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Polymetalloceylenes-Recent Developments

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Polymetalloceylenes-Recent Developments

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ABSTRACT

The polymetalloceylenes represent a class of macromolecular compounds in which units of a metallocene complex are directly and difunctionally interconnected so as to constitute a linear chain. This chapter represents an account of recent progress in the synthesis and spectroscopic characterization of the only two types of polymetalloceylene known to this date, *viz.* poly-1,1'-ferroceylene (obtained with \bar{M}_n up to 10 000) and poly-1,1'-ruthenocylene (obtained in the oligomer range). In addition, the partial oxidation of poly-1,1'-ferroceylenes, which gives poly(1,1'-ferroceylene-co-1,1'-ferricenylene) structures possessing mixed-valence characteristics, is treated, and a discussion is presented of potential applications for these organometallic polymer types and expected future developments in the polymetalloceylene field.

INTRODUCTION

Scientific challenge and technological usefulness both have combined to place the metallocenes into a most privileged position within the realm of organometallic research, and one finds this well reflected in the abundance of publications in the chemical, physical and patent literature. Although the great majority of communications deals with di- η -cyclopentadienyliron or ferrocene, many

other metallocene types less readily accessible than the iron-organic prototype have also in recent years attracted much research interest.

It has long been recognized that the incorporation of metallocene units into a polymeric backbone may give rise to certain bulk properties or combinations of pertinent chemical and physical features not found in the non-polymeric complex. Accordingly, the problem of metallocene polymerization has received appreciable attention, and the number of publications in the field of metallocene-containing macromolecules most likely exceeds that of all other communications on polymeric organometallic compounds. By far the largest proportion of polymeric metallocenes investigated over the past twenty-odd years comprises structures containing organic connecting segments in addition to the metallocene complex proper, the latter either being pendent or else constituting a component of the chain. Most of these investigations were conducted in the 1960 - 1970 decade and have been thoroughly and critically reviewed [1]. The evident preponderance of metallocene polymers containing organic connecting groups is entirely traceable to synthetic convenience. Countless reactions can be utilized in metallocene polymer synthesis provided only that suitable derivatization of a metallocene complex is accomplished through attachment of reactive functional groups of the familiar types conventionally employed for polymerization and capable of undergoing partial (in polycondensation) or total (in polyaddition) incorporation into the growing chain. This strategy allows the polymer chemist to prepare, and purify, the monomer(s) in a separate operation. The subsequent polymerization will then be brought about entirely by reaction of the functional side groups, and the metallocene complex proper, although capable of exerting some steric and electronic influence on these side group interactions, will not itself actively participate in the polymerization sequence. Whereas the synthetic problems associated with this polymerization approach in general are reasonably manageable, the preparative task

of polycondensing metallocenes in such a fashion as to obtain linear chains composed of metallocene units directly joined to each other by single bonds without the interposition of other bridging groups has proved to be a truly formidable one, requiring highly selected strategies and specialized laboratory techniques. A polymer thus generated by the direct interconnection of metallocene units, while correctly to be designated as a poly(metallocenediyl), is commonly referred to as a polymetallocenylene.

It is well at this point to examine in some detail the causes underlying the problems of polymetallocenylene synthesis. In the first place, there are severe restrictions in the number and kind of chemical approaches that lend themselves to the task of interconnecting metallocene units directly and in high conversion, only the most efficacious types of aryl-aryl coupling mechanisms being applicable here.

Secondly, one should remember that in metallocene polycondensation, just as in any other step-growth polymerization process, the number-average degree of polymerization, \bar{X}_n , is strongly dependent on the extent of reaction, p , that is, the conversion along the polymerization reaction path, and quantitative relationships derived from simple statistical considerations allow us quite accurately to determine \bar{X}_n as a function of p . For illustration let us consider an experiment in which the desired synthetic step proceeds to 50% conversion. While, by ordinary standards, the level of conversion attained may be rated as high, the same extent of reaction brought about in an experiment involving a polycondensation (at balanced stoichiometry) is calculated to give $\bar{X}_n = 2$, this rather trivial result indicating that a mere dimerization has been achieved. From the polymer chemist's viewpoint, such an experiment would, hence, be rated a total failure. Even a 90% conversion in the desired direction, highly respectable by the standards of non-polymer chemistry, is calculated to be insufficient for polymerization purposes, as, on a number-average basis, no more than ten monomer units are assembled in one product molecule. The conversion along the propagation path must indeed

very appreciably exceed that of the last-named example if satisfactory polymerization is to be accomplished, and the reaction type chosen must proceed almost exclusively in the desired direction, the extent of concurrent side reactions being restricted to fractions of a percent. In addition, the side reactions that do occur concurrently must be of such a nature as not to interfere with polymerization nor to cause the participation of by-products in the propagation sequence, as this would result in contamination of the polymeric end product.

Thirdly, since a strictly linear propagation scheme requires that exactly two interconnecting bonds be generated for every metallocene complex involved (save the two terminal units), it is clear that, whatever the coupling mechanism operative, it must ensure participation of no more and no less than two sites per complex. It is thus imperative that experimental conditions causing monofunctional or trifunctional behavior of a monomer unit in the feed or in the growing chain be meticulously avoided. Under typical conditions, the presence of a monofunctional (or monofunctionally reacting) compound in a concentration of only one mole percent may well reduce \bar{X}_n to one-half of what it would have been in the absence of such an impurity. Conversely, the same percentage of a trifunctionally reacting compound present in the feed suffices to cause appreciable crosslinking; in a polymerization proceeding to $\bar{X}_n > 100$, in fact, the entire batch would turn substantially insoluble under these conditions.

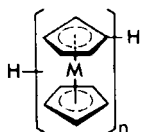
Although the two requirements of strict difunctionality and an extraordinarily high extent of reaction are not restricted to the synthesis of polymetallocenylenes but hold for all step-growth polymerizations, they are notoriously difficult to fulfil for reactions involving the direct coupling of aromatic nuclei. Such coupling reactions typically utilize organolithium, -copper, -nickel, and -magnesium chemistry, all of which are to a variable extent afflicted with the evils of detrimental side reactions and deviations from the desired functionality through loss or alterations of sensitive substituents in intermediary stages.

In the light of the problems pointed out in the foregoing, it is not surprising to find that the number of literature reports dealing with polymetalloenylenes has until now remained conspicuously small in relation to the coverage of metallocene-containing polymers in which the metallocene units are interlinked by organic bridging groups. Well in accord with the absolute predominance of ferrocene chemistry in all metallocene research, the published topics in polymetalloenylene chemistry are almost exclusively concerned with the polyferrocenylenes. Little information is available on polymeric chain structures composed of ruthenocene units, and nothing is known about other polymetalloenylene types.

The following sections will cover synthetic aspects of metallocene polymerization, as well as physical and chemical features of the known polymetalloenylenes. Concluding the chapter, an attempt will be made to delineate areas of promising research potential and point out future development trends in this challenging field of macromolecular chemistry.

POLYMERIZATION REACTIONS

As all polymers to be discussed in this chapter are derived from metallocenes of the dicyclopentadienylmetal type, they can summarily be represented by the structure shown below, in which M stands for a transition metal of Group VIII, specifically Fe and Ru. The centered position of the left-hand connecting bond in



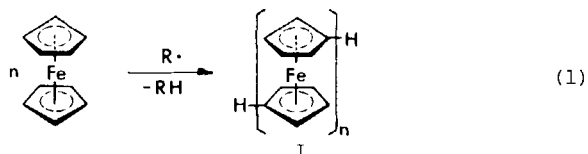
this formula indicates the possibility of homoannular (i.e. 1,2- or 1,3-type) or heteroannular (1,1'-type) substituent disposition. Although, as will be seen, almost all known polymetalloenylene

structures are of the heteroannular type, several tri-, tetra-, and pentanuclear compounds with $M = \text{Fe}$ have been described in which the internal units are homoannularly connected.

POLYFERROCENYLENES

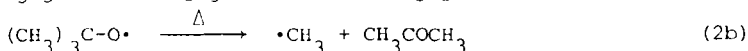
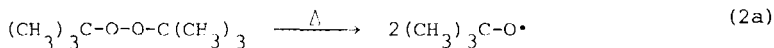
Poly-1,1'-ferrocenylenes. - Following the discovery of ferrocene in 1954, the exploration of the basic substitution chemistry of this prototype metallocene progressed at an extraordinarily rapid pace, and the first comprehensive coverage of the subject appeared as early as 1965 in the form of a proficiently written book [2]. However, most of the earlier studies of ferrocene substitution behavior involved the attachment of other groups to the metallocene complex, and little of the chemistry explored was applicable to the problem of polymerization by propagation through direct ferrocene-ferrocene bond formation. Seen in this light, the first synthetic approach toward polyferrocenylenes reported in 1960/1961 by the groups of Korshak and Nesmeyanov [3] must be valued as a courageous pioneering effort, triggering off, and stimulating, the great many research efforts subsequently undertaken in the field. This type of ferrocene polymerization, although lastly unsuccessful, presents an instructive example of a polycoupling reaction the outcome of which is dramatically affected by the various aforementioned requirements; it will, therefore, be discussed here in some detail despite ample coverage in previous reviews [1].

In principle the process, referred to as a polyrecombination, involves the step-growth polymerization of ferrocene via free-radical intermediates at elevated temperatures as summarized in scheme 1, and under suitable experimental conditions the authors [3]

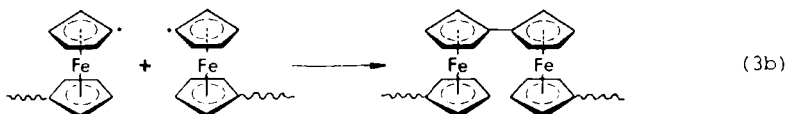
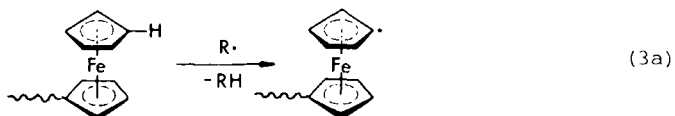


obtained in 5 - 16% yield soluble polymers to which they assigned the structure I of poly(ferrocene-1,1'-diyl) or poly-1,1'-ferro-

cenylene. Molecular masses were up to 7000. On the surface the reaction sequence looks simple enough: ferrocene monomer in the molten state (temperature $>200^{\circ}$) is exposed to a suitable free radical source, most typically *t*-butyl peroxide, whereupon intermediary *t*-butoxy and methyl free radicals, generated thermolytically from the peroxide (eqs. 2), extract a hydrogen atom from the



metallocene nucleus, leaving a ferrocenyl free radical. Two such metallocenyl radicals recombine in the first propagation step to yield biferrocene. Further hydrogen extraction from this species, followed by recombination of the resulting biferrocenyl free radical with a ferrocenyl radical, gives a trimer, and with increasingly larger oligoferrocenylenes as substrates for hydrogen extraction, and partners for recombination, the ultimate result expected is the formation of long-chain polyferrocenylenes. The overall polyrecombination reaction could thus be depicted by scheme 3 ($r = \text{H}$, ferrocenyl or polyferrocenyl).



I

However, in view of what has been said initially regarding the control of functionality and extent of reaction, doubts must arise as to the practicability of a polymerization process as implied in this scheme. Firstly, as the mono- and polynuclear substrates

offer more than two sites for reaction, one should, in an early stage of the reaction, expect a substituent disposition not only of the (sterically preferred) heteroannular type, but also of the two homoannular types; in more advanced stages, one should additionally expect tri- and polysubstitution, leading to the generation of branches and, ultimately, crosslinks. Secondly, as a minimum of two primary free radicals $R\cdot$ are required for the formation of a single ferrocene-ferrocene bond, it stands to reason that there should be significant competitive participation of nonferrocene-type compounds in the propagation reaction. Not only would one expect the primary free radicals, $\cdot\text{CH}_3$ and $\cdot\text{OC}(\text{CH}_3)_3$, to engage in alkylation and alkoxylation side reactions, but also such secondary products as acetone, *t*-butanol, methane, and methyl *t*-butyl ether, derived from the primary radicals by hydrogen capture or through other transfer reactions (e.g., $2(\text{CH}_3)_3\text{C-O}\cdot \rightarrow \text{CH}_3\text{COCH}_3 + \text{CH}_3\text{-O-C}(\text{CH}_3)_3$), must be considered as potential reaction partners. Even though their effective concentrations in the reaction mixture will be very small under proper experimental conditions of rapid dissipation and vaporization, hydrogen extraction from these aliphatic compounds will be sufficiently favored energetically over that from the aromatic ferrocene nucleus to permit the generation of derived free radicals in instantaneous concentrations high enough to cause alkyl and alkoxy substitution by recombination with free radical sites on ferrocene or ferrocenylene units of the growing chain.

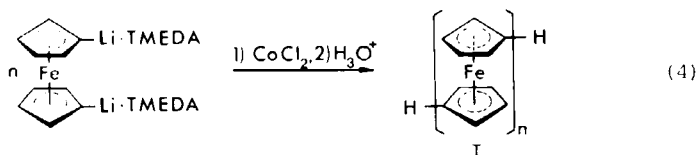
These various expectations were indeed borne out in later reinvestigations [4,5] by the identification of a number of diagnostically useful nonpolymeric by-products. Thus, the three isomeric trimers (1,2-, 1,3-, and 1,1'-diferrocenylferrocene) were isolated from low-molecular fractions, and large quantities of insoluble, crosslinked material (making up the entire product batch as conversions exceeded 90%) were collected in addition to the 9 - 27% of soluble, substantially linear products, attesting to both the lack of regioselectivity in the primary free radical attack and the potential polyfunctionality exhibited by the growing chain

system. Moreover, methylferrocene and a methylated biferrrocene were detected mass-spectrometrically, and in representative experiments both diferrocenylmethane and ferrocenylmethyl *t*-butyl ether were separated and identified as by-products, giving clear evidence for the active involvement of nonferrocene-type compounds derived from the peroxide reactant. In further support of this finding, the presence of methyl, methinyl and *t*-butyl substituents as well as aliphatic ether groups in the soluble oligomeric and polymeric products was ascertained spectroscopically, and micro-analytical results agreed with chain compositions such that, on the average, 1 - 2 aliphatic C atoms were incorporated for every ferrocene unit. Taking into account all evidence presented in the later studies, one is led to conclude that the recombination products, far from possessing a polyferrocenylene structure, were in fact composed of ferrocenylene and short polyferrocenylene units bridged and substituted by a variety of aliphatic groups. For reasons of polyfunctional substrate behavior and massive interference by side reactions, the ferrocene polyrecombination thus proves to be entirely unsuitable for polyferrocenylene preparation.

There has been no lack of attempts in the subsequent decade to synthesize I by other methods designed to provide an improved control of functionality, these efforts having in common the use or co-use, as monomers, of ferrocene compounds with preintroduced difunctionality. Thus, 1,1'-dihaloferrocenes, in admixture with monohaloferrocenes, were subjected to the conditions of Ullmann coupling in the melt phase, giving oligomeric I in high yields [6]. Similar results were obtained in experiments comprising the self-condensation of chloromercuriferrocenes via chloropalladated intermediates, the latter arising by palladium/mercury exchange in the presence of lithium tetrachloropalladate [7]. In a different approach, poly(mercuriferrocene), in which ferrocene units are connected by mercury bridges, was demercurated thermally [8] or with the aid of metallic silver [9], thereby yielding oligo- and polynuclear I. In other studies, difunctionality was introduced in an intermediate stage, *viz.* through lithiation of ferrocene;

the lithiation mixture, containing both mono- and dilithioferrocene, was allowed to undergo oligomerization by oxidative coupling in the presence of cobaltous ion [10]. These earlier investigations, most of which have been thoroughly reviewed and, therefore, will receive no further attention here, all suffered from various deficiencies with respect to 'cleanliness' of the reaction and so failed to produce polyferrocenylenes in an acceptable molecular mass range and/or free from structural imperfections brought about by alkylation or introduction of cyclopentadienyl substituents.

When, several years after the first description of lithiated ferrocene oligomerization, a method for the isolation and purification of 1,1'-dilithioferrocene was published by Rausch's group [11], a renewed attack was ventured on the knotty problem of ferrocene polymerization, again utilizing the oxidative coupling mechanism with cobaltous ion participation [12]. Use of the prepurified bis-TMEDA complex of 1,1'-dilithioferrocene (TMEDA = N,N,N',N'-tetramethylethylenediamine), rigorous exclusion of moisture and oxygen, and removal of the traces of carbon dioxide contaminating the commercial grade of argon purging gas all combined to advantage in those experiments to give rise to linear oligomeric and polymeric I (scheme 4). Although overall yields



were only moderate, the average degree of polymerization attained was about twice that of previous coupling products derived from lithiated ferrocenes, and the polymers were devoid of the alkyl and cyclopentadienyl substitution observed in the previous cases.





In search for ever more efficient ferrocene polymerization approaches, a major synthetic program, prompted by these encouraging results, was initiated three years ago in our laboratory. Latest methods of aryl-aryl coupling made available in organic chemistry

were utilized in this program and suitably adapted to the goal of difunctional propagation. In the first series of experiments [13], recourse was made again to preformed difunctional ferrocene derivatives, such as 1,1'-dihalides, 1,1'-bis-Grignard, and 1,1'-bis(chloromercuri)ferrocenes, which were allowed to homo-couple or cross-couple in the presence of various recently proposed co-reactant or catalyst systems. Table 1 summarizes reaction variables and results for this series of experiments.

Although, as the table shows, the results of these efforts, by and large, turned out to be rather unpromising, they will briefly be discussed in the following so as to high-light some of the basic difficulties, in particular those associated with deleterious side reactions, that one must expect to encounter in poly-coupling experiments.





The selfcoupling of chloromercuriarenes in polar solvents catalyzed by chlororhodiumdicarbonyl dimer has recently been added to the palette of the organic chemist as a highly efficacious aryl-aryl coupling procedure, which in the originators' hands [14] gave dimer yields as high as 80 - 90%. Similarly high yields were obtained in the selfcoupling of chloromercuriarenes in pyridine with metallic copper in the presence of palladium(II) chloride catalyst [15], this method representing an improvement over the earlier chloropalladate process which required full stoichiometry of the palladium salt [7]. Both methods, when applied to the bis(chloromercuri)ferrocene, failed to give polymeric I; only low-molecular oligomers were isolated in addition to appreciable quantities of unreacted bis(chloromercuri)ferrocene, chloromercuri-ferrocene, unsubstituted ferrocene, and other coupling or degradation products (entries 1 and 2, Table 1). Clearly, both the observed low reactivity of the HgCl group, entailing a low extent of reaction, and the significant degree of reductive demercuration, with concomitant lowering of monomer functionality, are the prime factors to be implicated in the utterly poor polymerization efficiency realized in the two reaction types.

TABLE I SYNTHESIS OF LOW-MOLECULAR POLYFERROCENYLENES BY VARIOUS COUPLING REACTIONS

Entry ^a	Reagents ^b (Molarity)	Catalyst (Molarity)	Solvent ^b	Time, Temp.	Overall Coupling Yield, %	\bar{M}_n of pre- duct frac- tion with $\bar{X}_n > 5^d$	Starting mtl. re- covered or by-pro- ducts isolated per ref. e
1	 HgCl (0.20)	LiCl (0.80)	DME ^f	24 h, reflux	15 - 25	- ^g	1,1'-bis(chloromer- curi)ferrocene, chloromercuriferro- cene, ferrocene (50 - 60%)
2	 HgCl (0.25)	PdCl ₂ (2.00)	Py	22 h, reflux	35 - 40	- ^g	As above (25 - 30%). In addition, [0.0]- ferrocenophane (~5%)
3	 MgBr ^h (0.60)	TiBr (1.80)	THF/Bz (1:1)	12 h, reflux	60 - 65	1700(5%)	Ferrocene and Br- and Ti-containing ferro- cenes (25 - 30%)
4	 Br (0.35)	Ni(COD) ₂ (0.70)	DMF	36 h, 45°	20 - 28	- ^g	(1,1'-Dibromoferro- cene), bromoferro- cene, ferrocene, other ders. (45 - 55%)

^aOnly one representative expt. (out of three expts. conducted at varied molarity and reaction time) is listed per entry.
^bDME = 1,2-dimethoxyethane; Py = pyridine; THF = tetrahydrofuran; Bz = benzene; Ni(COD)₂ = bis(1,5-cyclooctadiene)-nickel(0). ^cRange of yields from three different expts. ^dContent, in percent of total coupling product, given in parentheses. ^eOriginal method was used in each expt.; polymeric product was separated by fractionating precipitation from original solution with hexane. ^fReplacement of DME by hexamethylphosphoramide did not improve results. ^gNo fraction with $\bar{X}_n > 5$ was isolable. ^hPrepared by ref. 26.

TABLE 1 SYNTHESIS OF LOW-MOLECULAR POLYFERROCENYLENES BY VARIOUS COUPLING REACTIONS (Contd.)

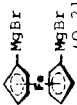
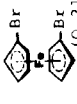
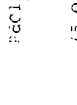


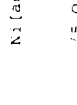
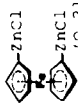
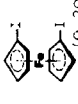
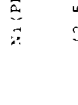
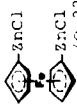
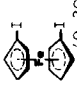
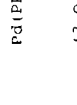
Entry ^a	Reagents ^b (Molarity)	Catalyst (Molarity)	Solvent ^b	Time, Temp.	Overall Coupling Yield, % ^c	\bar{M}_n of pro- duct frac- tion with $X_n > 5$	Starting mts. re- covered or by-pro- ducts isolated per ref. ^e	Original method per ref.
5	 I I (0.03)	-	DMF	30 h, 55°	35 - 42	1080(8%)	Iodoferrrocene, ferrocene, other ders. (35 - 40%)	18
6	 Br Br (0.14)	-	DMF	28 h, 50°	50 - 55	1550(6%)	Bromoferrrocene, ferrocene, other ders. (30 - 35%)	22
7	 Br Br (0.25)	Ni(PPh ₃) ₃ (0.012)	DMF	28 h, 50°	50 - 60	1420(7%)	1,1'-Dibromoferro- cene, bromoferro- cene, ferrocene, other ders. (25 - 35%)	21
8	 MgBr MgBr (0.10)	NiCl ₂ L ₂ (0.002)	THF	20 h, 0 - 50°	55 - 62	1525(9%)	Bromoferrrocene, ferrocene (15 - 20%)	19,20

^aOnly one representative expt. listed in each entry. Other expts. were conducted with minor modifications.

^bNi(PPh₃)₃ = tris(triphenylphosphine)nickel(0); Ni(PPh₃)₄ = tetrakis(triphenylphosphine)nickel(0); NiCl₂L₂ = dichloro-1,3-propylenebis(diphenylphosphine)nickel(II); DMF = N,N-dimethylformamide. ^cRange of yields from several expts.

^{d,e}See respective footnotes on preceding page. ^fPrepared in situ from dichlorobis(triphenylphosphine)nickel(II) and zinc powder (each 0.28 M). Triphenylphosphine (0.5M) additionally employed.

TABLE I SYNTHESIS OF LOW-MOLECULAR POLYFERROCENYLENES BY VARIOUS COUPLING REACTIONS (Contd.)

Entry ^a	Reagents (Molarity)	Catalyst ^b (Molarity)	Solvent ^b	Time, Temp.	Overall Coupling Yield, %	\bar{M}_n of product fraction ^c $\bar{X}_n > 5$	Starting mols. recovered or by-products isolated ^d	Original method ^e per ref.
9	  (0.21)  (0.21)	PdCl_2L_2 (5.0×10^{-3})	THF	48 h, 0° 0 - 50°	50	1650(71)	(1,1'-Dibromoferrocene), bromoferrocene, ferrocene (20%)	20
10	  (0.06)  (0.06)	$\text{Ni}(\text{acac})_2$ (5.0×10^{-4})	Et/Phz (1:1)	2 h, -15° 15 h, 25°	52	1350(54)	Iodoferrocene, bromoferrocenes, other ders. (38%)	24
11	  (0.21)  (0.20)	$\text{Ni}(\text{PPh}_3)_4$ (2.5×10^{-3})	Et/THF (1:6)	8 h, 25°	68	1480(8%)	Iodoferrocene, ferrocene (18%)	25
12	  (0.22)  (0.20)	$\text{Pd}(\text{PPh}_3)_4$ (3.0×10^{-3})	Et/THF (1:6)	9 h, 25°	60 - 73	1870(104)	Iodoferrocene, ferrocene (15 - 20%)	25

^a Only one experiment conducted in entries 9 - 11, three experiments in entry 12. PdCl_2L_2 = dichloro[1,1'-ferrocenylene-bis(diphenylphosphine)]palladium(II); $\text{Ni}(\text{acac})_2$ = bis(acetylacetonato)nickel(II); $\text{Pd}(\text{PPh}_3)_4$ = tetrakis(triphenylphosphine)palladium(0); Et = diethyl ether. ^c In entry 12, range of yields from three experiments conducted at different molarities. ^{d,e} See respective footnotes on first page of Table I.

An excellent method of aryl-aryl coupling, developed in the laboratories of McKillop and Taylor [16], involves heating of aryl-Grignard reagents with 1.5 molar equivalents of thallium(I) bromide in benzene. Representative biaryl yields are in the 75 - 99% range. This method, when applied to the 1,1'-bis-Grignard complex of ferrocene (entry 3), gave oligomer I in appreciably higher yields than determined in the two preceding entries; however, the degree of polymerization remained comparatively low despite rigorous exclusion of moisture, and, as before, large quantities of ferrocene were isolated. This indicates that demetalation, probably as dethallation from intermediary ferrocenylthallium species, represented a major side reaction entailing a significant reduction of functionality.

Aryl halides, as was shown in the laboratories of Semmelhack [17,18], Kumada [19-21], Kende [22] and others, undergo highly efficient reductive self-coupling under mild conditions in dimethylformamide in the presence of stoichiometric or near-stoichiometric, and even catalytic, quantities of ligand-coordinated nickel(0) species. When 1,1'-dihaloferrocenes were treated with stoichiometric amounts of either bis(1,5-cyclooctadiene)nickel(0) or tetrakis(triphenylphosphine)nickel(0) at 40 - 60° in DMF, only oligomeric I was isolated in low yields in addition to large percentages of monohaloferrocene, ferrocene, and degraded material (entries 4 and 5), the overall formation of these by-products being enhanced through use of more forcing experimental conditions, such as higher temperatures. Slight increases in both yield and degree of polymerization were achieved (entries 6 and 7) when the nickel species was prepared in situ as tris(triphenylphosphine)nickel(0) from dichlorobis(triphenylphosphine)nickel(II) and zinc, either in stoichiometric [22] or in catalytic quantities [21], excess zinc in the latter case regenerating the catalytically active Ni(0) complex. Again, however, the presence of ferrocene and monohaloferrocene was established in the final products. It is clear from these findings that reductive dehalogenation by low- or zero-valent nickel reduces

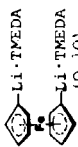
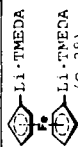
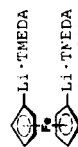
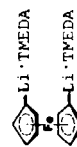
the monomer functionality even more drastically than was observed in the thallium-promoted Grignard coupling reactions.

Next, attention was turned to reactions utilizing mechanisms of cross-coupling between aryl halides and aryl-Grignard or arylzinc compounds. Much information published in recent years is available on aryl-aryl coupling of this type, catalyzed or promoted by miscellaneous transition metal complexes, and in several instances reported coupling yields have been well in excess of 80%. When applied to the system 1,1'-dihaloferrocene/1,1'-bis(bromomagnesium)-ferrocene, this approach gave rather variable results. For example, manganese(II) salts or catalysts [23] caused reductive dehalogenation of the halide by the Grignard reagent to be the principal process and so proved totally useless for the purpose. On the other hand, dihalodiphosphinenickel(II) compounds, as exemplified by dichloro-1,3-propylenebis(diphenylphosphine)nickel [19,20], were found to be reasonably efficacious catalysts in this type of reaction (entry 8), although defunctionalization at both reactants and concomitant suppression of chain growth was still observable. Use of the analogous dihalodiphosphine palladium complexes [20] as catalysts gave very similar results (entry 9). The nickel chelate, bis(acetylacetonato)nickel(II) [24], catalyzing the coupling of 1,1'-diiodoferrocene with the bis-Grignard derivative of ferrocene, proved less satisfactory, the sluggishness of the coupling reaction allowing defunctionalizing side reactions to become predominant (entry 10). A moderately efficient, albeit experimentally cumbersome, coupling process proved to be the reaction of 1,1'-bis(chlorozinc)ferrocene (from 1,1'-dilithioferrocene and zinc chloride) with 1,1'-diiodoferrocene in tetrahydrofuran solution in the presence of tetrakis(triphenylphosphine)-nickel(0) or the corresponding zero-valent palladium complex (entries 11 and 12), using the method of Negishi [25]. Good yields of coupling products were paired especially in the palladium complex-catalyzed experiments with higher average degrees of polymerization than in most of the preceding entries.

All oligo- and polyferrocenylene products prepared in this final series of experiments (Table 1) essentially conformed to structure I. The higher-molecular fractions, however, were found to be contaminated to a variable extent with non-extractable organic (1 - 5%) and inorganic (0.01 - 0.5%) impurities stemming from the catalyst systems, from the functional groups, or from degraded metallocene. Surveying the entire series of experiments one is led to conclude that, in view of both the observed contamination and the generally unsatisfactory degrees of polymerization attained, these selected types of coupling reaction, much as they should receive recognition as outstandingly useful synthetic tools in the organic chemistry of nonpolymeric compounds, fail to lend themselves to the preparation of polymetalloenylenes. Neither are they sufficiently 'clean' in the sense of earlier discussions in this chapter to preclude competition by such side reactions as demetalation, dehalogenation, and metallocene or catalyst degradation, nor do they proceed at rates fast enough relative to such other reactions to prevent their active participation in, and interference with, the propagation sequence. One finds this failure visibly reflected in the structural imperfections of the polymeric products, the low extents of reaction, and the low degrees of polymerization resulting from stoichiometric imbalances.

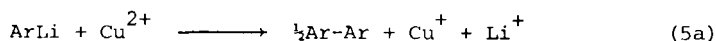
The second series of experiments, summarized in Table 2, was based on organocopper chemistry. As most copper-organic compounds are conveniently prepared from lithium-organic precursors, 1,1'-bis(lithio-TMEDA)ferrocene (again prepared and purified in the solid state^[11]) served as the principal starting material throughout this experimental series. While the straightforward oxidative coupling of the lithiated ferrocene with copper(II) halide, conducted over a wide range of temperatures, concentrations, and solvent polarity (entry 1), did not lead to marked improvements over the results of Table 1, the required high copper ion concentrations causing excessive ferrocene halogenation, dimer cyclization (*vide*

TABLE 2 SYNTHESIS OF POLYFERROCENYLENES FROM DILITHIATED FERROCENE

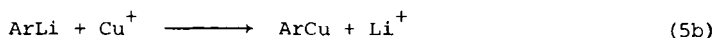
Entry ^a	Reagents (Molarity)	Solvent ^b	Time, Temp.	Overall Coupling Yield, %	\bar{M}_n of product fractions with $X_n > 5 \times 10^4$	Starting mols. recovered or by-products isolated	Ref.
1 ^f	 Li-TMEDA (0.10)	DBE	3 h, -70°C; 3 h, 25°C; 16 h, 110°C	25 - 42	1100 (26%) 2000 (6%)	Chlorinated ferrocenes and oligoferrocenylenes, ferrocene (30 - 50%); [0.0]ferrocenophane (5 - 10%)	27
2 ^g	 Li-TMEDA (0.28)	CuCl ₂ (0.21)	DME/THF (1:3)	22 h, 25°C	1300 (13%) 3400 (21)	As above (20 - 30%); [0.0]ferrocenophane (5 - 10%)	27
3 ^h	 Li-TMEDA (0.064)	CuCl ₂ (0.30)	DIO/Hx (3:2)	3.5 h, 25°C; 15 h, 50°C	1100 (12%) 3900 (1.5%)	Ferrocene (10 - 20%)	28
4 ⁱ	 Li-TMEDA (0.29)	-	DME/THF (1:1)	2 h, 0°C; 20 h, 25°C	1650 (31%) 3600 (16%)	Ferrocene (1 - 4%)	30

^a Only one representative expt (out of at least three expts. conducted at varied molarity and reaction time) is listed per entry. ^b DBE = di-n-butyl ether; DME = 1,2-dimethoxyethane; THF = tetrahydrofuran; DIO = dioxan; Hx = hexane. ^c Change of yields of linear material from different experiments. ^d Content, in percent of total linear coupling product, is given in parentheses. ^e All crude products were treated with Vitride reducing agent for dehalogenation (inefficient for Cl-containing products); oligomers and polymers were separated by fractionating precipitation with hexane. ^f Similar results in DME or DME/Bz; analogous results with CuBr₂. ^g Lower yield range in DBE. ^h Similar results with CuI (Cu:Li = 0.5) or in DIO/THF. ⁱ Similar results in DIO/DME. Slightly higher yields with Pd(O) or Cu(I) (~10⁻³) catalysts. Higher molecular masses (up to 6200 for 1st fraction), but poor composition and up to 10% ferrocene recovery, in DBE at 25 - 110°C.

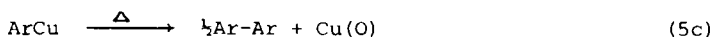
infra), and product contamination with copper, promising results were obtained in experiments in which the molar equivalent of copper(II) halide was halved (entry 2) [27]. This allowed for a fraction of the organolithium sites to undergo oxidative coupling with polyferrocenylene formation (eq. 5a; Ar = $\frac{1}{2}$ ferrocenylene), and for the resultant cuprous ion to suffer transmetalation with the



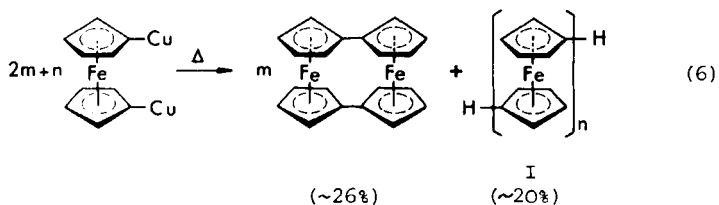
remaining organolithium functions in the reaction mixture to give ferrocenylenecopper(I) species (eq. 5b). Raising the reaction



temperature then brought about thermal coupling of the organocopper intermediates with generation of I (eq. 5c). The oligo- and



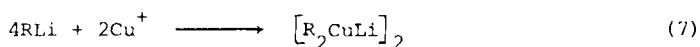
polyferrocenylenes thus prepared in 45 - 55% yield, although substantially of type I, still contained trace quantities of copper in addition to several percent of halogen present as halide end groups, effectively stopping chain growth. Furthermore, irrespective of substrate concentration, considerable portions of dimer intermediates underwent internal cyclization to [0.0]ferrocenophane. The optimization of ferrocenophane formation (scheme 6) under



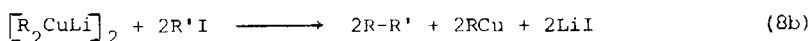
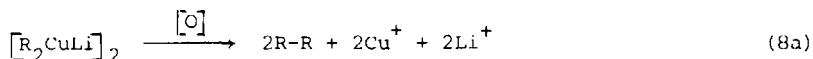
conditions of purely thermal coupling of ferrocenylenecopper(I) species [27], the latter generated in situ from 1,1'-bis(lithio-TMEDA)ferrocene and two molar equivalents of Cu(I) salt, suggests

that aggregated organocopper(I) complexes appearing as intermediates in the polycondensation of the dilithioferrocene complex under conditions of high relative copper ion concentrations may act as templates. Depending on steric factors and the degree of association and solvation, these may decompose either *via* internal or *via* intermolecular C-C bond formation, thus entailing either cyclization or polymerization.

With high instantaneous copper ion concentrations established as the principal cause of preferential ferrocenophane formation, subsequent experiments were conducted under conditions of organocuprate intermediacy [28]. Organocuprates, more copper-deficient than organocopper compounds and in the simplest form of the general structure $[\text{R}_2\text{CuLi}]_2$, have in recent years come to play an increasingly significant role as reactive nucleophiles in synthetic organic chemistry [29], their reactivity possibly deriving from the cooperative interplay of the two copper atoms in the dimeric complex. They are conveniently generated *in situ* from organolithium compound and copper(I) cation (eq. 7). Coupling may proceed either



with oxidative assistance by such other reactants as copper(II) cation or molecular oxygen (eq. 8a) or through nucleophilic attack



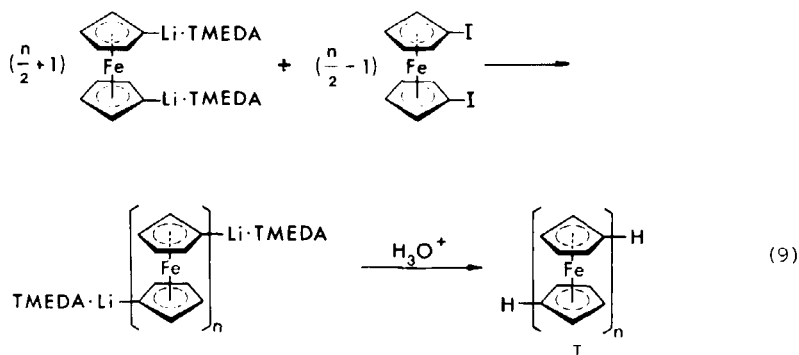
on organohalide (eq. 8b; R, R' = alkyl, aryl).

Both reaction types were utilized for ferrocene polymerization (R, R' = 1,1'-ferrocenylene) [28]. Whereas the former was found to be unsuitable because of oxidative side reactions and/or oxidant incorporation, the latter proved highly efficacious, affording I in 70 - 75% yield. The reaction mixtures in these experiments were ultimately heated to 50° in order to bring about full utilization, through thermal coupling, of the organocopper species generated

(eq. 8b) along with coupling product. A representative experiment, in which the cuprous salt needed (eq. 7) was prepared *in situ* from CuCl_2 (Cu:Li \approx 0.15), is summarized in entry 3.

Although, under these conditions, internal cyclization was negligible, the products I still were not entirely free from copper contamination. Attention was, therefore, focussed on the problem of direct solution condensation of the dilithioferrocene complex with diiodoferrocene (scheme 9) [30]. This polycondensation reaction, in the simplest mechanistic sense representing an aromatic nucleophilic substitution process, in initial experiments gave low \bar{p} and \bar{X}_n values resulting from use of insufficiently polar solvents and inadequately purified organolithium monomer. Later experiments, performed in di-n-butyl ether under considerably refined experimental conditions at ultimate temperatures of 50 - 100°, furnished polyferrocenylenes in excellent yields and degrees of polymerization. The polymers were marred, however, by the inclusion of (deprotonated) TMEDA chelating agent, as evidenced *inter alia* by low (0.2 - 0.5%) nitrogen contents; in addition, they showed an unusual aging behavior, manifested in the loss of initial solubility after several months of storage. The reaction conditions which, after much experimenting, were ultimately found to be optimal for clean and efficient propagation called for the use of strongly coordinating ether solvents, such as THF and DME, at temperatures not substantially exceeding 25° (entry 4). Overall ferrocene-ferrocene coupling yields thus amounted to 85 - 88%. The oligo- and polyferrocenylenes I were of the highest purity yet achieved and contained no detectable quantities of [0.0]ferrocenophane. The molecular mass of the top fraction (15 - 20% of total) reached the 3500 - 4500 range, although it was not possible even under the most rigorously controlled conditions entirely to suppress demetalation and dehalogenation, evidenced by the regeneration of up to 4% ferrocene and the comparatively large proportion of oligomeric material formed. Use of much higher temperatures in these experiments proved counterproductive; while bringing about minor

further increases in \bar{X}_n , this invariably led to interference by solvent and chelating agent with resultant deviations from the ideal structure I.

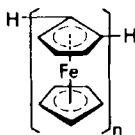


Other efforts further to enhance the \bar{X}_n ceiling in these organolithium-organohalide coupling reactions included catalysis by Pd(0) and Cu(I). Although preliminary findings suggest that minor additional molecular mass increases may be brought about by such transition metal catalysis, the effects are not very pronounced [30], and considerable refinement of this approach is needed if significant improvements are to result.

In summary, the experience emanating from the two series of experiments covered in Tables 1 and 2 shows that the prime requirements of highest product purity and a maximal extent of reaction, p , concomitant with highest possible \bar{X}_n , are not in general mutually compatible. All efforts to increase p , and thus \bar{X}_n , by 'pushing' the reaction to the right-hand side through the expediency of higher temperatures will almost invariably result in an enhanced extent of destructive side reactions and concomitant participation of catalyst components or by-products in the propagation sequence with unacceptable consequences regarding the conformance of the polymeric products to structure I. Accordingly, a compromise solution must be found in which the two requirements of product purity and high molecular mass are properly balanced. In the experiment of entry

4, Table 2, the conditions of which quite obviously are the most favorable developed to this date for the synthesis of polyferrocenylenes, this compromise is clearly evident.

Poly-1,2-ferrocenylenes.- Only a single investigation has been communicated the aim of which was the synthesis of oligoferrocenylenes comprising internal ferrocene units joined in a 1,2-disubstitution pattern. This project, studied by Rausch *et al.* [31], involved the mixed Ullmann coupling of iodoferrocene and 1,2-diiodoferrocene (or, less favorably, the homo-coupling of solely the diiodo monomer) in the presence of activated copper in the melt at 150°. The product mixtures, obtained in combined yields of 50 - 60° (appreciably less in the homo-coupling reactions), consisted for the most part of biferrocene formed by selfcondensation of iodoferrocene. As even in the homo-coupling of the diiodo compound some 20 - 30% of total coupling product constituted biferrocene, it is obvious that appreciable dehalogenation occurred in these Ullmann reactions, rendering the process unsuitable for polymerization purposes. The remaining oligomers, isolated in 0.4 - 4% combined yield in addition to the dimer, were 1,2-terferrocene (II, $n = 3$), the two (*meso*- and *d,l*-) 1,2-quaterferrocenes (II, $n = 4$), and several 1,2-quinqueferrocene isomers (II, $n = 5$).



II

Although the organolithium-organohalide polycondensation process and other polycoupling reactions utilized for the preparation of I could, in principle, be used as well for the synthesis of higher-molecular II, this has not so far been attempted.

No polyferrocenylenes containing ferrocene-1,3-diyl internal units have to this date been reported, undoubtedly for lack of

readily available starting materials, such as 1,3-dihaloferrocenes and derived 1,3-dilithio compounds.

POLYRUTHENOCENYLENES

The ruthenocene (di- η -cyclopentadienyrruthenium) and osmocene (di- η -cyclopentadienylosmium) complexes, together with ferrocene, represent the iron-group metallocenes, whose physical and chemical properties show much mutual resemblance because of the similarity of their molecular structures and valence electron systems. As a consequence, one should expect a similar behavior in polymerization reactions *via* the various approaches outlined above for I. However, with ring electron density markedly decreasing in the order ferrocene > ruthenocene > osmocene, one may predict an increasing propensity for reaction with nucleophiles in this order and, hence, an increasing reactivity in coupling processes in which the metallocene is used as the dihalo derivative. On the other hand, decreasing nucleophilicity may be anticipated, again in the order given, for the metallocene employed as the dilithio derivative. Although, most likely for reasons of high costs, no work has been done in the field of osmocene polymerization, limited data are available on ruthenocene polymerization behavior.

The first, cursory report on ruthenocene oligomerization, dating back to 1970, and devoid of experimental details, pointed out the feasibility of preparation of biruthenocene and higher homologs by Ullmann coupling of mono- and 1,1'-diiodoruthenocene [32]. A thorough study of this reaction in our laboratory [13] has confirmed that the coupling of haloruthenocenes in the melt phase proceeds indeed readily and in high overall yields as shown in scheme 10, giving bi-, ter-, and quateruthenocene (III, $n = 2-4$), as well as little higher-molecular material (entry 1, Table 3).

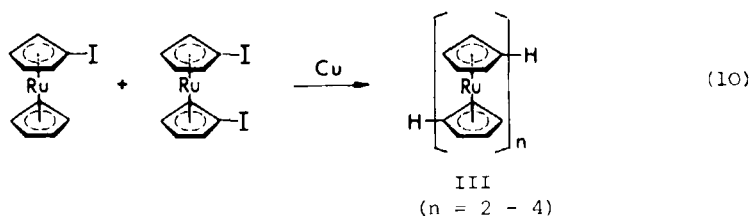

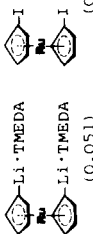
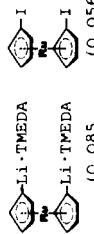
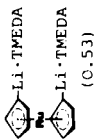


TABLE 3 SYNTHESIS OF LOW-MOLECULAR POLYRUTHENOCENYLENES FROM DIISOLATED AND/OR DIODINATED RUTHENOCENE

Entry ^a	Reagents ^b (Molarity)	Solvent ^c	Time, Temp.	Overall Coupling Yield, % ^d	\bar{M}_n of pro- duct frac- tions with $\bar{M}_n > 5000$	Starting mols. recovered or by-products isolated	Ref.
1		-	24 h, 130°C 2 h, 150°C	68	1160 (1%)	Iodoruthenocenes, ruthenocene (25%)	13
2 ^h	 (0.051)	DBE	20 h, 25°C 8 h, 70°C	24 - 40	1200 (15%) 1620 (1%)	As above (20 - 50%)	33,34
3	 (0.085)	THF/DIO (2:1)	2 h, -70°C 1 h, 0 - 25°C 12 h 50°C	38	1280 (9%) 2000 (0.5%)	As above (35%)	34
4	 (0.53)	CuCl ₂ DBE	1 h, 0°C 19 h, 25°C 1 h, 60°C	70	1250 (4%) 2400 (0.9%)	Chlorinated ruthenocenes, ruthenocene (18%)	35

^aOnly one expt. each was conducted and is listed in entries 1,3,4; only one expt. (out of four expts. conducted) is listed in entry 2. ^bLi-TMEDA stoichiometry unproven. ^cDBE = di-n-butyl ether; THF = tetrahydrofuran; DIO = dioxan. ^dIn entry 2, range of yields from four experiments. ^eContent, in percent of total coupling product, is given in parentheses. ^fAll crude products were treated with Vitride reducing agent for dehalogenation (ineffective for Cl-containing products); oligomers and polymers were separated by fractionating precipitation with hexane. ^gCu:I = 10. ^hSimilar results in DME and with Pd(O) or Pd(II) catalysts.

In order to maintain melt conditions throughout the reaction it is necessary to work with a mixture of mono- and dihalogenated ruthenocene, as the use of the dihalide alone leads to premature solidification of the melt and concomitant low coupling efficiency. Another drawback is the occurrence of ample dehalogenation, resulting in the generation of ruthenocene. The method as such is, therefore, not readily applicable to the preparation of higher-molecular III.

Surprisingly, the direct solution condensation of 1,1'-dilithio-ruthenocene (chelated with TMEDA) with 1,1'-diiodoferrocene (entry 2, Table 3) under the experimental conditions so successfully employed in the analogous ferrocene polymerization (entry 4, Table 2), turned out to be of little use, affording no more than 40% of largely oligomeric III. Catalysis by various transition metals or their low-oxidation-state salts caused no improvements [33,34]. Similarly inefficient proved to be the coupling of ruthenocenylenecuprate with diiodoruthenocene according to eq. 8b ($R = \frac{1}{2}$ ruthenocenylenecuprate), which gave predominantly oligomeric III ($n = 2 - 5$) in addition to less than 5% of higher-molecular compounds (entry 3, Table 3). One is led to conclude from these findings that the metalated ruthenocene complex possesses insufficient nucleophilicity for these types of coupling reaction to proceed efficaciously. On the other hand, the combined oxidative and thermal coupling, in DBE solution, of TMEDA-chelated dilithioruthenocene in the presence of copper(II) chloride (eq. 5, $Ar = \frac{1}{2}$ ruthenocenylenecuprate) [35] afforded coupling products in higher yields (70%) than realized in the corresponding dilithioferrocene polymerization, although, again, the degrees of polymerization attained were low, the major portion of III being in the oligomer range. In addition, as a result of end group chlorination by the cupric ion reagent, the products were found to contain up to 5% Cl resisting all attempts at removal by reductive treatment, and only by elaborate separation techniques was it possible to isolate the chlorine-free oligomers III, $n = 2 - 4$.

As shown by the tabulated data, the results obtained to-date in ruthenocene polymerization are by no means satisfactory, and a healthy challenge awaits the aspiring researcher in this field.

PROPERTIES AND USES

Considering the state of infancy in which polymetalloceNylene research is found to be at this time, the paucity of property and performance data in the literature should come as no surprise. In fact, with just one year elapsed since publication of the more practicable ferrocene polymerization procedures [27,28,30], one can hardly expect to find anything more than simple property descriptions and most certainly no records of completed development and application studies. Accordingly, the reader will find the information presented in this section to be comparatively heavy on polymer characterization data but very light indeed on the question of just what precisely these polymetalloceNylenes can offer in terms of scientific and technological use. Furthermore, since virtually all that is known about polymetalloceNylenes refers to the ferrocene polymers, one can only speculate at this time on the possible use of polymers derived from other transition metal complexes.

POLYFERROCENYLENES

Physical Properties. - All oligo- and polyferrocenylenes, irrespective of the substituent disposition at the internal recurring units, are high-melting solids ranging in color from orange-yellow or light orange in the low-molecular-mass region to orange-tan, tan-brown, and, ultimately, dark brown in the region of higher molecular masses. All individual homologs or fractions are to a varying extent soluble in halocarbons, aromatic hydrocarbons, and a number of dipolar, aprotic solvents. While the low-molecular members show a distinct saturation limit, reasonably high for the dimer and the trimers, yet low or very low for the homologs with $n = 4 - 6$, the higher-

molecular fractions (of the only known polymer type I) possess excellent solubility in these solvents and may be precipitated from solution by such non-solvents as methanol or hexane. Polymorphism, manifested in differences of the X-ray powder diagrams and, occasionally, in the melting behavior, has been noticed with representative trimers and doubtlessly is associated with higher homologs as well. The individual oligoferrocenylenes are characterized by distinct melting points, with highest values shown by the members with $n = 4 - 6$; a tabulation of m.p. data for the known oligomers is given in Table 4.

TABLE 4 MELTING POINTS AND SELECTED ELECTRONIC ABSORPTION MAXIMA OF KNOWN OLIGOFERROCENYLENES^a

Compound	M ^b	M. p., °C ^c	λ_{max} , nm (ϵ , M ⁻¹ cm ⁻¹) ^d			
Biferrocene (I, n = 2)	370	238 - 240	223 (22900)	263 (6100)	300 (4800) 456 (320) 295 (4250) 450 (300)	
1,2-Terferrocene (II, n = 3)	554	202 - 204 ^e	-	-	-	295 (3000) 449 (260)
1,3-Terferrocene		206 - 208	-	-	-	301 (4170) 455 (375)
1,1'-Terferrocene (I, n = 3)		229 - 230	226 (20200)	267 (6400)	305 (5500) 458 (480) 302 (5250) 454 (430)	
1,2-Quaterferrocene, meso (II, n = 4)	738	374 - 376	-	-	-	-
1,2-Quaterferrocene, d,1 (II, n = 4)		250 - 253	-	-	-	-
1,1'-Quaterferrocene (I, n = 4)		279 - 281	228 (17900)	270 (7900)	308 (6000) 460 (590)	
1,2-Quinqueferrocene, meso (II, n = 5)	922	345 - 350	-	-	-	-
1,1'-Quinqueferrocene (I, n = 5)		262 - 264	-	-	-	-

^aData collected from refs. 5,6,7,10,27,30,31. ^bBy mass spectrometry.

^cOnly highest m.p. given. ^dIn 1,2-dichloroethane (abs. ethanol for second-row data). First column: band system X, XI in ferrocene; second column: band system VII, VIII in ferrocene; third column: band system VI in ferrocene; fourth column: band system IV in ferrocene; band system designations by McGlynn's notation (ref. 17). ^ePolymorph melting at 187 - 189°.

The higher-molecular oligomers and polymers, available only as polydisperse fractions (i.e. mixtures of homologs) for the heteroannular type I, are characterized by broad melting ranges (Table 5); the melting temperatures pass through a minimum for fractions with major heptamer/octomer contents and exceed the 350° level at $\bar{X}_n > 20[30]$.

The exceptional heat resistance of the ferrocene unit has prompted extensive work, mostly under government contracts, directed toward the use of ferrocene-containing polymers in high-temperature and ablative applications[1]. However, only a single study has focussed on the thermal stability behavior of polymeric I[8]. The polymer, prepared by demercuration of poly(mercuriferrocenylene), when subjected to the thermogravimetric analysis test under argon, gave a respectable thermogram, indicating relative residual weights of 98, 85, and 75%, respectively, at 400° , 600° , and 800° . In contrast, a sample of a polyrecombination product synthesized by Korshak's process[3] and in the same molecular mass range of 2500 - 3000 showed markedly inferior thermostability, giving residual weights of about 70% at 500° and some 65% at 600° . No thermogravimetric analysis data on more recently synthesized poly-1,1'-ferro-

TABLE 5 MELTING RANGES AND SELECTED ELECTRONIC ABSORPTION MAXIMA OF FRACTIONATED POLY-1,1'-FERROCENYLENES^a

Fraction	\bar{M}_n ^b	Melting range, °C	λ_{\max} , nm (ϵ , $M^{-1}cm^{-1}$) ^c			
1	9900	> 350	228(17800)	269(6600)	308(5300)	461(650)
2	7200	> 350				
3	5800	> 350	228(18200)	270(7600)	309(5900)	460(630)
4	4700	> 350	227	270(7600)	309(5600)	460(650)
5	3200	230 - 250	228(19400)	270(8000)	310(5800)	460(610)
6	2900	215 - 230	228(18800)	269(7400)	309(5400)	461(600)
7	2100	165 - 180	229(18400)	269(7300)	309(5400)	461(580)
8	1850	140 - 150	228(18900)	269(7500)	309(5500)	460(580)
9	1300	135 - 145	227(19000)	270(7000)	308(5700)	461(620)
10	1100	205 - 215	228(18100)	268(7900)	308(6400)	461(590)

^aData from ref. 30. ^bBy vapor pressure osmometry. ^cIn 1,2-dichloroethane. Band system notation as in Table 4.

cenylenes have as yet been reported, but there is no reason to predict any significant further improvements over the results obtained on the demercuration product [8], as the polymer sample investigated was of high quality and in an acceptably high molecular mass range. It should be added at this point that the *thermo-oxidative* stability of poly-1,1'-ferrocenylene, as determined by thermogravimetric analysis in air, is very markedly lower than the thermal stability in the absence of oxygen. Catastrophic breakdown of the molecule occurs in the vicinity of 500^o, and this oxidative degradation is probably self-catalyzed.

The two cyclopentadienyl (Cp) ring ligands in ferrocene, despite an exceedingly low barrier to internal rotation ($\sim 3.7 \text{ kJ mol}^{-1}$), assume a preferential conformation both in the gas phase and in the crystal. Although, for many years, this was believed to be the staggered (D_{5d}) type, it was more recently established [36] by electron diffraction and X-ray studies that the gas-phase equilibrium conformation is eclipsed (D_{5h}), and even in the solid state below the λ -point transition at 164K the relative ring orientation tends more toward the eclipsed than the staggered conformational arrangement, whereas at room temperature rotational disorder prevails, allowing neither a D_{5d} nor a D_{5h} symmetry assignment. (For reasons of tradition and convenience, the staggered conformation is still being used in the literature, including the present chapter.) The dimer, in the crystalline state, likewise prefers a more eclipsed than staggered equilibrium conformation [37], and in the 1,1'-trimer one finds both the eclipsed (outer units) and the staggered (central unit) conformation [38]. The directly connected Cp rings in these two compounds are substantially coplanar, forming fulvalene-type ligand bridges. A lesser extent of coplanarity between directly joined rings can be inferred from nmr data for the two homoannular trimers, notably the sterically crowded 1,2-terferrocene (II, $n = 3$) [5,31,39], although corroborating structure determinations have yet to be performed, and the question of relative ring orientation remains an open one. No X-ray diffraction data are available for

the higher-molecular oligomers of I and II. It is safe to assume, however, that there will not be a given equilibrium conformation for each unit, and rotational disorder may even prevail throughout the entire chain.

As appears predictable from steric considerations, the ferrocene units in the dimer crystal assume a mutually transoid conformation. The same pattern holds for the 1,1'-trimer, and one may expect a preference for similar transoid arrangements of adjacent units in the higher-molecular homologs of both I and II, albeit doubtlessly associated with increased disorder in the high-molecular-mass ranges as a consequence of greater randomness of chain conformation.

There is no tilting of the rings in ferrocene, nor has such tilt been observed in biferrocene, and from the insensitivity to molecular mass changes of the chemical shift difference between α and β proton signals in the NMR spectra of the low-molecular oligomers of I (where such signals can still be distinguished) one may conclude that ring tilting is insignificant as well in polymeric I [27]. There is also no *a priori* reason for assuming tilt effects in oligomers or polymers of the homoannularly interlinked types, the second ring of each unit along the chain remaining unsubstituted and unconstrained.

Various spectroscopic techniques lend themselves to the characterization of oligo- and/or polyferrocenylenes, including mass spectrometry, solution NMR and electronic absorption spectroscopy, as well as infrared and Mössbauer spectroscopy.

Mass spectrometry has been applied to characterize some oligoferrocenylenes of structures I and II. While all oligomers have in common with the parent complex, ferrocene, a pronounced resistance to fragmentation as reflected in relatively high intensities of the parent ion peak and the corresponding doubly charged signal, this fragmentation resistance is more pronouncedly shown by the 1,2-type oligomers than by the 1,1'-type counterparts. Thus, for the trimer as well as the two tetramers of II the parent ion peak

represents the base peak, and the relative parent ion abundance for the *meso* pentamer is still 79% of the ion at m/e 738 representing the base peak [31]. In the analogous series of I, in contrast, reports from the same laboratory [6b] indicate the tetramer and pentamer to give, respectively, 61 and 6% parent ion peak intensity (relative to m/e 368). An interesting feature of the spectrum of the 1,2-trimer (II, $n = 3$) is the isotopic abundance distribution in the m/e 550 - 553 region characteristic of 1,2-triferrocenylenes generated from the trimer by expulsion of 2 H and subsequent cyclization. An analogous process involving loss of 2 H from one of the pentameric isomers is a strong possibility [31].

^1H NMR spectroscopy, while a highly valued tool in the identification of lower homologs ($n = 2,3,4$) of both homo- and hetero-annularly interlinked oligoferrocenylenes [5,10,31,39], is of little use for the characterization of higher-molecular fractions. At degrees of polymerization higher than 5 - 6, the individual proton signals coalesce to a broad multiplet showing a maximum near $\delta = 4$ ppm (benzene- d_6), the latter being insensitive in position to further molecular mass increases. As \bar{x}_n exceeds 20, the signal becomes featureless and undergoes minor additional broadening as a result of enhanced conformational probabilities, and no structural information can be extracted from it [30].

Considerably better use for structural elucidation of both lower- and higher-molecular polyferrocenylenes has been made of electronic absorption spectroscopy. The spectrum of the ferrocene parent complex has been extensively discussed, and transition assignments have been made, the papers by McGlynn's and Gray's groups being representative [40]. The maxima and extinction coefficients for a number of individual oligoferrocenylenes and a series of fractions of poly-1,1'-ferrocenylenes are listed in Tables 4 and 5, the extinction coefficients having been calculated per ferrocene unit for ready comparison. The polymer samples used for recording the data in Table 5 and those to follow in this section were obtained as per entry 4, Table 2.

The marked batho- and hyperchromic shifts apparent for all listed bands in the spectrum of biferrocene relative to ferrocene are a reflection of the conjugation achieved between the two directly joined, essentially coplanar Cp rings. However, on comparing the spectrum of biferrocene with that of the next higher heteroannular homolog, 1,1'-terferrocene, one notices but minor further red shifts and intensity increases [10,27], and as the degree of polymerization exceeds 4 both λ_{\max} and ϵ remain altogether constant within experimental error limits up to the highest \bar{M}_n value ($\sim 10\ 000$) determined. Confirming the long-known barrier function of the metal center with respect to the transmission of resonance from one ring to the other in the ferrocene complex, these findings are clear evidence of the lack of significant electronic delocalization along the polymer chain in the heteroannular polyferrocenylene and so accord well with the observed failure of this polymer type to conduct an electrical current (d.c. conductivity $\rho_{20} \approx 10^{-12} \text{ Ohm}^{-1} \text{ cm}^{-1}$) [41]. It is informative to compare the tabulated spectral data for the heteroannular trimer with those for the two homoannular counterparts. Whereas 1,3-terferrocene gives virtually the same λ_{\max} and ϵ values as shown by 1,1'-terferrocene, the pattern of 1,2-terferrocene, more closely coincident with that of the dimer, suggests appreciable resistance to coplanar alignment of the three directly joined Cp rings in the molecule [5]. This in turn permits the conclusion that poly-1,2-ferrocenylenes are unsuitable as models for the study of conjugation effects along polymer chains. The reduced steric hindrance to coplanar alignment in poly-1,3-ferrocenylenes would seem to suggest this polymer type to exhibit a very high extent of conjugation in chain direction as no metal barriers interrupting electronic charge delocalization along the backbone are interposed. However, the failure of 1,3-terferrocene to show enhanced batho- and hyperchromic shifts relative to the 1,1'-isomer indicates - and this is supported by molecular models, as well as by NMR data - that even a 1,3-substituent disposition does not permit unperturbed

coplanarity of the Cp rings involved in unit interconnection[39]. Accordingly, it appears doubtful whether a significantly extended domain of conjugation can ever be brought about in a polymer composed of 1,3-ferrocenylene units.

The infrared absorption features of homo- and heteroannular oligoferrocenylenes have been amply described[5,6b,10,31,34,39], and assignments of all fundamentals, skeletal vibrations, and modes of the C-C bond connecting adjacent ferrocene units have recently been proposed, based on the assumption that the local-symmetry concept is valid for the sandwich-type metallocenes[30]. In going from ferrocene to biferrocene and higher-molecular homologs of 1, one finds comparatively little change in the overall absorption pattern, except that, as a result of changing from local point-group symmetry C_{5v} of the unsubstituted Cp ring to C_{2v} of the mono-substituted ring, some degeneracy of frequencies is lifted, and 21 IR- and/or Raman-active ring-vibrational modes are expected in addition to skeletal modes and vibrational modes involving the ferrocene-ferrocene bond. While many of these absorb at frequencies more or less coincident with those of the pertinent ferrocene fundamentals, others give rise to new bands, noteworthy being the 'substitution' band near 1030 cm^{-1} (assigned [30] to an a_1 CH in-plane bending mode with admixed a_1 *sym.* ring-breathing component and C-C stretching of the ferrocene-ferrocene connecting bond). In addition, in violation of the '9,10- μ rule' of Rosenblum[42], which states that the contribution to the two strong ferrocene bands at 1000 and 1100 cm^{-1} vanishes for a Cp ring as it suffers substitution, biferrocene absorbs near 1000 and 1100 cm^{-1} in intensities much higher than expected for the 'loss' of one unsubstituted ring per unit, the reason being that new absorptions appear precisely at these positions as a result of substitution by another ferrocene unit. The same observation is made with all other oligo- and polyferrocenylenes. As Rosenblum's rule has proved widely usable for quantitative determinations of the contents of substituted rings in ferrocene compounds[43], its breakdown in polyferrocenylene chemistry represents a regrettable restriction of the diagnostic

tools available to the researcher for confirmation of the inherent substituent patterns in homo- and heteroannularly joined polyferrocenylenes.

As the IR spectra of low- and high-molecular I are compared, a striking insensitivity of band positions and multiplicities to increases in chain length is noticed (Fig. 1), this being a manifestation of the absence of vibrational coupling between adjacent recurring units and, hence, of the lack of significant vibrational interaction between the pair of ring ligands in the ferrocene complex. The observed behavior is well in accord with experience in the vibrational spectroscopy of non-polymeric ferrocene compounds, which are characterized by a similar lack of vibrational

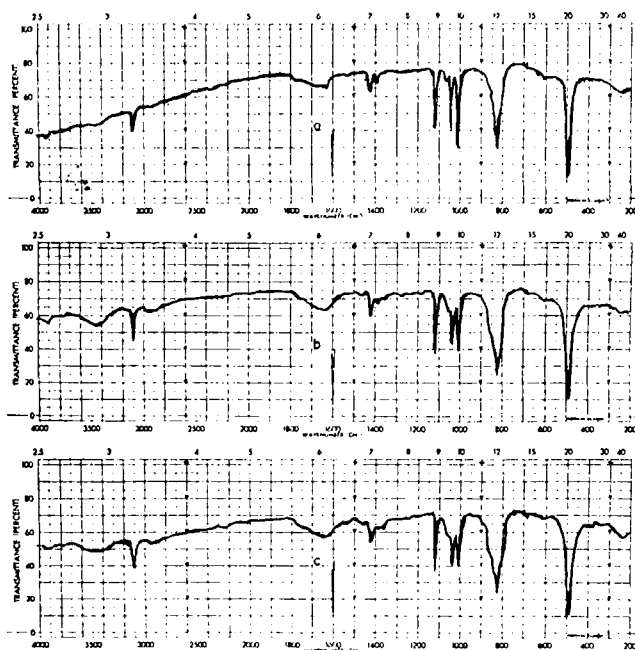


FIGURE 1 Infrared spectra (KBr pellet) of poly-1,1'-ferrocenylenes;
 a: fraction of I, $\bar{M}_n = 550$; b: fraction of I, $\bar{M}_n = 1600$;
 c: fraction of I, $\bar{M}_n = 4100$

coupling between the two Cp rings. It is of interest to note that the lack of positional shifts in higher-molecular I also applies to the skeletal infrared and Raman absorptions at 485 cm^{-1} (*asym.* ring-iron tilting and stretching) and 310 cm^{-1} (*sym.* ring-iron stretching), respectively, which indicates that heteroannular-type polymerization of the ferrocene nucleus entails no constraints in ligand tilting or metal-ligand stretching motions.

Mössbauer spectroscopy, while inconvenient or altogether impracticable for the investigation of most other metallocenes, has proved invaluable for the elucidation of structural and electronic features in ferrocene compounds [44]. Both ferrocene and biferrrocene give spectra virtually identical in chemical shift (δ) and quadrupole splitting (ΔE_q), and one finds this identity virtually retained as one goes to the heteroannular trimer and, thence, to higher-molecular I (Fig. 2). Typical Mössbauer parameters for selected oligomeric and polymeric fractions of I are contained in Table 6. The lack of \bar{M}_n dependence of δ and, hence, of the s-electron density at the metal center permits the conclusion that there is little or no d-electron interaction between adjacent ferrocene units, as such inter-unit delocalization involving d-electron density would certainly affect the s-electron charge distribution at Fe because of changes in screening.

The conclusion of lacking inter-unit d-electron delocalization in polymeric I, well in agreement with the electronic spectral behavior, finds support in the insensitivity to \bar{M}_n of the quadrupole splitting and, thus, of the electric field gradient at the iron nucleus. In the axially symmetric ferrocene molecule the electric field gradient, $-eq$, is entirely defined by $eq = V_{zz}$, V_{zz} being the z component of the electric field gradient tensor. The magnitude and sign of V_{zz} in ferrocene is primarily dictated by the compounded effect of the two d_o and four $d_{\pm 2}$ electrons occupying the the essentially non-bonding, metal-localized a_{1g} and e_{2g} orbitals, respectively. Therefore, in I, $n > 2$, the inter-unit overlap of e_{2g} orbitals with consequent delocalization should lead to enhanced

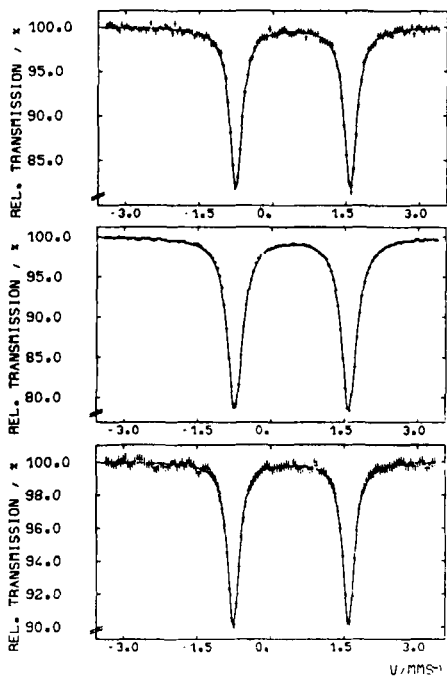


FIGURE 2. Mössbauer spectra ($^{57}\text{Co}(\text{Rh})$; 77K) of poly-1,1'-ferrocenyls; top: biferrrocene; center: 1,1'-terferrocenyl; bottom: fraction of I, $\bar{M}_n = 2500$.

TABLE 6. MÖSSBAUER PARAMETERS FOR SOME OLIGO- AND POLYFERROCENYLENES^a

Compound	Chemical shift δ , mm s^{-1}	Quadrupole splitting ΔE_Q , mm s^{-1}	Width at half height Γ , mm s^{-1}	Ref.
Biferrrocenyl (I, n = 2)	0.53	2.34	0.29	45
	0.52	2.37		46
1,1'-Terferrocenyl (I, n = 3)	0.53	2.32	0.34	45
Oligo-1,1'-ferrocenylene (I, n = 5)	0.53	2.33	0.29	45
Poly-1,1'-ferrocenylene (I, n = 10)	0.53	2.34	0.30	45
Poly-1,1'-ferrocenylene (I, n = 15)	0.53	2.34	0.26	45

^aAt 77 - 78K. All isomer shifts re-referenced to metallic iron. $^{57}\text{Co}(\text{Rh})$ source in ref. 45; $^{57}\text{Co}(\text{Cr})$ in ref. 46.

e_{2g} orbital diffusiveness and, hence, because of the proportionality of V_{zz} to $\langle r^{-3} \rangle$ (r = distance between electron and iron nucleus), to a significant decrease of $V_{zz} (e_{2g})$ and concomitant reduction of ΔE_q . Another piece of information to be gained from the observation of lacking molecular mass dependence of ΔE_q concerns the distance between the central iron atom and the Cp ligands. Both δ and ΔE_q have been found [47] to be critically dependent on the metal-ring distance in ferrocene compounds. The constancy of ΔE_q as the degree of polymerization increases, therefore, indicates that there is no significant change in the iron-ring distance in higher-molecular I relative to the dimer or, in fact, ferrocene itself. This finding may prove important in view of the impossibility of collecting X-ray diffraction data from the polymeric material.

Concluding the discussion of physical properties, a comment is due on the magnetic behavior of poly-1,1'-ferrocenylenes. In view of the lack of inter-unit electronic interaction along the chain in this polymer type, paired with an Fe-Fe distance expected to be too large (5.1 Å in a transoid conformation) to allow for direct metal-metal bond formation and antiferromagnetic coupling, one would anticipate diamagnetic behavior in both low- and high-molecular I. For poly-1,1'-ferrocenylenes prepared by the organolithium/organohalide coupling route (entry 4, Table 2), susceptibility measurements conducted in our laboratory have indeed established diamagnetism up to the \bar{M}_n range of about 5000. Higher-molecular fractions showed feeble paramagnetism; almost certainly however, this was due to paramagnetic contaminants, such as traces of adsorbed Fe^{3+} ion or ferricenium sites generated by inadvertent oxidation of ferrocene units (*vide infra*) and unremovable from the polymeric material by conventional extraction or reducing reprecipitation treatment. It should be added that, again because of contamination, polyferrocenylenes prepared by other methods were found to tend more toward the paramagnetic side than did those of entry 4, Table 2. Thus, polymers synthesized by oxidative and thermal coupling of ferrocenylenecopper or -cuprate species proved

to be weakly paramagnetic down to \bar{M}_n values of about 3000, and polymers from other preparations, *e.g.* those summarized in Table 1, retained feeble paramagnetism down to \bar{M}_n 1500 - 2500. The strong paramagnetism reported in early communications [3] for Korshak's polyrecombination products containing oligoferrocenylene segments in the chain (*vide supra*) must likewise be traced to magnetic impurities generated under the harsh reaction conditions [48]; indeed, recombination polymers synthesized in our laboratory and rigorously purified were found to be diamagnetic up to $\bar{M}_n \sim 2000$, and only faintly paramagnetic in higher molecular-mass ranges. In summary, at the present state of knowledge in the field, it appears safe to state that poly-1,1'-ferrocenylenes, *if* devoid of metallic or metal ion impurities, are diamagnetic at least throughout the molecular mass range so far attained experimentally, and there is no *a priori* reason for predicting paramagnetic behavior for higher-molecular-mass polymers still to be synthesized.

Chemical Properties.- The chemical behavior of polyferrocenylenes can manifest itself by reactions that may occur either at the ring ligands or at the central metal atom. In the former case, ring substitution is the general result, whereas, in the latter case, iron protonation or oxidation can typically be visualized. In addition, ligand exchange, which proceeds readily in ferrocene compounds under suitable conditions, must be considered as a possible reaction course in polyferrocenylenes. Since a ferrocene unit, in the process of undergoing substitution by another ferrocene group, gains in ring basicity because of the substituent's powerful electron donor action, the internal units in polymeric I, all flanked by ferrocene neighbor units, should be at least as susceptible as ferrocene itself to electrophilic attack, *e.g.* in alkylation or acylation, although reduced steric accessibility of reaction sites in the polymeric substrate will by necessity have a rate-retarding effect. Proneness to nucleophilic attack, on the other hand, should be lessened in the polymer relative to the monomeric

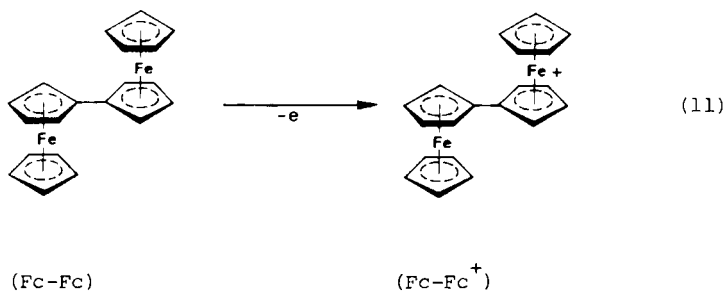
complex. These predictions have not so far been put to the test. Only biferrocene has been acetylated, but no polymer acylation or, in fact, any other chemistry affecting the ring ligands in polymeric I has to this date been investigated, although this task offers enormous challenge with respect to both the chemical approaches involved and the properties thereby to be gained.

The situation is different with regard to the chemistry involving the metal center, the topic of highest current priority in research being the change of metal oxidation state in oligo- and poly-1,1'-ferrocenylenes brought about in suitable oxidative environments. The reason for the special research interest in this topic can be traced to the mixed-valence properties expected in a partially oxidized polyferrocenylene. The mixed-valence phenomenon, stated in simplified terms, can be observed in a molecular entity comprising two or more atoms of a particular element (generally a transition metal) characterized by different oxidation states ('valencies') and in reasonable proximity to each other to allow a weak mutual electronic interaction. In such a system the valencies, although localized (trapped) in the ground state, can undergo exchange between the two (or more) sites by an optically induced intramolecular electron transfer requiring a comparatively small expenditure of energy. This exchange, referred to as intervalence transfer, manifests itself in a broad absorption band typically in the near-infrared; it leads to a reversal of the oxidation states such that immediately after completed electron transfer the donor center's coordination sphere possesses the vibrational coordinates of the acceptor center, and *vice versa*. The model proposed by Hush [49] has proven invaluable for the demonstration and understanding of intervalence transfer phenomena, and the groups of Hush, Day, and Taube [49-51] may be cited as the foremost pioneers in the fascinating field of mixed-valence physics and chemistry, which has in recent years become a focal point of research activities on account of its important ramifications into questions involving catalytic and biological electron transfer processes. While no details can be presented here, the reader is

referred to the many proficient articles and reviews that have since appeared in print on pertinent aspects of the mixed-valence phenomenon [52-55].

Because of the similarity in ligand environment in both ferrocene and its one-electron oxidation product, the ferricenium cation, it stands to reason that a system made up of two or more adjacent ferrocene units and partially oxidized so as to give rise to a sequence of iron centers with discrete, weakly interacting higher (Fe(III)) and lower (Fe(II)) oxidation states should lend itself exceptionally well to the study of the mixed-valence problem.

In the ferrocene monocation, Fc-Fc^+ (Fc = ferrocenyl, Fc^+ = ferricenyl), prepared from the neutral complex by partial oxidation with *p*-benzoquinone, iodine, or other oxidants (scheme 11) and



physically isolated as the picrate, triiodide, tetrafluoroborate, etc., such mixed-valence behavior has indeed been established in experimental efforts executed most painstakingly and on a broad front by Cowan *et al.* [52,56,57] and, subsequently, by the groups of Hendrickson [55,58], Meyer [53,59], and others. The electrophysical and spectroscopic data obtained on the cation are clear evidence of a system with trapped valences, the two oxidation states being localized, in the time scale of the characterization techniques used, each one on a given unit. (The contrasting behavior of [0.0]ferrocenophane monocation, which represents an 'average-valence' system with equal charge on both units, is on record [56].) The cation

possesses a (somewhat anion-dependent) magnetic moment ($\mu_{\text{eff}} \approx 2.2$ B.M.) similar to that of mononuclear ferricenium ion, and, as in the latter, highly anisotropic g values are derived from the ESR spectrum. In contrast to the ferricenium species, the dinuclear Fc-Fc^+ gives a well-defined spectrum at $T \gg 20\text{K}$ because of increased ESR relaxation time resulting from distorted symmetry in that cation and consequent increase in the splitting between the two Kramers doublets arising from the ${}^2\text{E}_{2g}$ ground-state configuration [57c]. The cation's electroconductivity, $\sigma_{20} \approx 10^{-8} \text{ Ohm}^{-1} \text{ cm}^{-1}$, is some five orders of magnitude higher than that of ferricenium ion (excepting the ferricenium-TCNQ⁻ salt, which is even more highly conducting because of anion participation) [57a]. This demonstrates convincingly that mixed valence provides a better path for electronic conduction than would be found in a system simply composed of non-interacting ferrocene and ferricenium units. The Mössbauer scan represents a superposition of the two quadrupole-split doublets pertaining to the ferricenium (outer doublet, $\Delta E_Q = 2.1 - 2.3 \text{ mm s}^{-1}$) and ferrocene (inner doublet, $\Delta E_Q = 0.3 - 0.4 \text{ mm s}^{-1}$) parts of the compound. While in most cases reported the two doublets appear in approximately equal intensity when recorded at 77 K, some anomalies have been observed near 300 K, where the inner doublet, apparently through contribution by a third, narrow doublet arising at this higher temperature, possesses a higher intensity than the outer one. The origin of the contributing resonance is not clear. It has been speculated that this newly appearing doublet represents an average-valence signal and thus indicates that the electron exchange rate between the two iron nuclei may approach $10^7 - 10^8 \text{ s}^{-1}$ at the higher temperature, leading to partial oxidation-state averaging within the time scale of the Mössbauer experiment [55,57b]. Mössbauer data obtained by applying an external longitudinal magnetic field [60] seem to indicate that the lone electron at the Fe(III) site is not metal-localized, as had previously been accepted, but rather occupies a predominantly ligand-based orbital, e.g. a π orbital of the fulvalene bridging ligand. This could indeed provide a conceivable path for thermal electron exchange and high-temperature

delocalization. Further attention should be paid to this important question. The most striking spectroscopic feature of the dinuclear cation is observed in the near-infrared absorption spectrum, recorded on solutions in polar solvents. The spectrum displays an intervalence transfer band at about 1900 nm for the process $\text{Fc}^+-\text{Fc} \rightarrow \text{Fc}-\text{Fc}^+$, and from both the frequency and width at half height of this band one is in a position to calculate the interaction parameter α in the simplified wave function of the mixed-valence cation [52,59]. The value derived, in the order of 10^{-1} , is in agreement with the weak-interaction-type mixed-valence case expected for the monocation.

In addition to the mono-oxidized biferrocene, the fully oxidized species, Fe^+-Fe^+ , has also been isolated and spectroscopically characterized [55,57b]. With each unit carrying a full positive charge in this dication, the conditions for mixed-valence behavior no longer obtain, and, accordingly, no intervalence transfer band is observed.

In an excellent follow-on study, ferrocene and the three oligomers I, $n = 2 - 4$, were investigated electrochemically [54]. Several partially or fully oxidized species were generated from the neutral compounds at controlled potentials, although no products were physically isolated. Half-wave potentials (*versus* SCE) determined for the various oxidation stages by cyclic voltametry in dichloromethane/acetonitrile are collected in Table 7.

It is seen that separate, discrete waves arise at increasingly higher potentials as the ferrocene units undergo successive oxidation, attesting to the discreteness of each oxidation state site and to the weak interaction between them. Also apparent is the increasingly stronger electrostatic repulsion that must be overcome with each new Fe(III) site introduced. Another trend of significance is the steady shift of $E_{1/2}$ to more negative values as one goes from ferrocene to the dimer, trimer, and tetramer. Well in accord with the stabilizing effect on a ferricenium unit exerted by each added electron-donating ferrocene group, the trend suggests that the propensity for mono-oxidation increases steadily, albeit

TABLE 7. HALF-WAVE POTENTIALS FOR PARTIALLY AND FULLY OXIDIZED OLIGOFERROCENYLENES^a

Parent compound	Oxidation step ^b	E _{1/2} , V ^c
Ferrocene	$\text{Fc} \xrightarrow{-e} \text{Fc}^+$	0.40
Biferrocene (I, n = 2)	$\text{Fc-Fc} \xrightarrow{-e} [\text{Fc-Fc}]^+$	0.31
	$[\text{Fc-Fc}] \xrightarrow{-e} [\text{Fc-Fc}]^{2+}$	0.65
1,1'-Terferrocene (I, n = 3)	$\text{Fc-Fc-Fc} \xrightarrow{-e} [\text{Fc-Fc-Fc}]^+$	0.22
	$[\text{Fc-Fc-Fc}]^+ \xrightarrow{-e} [\text{Fc-Fc-Fc}]^{2+}$	0.44
	$[\text{Fc-Fc-Fc}]^{2+} \xrightarrow{-e} [\text{Fc-Fc-Fc}]^{3+}$	0.82
1,1'-Quaterferrocene (I, n = 4)	$\text{Fc-Fc-Fc-Fc} \xrightarrow{-e} [\text{Fc-Fc-Fc-Fc}]^+$	0.16
	$[\text{Fc-Fc-Fc-Fc}]^+ \xrightarrow{-e} [\text{Fc-Fc-Fc-Fc}]^{2+}$	0.36
	$[\text{Fc-Fc-Fc-Fc}]^{2+} \xrightarrow{-e} [\text{Fc-Fc-Fc-Fc}]^{3+}$	0.61
	$[\text{Fc-Fc-Fc-Fc}]^{3+} \xrightarrow{-e} [\text{Fc-Fc-Fc-Fc}]^{4+}$	0.89

^aData from ref. 54. ^bFc = ferrocenyl (terminal) or 1,1'-ferrocenylene (internal). Brackets indicate uncertainty of position(s) of ferricenium unit(s) in the chain. ^cVersus SCE at 24^o, in dichloromethane/acetonitrile (1:1), 0.1 M tetra-n-butylammonium hexafluorophosphate.

in decreasing increments, as n grows from 1 to 4 and, thence, to higher values. A long chain of I, in fact, may suffer mono-oxidation spontaneously and with profound effects on the solubility in nonpolar solvents.

The partial oxidation of the oligomers with n > 2 in certain instances provides more than one possibility of positioning the ferricenium unit(s) in the chain, and oxidation state isomerism may thus result. Uncertainties in the unit sequence are reflected in the bracket denotation used in the table. Although one may predict certain arrangements to be energetically favored over others, the energy differences are not large; from electrochemical arguments, for example, the difference in free energy between the two dicationic isomers derived from terferrocene, $\text{Fc}^+-\text{Fc}-\text{Fc}^+$ and $\text{Fc}^+-\text{Fc}^+-\text{Fc}$, has been estimated to be as small as 11.5 kJ mol⁻¹ [54], the first-mentioned isomer being the more stable one for obvious electrostatic reasons.

Table 8 contains the intervalence transfer band maxima measured in the same study on the electrochemically obtained salt solutions (entries 1 - 4, column A). Preliminary absorption data for the same mono- and dications obtained in the author's laboratory by chemical oxidation of the neutral parent compounds have been juxtaposed in the table for comparison (column B). Because of the broad band structure, error limits for λ_{\max} are high, and this must be taken into account in any comparative evaluation. Excepting the entry 2, the tabulation shows the expected trend of intervalence transfer energies, although significant quantitative differences between the two series of results in columns A and B can be observed. Thus, the transition in the trinuclear dication (entry 3), being unsymmetrical and leading to a higher-energetic isomer, should, and

TABLE 8 INTERVALENCE TRANSFER ABSORPTION OF PARTIALLY OXIDIZED OLIGO- AND POLYFERROCENYLENES^a

Entry	Cation ^b	Predicted transition ^c	λ_{\max} , nm	
			A ^d	B ^d
1	$[\text{Fc-Fc}]^+$	$\text{Fc}^+-\text{Fc} \rightarrow \text{Fc-Fc}^+$	1900	1790
2	$[\text{Fc-Fc-Fc}]^+$	$\text{Fc-Fc}^+-\text{Fc} \rightarrow \text{Fc}^+-\text{Fc-Fc}$	1990	1780
3	$[\text{Fc-Fc-Fc}]^{2+}$	$\text{Fc}^+-\text{Fc-Fc}^+ \rightarrow \text{Fc}^+-\text{Fc}^+-\text{Fc}$	1670	1625
4	$[\text{Fc-Fc-Fc-Fc}]^{2+}$	$\text{Fc}^+-\text{Fc-Fc}^+-\text{Fc} \rightarrow \text{Fc}^+-\text{Fc-Fc-Fc}^{+e}$	1790	1770
5	$[\text{I}, n = 11]^{5.5+}$	$-\text{Fc}^+-\text{Fc-Fc}^+-\text{Fc-Fc}^+-$		1800
6	$[\text{I}, n = 24]^{12+}$	"		1800
7	$[\text{I}, n = 11]^{3.5+}$	$-\text{Fc}^+-\text{Fc-Fc-Fc}^+-\text{Fc-}$		1850
8	$[\text{I}, n = 24]^{8.5+}$	"		1840

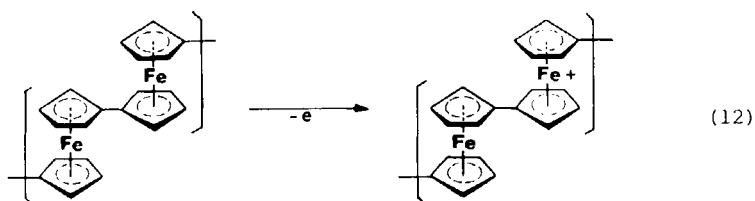
^aIn dichloromethane/acetonitrile, 0.1 M (n-Bu)₄NPF₆ (electrochem. oxidized) or acetonitrile (chem. oxidized), under Ar. ^bAnion is PF₆⁻ (electrochem. oxidized; from supporting electrolyte, products not isolated) or BF₄⁻ (chem. oxidized with p-benzoquinone/HBF₄). ^cAll products in vibrationally excited state. Transitions in entry 4 and higher entries speculative.

^dProducts by electrochem. oxidation (column A; from ref. 54) or chem. oxidation (column B; unpublished results, author's laboratory). Estimated uncertainty ± 10 nm for entries 1 - 4; ± 20 nm for entries 5 - 8.

^eThe less probable $\text{Fc}^+-\text{Fc-Fc}^+-\text{Fc} \rightarrow \text{Fc}^+-\text{Fc}^+-\text{Fc-Fc}$ [54] should produce a band at higher energy observed.

does, give a maximum shifted to shorter wavelength in relation to the monocation's band (entry 2). The latter, perhaps for reasons of unsymmetric transition, turns out to be at slightly higher energy than the dinuclear monocation's maximum if column B data are considered. Inexplicably, however, the reverse holds for the values of column A. In the tetranuclear dication (entry 4) the energetic demand for the depicted transition should be similar to that in terferrocene monocation, and the values listed in column B indeed are close, whereas, again, the data of column A do not conform. With the chemical oxidation work still in progress and the findings subject to correction, it is too early to draw significant conclusions from these comparative observations.

Extending the investigations discussed in the foregoing, work is progressing in the author's laboratory towards the goal of preparing partial oxidation products of I, $n > 4$. The chemical oxidation of polymeric I as exemplified in the segment structure of scheme 12 for the case of an exactly half-oxidized polycation,



while straightforward in principle, presents extraordinary practical difficulties arising from (i) poor solubility or absolute insolubility of most of the polysalts formed, (ii) extreme sensitivity of the higher-oxidized polycations in the dissolved state to impurities capable of acting as reductants and thus causing uncontrollable decreases in ferricenium contents, (iii) inability of most oxidizing systems to provide rigorous stoichiometric control of the oxidation process, and consequent variations in the degree of oxidation attained, and (iv) polysalt resistance to combustion, causing problems in the elemental analysis required for accurate structural

definition. For example, such conventional oxidants as $\text{H}_3\text{O}^+/\text{O}_2$, Ce^{4+} , tetracyanoquinodimethane, and dichlorodicyanoquinone, which have been successfully employed for the oxidation of biferrocene [55-58] or short oligoferrocenylene segments in polyrecombination products of ferrocene [61], have proved to be entirely useless for polyferrocenylene oxidation because of unreproducible degrees of oxidation achieved and/or product insolubility. The only system so far found to be moderately efficacious is $\text{H}_3\text{O}^+/\textit{p}$ -benzoquinone, applied by adding HBF_4 and *p*-benzoquinone to the THF or benzene solution of the neutral parent polymer. While, again, giving rather unreproducible degrees of oxidation as a consequence of its propensity for undergoing both one-electron and two-electron reduction, this oxidant furnishes polysalts retaining initial solubility in rigorously purified solvents, such as acetonitrile or nitromethane. Polysalts so prepared tend to remain soluble for a period of 24-28h, permitting analytical or spectroscopic determination of desired solution properties within the limited time span. Once insoluble, the polysalts can no longer be resolubilized without concomitant destruction. As no significant differences in elemental composition and spectroscopic solid-state properties have so far been observed between products prior to, and after, the loss of solubility, one may speculate that this peculiar 'aging' characteristic is brought about by packing differences in the lattice, perhaps as a result of gradual solvent diffusion from the precipitated crude salt. Structural analyses of polysalts sufficiently low-molecular to provide a reasonable degree of crystallinity may help to shed some light on this problem.

Preliminary characterization so far performed on the poly(ferrocenylene-*co*-ferricenylene) polysalts prepared in different Fc/Fc^+ ratios and at various \bar{x}_n levels includes Mössbauer and electronic absorption spectroscopy. Whereas elemental analysis, for reasons pointed out above, has proved inadequate for reliable determinations of the ferricenium contents, Mössbauer spectroscopy is well suitable for this purpose, since the recoilless fractions of both the

ferrocene and the ferricenium moieties are sufficiently similar to permit direct signal area comparison at 77K. (At much higher temperatures, anomalies arise as earlier reported for the dinuclear case [55,57b].) The δ and ΔE_Q parameters determined for a large number of polycations possessing molecular masses of 1000 - 5000 and ferricenium contents of 35 - 60%, although showing some scatter from sample to sample, are in the ranges of $\delta = 0.50 - 0.57 \text{ mm s}^{-1}$, $\Delta E_Q = 2.20 - 2.47 \text{ mm s}^{-1}$, for the outer (ferrocene) doublet and of $\delta = 0.51 - 0.59 \text{ mm s}^{-1}$, $\Delta E_Q = 0.39 - 0.46 \text{ mm s}^{-1}$, for the inner (ferricenium) doublet. They are not substantially different from the corresponding values for the ferrocenylferricenium cation [45,46,58] (Fig. 3). It thus appears that at least within the range of ferricenium contents so far investigated, there is no \bar{x}_n -dependent shift toward higher or lower values of either δ or

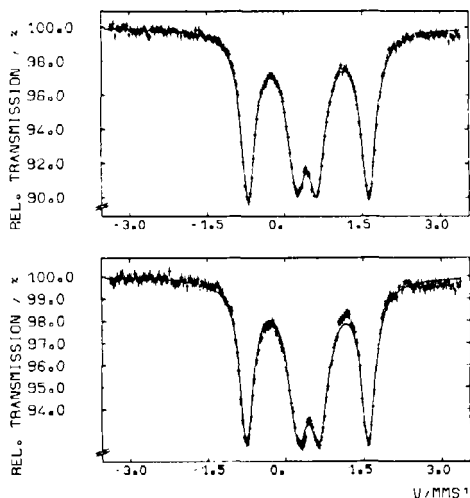


FIGURE 3. Mössbauer spectra ($^{57}\text{Co}(\text{Rh})$; 77K) of partially oxidized di- and polynuclear 1; top: ferrocenylferricenium tetrafluoroborate; bottom: poly(ferrocenylene-ferricenylene tetrafluoroborate).

ΔE_q and, hence, little or no change in s-electron density and electric field gradient at the iron nuclei of the individual Fc and Fc⁺ units. This suggests that the extent of electronic interaction between adjacent units, and, thus, the mixed-valence behavior, is not significantly altered as the ferrocenylene-ferricenylene system becomes repetitively linked into a linear chain of higher molecular mass.

The intervalence transfer band maxima determined for a number of fractions of partially oxidized I are in qualitative agreement with this inference. The bands are distinctly broader than observed with the dinuclear cation as a consequence of the simultaneous occurrence of many nearly isoenergetic transitions. As seen from the exemplifying λ_{\max} values listed in Table 8 (entries 5 - 8), there is no molecular-mass dependence of the intervalence transfer energy within the range, $n \approx 10 - 25$, and, in accord with expectation, the energetic demand is lowered as the degree of oxidation decreases sufficiently below the 50%-level to permit the random occurrence of two adjacent uncharged units in the chain (*cf.* entries 7,8 *vs.* 5,6). However, the comparatively high wavelength range of 1800 - 1850 nm in which these bands are observed is somewhat puzzling. The transitions in entries 5 and 6, for example, should not be favored energetically over that in entry 3 and, hence, should give rise to maxima closer to 1650 nm. This apparent inconsistency requires further study, although a possible explanation may be found simply in greater experimental difficulties experienced in dissolving the polymer rapidly and yet completely anaerobically, which in turn may have led to effectively lowered ferricenium contents of the solutions investigated.

The few data presented in this section, although rather tentative and incomplete as the experimental program continues, suffice to permit the prediction that polysalts composed essentially of alternating Fc and Fc⁺ units (scheme 12) and comprising electronically balanced anions will not exhibit electrophysical

properties substantially different from those of the simple dinuclear ferrocenylferricenium salts previously investigated [52-58]. Specifically, increases in electroconductivity appear to be out of the question, as do any major changes in the magnetic properties and ESR parameters that would point to enhanced electronic delocalization along the polycation's chain. While, to this date, no information on structures with very much higher or lower ferricenium contents has been made available, surprise findings with respect to the electrophysical behavior of such structures are quite unlikely.

Potential Uses.- In view of the limited accomplishments made until now in the synthesis of pure polyferrocenylenes of high molecular mass, the absence of application and performance reports in the literature is not unexpected. In the following, an attempt will be made, based on known applications of ferrocene itself, to point out potential use areas for the polymer. Only some of the more recent literature sources for ferrocene applications will generally be cited in this context, although earlier sources, most of these well reviewed [1,2,62], will occasionally be quoted if particularly significant. In the majority of use areas discussed below, the principal advantage of employing the polymer in place of ferrocene proper lies in the firm anchoring and immobilization of the active metal site thereby achieved. The parent complex is highly volatile and tends to migrate and evaporate from polymeric and other substrates into which it is compounded, leading to rapid depletion of metal contents, especially at elevated temperatures.

The excellent heat resistance of the ferrocene complex, paired with outstanding stability under the impact of high-energy ultraviolet radiation as encountered outside the terrestrial atmosphere, has prompted much research on ferrocene-containing space vehicle coatings and related compositions [63]. At the low gas densities observed in the upper atmosphere or in outer space, the question of retaining the metallocene in the framework of the coating is a particularly pressing one, and use of high-molecular polyferro-

cenylenes should contribute significantly to an enhanced integrity of the coating material.

A feature of considerable importance in connection with the well-known functioning of the ferrocene complex as a burning rate accelerator and combustion catalyst is the metal atom's ability to exist in two different oxidation states and thus act as an efficient electron transfer agent. In many areas of combustion catalysis until now reserved for ferrocene or some of its derivatives, *e.g.* in fuels (including hypergolic ones), pyrotechnic compositions, and solid rocket propellants [64], use of polyferrocenylene should, for the aforementioned reason, offer particular advantage. The same argument holds for the use of polyferrocenylene in place of ferrocene as an additive in cable insulating materials to reduce dielectric breakdown [65], as a heat- and light-stabilizing component in numerous polymeric materials [66], as an additive exerting a photo-sensitizing effect in polymers or in photographic compositions and other light-sensitive reproduction materials [67], and as a constituent of epoxy resins, poly(vinyl chloride) (PVC), polyurethane, and other plastics to improve fire resistance and flame retardance [68]. The last-named topic is of highest current interest in materials technology, notably in aircraft and automotive interior designing, as well as in high-rise building and factory construction. Intimately connected with this question of flame retardance is the problem of smoke suppression. Smoke and fumes developed in an enclosed fire location tend to pose more serious hazards to life than open fires, and successful suppression of smoke evolution from burning organic matter, notably plastics and rigid foam insulating materials, is therefore frequently a vital design feature. The efficacy of ferrocene in suppressing or inhibiting smoke development in PVC and other polymeric materials is on record [69], and the use of polymeric I in lieu of ferrocene is a suggested approach. A related problem concerns the liberation of HCl during the combustion of PVC-type materials with sometimes dramatic consequences. Ferrocene has been tested successfully as an additive suppressing HCl evolution [70], and,

again, the polymeric product, unable to diffuse and migrate out of the PVC composition, should show an even better performance than the monomer.

Other applications in which the substitution of polyferrocenylenes for the monomer should offer distinct advantages include use in radiation resist compositions and semiconductor devices [71], in cutting fluids to enhance the durability of cutting tools [72], in petroleum distillates for the removal of unsaturated ingredients [73], as synergists for insecticides and acaricides [74], as a co-initiator of the free-radical polymerization of methyl methacrylate [75], as a curing accelerator in unsaturated polyester-polyacrylates [76], and as a hardening agent for oligoacrylates on cadmium surfaces [77]. In view of the ready oxidizability of ferrocene and its proneness to complexation with electron acceptors, a particular challenge should be found in the use of polyferrocenylenes as polymeric charge transfer complexes and, in the partially oxidized state, as electron exchange resins and in certain electrophysical applications where the magnetic and mixed-valence characteristics are of interest. A case in point is the creation of surface-attached electroactive ferrocene centers on graphite or platinum electrodes, as well as on semiconducting, silicon-based photoelectrodes of greatest current interest in photoelectrochemical energy conversion projects [78]. Polyferrocenylenes can probably be deposited readily from solutions of the neutral material. Once deposited, the coating may be partially oxidized, whereupon it will lose its solubility not only in nonpolar solvents but, after some 'aging' time, also in such polar solvents as nitromethane or acetonitrile; this should result in effective immobilization on the electrode surface.

A discussion of potential polyferrocenylene applications would be incomplete without covering the important field of medical and medicinal use. Many ferrocene derivatives have been developed, in some cases with considerable success, as hematinics, antibiotics, haptens and antineoplastic agents, as specific enzyme inhibitors, tagging agents and labels in various forms, as a pharmacon promoting

liver regeneration, and for conversion into the gamma-emitting ^{52}Fe radionuclide to be used in nuclear medicine [79]. Hydrophilic behavior in the oxidized state and low toxicity both combine to render the ferrocene complex a ready substrate for medicinal applications. However, its rapid metabolism in the living organism presents a considerable disadvantage in most of its physiological and pharmacological functions, and replacement by a polymeric structure is likely to retard the metabolic process in addition to preventing unduly fast removal from the site of action through diffusion or resorption. This should be particularly advantageous in hapten and other chemoimmunological, as well as labeling and radiochemical applications.

POLYRUTHENOCENYLENE

Only the heteroannularly inter-linked compounds III will be treated in this section, no homoannular isomers being known, and the discussion will be restricted by necessity to the oligomeric homologs prepared until now.

Physical Properties.- The oligo-1,1'-ruthenocenylenes III are colorless or cream-colored solids. The dimer and trimer both crystallize as well developed needles and, like the tetramer, possess melting points below 300° (Table 9). Although homologs with $n > 4$ have not so far been separated as pure compounds, one may expect their melting points to show a similar trend as observed in the ferrocene polymer series, increasing beyond 300° at $n = 4 - 6$; higher fractions, as represented by entry 4 of the table, being polydisperse, should show a dip in the melting point-temperature relationship, followed by a steady increase beyond 350° as degrees of polymerization of 15 - 20 are exceeded. The solubility behavior of the oligomeric ruthenocenes is similar to that of the corresponding ferrocene analogs, although the low-molecular members of the series are characterized by lower saturation limits. High-molecular III, not as yet synthesized,

should possess excellent solubility in aromatic solvents and halocarbons.

While no thermostability testing has been performed owing to the unavailability of higher-molecular material, it is safe to predict, on the basis of comparative thermogravimetric analysis data reported for methylene-bridged ruthenocene polymers [80], that high-molecular fractions of III will be superior in heat resistance even to the polyferrocenylones.

The ruthenocene crystal is pentagonal prismatic (D_{5h}), *i.e.* the ring conformation is eclipsed, and the barrier to internal rotation is slightly higher than in ferrocene [81]. No X-ray structure data are available as yet on any crystalline oligomer; yet steric considerations suggest a transoid conformation with respect to the two metallocene units in the solid dimer, as in biferrocene, and the higher oligomers and polymers most likely are arranged in predominantly transoid conformations as well. Preliminary spectroscopic evidence (*vide infra*) agrees with an essentially coplanar alignment of the fulvalene-type bridging ligands in all oligomeric samples investigated (Table 9). There is no spectroscopic evidence for tilting of the Cp rings in oligomeric III, and no tilting is expected in compounds of higher molecular mass.

The spectroscopic data collected until now are few; with both mass spectrometry and NMR spectroscopy, as in the ferrocene series, found to be of little use in the higher polymeric range, the only major techniques employed are electronic and infrared absorption spectroscopy. The electronic spectrum of the ruthenocene parent complex has been described and analyzed, the aforementioned two papers being typical [40]; it resembles closely the ferrocene spectrum, although all pertinent transition energies are higher, and the maxima appear correspondingly shifted to lower wavelengths. The electronic spectra [13,33,35] of III, $n = 2 - 4$, similar to the ruthenocene spectrum, exhibit the characteristic ligand-field band near 320 nm due to the two d-d transitions, $a_1' \rightarrow e_1''$ and $e_2' \rightarrow e_1''$, and the two charge-transfer bands in the UV region near

250 and 265 nm, corresponding to the band systems V, IV and II in Gray's notation [40]. The three maxima are listed in Table 9, with ϵ , again, calculated per metallocene unit. Much as in the ferrocene series, the UV bands suffer appreciable red shifts and intensity increases as the ruthenocene molecule dimerizes, this being the result of the introduction of the fulvalene ligand bridging the two metal atoms. The trend becomes much less pronounced as one goes from the dimer to the trimer, and only small additional shifts in the indicated direction can be observed in the tetramer. The data obtained on the oligomer fraction (entry 4, Table 9) suggest that no further shifts occur as n exceeds 4 - 5. (For the seeming failure of the ligand-field band maximum to follow the overall trend of bathochromic shifts, see [33].) It appears from these results that the two Cp rings constituting each fulvalene-type ligand are substantially coplanar. It is, furthermore, apparent that the central metal atom in ruthenocene is not capable of transmitting significant electronic effects from one Cp ring to the other; accordingly, electronic interaction between adjacent 1,1'-ruthenocenylenes in III is essentially limited to delocalization *via* the fulvalene bridge. Hence, no significant extent of electronic charge delocalization along the polymer chain of III is indicated by the UV data. The situation is thus, not unexpectedly in view of the similar electronic structure and bonding characteristics, quite comparable with that in the ferrocene polymer series I, and one may safely predict that this lack of electronic inter-unit interaction will find confirmation in the ^{99}Ru Mössbauer spectra, the diamagnetic behavior and the electrical insulation characteristics yet to be determined on polymeric III.

The vibrational spectrum of ruthenocene has been treated extensively [82]. As would be expected from the practically independent vibrational behavior of each Cp ring, the ring-vibrational fundamentals are observed at positions close to, or coincident with, those in the ferrocene spectrum. Quite accordingly, one finds [33] the IR spectra ($4000 - 500 \text{ cm}^{-1}$) of birutheno-

TABLE II. MELTING POINTS AND SELECTED ELECTRONIC ABSORPTION
MAXIMA OF FERROCENE OLIGORUTHENOCENYLENES^a

Compound	M_n^b	M.P., °C	λ_{max} , nm ($\epsilon, M^{-1} \text{ cm}^{-1}$) ^c
ferrocene (III, n = 2)	400	248-249	249(6400) 261(5300) 322(670)
1,1'-ferrocenophene (III, n = 3)	690	276	252(2400) 265(8600) 322(1050)
1,1'-quateruthenocene (III, n = 4)	970	269-271	253(5400) 265(8500) 323(1300)
1,1'-oligoruthenocenylenes (III, n = 4)	1420	210-230	253(9600) 264(8050) 323(1290)

^aFrom entries 13, 13, 21, ^bby mass spectrometry (for ^{102}Ru) in first three entries, by vapor pressure osmometry in last entry. ^cin 1,2-dichloroethane. Molar extinction coefficient ϵ calculated per metallocene unit.

cene and the higher homologs to be strikingly similar to the spectra of the corresponding ferrocene oligomers discussed in a previous section, showing the characteristic substitution band in the vicinity of 1030 cm^{-1} and the absorptions near 1000 and 1100 cm^{-1} , the latter invalidating the '9,10- μ rule'. The only significant differences, relative to the ferrocene counterparts, appear in the region of the unsymmetric skeletal vibrations below 500 cm^{-1} where, as in the spectrum of ruthenocene itself, shifts to lower frequencies are observed. Characteristically, and, again, as in the case of I, there are no molecular-mass-dependent band shifts over the entire $4000 - 250 \text{ cm}^{-1}$ region, attesting to the absence of significant vibrational interaction between neighboring ruthenocene units, as well as to the lack of any constraints in the ligand tilting and metal-ligand stretching modes as n increases beyond 2 - 3.

Chemical Properties.- The ruthenocene complex, while offering certain parallels with ferrocene in its chemical behavior [2], shows a number of features in which it differs markedly. Thus, reduced electronic charge in the σ carbon orbitals of the Cp rings relative to ferrocene leads to decreased ring basicity with concomitantly

diminished reactivity towards electrophiles. As a consequence, electrophilic ring substitution is disfavored, and nucleophilic substitution favored, in relation to ferrocene. In contrast, the metal basicity is greater in ruthenocene than in the iron congener; therefore, ruthenium protonation and other electrophilic metal substitution reactions are facilitated. None of these reaction types have been 'tried out' as yet on oligomeric III.

The difference between the two metallocenes is particularly striking in the central metal's oxidation/reduction behavior. Whereas ferrocene suffers one-step, one-electron oxidation to the Fc^+ cation regardless of the oxidation method employed, the ruthenium complex is capable of undergoing both one-step, one-electron and one-step, two-electron oxidation reactions depending on the oxidative environment [83]. Thus, reversible loss of one electron, giving rise to the generation of the ruthenocenium monocation, is brought about photooxidatively in the presence of halocarbons. The same result is obtained electrochemically at the dropping mercury electrode. The polarographically determined half-wave potential is less positive than that of the Fc/Fc^+ system, indicating a greater propensity for oxidation in the ruthenocene case. Quite in contrast, if ruthenocene oxidation is accomplished chemically (e.g. by iodine, FeCl_3 , or $\text{H}_3\text{O}^+/\text{p}$ -benzoquinone) or electrochemically at the platinum electrode, one finds a greater resistance to oxidation than in the iron complex, the half-wave potential having more than doubled (i.e. increased toward more positive values), and the product is the ruthenocenium dication with formal Ru(IV), generated irreversibly by a two-electron step. Whether the ruthenocene nucleus suffers oxidation more, or less, readily than the ferrocene complex thus depends critically on the oxidation method employed. Although no work has been performed in the area of oligoruthenocenylenes oxidation, this research field should offer high rewards in view of the unusual oxidation/reduction behavior of the monomer. For example, the controlled, reversible one-electron oxidation (at the dropping mercury electrode) of a fraction of the

ruthenocene units in a polynuclear compound can be expected to furnish mixed-valence salts as in the analogous ferrocene polymer case, although, in the light of the decreased donor power of the ruthenocene system in relation to ferrocene, there is less likelihood of a trend of increasing ease of monooxidation in the poly-ruthenocenylenene chain as n grows beyond the value of 2. Electrochemical treatment at the platinum electrode may lead to two-electron oxidation as in the mononuclear compound, although perhaps with enhanced reversibility in the polymer system. On the other hand, the mildly electron-withdrawing effect of adjacent ruthenocene units may raise the potential for the two-electron oxidation step sufficiently to render one-electron oxidation more favorable, in clear departure from the mononuclear case. Another challenging task to explore concerns the polymer behavior under conditions of chemical oxidation. Thus, it should be of interest to find out whether the mode of oxidation can be changed to that of one-electron oxidation if a ruthenocene unit tied into a chain is treated with chemical oxidants (including the ferricenium cation) possessing a redox potential intermediate between the potentials of the ruthenocene/ruthenocenium monocation and ruthenocene/ruthenocenium dication systems. With access to the metal center likely to be curtailed in a polymeric substrate, the simultaneous availability at the reaction site of two one-electron-type oxidant molecules may no longer be assured, and the mechanism of chemical oxidation could conceivably be altered so as to facilitate the kind of one-electron oxidation step observed at the dropping mercury electrode. This would, of course, also result in a change of magnetic properties, as the dication of ruthenocene is diamagnetic, whereas one-electron oxidation entails paramagnetic behavior.

Potential Use.- As only preliminary communications regarding oligomeric III, and no reports on polymeric III, have until now become available, there is little reason to discuss major use areas at this point. The high cost of the parent complex, not exactly

conducive to large-scale development and evaluation work, will doubtlessly have a retarding effect on application research. However, specialty fields may well call for the use of polyruthenocenylenes where costs are no primary consideration. The combined heat and radiation resistance of ruthenocene, superior even to that of ferrocene, should, for example, warrant the development of space vehicle or instrument coatings containing polyruthenocenylenes. The parent complex shows low-temperature phosphorescence and is an efficient triplet quencher, use of which could be made in polymer applications. The most outstanding potential for investigation, however, is offered in nuclear medicine, where excellent groundwork involving the use of labeled ruthenocene derivatives has been performed by Wenzel, the foremost researcher in this field [84]. The ^{103}Ru radionuclide is both a β (0.21 MeV) and a γ emitter (0.50 MeV) with a useful half-life of 40 d. The β emission lends itself to whole-body autoradiography, and the γ emission can be utilized for the labeling of ruthenium compounds applied as pharmaca or for diagnostic purposes. Accordingly, ruthenocene compounds labeled with ^{103}Ru have found extensive use in nuclear-medical research, *e.g.* for the study of organ distribution and, most recently, for the labeling of cytostatic drugs used as inhibitors of tumor growth. These findings suggest challenging possibilities for macromolecular, labeled ruthenocenes. The introduction of the ^{103}Ru nuclide into oligo- and polynuclear III can possibly be accomplished with reasonable efficiency through thermal exchange with $^{103}\text{RuCl}_3$ by Wenzel's method developed for the labeling of ruthenocene compounds [85].

SUMMARY AND CONCLUSIONS

Only two types of polymetallocenylene have been synthesized until now: poly-1,1'-ferrocenylenes and poly-1,1'-ruthenocenylenes. Of the many reaction paths toward polyferrocenylenes investigated

in recent years, including various coupling reactions involving organo-magnesium, -zinc, and -copper intermediates, the direct, low-temperature polycoupling reaction of 1,1'-dilithioferrocene with 1,1'-diiodoferrocene has proved its superiority over other approaches, giving soluble, linear poly-1,1'-ferrocenylene in yields of ca 85% and with molecular masses of up to 4000 (10 000 upon subfractionation). The polymer gives IR and NMR spectra indicative of the absence of molecular-mass-dependent inter-unit vibrational and ring-current interactions, and the same insensitivity to molecular mass changes (at $\bar{x}_n > 4$) of the electronic charge transfer and d-d transitions is apparent from the electronic absorption spectra, suggesting insignificant electronic charge delocalization along the polymer chain. The Mössbauer spectra, yielding virtually identical chemical shift and quadrupole splitting parameters irrespective of the degree of polymerization, suggest the absence of inter-unit d_{σ} - and $d_{\pm 2}$ -electron delocalization, thus confirming the electronic absorption data. In accord with this spectroscopic behavior, the polymer, within the molecular mass range investigated, does not conduct an electrical current and in the low-molecular-mass region is diamagnetic, although feeble paramagnetism, presumably due to impurities, has been determined on higher-molecular samples. Partial oxidation of oligo- and poly-1,1'-ferrocenylenes, difficult to control by chemical means and probably very much easier to accomplish electrochemically, gives rise to the formation of polysalts containing cationic sites in the chain; these polysalts accordingly exhibit weak-interaction-type, mixed-valence behavior, showing the typical intervalence transfer absorption in the near-infrared. However, significant electronic or magnetic interaction along the backbone of these poly(1,1'-ferrocenylene-co-1,1'-ferri-cenylene) structures is not indicated by the spectral data at hand, and electro-conduction properties are not expected.

Very much less than in the ferrocene polymer case is known about the second polymetallo-cenylene type, *viz.* poly-1,1'-rutheno-cenylene. Only oligomeric compounds or fractions have been obtained

to this date, the most successful synthetic approach involving the combined oxidative and thermal coupling of TMEDA-chelated 1,1'-dilithioruthenocene. Preliminary spectroscopic findings demonstrate the same lack of inter-unit vibrational and electronic interaction as observed in the ferrocene polymer series, and there is no reason to expect changes in spectroscopic and electronic properties as higher-molecular-mass ranges will be made available. Novel electro-physical behavior might, however, be expected in partially oxidized polyruthenocenylenes, where, depending on the oxidation method employed, monocationic or dicationic sites may appear in the chain.

The areas of potential use for both polyferrocenylene and polyruthenocenylene are quite diversified and range from radiation and heat protection, stabilization or sensitization functions, polymerization initiation and combustion catalysis to flame retardance and smoke suppression as well as a multitude of medical or biological applications. Whereas costs are not a major consideration with the polymers derived from the inexpensive iron complex, the price of ruthenocene is too high to allow for the economic utilization of the polyruthenocenylenes in many a technological field, and, hence, applications will be restricted to specialty areas where particular benefits can be achieved with polymer use in very small quantities or at low concentrations, such as in catalytic or certain medical applications. No major use can be foreseen for the analogous polyosmocenylenes, should these ever be synthesized, as their cost situation is even more precarious than that of the polyruthenocenylenes.

It need not be emphasized that the molecular mass ranges presently reached for polyferrocenylene, not to mention those for polyruthenocenylene, leave much to be desired, since many applications require mechanical properties attainable only at a minimum molecular mass of 25000 - 30000, and even the most painstaking subfractionation of currently available bulk polymer will not provide such material economically. On the other hand, it appears doubtful whether the presently available synthetic methods of

aryl-aryl coupling leave room for much improvement in the ferrocene step-growth polymerization with respect to the overall degree of polymerization. Although further experimental refinements can be expected, the major drawback inherent in all the types of coupling reaction so far utilized, *viz.* defunctionalization with concomitant depression of p and \bar{x}_n , clearly sets a limit to what can be achieved in this respect. As long as organolithium, Grignard, or organocopper compounds are used as monomers, either directly or prepared *in situ*, it is obvious that the problem of loss of difunctionality owing to existing equilibria with mono- and unsubstituted (and, occasionally, higher substituted) parent compounds must be accepted even if the most stringent experimental conditions to ensure absence of impurities are observed. Therefore, in addition to investigations of catalytically useful additives in the heretofore practiced coupling reactions, in an effort to enhance the polycondensation rates relative to side reactions, it will be necessary to search for entirely different monomers or monomer pairs, each compound having two non-equilibrating functional substituents capable of fast reaction in the propagation sequence and yet sufficiently unreactive with solvents, catalysts or other components to retain its difunctionality throughout the polymerization reaction. Dihalogenated metallocenes might be suitable as monomers of this type, to be subjected, for example, to solution polycondensation by the Ullmann coupling technique with the aid of a recently developed copper reagent possessing improved activity [86], although even then some loss of functional groups through reductive dehalogenation may not be avoidable.

A different approach, potentially useful not only for polyferrocenylene preparation but also for the synthesis of other polymetallocenylenes, could utilize the preformed fulvalene dianion as the ligand-forming monomer, propagation proceeding through double-complexation with metal cation, M^{2+} . While the method of fulvalene dianion generation from cyclopentadienide [56,87] is unsuitable for clean propagation because of the prominent occurrence

of side reactions, such as ligand dimerization and diene polymerization, the generation of the dianion through electrochemical reduction of [O.O]ferrocenophane by El Murr's procedure [88] might be feasible, provided that the solubility problem with this compound can be overcome. At the present state of knowledge, in fact, this procedure can be judged to provide the only conceivable synthetic access to such other metallocene polymers as polycobaltocenylene or polynickelocenylene, which cannot be prepared by the coupling procedures used for polyferrocenylene synthesis as the parent metallocenes have so far neither been successfully lithiated nor been found themselves to suffer a clean substitution by organolithium reagents. Polycobaltocenylene is of potential interest in the partially or fully oxidized forms. Both types of polymer should possess properties required in certain polyelectrolyte and membrane applications. In addition, the partially oxidized material should provide mixed-valence features, and the fully oxidized product, to judge from the considerable stabilization achieved in the cobaltocenylene system on loss of the unpaired, high-energy valence electron, can be expected to possess extraordinarily high thermo-oxidative (and, presumably, radiative) stability, being far superior in this respect to any other metallocene polymer type that can be visualized.

In summary, the foregoing sections show that, while some promising entries into polymetallocenylene chemistry have been made, only poly-1,1'-ferrocenylene and its partial oxidation products have been subjected to major exploration. Some rather formidable experimental hurdles remain to be overcome if both polyferrocenylene and polyruthenocenylene are to be obtained in a mechanically useful molecular mass range of 25000 - 30000, and new synthetic strategies will have to be designed for the preparation of polymers derived from other transition metal complexes. There can be no doubt, however, that the synthetic aspects and application goals both provide challenge enough to render further chemical and physical research in the field a highly rewarding task.

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