymers derived from them were found to be considerably more soluble in pyridine than previous materials [93]. A mixed ferrocene–titanocene–ferrocene triad has also been reported and it is suggested that polymeric systems containing this stuctural motif might be useful in catalysis [94].

Laguna and coworkers have recently published the structure of the coordination polymer $[Ag\{Fc(S_2CNEt_2)_2\}]_n[ClO_4]_m$ **49** (Fig. 11), obtained from the reaction of $Fc(S_2CNEt_2)_2$ with $AgClO_4$ [95]. The authors suggest that it represents the first example of the η^5-Cp rings of ferrocene bonded to another metal centre through the π-system. It however should be noted that $Fe_2Cp_3^+$ has been observed in the gas phase [96]. The solid complex precipitates from diethyl ether, is air stable and behaves as a 1:1 electrolyte in acetone. The structure of this complex is related to the well known charge-transfer complex formed from TCNE and ferrocene which forms a quasi-one-dimensional chain in the crystal lattice [97]. The most recent example of an intimately π-stacked linear ferrocene system comes from the laboratory of Nakajima who has successfully synthesised a number of multidecker sandwich polyferrocene clusters by cocondensation of laser vaporised vanadium and ferrocene. The clusters were detected by mass spectrometric means and were characterised as one-dimensional stacks with up to four ferrocene units separated by three vanadium atoms [98].

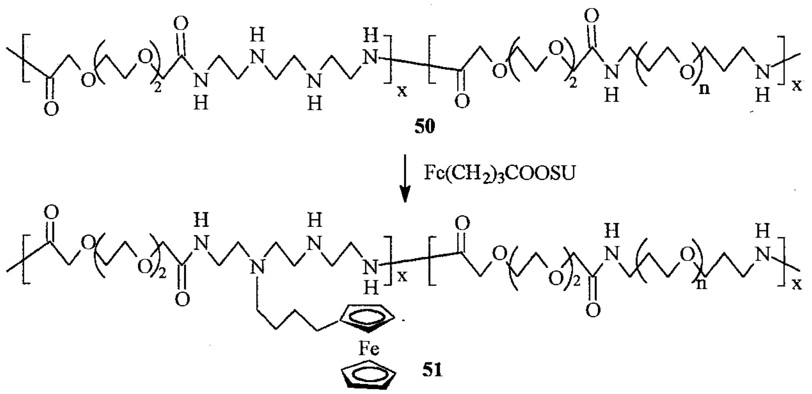
3. Polymers with ferrocene in the side chain

The incorporation of ferrocene into side chains along a polymeric backbone may be achieved in two ways. Either the polymer is constructed from monomeric units already bearing the metallocenes or it is laterally functionalised at a later stage. There are a huge number of widely diverse examples of both of these approaches in the literature and a full discussion of the topic is beyond the reach of this short review. The reader is directed to the many excellent reviews and books covering this topic up to the last few years [99]. Instead methodologies, trends and uses will be illustrated by examples taken from the recent literature.

3.1. Peripheral functionalisation of organic polymers

The incorporation of ferrocenes in the side groups of polymers has been achieved by the modification of conventional organic polymers. For example addition of ferrocene carboxaldehyde to poly(allylamine) [100], quaternisation of poly(vinylpyridine) with ferrocenylmethyltrimethyl ammonium iodide [101] or treatment of polyacrylic acids with ferrocenyl alcohols [102].

One area where ferrocene is recently experiencing a burgeoning degree of interest is in cancer research. The antiproliferative activity of certain water-soluble ferricenium salts against a number of murine and tumour lines has been known for some time [103] and Neuse and coworkers have made considerable progress in this area. This pioneering work serves to illustrate a methodology directed towards the lateral modification of organic polymers with ferrocene substituents. In early work bioactive ferrocenyl groups were bioreversibly bound through pendant amide linkages to polyamides and it was anticipated that these macromolecular carriers would act as protective transport vehicles to convey the metallocene agent to the site of action. The water-soluble materials displayed outstanding antiproliferative activity in vitro against human cancer lines. Lately Neuse and coworkers have derivatised similar polymers in which the amine point of attachment was an intrachain constituent, thus bringing the metallocene into closer contact with the polymer backbone (Scheme 12) [104]. This strategy was designed to probe the pharmokinetic fate of these ‘pro’drugs and the dependence of bioactivity on the accessibility of the



Scheme 12.

biofissionable linkages. A variety of polyamides, e.g. **50**, prepared by diester–diamine polycondensation or Michael-type polyaddition were studied and modified by addition of *N*-succinimidyl 4-ferrocenylbutanoate ($Fc(CH_2)_3COOSU$) to afford high metallocene loadings in reasonable yields 35–70% as exemplified by **51**.

In a related approach the ferrocenes were distributed along polyaspartamide or oligo(ethylene oxide)-containing polyamides by coupling 4-ferrocenylbutanoic acid with **52** affording biofissionable esters **53** (Scheme 13) [105].

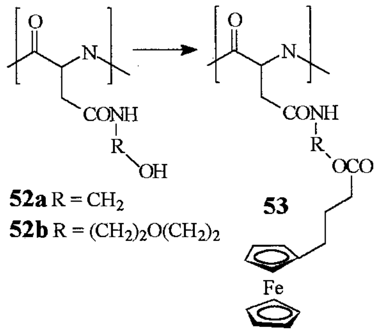
These completely water-soluble polymers were found to contain 2.5–5.5% incorporation of iron corresponding to up to 30% loadings.

The cytotoxic properties of some of the amide-linked polymers against the LNCaP human metastatic prostate adenocarcinoma line are in press. These compare well to the square-planar cisplatin-type anticancer drug systems [106] and this augurs well for such an approach to cancer therapy.

In an alternative approach to the above methods, several groups are studying the use of palladium coupling for the derivatisation of organic polymers, in particular oligonucleotides. Given the stability, reversible redox properties and ready functionalisation of ferrocene it is inevitable that it should find utility as a label for biomolecule sensing and characterisation purposes by electrochemical means. Yu et al. have been developing microsensors for the detection of nucleic acids and have recently reported the incorporation of ferroceneacetylene into oligonucleoitides by Sonagashira coupling between ferroceneacetylene and iodinated uridine bases [107]. The authors suggest that the new ferrocene containing phosphoramidites in which the substituted uridine bases are conjugatively linked to the metallocene can then be incorporated into any position of a DNA sequence using automated DNA synthesis techniques. The same group has very recently reported the inclusion of ferrocene at the 2′-ribose position in two novel phophoramidites via a butoxy-linker [108]. Automated DNA synthesis with these modified bases was used to afford DNA sequences with ferrocene appended at various positions along the oligonucleotides. No effect was found on the stability of the modified DNA and electrochemical studies indicated that the modified materials were indeed electrochemically active.

Grinstaff and coworkers have reported a similar derivatisation of an iodouridine (5IdU) residue whilst the oligonucleotide under construction was still bound to the column on an automatic synthesiser during DNA construction [109]. Phosphoramidite couplings with standard bases were performed followed by introduction of a 5IdU residue. The column was removed from the synthesiser, dried and charged with ferrocenyl propargylamide, $Pd(Ph_3)_4$ and CuI. It was refilled with solvent and shaken for 6 h followed by flushing and drying before replacement on the sythesiser. Routine synthesis was then resumed in order to complete the required oligonucleotide (Fig. 12). In this way site-specific ferrocene modified duplexes **54**, were obtained which appeared to exhibit little disruption of their structure relative to unmodified materials.

Ferrocene has also been incorporated into DNA as a capping group in order to function as a reporting moiety [110]. Fang and coworkers have prepared a sequence-known DNA strand of 256 base pairs which



Scheme 13.

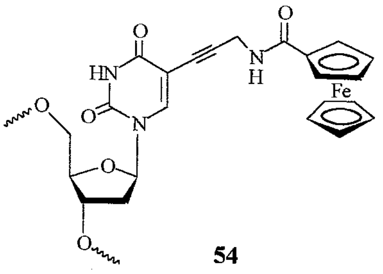
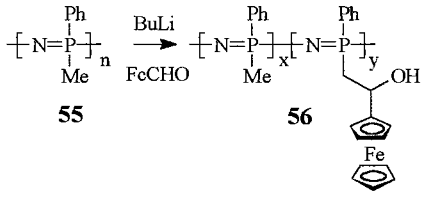
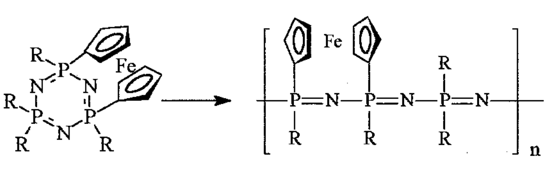


Fig. 12. The ferrocene-modified portion of an oligonucleotide.



55 **56**

Scheme 14.



57 **58**

R= F, OCH_2CF_3, Ar, Alkoxy, Alkyl, Ferrocenyl

Scheme 15.

was labelled with aminoferrocene at the 5′-end [111]. Sequence unknown samples were immobilised on electrodes and immersed in a solution of the DNA probe labelled with ferrocene. Only the complementary sequence (cDNA) could form double stranded DNA with the reporter strand and modify the probe. The anodic peak current was found to be linearly related to the concentration of the cDNA in the unknown sequence.

It is not only organic polymers that have been peripherally modified. Wisian-Neilson et al. demonstrated that polyphosphazenes could be functionalised with pendant ferrocenes by reaction of the deprotonated polymer **55** with ferrocene carboxaldehye (Scheme 14) [112]. It was evident from inspection of NMR spectra that 45–50% of the methyl groups had been substituted corresponding to 90–100% reaction yield based on the amount of butyllithium used. The molecular weight determinations of up to $M_w = 253\,000$ and $M_n = 83\,000$ by GPC–HPLC analysis, indicated that no degradation of the polymer backbone had occurred during this process. Cyclic voltammetry studies of the materials **56**, showed reversible oxidation waves and an increase in the number of ferrocene substituents was found to increase the charge-transfer efficiency for the phosphazine polymer in solution and as a film deposited on an electrode surface [113].

3.2. Ring-opening polymerisations

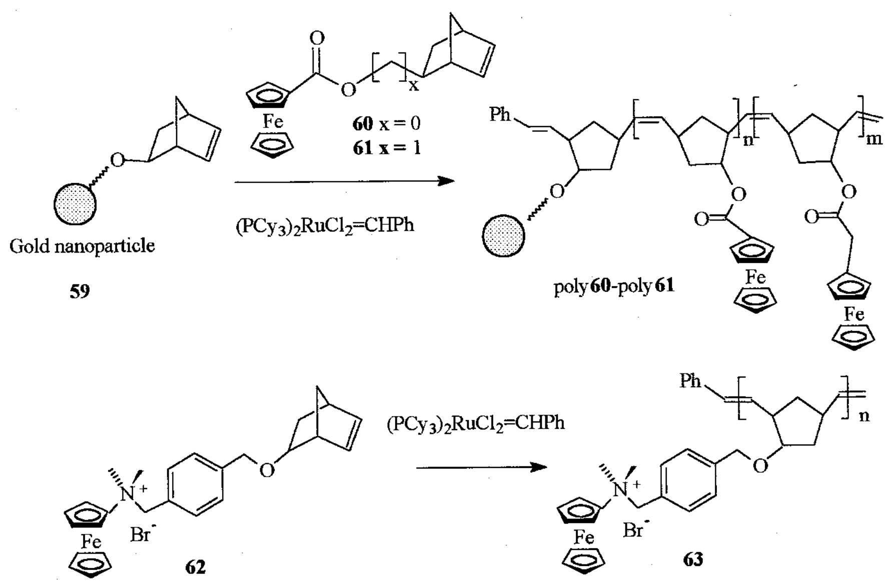
Of course ROP routes are not restricted to producing main-chain metallocene polymers. Allcock et al. have developed a very elegant methodology to access these compounds by the use of strained cyclic phosphazines to produce ferrocene-substituted inorganic polymers related to those shown above [114]. These side-chain polymers **58**, represent a very unusual structural motif in which the ferrocene is bound to the main chain in a 1,1′-binding mode (Scheme 15). In order to accomplish this, a transannular ferrocenoyl group was introduced into a cyclic phosphazine ring thus imparting the necessary ring strain for ROP. The degree of strain was evident from its non coplanarity as determined by an X-ray crystallographic study [115] and depending on side group-substitution patterns, these compounds would undergo polymerisation or ring expansion [116].

The mechanism of the polymerisation was investigated by the authors and it was found that fully organo-substituted ferrocenylphosphazines polymerise thermally in the absence of any added initiator. These results provided the first example of the uninitiated ROP of cyclotriphosphazines lacking P–halogen bonds. Intriguingly the reaction was not necessarily regiospecific with head-to-tail and head-to-head structural arrangements being noted for the first time. In contrast to the pendant ferrocene polymers **56**, these materials exhibited irreversible electrochemistry [117].

Ring-opening metathesis has also been applied to the synthesis of side chain ferrocenyl polymers and Mirkin and coworkers have used this approach to both build and immobilise side chain ferrocene polymers on gold nanoparticles [118]. A ROMP active norbornene segment was appended to a gold nanoparticle to afford **59**. Addition of the ROMP catalyst $(PCy_3)_2RuCl_2{=}CHPh$ (Cy = cyclohexyl) followed by the ferrocenyl-substituted norbornenes **60** or **61**, gave the required tethered redox active polymer chains (Scheme 16). Addition of **60** followed by polymerisation and then introduction of **61** followed by a further period of polymerisation gave the hybrid poly**60**–poly**61** layered particles. In a subsequent publication the authors used the same ROMP approach to synthesise the water-soluble polymer **63** from the amphiphilic ferrocenyl-modified norbornene **62** [119]. The authors suggest that the immobilisation of such water-soluble polymers on nanoparticles may provide useful biological diagnostic tools.

3.3. Metal-catalysed polymerisation

As noted earlier the logical way to obtain ferrocene-substituted polyenes would be to polymerise ethynylfer-



Scheme 16.

rocene but many early attempts produced poorly characterised polymers with unconvincing physical properties [120]. Recently the Schrock metathesis catalyst Mo(N-2,6-$Me_2C_6H_3$)($CHCMe_2Ph$)[$OCMe(CF_3)_2$]$_2$ has been employed to polymerise ethynylferrocene and well-defined soluble materials with up to 50 double bonds were formed [121]. Copolymerisations with 7,8-bis(trifluoromethyl)tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene] produced materials which on heating underwent retro Diels–Alder reactions to produce copolyenes in the so-called Feast approach [122]. Buchmeiser has extended the Schrock carbene approach to produce the polymer **64** with mesogenic side-chains by the living polymerisation of 4-(ferroceneylethynyl)-4′-ethynyltolan and in contrast to the original studies, found that the reaction starts virtually solely by β-addition to the metal=carbon double bond of the initiator (Fig. 13) [123]. The polymer which again contained up to 50 metallocenes was more soluble than poly(ethynylferrocene) and comparable in stability to it which may be due to 'steric shielding' of the conjugated alkenyl backbone.

Buchmeiser et al. have also reported the formation of polymers from a variety of other alkynes and surprisingly long effective conjugation lengths have been observed in the case of the polymer **66** (60 repeat units) having a 1,2-substitution pattern about the phenyl rings in the side-chains (Fig. 14) [124]. This was attributed to long-range π-stacking interactions which may be of the type shown in Fig. 14. A detailed ^{57}Fe Mössbauer study has been carried out on related materials [125].

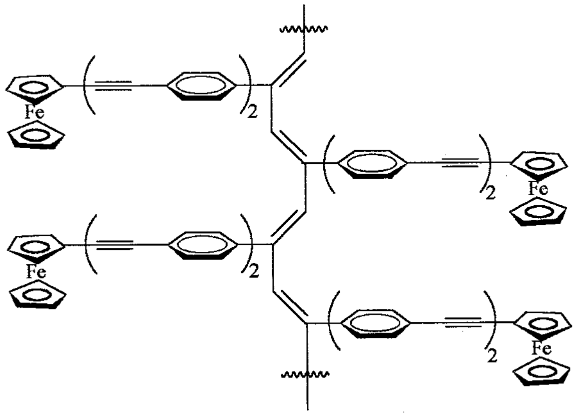


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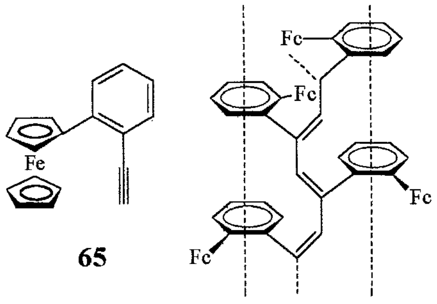
Fig. 13. Ferrocene-containing mesogenic side-chain polyene.



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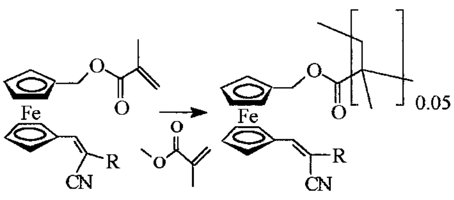
66

Possible π-stacking array

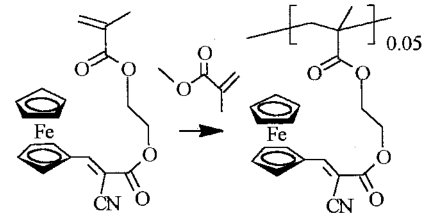
Fig. 14. π-stacking facilitates long effective conjugation lengths.



67 **68**

68a R = CO_2Et
68b R = 4-BrC_6H_4- Mn = 30000
68c R = Py Mn = 21000
68d R = CN Mn = 13000

Scheme 17.



69 **70**

Scheme 18.

3.4. Free radical polymerisation

Probably the earliest example of a polymer with pendant metallocene groups was obtained through the free radical addition polymerisation of vinylferrocene [126] to form poly(vinylferrocene) (PVF) [99] and perhaps it may be regarded as the 'parent structure' for this class of compounds. A variety of other alkenyl-substituted ferrocenes have been similarly polymerised, including acrylates, methacrylates and isopropenylferrocenes. Vinyl ferrocene has also been copolymerised with other alkenyl compounds [127].

The nonlinear optical properties of organometallic species have received a great deal of attention recently due to their tunable structural characteristics, accessible multiple oxidation sates, high dipole transition moments and charge-transfer transitions in the UV–vis region [1,128]. In many recent papers dealing with ferrocene-containing polymers the potential of these systems for NLO applications is often suggested but there have been very few studies specifically directed towards this topic [129]. Notably Wright et al. have examined the incorporation of some simple ferrocene-containing chromophores into both the backbone [130] and side-chain sides of polyacrylates. The latter studies serve to illustrate both the radical methodology for the synthesis of metallocene-containing side chain polymers and their potential for second and third harmonic responses.

In the first example of a $\chi^{(2)}$ organometallic polymer to be prepared the authors polymerised the monomer **67a** with methylmethacrylate under free-radical conditions to produce the copolymer **68a** (Scheme 17) [131]. Films were cast on microscope slides and the material was aligned by corona poling to produce the required noncentrosymmetric environment. Second-harmonic-generation (SHG) measurements were performed with a Nd:YAG laser at 1064 nm and the material was found to exhibit an SHG efficiency four times that of the quartz standard.

Further, NLO-phores **67b**–**d** were synthesised and incorporated into polymer matrices in this way producing materials **68b**–**d**, with molecular weights varying from $M_n = 8000–43\,000$ [132]. The structure of the chromophores was varied by the placement of either the –CN acceptor moiety (Scheme 17) or the ferrocene (Scheme 18) at the terminus of the side chain, in order to probe their orientation and relaxation behaviour within the polymer matrix. Corona poling of cast films of the materials at $T_g + 25$ followed by SHG measurements showed them all to exhibit responses except **68c**. The authors concluded that packing of the NLO-phore within the polymer matrix is very important for orientational stability over time. It is also interesting to note that the copolymers **68,** showed faster relaxation times since the chromophore is effectively decoupled from the polymer backbone by virtue of the 'ball bearing' nature of ferrocene (Scheme 18) [91].

3.5. Electrochemical polymerisation

The derivatisation of electrode surfaces is an area of very active research and to date poly(vinylferrocene) PVF thin films deposited on conductive substrata are among the most studied modified electrodes [3,133]. Oligomeric and polymeric materials bearing ferrocene as a terminal 'reporter' group have also been attached to electrode surfaces for example poly(ethylene glycol) chains PEG–Fc have been bound to glassy carbon electrodes by amide linkages [134] or attached to the outermost monolayer of self-assembled immunoglobulins on similar electrodes [135]. Thiol-substituted polyacrylates have been self assembled on gold electrodes and either terminate in ferrocene themselves [136] or form host–guest polymers with ferrocene-terminated poly(oxyethylenes) [137]. Polymers with many ferrocene domains along their length have been synthesised by direct electrochemical means, for example ferrocene-modified thiophenes produced unstructured monolayers by direct aniodic coupling from the solution [138]. Very recently Rault-Berthelot et al. have examined the electrochemical synthesis of polyfluorenylidene with a pendant ferrocene to produce fully conjugated polymers which were electroactive in non-aqueous and aqueous media [139]. Zotti et al. have reported the formation of self-assembled monolayers of heterocycle-substituted ferrocenes and their coupling to produce polyconjugated layers on the electrode surface (Fig. 15) [140]. Both polythiophene and polypyrrole monolayers were formed on indium-tin-oxide (ITO) substrates and the authors noted that the rate of self assembly was much higher when the ferrocene was oxidised. They tentatively suggested that this effect may be due to polar interactions of the ferrocenium heads via anion bridging. Unfortunately only the thienyl systems formed a polymeric layer (shown schematically in Fig. 15) on anodic coupling.

The derivatisation of electrode surfaces with redox receptors may open the way to new electrochemical sensors [141]. Electropolymerisation of ferrocene–crown ether bearing pyrroles has allowed the coating of electrode surfaces with polymer films which showed recognition towards Group II metal cations [142] and very recently Moutet and coworkers have reported the electrosynthesis of poly-1,1-bis(bipyridyl)-substituted ferrocene derivatives [142]. Compound **71** (Fig. 16) had previously been shown to be a convenient structure for the electrochemical recognition of Cu^{I} and Ni^{II} in homogeneous solution [143] and intriguingly the authors found that electrodes modified by the polymer displayed coordinating ability only towards Cu^{I} ions.

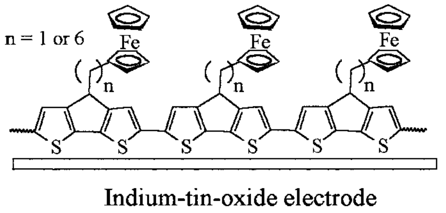
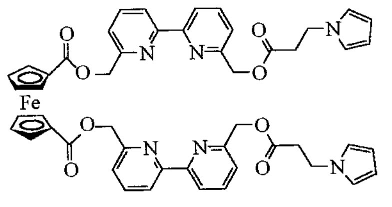
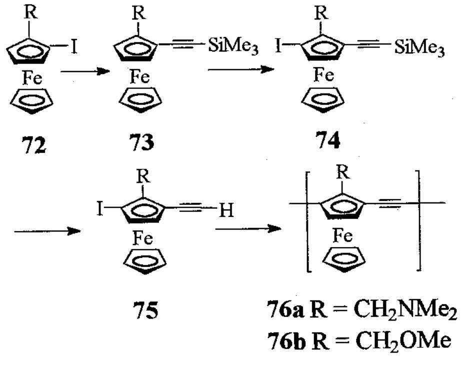


Fig. 15. Self assembled monolayers polymerise at the electrode.



71

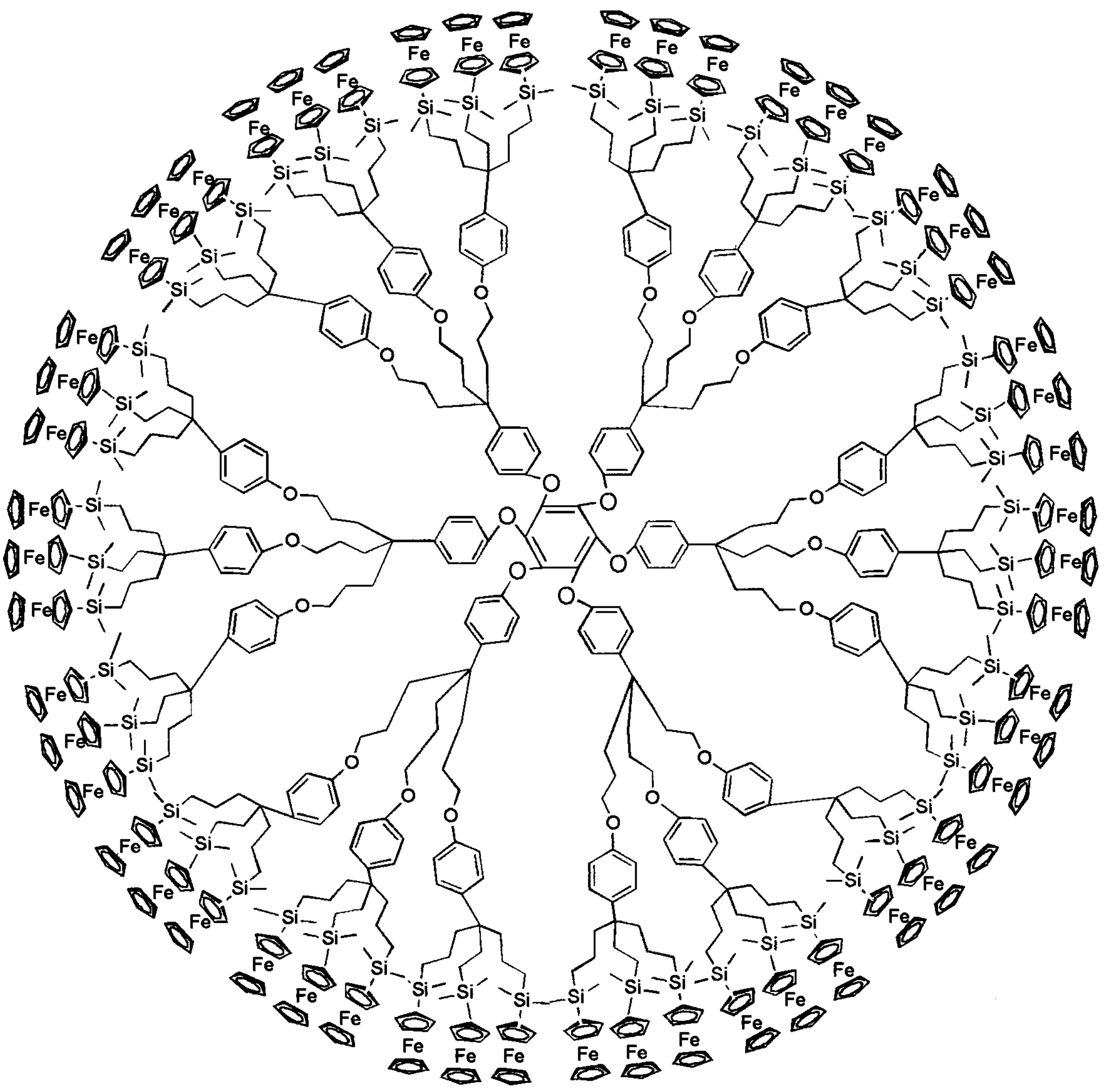
Fig. 16. Ferrocene-containing electrochemical Cu(I)/Ni(II) probe.



Scheme 19.

4. Embedded side-chain polymers

The least well represented of all the polymers containing ferrocene are members of the class **B1**, in which the ferrocene units are linked together through only one of the cyclopentadienyl rings. This produces an embedded side-chain architecture in which the iron atom is removed from the polymer backbone and becomes the lateral point of attachment for the side chains. The earliest examples of these structures were probably formed in experiments by Korshak and Nesmeyanov aimed at producing polyferrocenylenes by the polyrecombination of ferrocene. The authors assumed that all the possible 1,2-, 1,3- and 1,1′-modes of attachment within the resulting polymers would be obtained [8]. This was confirmed by Rosenberg and Neuse in their re-examination of these reactions [144]. In more recent work Herberhold et al. have reported the formation of oligomeric sulfur-bridged ferrocenes from radical reactions, showing this pattern of 1,2- and 1,3-attachment [145]. Abd-El-Aziz et al. have prepared materials in which $CpFe^{+}$ moieties were appended to a polyarylether (benzenoid) backbone and the number of metallic units has been varied from 2 to 35 [146]. Whilst the syntheses by Abd-El-Aziz were systematic, mild and reasonably general, of course these materials do not contain ferrocene per se. It was not until very recently that this molecular architecture was addressed in a systematic way to produce ferrocene-containing polymers by Plenio and et al. [147]. Starting from ferrocene it is difficult to directly introduce a 1,3-substitution pattern and so the route to these materials began with an *ortho*/*ortho*-directing strategy to build up the monomers **75** (Scheme 19). Deprotection of the silylacetylene **74a** ($R = CH_2NMe_2$) followed by Sonogashira coupling produced a dark red glassy material **76a**, which was readily soluble in polar solvents. This was attributed to the fact that the polymer is a diastereomeric mixture with random orientations relative to the backbone. The initial choice of CH_2NMe_2 as the directing group, whilst being readily derivatised, was found to be a hindrance towards electrochemical characterisation or molecular weight determination and in a subsequent publication the authors reported its replacement by CH_2OMe [147a]. The new monomers **75b**, were prepared as enantiopure compounds and polymerised as before to produce a material with an estimated molecular mass up to 10 kDa. This work provides the first example of a chiral organometallic polymer deriving its optical activity ($[\alpha]_{\mathrm{D}}^{20} = -198.0$ per



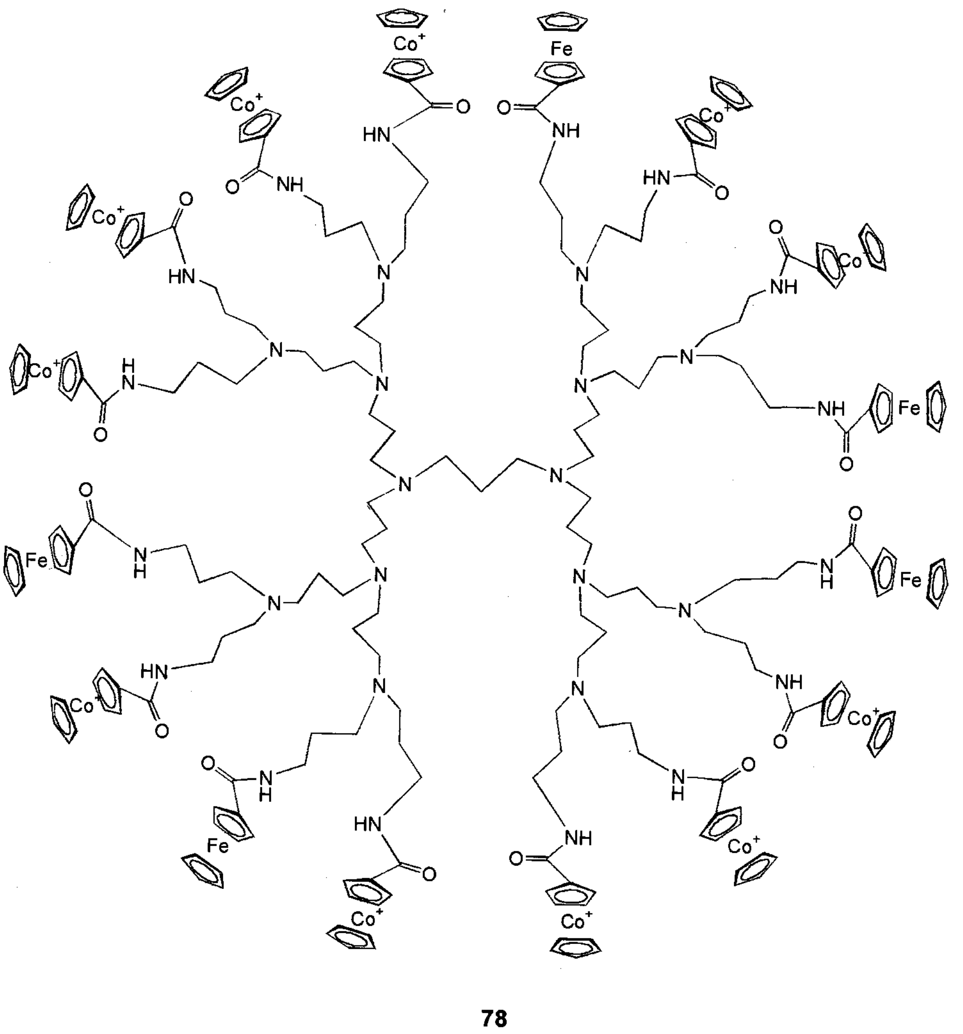
77

Fig. 17. Astruc's 54-ferrocene dendrimer.

ferrocene unit) from the planar chirality of 1,3-disubstituted ferrocenes. Evidence for extended electronic communication between the iron centres has been provided by UV and CV measurements and preliminary results suggest that they may be in better communication that the corresponding polymers prepared from 1,1′-disubstituted ferrocene monomers.

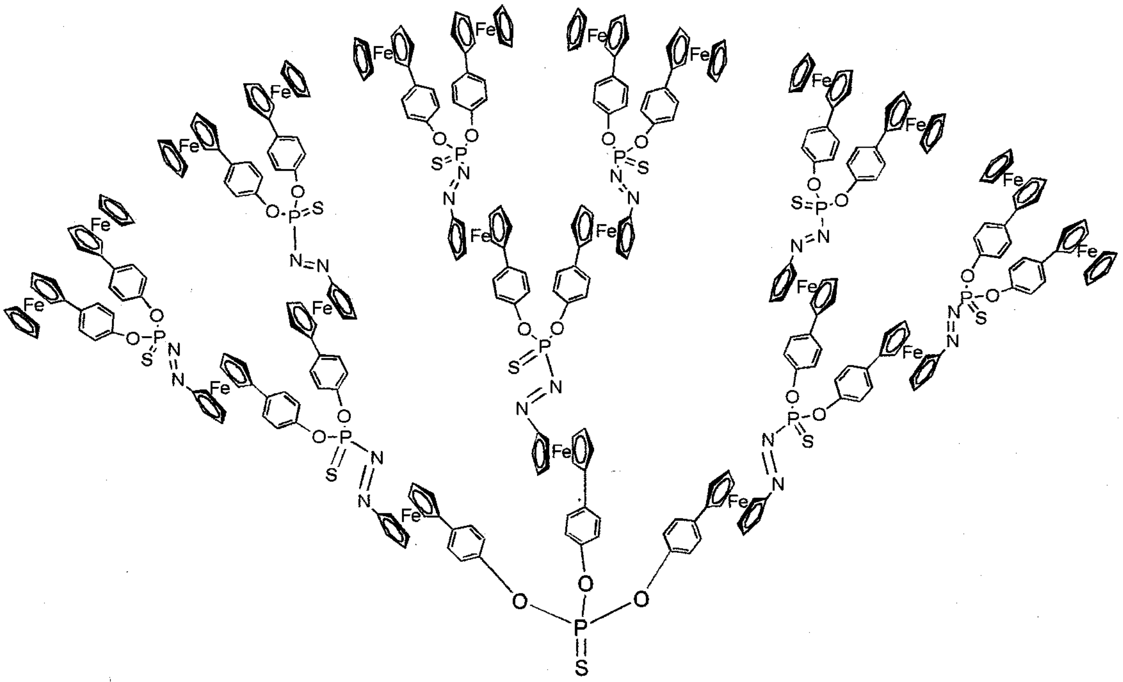
5. Dendrimers

The chemistry of dendrimers has been enjoying rapid development in recent years and many organometallic species have been incorporated into their structures [148]. Ferrocene-containing dendrimers have attracted a lot of interest since the first experiments to link ferrocene to the surface of small silicon-containing dendrimers [149]. Lately a good deal of this work has been reviewed [20,150]. Ferrocene may form the centre of the dendritic system [151] or be attached to the peripheries. Astruc and coworkers have recently reported a rapid convergent route to form structures of the latter type (Fig. 17) [152]. The four-step synthesis produced a 54-ferrocene dendrimer **77** which could be reversibly oxidised in DMF in a single 54-electron wave or by chemical means with NO^+, illustrating that access to precise redox active nanoscopic molecules is possible in this way. The material was used to modify a platinum electrode and the authors note that such materials may have the potential to find uses as sensors or molecular batteries. Cuadrado and coworkers have synthesised peripherally heterogeneous dendrimers containing ferrocene and cobaltocenium units located simultaneously on the surface of the dendritic structure by condensation reactions (Fig. 18) [153]. Intriguingly the dendrimers **78** based on diaminobutane did not display an equal loading of ferrocenes and cobaltocenium ions even when equimolar amounts of the metallocene precursors chlorocarbonylferrocene and chlorocarbonylcobaltocenium hexaflourophosphate were used. A significantly higher loading of cobaltocenium units was observed and in a later model study the authors concluded that chlorocarbonylcobaltocenium hexaflourophosphate is more reactive towards amines in comparison with the neutral ferrocene derivative due to the positive charge on the cobaltocenium moiety [154]. The convergent synthesis of a nona-ferrocenyl dendrimer using a topologically new tritopic dendron has recently been reported and avoids the neccesity of surface modification (as above) of the preformed dendrimer as the ultimate step [155]. Balvoine and coworkers have recently reported the first preparation of materials containing layers of ferrocene units [156] The first, in which ferrocene makes up the core of the dendrimer was synthesised from 1,1′-ferrocenedicarboxaldehyde and dichloro(methylhydrazino)phosphine sulfide followed by successive condensations of 4-hydroxybenzaldehyde sodium salt and the sulfide. The methodology adopted to synthesise the second class in which ferrocene units were located in three layers throughout the dendrimer was achieved by similar strategy with intermediate condensations of 1′-(4-hydroxylphenyl)ferrocenecarboxaldehyde sodium salt to afford structures of type **79** (Fig. 19). Dendrimers with ferrocene occupying positions only at the periphery were synthesised by successive condensations of 4-hydroxybenzaldehyde sodium salt with dichloro(methylhydrazino)phosphine sulfide to afford giant materials of up to nine generations which were capped with ferrocene to produce macromolecules with a theoretical count of up to1536 ferrocenyl groups



78

Fig. 18. Cuadro's mixed ferrocene-colbaltocenium dendrimer.



79

Fig. 19. Balvoine's multiple layered ferrocene dendrimer.

on the surface. CV studies of the dendrimer having three consecutive layers of ferrocenes showed that the inner two layers were oxidised simultaneously but the outer layer required a higher potential. All the ferrocenes at the surface of the giant dendrimers were oxidised at the same potential demonstrating their electrochemical independence.

6. Conclusions

The preceding discussion is intended to inform the reader of the diverse structures and some of the many uses of ferrocene-containing polymers. These materials have been known for some time now and the work outlined here represents only the most recent developments in the field. Nevertheless there remains considerable room for growth in this exciting area. In particular it is only very recently that chiral ferrocene-containing polymeric systems have been synthesised and the recognition that these may be of use in catalysis, sensing and optical applications is an important step forward. It is hoped that this review may stimulate further research into this fascinating class of compounds.

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