

Organometallic Polymers

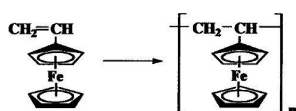
- Polymers with organometallic moieties as pendant groups
- polymers with organometallic moieties in the main chain
- condensation polymers based on ferrocene
- on rigid rod polyynes
- poly(ferrocenylsilane)s
- applications of Poly(ferrocenylsilane)s and related polymers,
- applications of rigid-rod polyynes,
- polygermanes
- polystannanes,
- polymers prepared by ring opening polymerization
- organometallic dendrimers.

Polymers with organometallic moieties as pendant groups

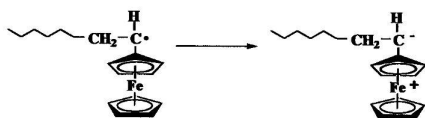
The addition polymerization of vinylferrocene to give organic polymers with pendent ferrocenyl side groups . This type of polymerization reaction has been attempted with the use of free radical, cationic, anionic, and Ziegler–Natta methods.

Free-Radical Initiation

For free radical polymerization reactions, the initiating radicals must be generated from azo-initiators because peroxides cause oxidation of the metal. In polymerizations the side group ferrocene units are the source of both the thermal stability of the product polymers and complications inherent in the free radical polymerization process.



For example, electron donation from the iron atoms to a growing radical chain end can convert an active radical to an anion which terminates the polymerization. The Fe⁺ center then rearranges to form a paramagnetic, ionically bound Fe(III) species.



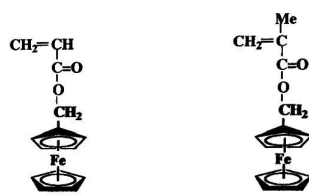
Ultimately this leads to extensive chain-transfer,

limitation of

the chain length, and formation of branched structures. This does not occur if the ferrocene unit is insulated from the vinyl group by a spacer unit, because these monomers polymerize normally. For example, monomer gives polymers with molecular weights as high as 250,000.

However, the electron-transfer process

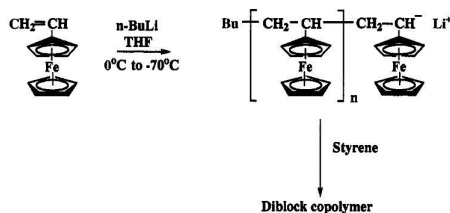
Molecular weights in the range of 6,000–35,000 have been reported for soluble, free-radical-generated poly(vinylferrocenes), which correspond to degrees of polymerization of about 28 to 160. Both vinylferrocene, and ferrocenylmethacrylate, undergo random free-radical copolymerization with styrene or methyl methacrylate to give soluble polymers. With copolymers with molecular weights as high as 250,000. Related organometallic monomers, such as the cyclopentadienylchromium complexes, have also been homo- and copolymerized, using free radical initiation. Here, too, the transition metal generates an electron-rich vinyl group which



deactivates the monomer.

More recently Nuyken and coworkers have polymerized highly purified vinylferrocene using anionic initiation.

Initiation of the polymerization was accomplished with the use of n-butyllithium or distyrylsodium or potassium (produced from styrene and sodium or potassium naphthalenide). The reaction takes place in tetrahydrofuran (THF) solvent at $-70\text{ }^{\circ}\text{C}$ to $0\text{ }^{\circ}\text{C}$ to give soluble oligomers with molecular weights in the range of 6,000 to 7,500. This corresponds to degrees of polymerization of 28 to 35. The oligo-vinylferrocene produced in this way has a



Tg of $219\text{ }^{\circ}\text{C}$.

In addition to the homopolymerization of

vinylferrocene, it is possible

to initiate the polymerization of vinylferrocene from the active end or ends of anionically produced polystyrene or poly(methyl methacrylate) to give di- or triblock copolymers.

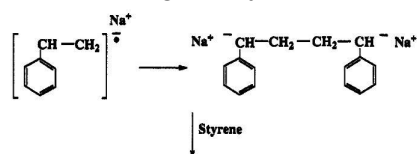
Moreover, the living poly(vinylferrocene)

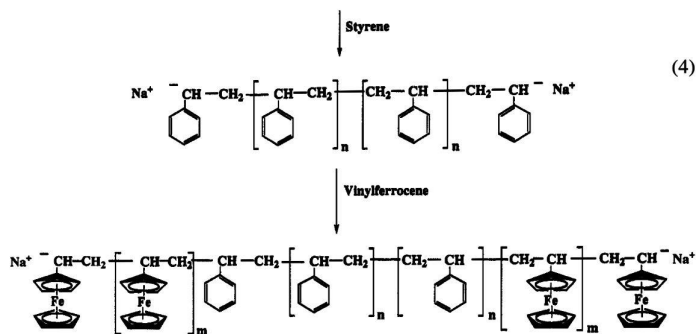
anion initiates the polymerization of styrene to give diblock copolymers.

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Condensation Polymerizations

Condensation polymerization of functional ferrocenes generally yields medium- or low-molecular-weight polymers with broad molecular-weight distributions.





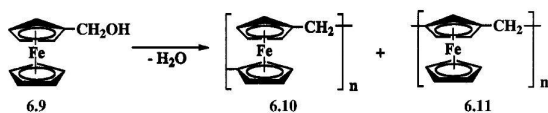
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ferrocenyl carbinol, has been condensation-polymerized to polymers in the presence of boron trifluoride etherate or zinc chloride.

Another condensation approach links cyclopentadienyl rings directly without the presence of a bridging group. Thus, ferrocene, when treated with a peroxide free-radical source is reported to yield species of type Perhaps surprisingly, in view of recent work, these polymers showed no significant electronic conductivity. However, oligomer in which a sequence of conjugated units separated the cyclopentadienyl rings, is purple in color. It is possible that the concept of "doping" conductive polymers with oxidizing or reducing agents to generate conductive species was not understood at that time.

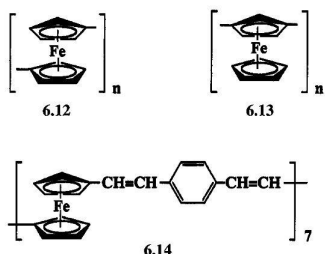
Higher molecular weight polymers (40,000–50,000) have been reported from condensation reactions between monomer and silanediols. Polymer can be melt-fabricated into films or fibers, which probably reflects the presence of roughly 100 repeating units per chain. However, the separation of the ferrocenyl units by the organic linker groups reduces the influence of the organometallic component.

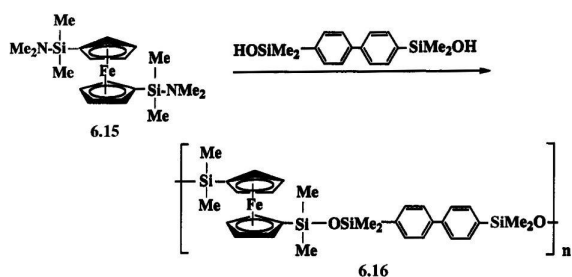
The advantage of these polymers over poly(vinylferrocenes) or related species with pendent organometallic units is that the condensation polymers have ferrocene units in the main chain where they can exert their maximum influence on polymer thermal stability.



The disadvantage of the condensation

products is that, except in the last, the molecular weights are too low to favor fiber or flexible film formation.



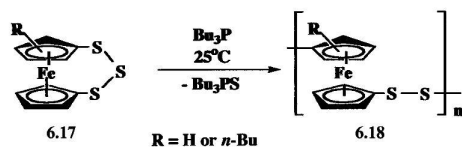


Nevertheless, this work indicated the potential usefulness of polymers with metallocene units in the main chain.

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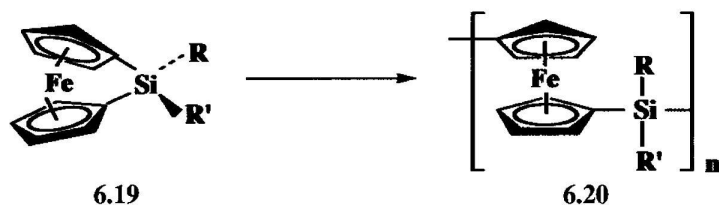
Ring-Opening Polymerization

As discussed, addition and condensation polymerizations generally yield ferrocene-containing polymers that are of relatively low molecular weight. In many cases the polymerization reactions are driven by the release of ring strain. Rauchfuss appears to have been the first to report a ring-opening polymerization that incorporates the ferrocene units into a polymer backbone. Monomer reacts at room temperature with tributylphosphine to yield polymer via a desulfurization process as



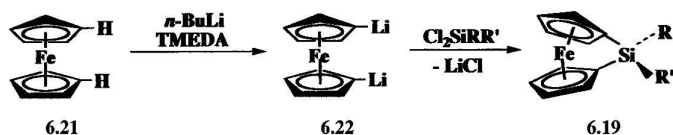
shown in reaction.

Although polymer 6.18, where R = H is insoluble, its analogue with R = *n*-Bu is soluble in a variety of organic solvents and has average molecular weights near 40,000 ($n = 160$) but with a broad molecular weight distribution and with the highest molecular weight values being more than 150,000. This polymer could be reversibly oxidized electrochemically, with the first oxidation occurring at alternating Fe atoms along the chain. Another method involves the ring-opening polymerization of silicon-bridged ferrocenes ("ferrocenophanes") such as 6.19 to form a wide range of high polymers with the general structure 6.20 as illustrated in



These polymers have molecular weights in the 10^5 – 10^6 range, which corresponds to 500–5,000 repeating units.

Ring-strain in monomers of type 6.19 can be detected by the marked tilting from coplanarity of the cyclopentadienyl rings. This tilting generates approximately 60–80 kJ/mol of ring-strain, which is relieved during polymerization. The monomers are synthesized by the reaction of dilithioferrocene (6.22) with a dichlorodiorganosilane, as shown in reaction .

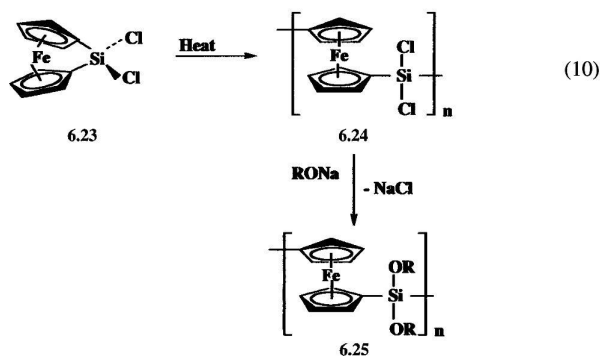


Dilithioferrocene is produced by

deprotonation of ferrocene (6.21) with an alkyllithium reagent. Similar techniques are employed to produce monomers with germanium, phosphorus, and sulfur in place of silicon.

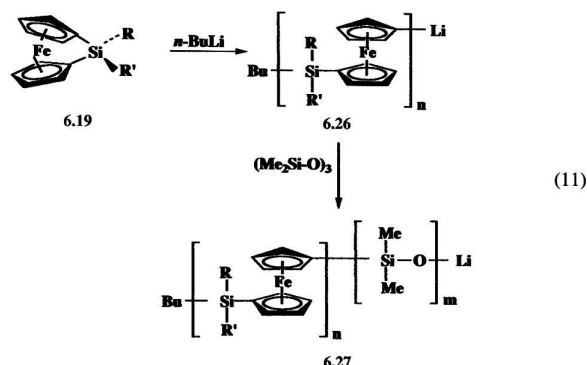
From an experimental viewpoint the polymerization of 6.19 where R and R' are both methyl groups, takes place in the bulk (molten) phase in sealed glass tubes at 130 °C and the reactions are complete in less than one hour. The yellow polymer is formed in almost quantitative yield and is soluble in solvents such as THF. The molecular weight is in the range of 3×10^5 to 5×10^5 (1,300–2,000 repeating units). The polymerizability of 6.19 is relatively insensitive to the types of side groups attached to silicon. Side-group combinations that allow polymerization are where R/R' includes Cl/Cl, H/Me, Me/Me, H/H, Et/Et, Bu/Bu, Hex/Hex, Me/CH₂CH₂CF₃, Me/CH=CH₂, Me/C₁₈H₃₇, Me/Ph, Me/ferrocenyl, and Me/norbornenyl. Polymerization

also occurs with the monomer Ph/Ph at 200–235 °C, but the resultant polymer is insoluble. Thus, polymerization of the monomer with Cl/Cl groups on silicon (6.23) can be followed by chlorine replacement reactions to give polymeric species with OMe/OMe, OEt/OEt, O(CH₂)₁₁CH₃, OPh/OPh, or R₂N/R₂N side units

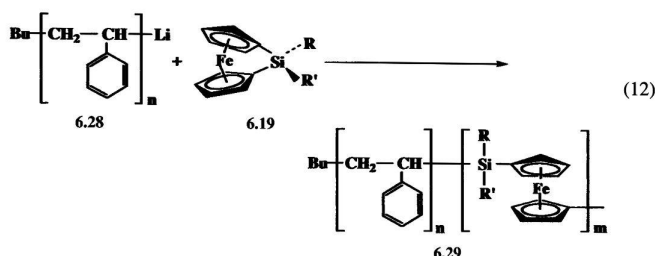


More control over the polymerization process is achieved by anionic rather than purely thermal initiation. Thus, the use of n-BuLi as an initiator in THF solvent at 25 °C gives narrow molecular-weight distributions (pdi < 1.2), and the molecular weights can

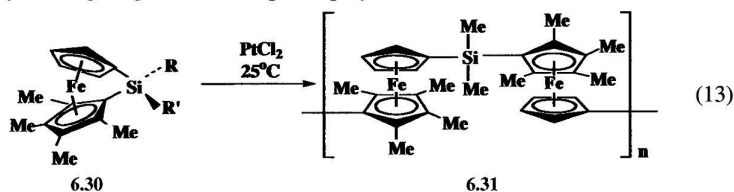
be controlled by the ratio of initiator to monomer because each initiator molecule will give rise to only one polymer chain. This polymerization is illustrated in



together with use of the living anionic chain end in 6.26 to initiate ring-opening polymerization of a cyclosiloxane to give a block copolymer (6.27). Alternatively, the living chain end of anionically produced polystyrene (6.28) will initiate polymerization of 6.19 to give styrene-ferrocenylsilane block copolymers (6.29)



In addition to the *n*-BuLi-initiated polymerizations, it is possible to induce ring-opening polymerization using initiators derived from Pt (I), Pt (0), or Rh (I). These are mild initiators that function at room temperature and are believed to participate through the formation of colloidal metal particles. An advantage of these initiators is that they can be used even though the monomer is not exceptionally pure. Molecular-weight control is achieved by the addition of different amounts of Et₃SiH which serves as an end-capper for the chains. These colloidal metal initiators also provide access to regioregular, crystalline poly(ferrocenylsilanes) (6.31) from monomers with both cyclopentadienyl and tetramethylcyclopentadienyl (6.30) type rings



by CpH-OSi rather than CpMe-OSi cleavage). By contrast, the uncatalyzed thermal process yields regioregular but amorphous polymers.