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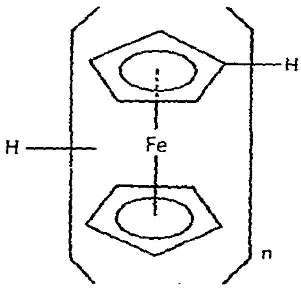
SHORT COMMUNICATIONS

Metallocene polymers
XIX. Polyferrocenylenes

The synthesis of polymers exclusively composed of ferrocenylene recurring units (I) has been the goal of many research efforts in recent years. Korshak and Nesmeyanov with co-workers[1-3] were the first to report a polyrecombination reaction involving the action of tert-butyl peroxide on ferrocene, in which polyferrocenylenes I with number-average molecular weights ($\bar{M}_n$) up to 7000 were claimed as products. However, the inconsistency with structure (I) of the elemental compositional data given by Korshak[2] prompted other workers[4] to re-examine this synthesis, and it was found that the recombination products, rather than constituting pure (I), consisted of small polyferrocenylene segments interlinked by methylene and aliphatic ether groups, these linking groups having arisen *via* methyl and tert-butoxy radicals stemming from thermal decomposition of the peroxide reactant. Spilners and Pellegrini[5] as well as Hata and co-workers[6] obtained polyferrocenylenes, some of these painstakingly isolated as individual compounds, by a radical coupling reaction from lithioferrocenes; yet in both instances the molecular weights reported



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were in the low range 450–1450, classifying the products as oligomers. Independently, Rausch[7] reported the formation of polyferrocenylene in trace quantities by reaction of poly(mercuriferrocenylene), $\{C_{10}H_8Fe\text{-}Hg\}_x$, with silver at 300°; again, however, the product's molecular weight was quite low as judged from the crystalline nature of the compound and its capability of subliming*.

We now wish to report the synthesis of soluble polyferrocenylene (I) with molecular weights in the range 2000–3500 by subjecting Rausch's poly(mercuriferrocenylene)[7] to homolytic fission of the carbon–mercury bond in the presence of molten ferrocene as solvent. When poly(mercuriferrocenylene) (one mole) was fused for 1–5 h with excess ferrocene (10–20 moles) at 245–260° under dry, oxygen-free nitrogen, linear, soluble polyferrocenylene (I) was formed in 10–20% yield. In a typical experiment, the melt of 0.3 mmole of poly(mercuriferrocenylene) (m.p. 292–295°) and 33.0 mmoles of ferrocene was stirred for 1.5 h at 255°. Another 15.0 mmoles of ferrocene were added in small portions during this period, starting after the first 0.5 h. The cold, solidified melt was extracted with hexane to remove ferrocene and small quantities of oligonuclear by-products. From the residue containing crosslinked matter, metallic mercury, unreacted starting material and Polymer (I), the latter was extracted with benzene and was precipitated from this extract by isopropanol. Reprecipitation in the same manner furnished the product in 12.5% yield (Found: C, 65.38; H, 4.50; Fe, 30.18; mol.wt., 3110. $C_{170}H_{138}Fe_{17}$, calcd.: C, 65.23; H, 4.44; Fe, 30.33%: mol.wt., 3130.) as a tan, powdery solid which did not melt up to 300°, yet readily dissolved in benzene, dioxane, chloroform, etc. The infrared spectrum closely resembled that of biferrocenyl[8] except for the attenuated 9,10-μ bands indicative of unsubstituted cyclopentadienyl rings[9]. The residual absorption shown at these latter two positions appears to be too strong to be solely accounted for by ferrocenyl end-groups, thus pointing to the existence of small populations of ferrocenyl side-groups, as well as of homoannularly rather than heteroannularly disubstituted ferrocenylene units in the polymer. The NMR spectrum showed only a broad ferrocene proton resonance extending from about τ 5.6 to τ 6.2, with three major peaks emerging near τ 5.7, 5.9 and 6.1, *i.e.*, in the vicinity of signals due to α-, β-, and unsubstituted ring protons in biferrocenyl[10] and trinuclear ferrocenes[4].

With melt temperatures raised to 260–265° and/or heating periods extended to 3–5 h (further addition of ferrocene being required in such cases to compensate for losses due to evaporation), yields in (I) increased up to 20% and M_n values measured were up to 3500. Under these conditions, however, the reactions were not always strictly reproducible, occasionally giving polymers from which weak IR (3.45–3.50μ) and NMR ($\tau \sim 4.5$ and 7.6–8.8) absorption indicated the presence of minute contents of alkenyl or cycloalkenyl moieties probably formed by cleavage of the metal-to-ring bond.

The reaction leading to (I) is likely to proceed through stepwise homolytic cleavage of carbon–mercury bonds in the poly(mercuriferrocenylene), followed by recombination (eqn. 1) of the resulting radical fragments with generation of a direct ferrocenylene–ferrocenylene bond.

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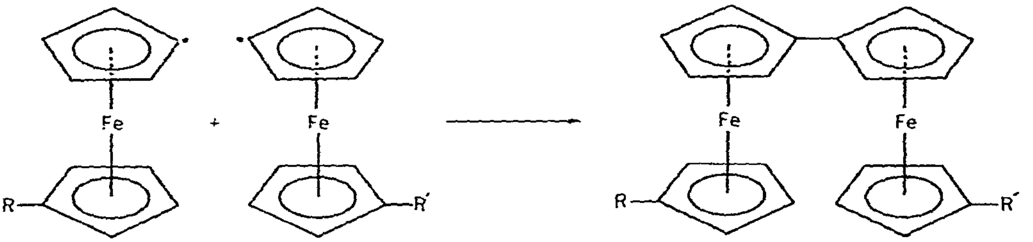
* Rausch also suspected the existence of (I) in the insoluble residues of his experiments[7]. The insolubility in organic solvents, however, indicates the suspected product, if indeed present in the residues, to be of a crosslinked type.



In keeping with the stepwise elimination of mercury in this process (R, R' in eqn. 1 representing residual poly(mercuriferrocenylene) chains in the initial stage, residual polyferrocenylene chains in the final stage of the reaction), the resulting polymers were found to possess gradually decreasing contents of mercury bridges with progressing polymerization. For instance, polymers isolated from experiments conducted over heating periods limited to 0.3–0.8 h contained 1–6% Hg; in addition, they showed an infrared band at 8.8μ apparently characteristic of the ferrocenylmercury system. The isolation of biferrocenyl and 1,1'-terferrocenyl* from the hexane extracts and precipitation filtrates in all experiments suggests that the ferrocenyl end-groups in (I) arose by recombination of the polynuclear radical fragments in eqn. (1) with hydrogen atoms extracted from the surrounding ferrocene medium. This step would appear to be facilitated by the relatively low stability expected for these radical fragments. The ferrocenyl radicals resulting from hydrogen extraction will likewise participate in a termination process (R' = H); to a minor extent, depending on their instantaneous concentrations they may also recombine with another species of their kind (R, R' = H), giving biferrocenyl. It is apparent that hydrogen atoms may not only be extracted from monomeric ferrocene, but also from any polynuclear species arising in the process of recombination. Since this hydrogen extraction may produce radical sites at any one position, α, β, or heteroring, relative to existing substituents[4], it is not surprising to find minor deviations from the expected heteroannular bonding disposition in the polyferrocenylene of the present study, as was pointed out above. Furthermore, in the light of this multitude of potential radical sites available, coupled with the possibility of transmercuration steps[13], the copious formation of crosslinked material and concomitantly low yields of linear (I) observed in this investigation can readily be rationalized.

Polymers (I), when subjected to thermogravimetric analysis (TGA) in argon environment at a heating rate of 15°/min., showed relative residual weights in the vicinity of 98, 85, and 75%, respectively, at the 400, 600, and 800° marks. This thermostability performance, while distinctly superior to that observed with the less ideally composed polyrecombination products of the earlier study[4], appears somewhat less impressive when viewed in comparison with ferrocene itself, whose capability to dissipate absorbed thermal energy by non-deleterious molecular vibrations has been well documented[14–16]. The failure of the polymer system (I) to show still higher

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* The heteroannular substituent disposition on the central ferrocenylene group in this termer (m.p. 228–229°) was ascertained by NMR data. The compound, hence, is probably identical with the 1,1'-terferrocenyl, m.p. 226.5–227.2°, obtained by Hata[6]. On the other hand, Nesmeyanov and coworkers[11] assigned this heteroannular structure to a product with m.p. 212.5–214.5°; Nesmeyanov's assignment was later confirmed by X-ray studies[12]. Efforts on an independent synthesis of our termer are in progress.

resistance to thermal attack than indicated by TGA reflects a comparatively low degree of electron delocalization. This restriction of resonance effects, well in agreement with the UV spectrum, which shows only insignificant batho- and hyperchromic shifts relative to biferrocenyl, is probably a consequence of the predominance of heteroannular substitution along the polymer backbone*. The essential lack of interannular resonance (*i.e.*, of conjugation across the central iron atom) in 1,1'-disubstituted ferrocene compounds has been convincingly demonstrated elsewhere[17-20].

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* It would be of interest in this connection to synthesize and investigate the thermal properties of a polymer essentially composed of ferrocenylene units substituted at relative positions 1,3 rather than 1,1'.