Acknowledgment. The authors thank William D. Parmelle for his help in carrying out some of the experimental work and Herman Yeh of NIH for his suggestions on the NMR experiments.

References and Notes

(1) NIH Visiting Fellow.
(2) G. J. Fleming, *J. Appl. Polym. Sci.*, 13, 2579 (1969).
(3) G. J. Fleming, *J. Macromol. Sci.*, **3**, 531 (1969).
(4) Reme, *Ber.*, **23**, 3135 (1890).
(5) S. F. Kilin and I. M. Rozman, *Opt. Spektrosk.*, **17**, 431 (1964).
(6) D. G. Pereyaslova et al., *Zh. Prikl. Khim.* (*Leningrad*), **43**, 912 (1970).
(7) V. D. Kotsubanov et al., *Opt. Spektrosk.*, **25**, 727 (1968).
(8) V. D. Kotsubanov et al., *Zh. Prikl. Spektrosk.*, **10**, 152 (1969).
(9) G. A. Abakumov et al., *Pisma Zh. Eksp. Teor. Fiz.*, **9**, 15 (1969).
(10) A. Heller, *J. Chem. Phys.*, **40**, 2839 (1964).
(11) T. Nakaya and M. Imoto, *Bull. Chem. Soc. Jpn*, **39**, 1547 (1966).
(12) Badische Anilin and Soda Fabrik A-G, German Patent 1 108 219 (June 8, 1961).
(13) P. Ruggli, A. Zimmermann, and R. Thouvay, *Helv. Chim. Acta*, **14**, 1250 (1931).
(14) W. Borsche, *Justus Liebigs Ann. Chem.*, **386** 351 (1911).
(15) E. D. Bergmann and M. Sulybacher, *J. Org. Chem.*, **16**, 84 (1951).
(16) A. E. Pierce "Silylation of Organic compounds", Pierce Chemical Co., 1968.
(17) M. Hasegawa et al., *J. Polym. Sci., Part A-1*, **7**, 743 (1969).
(18) Sadtler Standard NMR Spectrum No. 7378, Sadtler Research Laboratories, Inc., Philadelphia, Pa.
(19) R. Burwell, *Chem. Rev.*, **54**, 615 (1954).
(20) S. Tanake et al., *J. Pharm. Soc. Jpn.*, **73**, 38 (1953).
(21) G. Feutrill and R. Mirrington, *Tetrahedron Lett.*, 1326 (1970).
(22) V. B. Lushchik and S. S. Skorokhodov, *Polym. Sci USSR* (*Engl. Transl.*), **14**, (1), 69 (1972).
(23) K. H. Konig, W. Schulze, and G. Moller, *Ber.*, **93**, 555 (1960).
(24) C. G. Haynes et al., *J. Chem. Soc.*, 2823 (1956).
(25) B. S. Thyagarajan, *Chem. Rev.*, **58**, 439 (1958).
(26) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. 1, Wiley, 1967, 142.
(27) H. Feuer, Ed., "The Chemistry of the Nitro and Nitroso Groups", Part I. Interscience, New York, 1969, p 112.
(28) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "High Resolution NMR Spectra Catalog", Varian Associates, Palo Alto, Calif., 1962.
(29) S. Misumi et al., *Bull. Chem. Soc. Jpn.*, **34**, 1833 (1961).
(30) S. Misumi et al., *Bull. Chem. Soc. Jpn.*, **35**, 143 (1962).
(31) T. Ito et al., *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 1943 (1975).

The Organolithium Organohalide Coupling Reaction as a Synthetic Route to Poly(1,1'-ferrocenylenes)[1]

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ABSTRACT: Poly(ferrocenylenes) are synthesized by a step-growth polycoupling reaction involving 1,1'-dilithioferrocene (chelated with *N,N,N',N'*-tetramethylethylenediamine) and 1,1'-diiodoferrocene as monomers. The reactions are performed at temperatures ranging from −20 to 80 °C in ether solvents. Best results with regard to overall polycoupling efficiency (i.e., yield and molecular mass of coupling products) and product purity are obtained in a dimethoxyethane/tetrahydrofuran medium at temperatures not exceeding 25 °C. Under these conditions, the total yield of the light tan to light orange-brown, soluble poly(ferrocenylenes) amounts to more than 85%, and the number-average molecular mass of the highest molecular fraction constituting some 16% of total product approaches 4000. The addition, at early stages, of catalytic amounts of Cu(II) or Pd(II) salts to the reaction mixture with a view toward utilizing the intermediacy of reactive organocopper or organopalladium species does not lead to further substantial increases in the overall degree of polymerization. Subfractionation from benzene solution under anaerobic conditions gives subfractions with $\bar{M}_n$ in the 1000–10000 range. Preliminary magnetic susceptibility measurements indicate the polymers to be less contaminated by paramagnetic impurities than the poly(ferrocenylenes) synthesized in previous investigations, an observation of critical importance for future electrophysical studies. Spectroscopic data, supported by the results of nonpolymeric model reactions providing evidence for the absence of a ferrocyne mechanism indicate that propagation proceeds without loss of the heteroannular substituent disposition on the reactants and so are in agreement with a structural representation (**3**) implying a 1,1' type of unit interconnection along the polymer chain.

The problem of biaryl formation through coupling of aryllithium with haloarenes has been a topic of continued research interest ever since Gilman's and Wittig's pioneering work[3] on arene metalation and the no less significant contributions, mostly by Wittig, Roberts, and Huisgens, in the chemistry of dehydrobenzene (aryne).[4] With the proper choice of solvent and halogen substituent, biaryl formation may proceed to yields of 70% and higher, rendering this type of coupling reaction under favorable conditions a useful synthetic tool in the preparation of simple and mixed biaryls.

In the course of our continuing program aimed at the synthesis of compositionally pure poly(metallocenylenes)[2,5] for electrophysical and intervalence transfer studies, we investigated, as a logical outgrowth of aryl coupling chemistry, the interaction of lithio- and haloferrocenes.

Although ferrocenyl halides must be rated as poor substrates in nucleophilic substitution reactions by addition–elimination because of the appreciable basicity of the metallocene nucleus, the lithioferrocenes, especially when chelated for enhanced nucleophilicity with TMEDA (tetramethylethylenediamine),[6] should function as excellent nucleophiles in metallocenyllithium/halometallocene reactions. In one of the more recent studies of aryl–aryl coupling involving the reaction of phenyllithium with the four *p*-halotoluenes in the presence or absence of amine catalysts and TMEDA chelating agents, the fluoro-, chloro-, and bromotoluenes were found to couple through an elimination–addition sequence (benzyne mechanism), and only the iodo compound underwent direct displacement concurrently with the elimination–addition process.[7] Although no systematic studies of the coupling behavior of the haloferrocenes under similar conditions have been reported, limited information is available on the metalation chemistry of chloroferrocene. Thus, treatment of chloroferrocenes with alkyllithium

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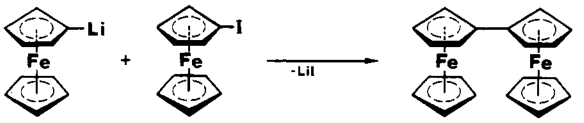
agents results in α-lithiation,[8] hence creating a potential precursor of ferrocyne, and an extended investigation of *n*-butyllithium/chloroferrocene systems[9] has indeed provided strong evidence for an elimination–addition mechanism subsequent to α-lithiation, albeit operating concurrently with predominating[10] metal–halogen exchange and resultant dehalogenation. Despite its demonstrated capability of generating ferrocyne species through the agency of butyllithium, chloroferrocene reportedly[9a] fails to couple with lithioferrocene to give biferrocenyl, suggesting ferrocenyl anion to be insufficiently basic to achieve halide abstraction from the α-chloroferrocenyl anion intermediate expected to be appreciably stabilized toward further elimination on account of the increased p character of both the anionic carbon center and the adjacent substituent-bearing carbon atom. Iodoferrocene differs from the chloro compound in that it does show some reactivity with lithioferrocene, as is apparent from an earlier literature report[11] describing the reaction of *n*-butyllithium with iodoferrocene (at 0 °C in ethyl ether). Again, appreciable metal–halogen exchange took place under these conditions; additionally, biferrocenyl was formed in 20% yield. The dimer, quite evidently, arose through coupling of some of the generated lithioferrocene with the remaining iodo compound (eq 1).



(1)

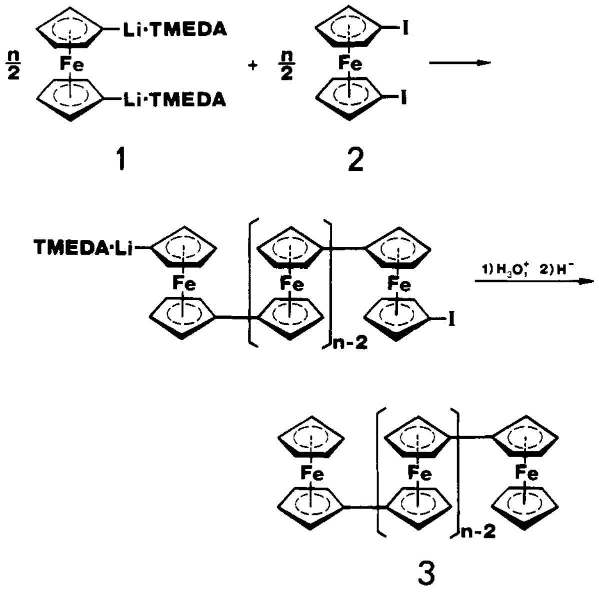
The failure of lithioferrocene to react with chloroferrocene, which should be a better substrate for ferrocyne formation than the iodo derivative, suggests the reaction in eq 1 proceeds through direct nucleophilic substitution, and there may be little, if any, contribution by an elimination–addition process.

On the basis of these earlier findings, it appeared to us that iodoferrocenes should represent useful monomers in coupling reactions leading to poly(ferrocenylenes). Accordingly, we investigated the 1,1′-dilithioferrocene/1,1′-diiodoferrocene interaction under conditions of step-growth solution polymerization. Pertinent results of these efforts are described in the following.

Results and Discussion

Exploratory work in our laboratory[12] had shown earlier that the yield of biferrocenyl in the process of eq 1 can be doubled relative to that of the reported work[11] when lithioferrocene is treated with an equimolar quantity of iodoferrocene in di-*n*-butyl ether (DBE) at 50–80 °C, and nearly trebled when the reaction is carried out in the presence of TMEDA as chelating agent, the latter increasing the nucleophilicity of the lithium compound. These results provided the basis for polymerization studies involving the difunctional starting materials, 1,1′-dilithioferrocene (TMEDA chelated) (**1**), and 1,1′-diiodoferrocene (**2**) (eq 2). As in previous investigations, the chelated dilithium compound was prepared and isolated in the solid state,[6] which aided in the removal of excess contaminating butyllithium.

In a representative experiment, dilithium complex **1**, suspended in DBE, was treated with diiodide **2** at −20 to 40 °C under the conditions summarized in Table I (experiment 1). The molar ratio of **1**–**2** was such as to provide a slight excess of lithiated compound in order to compensate for losses due to internal quenching. Acidic hydrolysis in the absence of air and carbon dioxide and further workup of the crude coupling product by treatment with a reducing agent for removal of iodo end groups,



(2)

followed by a sequence of selective extraction, crystallization, and precipitation steps as employed in previous work,[2] provided in excellent yield four fractions of linearly structured, soluble **3**. These, as before, were designated in decreasing order of molecular mass as fractions I, II, III, and IV, respectively. It is seen that the polymerization efficiency in terms of C–C bond formation, as reflected in the fraction yield and $\bar{M}_n$ data given in the table, exceeds that of previous experiments including even the most recent results[2] based on the organocuprate/iodide coupling mechanism, which has in many a case proved its superiority over noncopper-assisted nucleophilic aromatic substitution.[13] No significant changes in yield and $\bar{M}_n$ resulted from either doubling or halving the combined molar reactant concentration, or from doubling the total stirring period, nor were any such changes noticed when the experiment was initiated with equimolar amounts of **1** and **2** and a 15 mol % excess of **1** added at a later stage (footnote *e*, Table I). When, however, the initial **1**–**2** molar ratio was increased substantially beyond a value of 1.1, there resulted an expected proportionate decrease in the overall degree of polymerization in spite of increased temperatures in later stages; on the other hand, the products were devoid of iodo end groups without requiring a reductive treatment. Experiment 2 exemplifies this case.

With the molar reactant ratio maintained at about 1.1, yet the low-temperature stirring period omitted and the ultimate temperature raised to ~70 °C (experiment 3), the yield increased further by some 5% relative to experiment 1, and a corresponding increase in $\bar{M}_n$, notably conspicuous in fraction I, was observed, rendering this experiment the most successful one with respect to the overall degree of polymerization attained. A run conducted under similar conditions, yet with benzene added as a cosolvent in an attempt to enhance polymer solubility, gave distinctly lower yields, presumably owing to reduced solvent polarity (experiment 4). This effect manifested itself even more dramatically in a run performed in benzene alone (footnote *j*, Table I).

The poly(ferrocenylenes) of experiments 1–4, although possessing the elemental composition and spectroscopic characteristics required for **3**, differed from the products of the preceding investigations[2,5] in external appearance, being distinctly darker colored, and in purity, being contaminated by minute quantities of the chelating agent as manifested in small (0.2–0.5%) nitrogen contents. In addition, perhaps as a consequence of this contamination,

Table I
Poly(1,1′-ferrocenylenes) from 1,1′Dilithioferrocene-Bis(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) and 1,1′-Diiodoferrocene

	reactants, mmol[a]		molar ratio		reaction time, h;	coupling products 3[d]		
expt	1	2	1-2	solvent[b] (mL)	temp,[c] °C	fraction	yield, %	$\overline{M}_n$
1	15.3 (0.085)	14.4 (0.080)	1.06[e]	DBE (180)[f]	1, −20; 4, 25; 16, 40	I	9.8	3800
						II	14.2	1700
						III[g]	9.2	738, 922
						IV	48.1	500
						total	81.3	
2	16.3 (0.116)	8.7 (0.062)	1.87	DBE (140)[f]	8, −8; 12, 25; 16, 65; 6, 80	I	6.8	3300
						II	6.2	1400
						III	19.7	
						IV	46.3	450
						total	79.0	
3	14.8 (0.037)	13.7 (0.034)[h]	1.08	DBE (400)[i]	2, 25; 19, 72	I	6.9	6200
						II	8.3	1550
						III	15.6	738, 922, 1106
						IV	55.4	600
						total	86.2	
4	14.0 (0.088)	13.7 (0.086)	1.02	DBE (80)[j] BZ (80)[i]	4, 25; 17, 80	I	8.0	4500
						II	5.8	1700
						III	4.8	738, 922
						IV	47.1	500
						total	65.7	
5	14.3 (0.286)	13.7 (0.274)	1.04	THF (25) DME (25)[k]	2, 0; 20, 25	I	14.4	3800
						II	26.8	1650
						III	29.2	738, 922
						IV	16.0	550
						total	86.4	
6[p]	16.9 (0.313)	13.7 (0.254)	1.23	THF (27) DME (27)[m]	2, 0; 20, 25	I	11.9	4800
						II	21.7	1150
						III	36.7	738, 922, 1106
						IV	18.3	550
						total	88.6	
7[q]	15.8 (0.439)	13.7 (0.381)	1.15	THF (36)[n]	2, 0; 19, 25[o]	I	14.7	3500
						II	18.1	1500
						III	35.1	738, 922, 1106
						IV	21.2	500
						total	90.1	

[a] Quantities of reactants **1**, **2**, and MCl_2 (M = Cu in experiment 6, Pd in experiment 7) given in mmol (in parentheses, concentrations in mol L^{-1}; based on combined solvent volume in experiments 4-6). Reactant **1** prepared throughout from 20 mmol of ferrocene and isolated in the solid state; listed amounts taken as being equal to molar quantities of ferrocene reacted (see text). [b] DBE = di-*n*-butyl ether; BZ = benzene; THF = tetrahydrofuran; DME = 1,2-dimethoxyethane; in parentheses, volume in mL. [c] Temperatures ±3 °C. [d] Yields based on amount of **2** given in third column; in addition, 5–8% (1–4%) ferrocene recovered in experiments 1–4 (experiments 5–7) from crude products by sublimation. $\overline{M}_n$ of fractions I, II, and IV determined by vapor pressure osmometry, rounded off to nearest 50; of poorly soluble fractions III by mass spectrometry (molecular ion peaks of principal components only). Anal. found for fraction I (II, III, IV), experiment 6: 65.51 (64.94, 65.10, 64.99); H, 4.69 (4.89, 4.92, 5.07); Fe (ash), 29.83 (30.03, 30.26, 29.79). Anal. Calcd for $(C_{10}H_8Fe)_n$: C, 65.27; H, 4.38; Fe, 30.35. For $H(C_{10}H_8Fe)_3H$(554.09): C, 65.03; H, 4.73; Fe, 30.24. [e] Similar results in experiment conducted as before except that the initial **1–2** molar ratio was 1.0, and an additional 15 mol % was added as DBE slurry at 0 °C after the completed 40 °C stirring period. [f] Solid **1** suspended in one-half of the DBE volume listed, and the mixture was cooled to −10 °C; the solution of **2** in the remaining one-half volume of DBE was added at this temperature; stirring continued as indicated in the subsequent column. Treatment with VITRIDE reducing agent omitted in experiment 2. [g] Fraction III containing traces (0–0.2%) of [0.0]ferrocenophane. [h] Similar results with all molar concentrations doubled. [i] Solid 1 suspended at 25 °C in 300 mL of DBE in experiment 3 (80 mL of DBE in experiment 4); the solution of **2** in the remaining 100 mL of DBE in experiment 3 (80 mL of BZ in experiment 4) was added at this temperature; stirring continued as indicated. [j] Total yield reduced to 55%, with corresponding reduction of $\overline{M}_n$, if DBE was replaced by a double volume of BZ. Found: N, 0.56. [k] Solid **1** suspended at 0 °C in 25 mL of THF and a solution of **2** in 25 mL of DME was added at this temperature; stirring was continued as indicated. [l] Almost identical results with a fivefold quantity of $CuCl_2$ added; molar ratio **1/2** ≃ 1.1. [m] Solid **1** suspended at 0 °C in 27 mL of THF; $CuCl_2$ was added over a 5-min period at this temperature; the mixture was stirred for 2 h at 25 °C; a solution of **2** in 27 mL of DME was added at this temperature; stirring continued as indicated. [n] Solid **1** suspended at 0 °C in 30 mL of THF; **2** was added at this temperature, dissolved in 6 mL of THF containing $PdCl_2$ (previously boiled for 10 min to aid dissolution of Pd salt; some $PdCl_2$ remaining undissolved at this stage); stirring continued as indicated. [o] Same results with the stirring period at 25 °C reduced to 14 h. [p] Additional reactant:[a] MCl_2, 0.169 (3.13×10^{-3})[l]. [q] Additional reactant:[a] MCl_2, 0.022 (6.1×10^{-4}).

they displayed an unusual aging behavior, turning partially insoluble in the common aromatic and halocarbon solvents after several months of storage under ambient conditions.

In an effort to accelerate the nucleophilic attack step relative to competing side reactions, additional experiments were performed in a variety of more strongly coordinating media. While combinations of DBE with pyridine, hexamethylphosphoramide, and similarly basic solvents failed to give satisfactory results, appreciable improvements were realized with a number of glycol ethers. 1,2-Dimethoxyethane (DME) offered itself as a particularly suitable solvent because of its conveniently low boiling point (83–84

°C). In order to enhance the polymer-solubilizing capacity of the medium (higher molecular mass **3** fails to be dissolved in glymes), it proved advantageous to add tetrahydrofuran (THF), although in that case the reaction temperatures were not allowed to exceed 25 °C, thereby minimizing cleavage of the sensitive cyclic ether component.[14] A representative experiment using DME/THF solvent is listed in Table I as experiment 5. It is seen that excellent fraction yields were paired in this experiment with an overall degree of polymerization almost as high as in the preceding runs. (Subfractionation of fraction I by reprecipitation in such a manner as to produce a precipitate about equal in quantity to that of fraction I, experiment 4, gave material possessing $\bar{M}_n$ 5900.) Furthermore, the various product fractions of this and similarly conducted experiments, bright yellow-tan or light orange-brown in color and exclusively of linear structure,[15] were free from inclusions of chelating agent, and no aging effects with concomitant loss of solubility were noticed over an observation period of 6 months. A preliminary magetic investigation showed the polymeric fractions as isolated to be diamagnetic or, most likely owing to trace contents of ferricenium units, faintly paramagnetic. In contrast, polymer fractions stemming from experiments 1–4 or from the earlier copper-assisted reactions[2,5] possessed distinctly stronger paramagnetism, and those derived from cobalt-assisted condensations[16] gave susceptibilities more positive by several orders of magnitude. The polycondensation products of experiment 5 thus represent poly(ferrocenylenes) of distinctly higher magnetic purity than shown by those of the preceding experiments. A systematic investigation of the magnetic behavior of **3** as a function of temperature and molecular mass, of paramount importance in electrophysical characterization work, is in progress and will be dealt with in a future publication.[17]

Several experiments were performed under similar conditions as in experiment 5 except with catalytic quantities of copper(II) chloride added at the initial stage. The organocuprate R_3CuLi_2 (and possibly "higher order" cuprates of the type $R_nCuLi_{(n-1)}$, $n > 3$),[18] formed from RLi and Cu^+ ion (the latter arising by reduction of Cu^{2+} through the action of RLi[5]) and steadily regenerated (eq 3a, $n \geq 3$) as long as an excess of organolithium species is

$$R_{(n-1)}CuLi_{(n-2)} + RLi \rightleftharpoons R_nCuLi_{(n-1)} \qquad (3a)$$

present, should act here as the highly reactive[18] nucleophile in the propagation process (equation 3b; R = $^1/_2$(ferrocenylene); $n > 2$) in lieu of the simple organolithium reactant of eq 2. The polycondensations performed under

$$R_nCuLi_{(n-1)} + RI \rightarrow RR + R_{(n-1)}CuLi_{(n-2)} + LiI \qquad (3b)$$

such conditions and exemplified by experiment 6 indeed proceeded smoothly, giving product fractions of the same high purity and in similarly high yields as attained in experiment 5. However, as can be seen from the $\bar{M}_n$ values listed, there was no substantial further increase in the overall degree of polymerization. Similar results were obtained in a run (experiment 7) catalyzed by metallic palladium (generated from palladium(II) chloride through the action of RLi), the catalytic efficaciousness of which in related organohalide/Grignard compound coupling reactions is on record.[19] The lack of further significant $\bar{M}_n$ increases in experiments 6 and 7 in comparison to experiment 5 suggests that the propagation reaction was not appreciably faster in the former two experiments than in experiment 5 relative to internal quenching as the major cause of annihilation of ferrocenylene anion sites. Assuming the anion addition to halide substrate to be the rate-determining step in the overall substitution process, we conclude that the nucleophilic attack of RLi is already accelerated so efficiently through the coordinative assistance of the chosen DME/THF solvent system that synthetic manipulations involving the intermediacy of organocopper or organopalladium species have no significant further bearing on the rate of nucleophilic attack, thus rendering more or less identical the overall degrees of polymerization attained in all three reaction types.

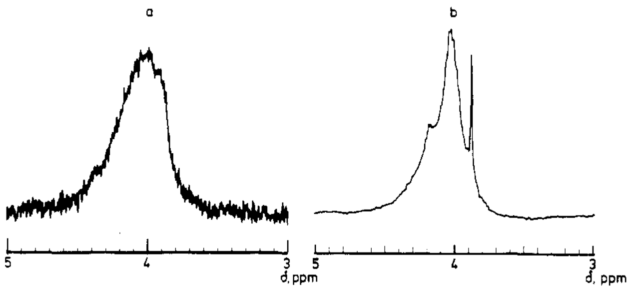


Figure 1. ^1H NMR spectra of **3** (ferrocene protons) in benzene-d_6 (100 MHz). Shifts, δ, in ppm downfield from Me_4Si: (a) fraction with $\bar{M}_n$ = 2800; (b) fraction with $\bar{M}_n$ = 950.

The poly(ferrocenylenes) synthesized in experiments 5–7 were investigated by ^1H NMR, IR, and electronic absorption spectroscopy. The ^1H NMR spectra (benzene-d_6, 100 MHz) of **3** in the higher molecular mass region ($\bar{M}_n$ > 2500) featured the same broad and monolithic resonance signals as in previous work,[2,5] extending from δ 3.8 to 4.4 ppm with a maximum near 4.05 (Figure 1a). At slightly lower degrees of polymerization the signals developed shoulders near 4.2 and 3.9 ppm. As the degree of polymerization (and thus the number of possible conformers) decreased further ($\bar{M}_n$ < 2000), the signals showed increasing resolution, with one or more sharp singlets due to protons of the terminal unsubstituted rings emerging in growing intensities from the 3.9-ppm shoulder (Figure 1b). The peak heights of these singlets tended to be lower than observed with corresponding fractions of previous syntheses,[2,5] which would seem to suggest a slightly lower extent of heteroannularity in the earlier polymers. However, the substantial "background" resonance due to substituted rings in the 3.8–4.0-ppm region disallows a quantitative evaluation of singlet peak intensities for the purpose of assessing the relative contents of unsubstituted rings,[2] especially in view of the observation that these peak heights were to some extent sensitive to both temperature and solvent effects and, hence, appeared to depend at least in part on conformational changes in solution.

The IR spectra of **3** (Figure 2) were recorded in the region of 4000–300 cm^{-1} on KBr pellets. The scans of oligomeric material (fractions III and IV) essentially represented superpositions of the known spectra of oligomers (**3**, n = 2–6) reproduced in print by Watanabe et al.[20] Apart from somewhat reduced resolutions and minor intensity alterations, notably in the 1420–1350 and 1100–1000-cm^{-1} regions, the spectra of **3** in higher $\bar{M}_n$ ranges (fractions I and II) were practically coincident with those of the oligomeric material, which may be taken as a reflection of the lack of significant vibrational interaction between the rings in ferrocene[21] and resultant insensitivity of band positions to the degree of polymerization. As the vibrational spectra of oligomeric and polymeric **3**, although in part commented upon,[20,22] have never been treated before in detail, we present a summary of proposed assignments in Table II. Greatly facilitated by the availability of earlier vibrational analyses of certain ferrocene compounds bearing monosubstituted rings,[23] these assignments were made with the aid of the local-symmetry

Table II
Infrared Absorptions of the Poly(ferrocenylene)System[a]

freq obsd, cm^{-1}	intensity	symmetry class	approx description of mode	origin of mode in ferrocene
3080-3095^b	w	a$_1$ (2×)	CH stretching	ν_1, ν_{12}, ν_{17}, ν_{23}
		b$_1$ (2×)	CH stretching	
1538			solid-state band^c	
1410-1419^{b,d}	m	a$_1$	CC stretching	ν_{15}, ν_{20}
1385	w-m	a$_1$	CC stretching	ν_{26}^{e}
1363	w	b$_1$	CC stretching	ν_{15}, ν_{20}
1350	vw	b$_1$	CC stretching	ν_{26}^{e}
1183	vw	b$_1$	CH ∥ bending	ν_5, ν_7
1105-1114^f	s	a$_1$	CH ∥ bending	ν_{24}
		a$_1$	C-Fc stretching^g	$\nu_{23}(\nu_3, \nu_{10})$
1052^b	w-m	a$_2$	CH ⊥ bending	ν_{25}
1028-1032	ms-s	a$_1$	CH ∥ bending	ν_{13}, ν_{18}
		a$_1$	sym ring breathing^i	ν_3, ν_{10}
1001^h	s	b$_2$	CH ⊥ bending	ν_{25}
885	w	b$_1$	CH ∥ bending	ν_{13}, ν_{18}
855-860	m (sh)	b$_1$	ring distortion ∥	ν_{27}
840^j	m (sh)	a$_2$	CH ⊥ bending	ν_{14}, ν_{19}
830^j	s (sh)	a$_1$	ring distortion ∥	ν_{27}
815^{b,k}	vs	b$_2$	CH ⊥ bending	ν_2
680^l	w	b$_2$	ring deformation ⊥	ν_{28}
610-620^l	vw-w	a$_2$	ring deformation ⊥	ν_{28}
485^{b,m}	vs		asym ring-metal tilting	ν_{21}
			asym ring-metal stretching	ν_{11}
400	vw		sym ring-metal tilting	ν_{16}
310^n	s		sym ring-metal stretching	ν_4
o		b$_1$	C-Fc ∥ bending	ν_{24}
p		b$_2$	C-Fc ⊥ bending	ν_{14}, ν_{19}
p			ring-metal-ring bending	ν_{22}

[a] In the spectral region 4000-300 cm^{-1}, on KBr pellets. Frequencies given as averages (ranges, if variation, $> \pm 2$ cm^{-1}), observed on samples of 3, $n > 2$. Symmetry classification for approximated C_{2v} point group symmetry. Numbering of ferrocene modes per ref 21a. Last column lists active modes only. [b] Doublet or multiplet structure shown by oligomeric material. [c] Absent in solution spectra; generally absent in solid-state spectrum, but occasionally appearing upon reprecipitation. Raman band observed near 1540 cm^{-1}. [d] Contains contribution by ν_{20} of the unsubstituted terminal ring. [e] Ascribed to 1356-cm^{-1} ferrocene band following ref 21b but contrasting with ref 21a. [f] Doublet with maximum near 1113 cm^{-1}, includes contribution by ν_{10} of the unsubstitute terminal ring. [g] Plus admixed symmetric ring breathing; mode should be substituent sensitive. [h] Includes contribution by ν_{18} of the unsubstituted terminal ring. [i] Plus admixed C–Fc stretching; mode should be substituent sensitive. [j] Order of assignments for 840- and 830-cm^{-1} bands based on intensity considerations. [k] Includes contribution by ν_9 of the unsubstituted terminal ring, possibly represented by a shoulder near 805 cm^{-1}. [l] Assignments based on intensity considerations; ν_{28} assumed $\gg 500$ cm^{-1} (see ref 21a); Raman band appearing at 680 cm^{-1}. [m] Includes contribution by ν_{11} and ν_{21} of the unsubstituted terminal ring. [n] Raman band. [o] Not observed. [p] Outside of the frequency region investigated; bands expected at 170-200 cm^{-1}.

concept, the use of which in the ferrocene case appears justified on the basis of the essentially independent vibrational behavior of the two rings in the complex.[21] The concept, applied with considerable success in the earlier analyses,[23] treats the spectrum of a metallocene complex as a superposition of the partial spectrum of the ring ligands on that of a pseudo-three-mass model representing the ring–metal–ring system. To the monosubstituted rings (we neglect the spectral features of the two unsubstituted end group rings largely or completely hidden in the spectrum of the backbone constituents), C_{2v} point group symmetry can be ascribed in an approximation which ignores the substituent group's orientation.[23a] One should thus, in addition to the five skeletal modes involving ring–metal vibrations, find 21 IR and/or Raman active modes due to cyclopentadienyl ring vibrations, viz., 8 × a$_1$, 7 × b$_1$, 3 × a$_2$, and 3 × b$_2$, as well as three modes (a$_1$, b$_1$, b$_2$) associated with the C–Fc bond (Fc = ferrocenyl or ferrocenylene). Classes a$_1$ and b$_1$ in this scheme represent in-plane vibrations, whereas a$_2$ and b$_2$ describe out-of-plane modes. The tabulation includes the 29 ring, C–Fc, and skeletal modes expected. It was not possible to utilize Raman spectroscopy for corroboration of the assignments made, as no fundamentals other than the totally symmetric ring-metal-ring stretching band near 310 cm^{-1} and the (unexpectedly intense) out-of-plane b$_2$ ring deformation band at 680 cm^{-1} could be distinguished from the spectral background, even upon signal averaging (20 scans), in the (Kr$^+$ excited) laser-Raman spectra of polymeric **3**.

The absorption range from 1000 to 1120 cm^{-1} deserves special comment. The spectra of all fractions of **3**, just as previously observed for oligo- and polymeric samples,[5,20,22] showed strong absorption at the positions near 1110 and 1001 cm^{-1}. This is unusual, as the appearance of peaks at the two frequencies generally is indicative of the presence of an unsubstituted ferrocene ring ('9,10-μm rule).[24] Since the concentration of unsubstituted rings is too small in the present cases to account for the strength of the two bands observed, especially so in higher molecular samples, the peaks clearly derive intensity only to a very minor extent from the respective modes of unsubstituted ferrocene. By comparison with 1,1′-dihaloferrocenes and 1,1′-dimethylferrocene,[23] and using the Steele–Whiffen inequality rule,[25] we have assigned the 1110-cm^{-1} absorption to an a$_1$ C–Fc stretching mode, most likely mixed with the a$_1$ symmetric ring-breathing vibration derived from the ν_3 or ν_{10} ferrocene bands. The a$_1$ in-plane bending mode arising from ν_{24} in ferrocene is expected to contribute to this multiplet absorption, as is the ν_{10} end-group vibration. The C–Fc stretching peak should be mass sensitive, and the rather invariant position of the band group in both low- and high molecular mass compounds then suggests the ferrocenyl and polyferrocenylene moieties attached to a particular unit to behave like a rigid substituent of constant point mass. The band near 1050 cm^{-1}, very weak (and sometimes split into a multiplet) in oligomeric, but

Table III
Selected Subfractions of 3

fraction[a]	$\overline{M}_n$[b]	melting behavior,[c] °C	λ_{max} (ϵ)[d]			
1	9900	infusible < 350	228 (17800)	269 (6600)	308 (5300)	461 (650)
2	7200	infusible < 350				
3	5800	infusible < 350	228 (18200)	270 (7600)	309 (5900)	460 (630)
4	4700	infusible < 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)	460 (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)
11	738-922	195-210	228 (18400)	269 (8000)	310 (6200)	461 (600)

[a] Obtained by fractionating precipitation of fractions I and II, experiment 6 (fraction 11, by hot toluene extraction of residue A; see Experimental Section). [b] By vapor pressure osmometry on benzene solutions; 37 °C (for fraction 11 by mass spectrometry). [c] Determined in sealed capillaries. [d] In nm (L mol^{-1} cm^{-1}); see ref 5 for details and discussion.

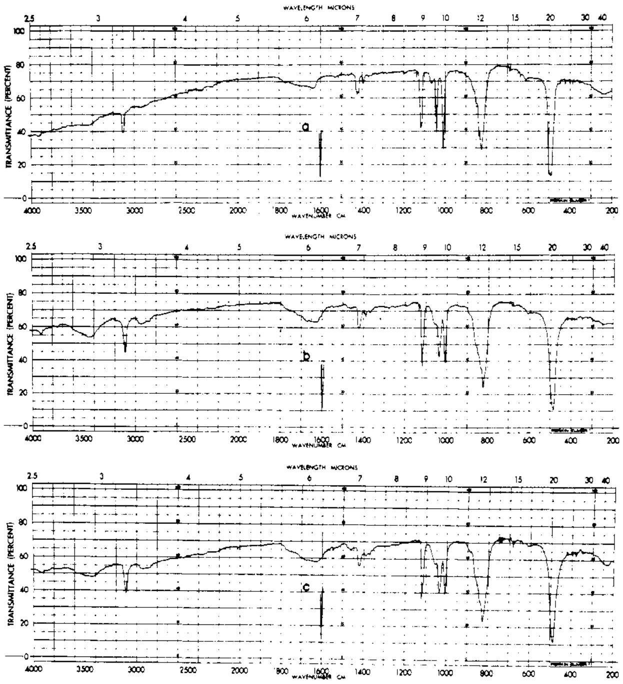


Figure 2. IR spectra of 3 (KBr pellets), calibrated with the polystyrene spectrum (spike at 1601 cm^{-1}): (a) fraction with $\overline{M}_n$ = 550; (b) fraction with $\overline{M}_n$ = 1600; (c) fraction with $\overline{M}_n$ = 4100.

somewhat stronger in polymeric **3**, can be ascribed to an IR-forbidden a_2 CH out-of-plane bending mode on account of its generally low intensity. Derived from ν_{25} in ferrocene, it finds its allowed b_2 counterpart in the band of high intensity appearing at 1001 cm^{-1}. The strong absorption in the range 1028–1033 cm^{-1}, typical of the substituted ferrocene ring (a feature near 1025 cm^{-1} has been observed by us in the spectra of each one of a large number of mono- and polysubstituted ferrocenes investigated over many years), can be assigned to the a_1 symmetric ring-breathing mode derived from ν_3 and ν_{10} in ferrocene and mixed with the C–Fc stretching vibration. The analogous mode in 1,1′-dimethylferrocene was assigned[23a] to a band in this vicinity. The band's broadness and strength variability suggests an additional contribution, most probably by the a_1 component of the in-plane CH bending mode derived from the 1000-cm^{-1} band (ν_{13}, ν_{18}) in ferrocene. The corresponding b_1 band is found at 885 cm^{-1}.

A further comment concerns the absorption region in the vicinity of 800 cm^{-1}. This constitutes a multiplet of considerable width, and while a maximum emerges consistently near 815 cm^{-1}, the majority of contributing bands appear merely as a series of narrowly spaced shoulders. Combined with the obvious uncertainties in the previous spectral interpretations of the dihaloferrocenes and the dimethyl compound,[23] this renders impracticable the use of the inequality rule. Therefore, excepting the very strong maximum at 815 cm^{-1} whose interpretation as a b_2 deformation band appears safe on the basis of its strength, the suggested assignments in this region remain somewhat speculative.

In addition to the ferrocenylene absorption pattern discussed in the foregoing, the spectra of higher molecular mass **3** contained very weak to weak absorption in the aliphatic CH stretching region of 2870–2950 cm^{-1}. As in previous work,[5,16] we were unable to relate the bands to any particular synthetic (and resulting structural) features. The absence of ^{1}H NMR signals at 2.2–3.4 ppm rules out the involvement of TMEDA (preceded by lithium–hydrogen interchange at one of the methyl groups[6b]) or cyclopentadienyl end groups (resulting from iron–ring bond cleavage), both of which should give methylene resonances in this region. The olefinic protons of the cyclopentadienyl or resultant Diels–Alder adduct structures comprising cyclopentenyl segments should additionally resonate in the vicinity of 6 ppm,[26] where in fact no peaks were ever noticed. The same arguments hold for alkylation or alkoxylation following ether solvent cleavage,[14] which should give rise to resonances at positions in the aforementioned range extending to the low-field side of about 2.2 ppm.[27] The weak signals generally exhibited at 0.9–1.5 ppm suggest hydrocarbon solvent residues physically adsorbed and tenaciously retained by the polymers to be the main cause of the aliphatic CH stretching IR absorption observed.

The electronic absorption spectra of **3**, recorded as before[5] on 1,2-dichloroethane solutions over the 200–500-nm region, proved essentially identical with those of corresponding fractions obtained by other synthetic methods. Some representative spectral data, obtained on subfractionated material in the $\overline{M}_n$ range 1100–10000, can be found in Table III. The λ_{max} and ϵ values, coinciding with the respective maxima of pure heteroannular tetramer (**3**, n = 4), are in accord with an exclusively heteroannular substitution pattern in the poly(ferrocenylene) chain as implied in the structure written (eq 2). Furthermore, they confirm the previous observation[5,22a] that there is no increased conjugation in homologues of **3** as n exceeds the value of 4, supporting the earlier contention[17a] that only a very minor extent of electronic charge is delocalized across the iron center in the ferrocene system.

The heterannular substituent disposition manifested in the electronic absorption data would seem to rule out the operation of an elimination–addition (ferrocyne) mechanism, as this should lead to the incorporation into the chain of 1,2-disubstituted units generated from intermediary di- and poly(ferrocenyl) anions in which the anionic site is located at a carbon atom in position α to the bond connecting the ring to the penultimate recurring unit. Such 1,2-ferrocenylene groups should possess a less coplanar alignment of adjacent cyclopentadienyl rings than is accomplished in the 1,1′-isomer structure and so should cause minor but distinct high-frequency shifts of the electronic absorption maxima.[28] In an effort to demonstrate more directly the lack of involvement of ferrocyne intermediates, we examined the NMR spectra of typical oligomer fractions of predominant trimer composition, e.g., fractions IV, experiments 5 and 6, for the appearance of signals, if any, in the region downfield from about 4.3 ppm. The 1,2-isomer, 1,2-diferrocenylferrocene,[22b,29] gives a strong resonance near 4.4 ppm; its formation (from a ferrocyne precursor) and presence in the fraction should thus be manifested by signals at the given position, as the heteroannular trimer (**3**, n = 3) shows no significant features to the low-field side of its strong 4.25-ppm resonance. The examination revealed significant resonances only to the high-field side of 4.3 ppm, demonstrating that the 1,2-trimer was not admixed to a clearly detectable extent.[30] The presence of very small percentages of this trimer still may not be ruled out, as a weak NMR signal at 4.4 ppm might well go undetected in the broadened base of the main resonance multiplet. Therefore, in a separate series of experiments, we reinvestigated the lithioferrocene/iodoferrocene coupling reaction of eq 1 in DBE medium, quenching portions of the reaction mixture at various times either with dimethyl sulfate or with deuterium oxide. Further treatment of the quenched samples by chromatography and mass spectrometry failed to reveal the presence of methylated or monodeuterated biferrocenyl species. Furthermore, no 1,2-terferrocenyl, expected to result from attacks by biferrocenyl α-anion intermediate on iodoferrocene, was isolated. Although these negative findings do not per se represent proof of the absence of ferrocyne intermediacy, since detection of the α-anionic site could fail if internal quenching proceeds at appreciably higher rate than further attack of the anion on haloferrocene, we do not, judging from the high ratios of $C_{10}H_9DFe$–$C_{10}H_{10}Fe$ in the recovered ferrocene portion, consider internal quenching an important competing process. Intermediate ferrocyne formation may thus, in accord with earlier arguments (cf. introduction), be neglected as a mechanistic feature in the lithioferrocene/iodoferrocene coupling reaction of eq 1 and, by inference, in the polycoupling sequence of eq 2. Accordingly, one may assume that both the dimer-forming reaction and the polymer-producing sequence proceed predominantly if not exclusively by direct nucleophilic substitution.

Experimental Section

Melting points, uncorrected, were determined in evacuated and sealed capillaries. IR spectra (on KBr pellets) were recorded with a Perkin-Elmer 521 spectrophotometer. A Varian HA-100 spectrometer was used for scanning the ^{1}H NMR spectra (on benzene-d_6 solutions; shifts, δ, in ppm downfield from Me_4Si); spectra of difficultly soluble samples were taken at 65–70 °C. Electronic absorption spectra were obtained on 1,2-dichloroethane solutions (N_2 saturated) with a Pye Unicam SP1800 spectrophotometer; cells with 1-cm path length were used for quantitative work (1-mm cells for improved positional determination of the 225-nm band partially hidden in the solvent cut-off peak). Mass spectra were obtained with the aid of a Varian-Mat CH5 mass spectrometer at 70 eV ionizing voltage and 200–270 °C inlet temperature. Raman spectra (on solid samples) were recorded with a Coderg T800 spectrometer (triple monochromator, 800-mm focal length) containing a Datarama on-line computer system and fitted with an RCA 31034 A-04 gallium arsenide photomultiplier tube, a A5C1 photon counter, and a 300-S prism premonochromator. A Spectra-Physics Model 165 Krypton ion laser (647 nm) served as the excitation source (output power at the sample 40 mW; no fluorescence or sample degradation observed). A Knauer vapor-pressure osmometer was used to determine the relative molecular masses (number average, $\bar{M}_n$) on benzene solutions at 37 °C. Elemental analyses were performed by the Microanalytical Division, National Chemical Research Laboratory, Pretoria.

Solvents, Reagents. 1,2-Dichloroethane, Analytic Grade, was purified for spectroscopic use by refluxing it over calcium hydride for 12 h, followed by distillation from this hydride under nitrogen prior to use. Hydrocarbon and ether solvents, TMEDA (*N,N,N′,N′*-tetramethylethylenediamine), and ferrocene, as well as the argon gas used for preparatory work, were purified as in earlier work.[5] The commercially available chlorides, $CuCl_2$ and $PdCl_2$, were dried over P_2O_5 for 24 h at 120 °C (0.05 torr) prior to use. All solid reagents were additionally dried and deoxygenated in the reaction vessel or addition tube by a threefold flaming/Ar purging/evacuation cycle. 1,1′-Diiodoferrocene was prepared and purified as described.[2] VITRIDE T Reducing agent (sodium bis(2-methoxyethoxy)aluminum hydride, Eastman; 70% in toluene) and *n*-butyllithium (Merck, 1.5 M in hexane) were used as received.

Lithiation of Ferrocene. All operations were performed under an Ar blanket in the absence of moisture and oxygen. Glassware and transfer equipment in lithiation work and subsequent polymerization experiments were flamed and Ar purged. In a 500-mL, four-neck, round-bottom flask equipped with suitable gas in- and outlet tubes and fritted glass filtering adaptor, 3.72 g (20 mmol) of ferrocene was lithiated in hexane with *n*-butyllithium (40 mmol) in the presence of TMEDA (40 mmol) as described in detail elsewhere.[5,6] The 1,1′-dilithioferrocene–$(TMEDA)_2$ chelate **1**, separated from the supernatant hexane phase by removing the latter through the filtering adaptor under slight Ar pressure for collection in a preevacuated receiver flask, was washed with hexane in the reaction vessel as before.[5] The amount of **1** actually present in the vessel after washing, as entered in the second column of Table I for the individual polymerization experiments, was determined indirectly by calculation, subtracting from the starting amount of ferrocene (20 mmol) the molar amount of ferrocene recovered from the combined hexane phase and hexane washings after hydrolysis.

Polycondensation Reactions. Table I summarizes the experimental variables for selected uncatalyzed (experiments 1–5) and catalyzed (experiments 6 and 7) polymerizations. The experiments were carried out in the reaction vessel used for ferrocene lithiation, and the quantity of ferrocene used to prepare the starting chelate **1** was the same (20 mmol) in all runs.

Uncatalyzed. Following the addition of the specified type and volume of solvent to the solid **1** contained in the reaction flask, a cooling bath was applied (not required in experiments 3 and 4), and the suspension was magnetically stirred for a short period to achieve thermal equilibrium at the specified temperature. A solution of **2** in the specified type and volume of solvent was added within 1–2 min to the stirred mixture at that temperature. For convenience and in order to avoid delays in the further performance of the experiments (hydrolysis of the hexane mother liquor and washings after lithiation, as well as collecting and drying of recovered ferrocene, requires more than 1 h), a fixed molar quantity (13.7 mmol) of **2** was used beginning with experiment 3. Stirring was continued under a steady stream of Ar in the dark under the conditions tabulated. The product was worked up by adding, at 0 °C, 20 mL of thoroughly Ar-flushed 1-M aqueous hydrochloric acid containing 4 g of $SnCl_2$ (to preclude oxidation to ferricenium cation) and shaking the mixture intermittently over a 15-min period. Some Insoluble polymeric material was filtered off. The organic phase of the filtrate was thoroughly washed with deoxygenated water and combined with the similarly washed polymeric residue. Solvent removal by rotatory evaporation at 40 °C (0.1 torr) left a semisolid residue, which was dehydrated by the addition of 100 mL of toluene and subsequent removal of 25–30 mL of liquid through azeotropic distillation. Following the addition of 25 mL of VITRIDE T, the mixture, blanketed with argon, was heated under reflux for 4–6 h and, after cooling to 0 °C, was poured with stirring into 200 mL of ice-cold, deoxygenated 1-M aqueous HCl containing 3 g of $SnCl_2$. After removal of the aqueous phase, the toluene layer (including some precipitated solid material) was thoroughly washed with water, and the solvent was removed as before by rotatory evaporation. The residue was extracted exhaustively with boiling hexane (extract A), followed by brief (3–5 min) extraction with a 100-mL portion of boiling toluene, leaving behind some undissolved product (residue A). The toluene extract was filtered while hot through hardened filter paper to remove traces of finely suspended matter; it was then concentrated under reduced pressure to 35 mL and allowed to stand overnight under N_2 at 0 °C, whereupon a portion of light orange-brown, oligomeric homologues of **3** crystallized. The separated material was briefly washed with hot hexane and set aside as part of fraction III. The mother liquor was stirred with 10–20 mL of hexane, allowing a few milligrams of dark, impure polymeric material to precipitate, which was discarded. (This operation was not required in experiment 5.) Further addition of hexane (35 mL) furnished a dark brown (yellow-tan in experiment 5) precipitate of higher molecular mass **3**; filtered off and washed with hot hexane, it was designated as fraction I. Evaporation of the filtrate to dryness under reduced pressure and hexane washing as before left a light orange-brown solid, labeled fraction II. Solvent removal from the combined initial hexane extract (extract A) and all hexane washings gave a light orange, crystalline residue, which, after separation of admixed ferrocene by sublimation (24 h at 65 °C (0.5 torr)) and brief washing with pentane, was designated as fraction IV. Finally, residue A was successively extracted with several 30-mL portions of toluene and chlorobenzene at the boiling temperatures, and the combined extracts were concentrated to a few milliliters, giving another portion of poorly soluble, oligomeric **3**; this was combined with the oligomer material that had crystallized from the first toluene extract and was labeled fraction III. All product fractions were dried for 3 days at 70 °C (0.05 torr). The highest and lowest molecular fractions (fractions I, II, and IV) possessed excellent solubility in halocarbons and aromatic hydrocarbons as well as in tetrahydrofuran and such dipolar aprotic solvents as hexamethylphosphoramide and tetramethylurea. Fractions III, composed predominantly of the tetra-, penta-, and hexanuclear homologues known to possess low solubility,[20] required large volumes of arenes or haloarenes at the boiling temperatures for satisfactory dissolution.

Catalyzed. In the copper-catalyzed polymerization run (experiment 6), 27 mL of THF was added under Ar to the solid chelate **1** contained in the reaction flask as in the preceding experiments. To the stirred suspension, cooled to 0 °C, the finely powdered copper(II) chloride was added from an angular side tube preattached to the flask, the stirred mixture was allowed to warm up to 25 °C, and stirring was continued at this temperature for 2 h so as to ensure complete reduction to Cu^+ salt and organocuprate formation. Precooling of the mixture to 0 °C was followed by the addition of **2** dissolved in 27 mL of DME, and stirring was continued in the dark as stated in the table.

The palladium-catalyzed reaction (experiment 7) was conducted by dissolving the finely powdered palladium(II) chloride in 6 mL of boiling THF under Ar (traces left undissolved), dissolving **2** after cooling to 25 °C, and adding this solution rapidly to the stirred suspension of **1** in 30 mL of THF at 0 °C in the reaction flask. Further stirring proceeded in the dark as tabulated.

The workup procedures used in both experiments, resulting in the separation of fractions I–IV listed, were the same as employed in experiment 5, except that in the copper-catalyzed run (experiment 6) a washing operation with aqueous ammonia was interposed as described elsewhere[5] in detail.

Subfractionation. A 1.5-g batch of fraction I of a scaled-up preparative run conducted under the conditions of experiment 6 was subfractionated under Ar by conventional fractionating precipitation from 1.5% benzene solution with hexane as the nonsolvent (both media Ar purged and saturated with ascorbic acid to prevent oxidation). After collection of the first five subfractions (each weighing 50–150 mg), the remaining solution, concentrated to 100 mL, was combined with the benzene solution (5%) of 1.5 g of fraction II of the same preparative run. Subfractionation was continued (fraction weights 250–300 mg), until a total of 10 subfractions were collected. The material remaining in the final mother liquor was not considered for the present purpose. All subfractions were washed successively with hexane and pentane and were dried for a minimum of 45 h at 75 °C (0.05 torr). In addition, samples were post dried for 1.5 h at 250 °C (0.05 torr) ($\bar{M}_n > 2500$) and 150 °C (0.05 torr) ($\bar{M}_n < 2500$). No differences in solubility behavior relative to unsubfractionated material were noticed; the two highest molecular fractions were of a dark brown color, however, and even the subsequent two fractions were darker than the parent batch.

The number-average molecular masses and melting-range data for ten representative subfractions, as well as for a fraction predominantly composed of tetra- and pentameric **3** (isolated from the hot toluene extracts of residue A[31]), are listed in Table III, which also contains the maxima and extinction coefficients taken from the electronic absorption spectra.

Acknowledgment. This investigation was generously supported by the South African Atomic Energy Board. It is a privilege to acknowledge the kind assistance by Dr. G. J. van Schalkwyk in providing the laser-Raman spectra, and by Drs. K. G. R. Pachler and P. L. Wessels, CSIR, in recording the NMR spectra. The authors also thank Miss Theresa N. Mzimela for her cooperation in the remaining spectroscopic and analytical work, and Mr. M. Buker for assisting this and previous experimental efforts with his most proficient glass-blowing skills.

References and Notes

(1) Part 37 in the series *Metallocene Polymers*. For Part 36, see ref 2.

(2) E. W. Neuse and L. Bednarik, *Transition Met. Chem.*, in press.

(3) (a) H. Gilman and R. V. Young, *J. Am. Chem. Soc.*, **56**, 1415 (1934); **57**, 1121 (1935); (b) H. Gilman and J. W. Morton, *Org. React.*, 8, 258 (1954), and leading references therein; (c) G. Wittig, U. Pockels, and H. Dröge, *Ber.*, **71**, 1903 (1938); (d) G. Wittig, *Acc. Chem. Res.*, **7**, 6 (1974), and references cited therein.

(4) Early references are given,[4a–c] and excellent reviews covering subsequent work are available.[4d,e] (a) G. Wittig, *Naturwissenschaften*, **30**, 696 (1942); *Angew. Chem.*, **66**, 10 (1954); (b) J. D. Roberts, H. E. Simmons, Jr., L. A. Carlsmith, and C. W. Vaughan, *J. Am. Chem. Soc.*, **75**, 3290 (1953); (c) R. Huisgen and H. Rist, *Naturwissenschaften*, **41**, 358 (1954); (d) R. Huisgen in "Organometallic Chemistry", H. Zeiss, Ed., Reinhold, New York, 1960, Chapter 2; (e) R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes", Academic Press, New York, 1967.

(5) E. W. Neuse and L. Bednarik, *Transition Met. Chem.*, in the press.

(6) (a) M. D. Rausch, G. A. Moser, and C. F. Meade, *J. Organomet. Chem.*, **51**, 1 (1973); (b) M. D. Rausch and D. J. Chiappenelli, *ibid.*, **10**, 127 (1967).

(7) (a) L. Friedman and J. F. Chlebowski, *J. Am. Chem. Soc.*, **91**, 4864 (1969). In addition, these workers observed extensive metal–halogen exchange in reactions involving the bromo- and iodotoluenes. Halogen–lithium interconversions of this kind, some of appreciable synthetic usefulness,[7b] are equilibrium processes, in which the more electronegative (acidic) carbanion is favored,[7c] and probably involve multicenter transition states.[3d] (b) R. Jones and H. Gilman, *Org. React.*, **6**, 339 (1951). (c) H. J. S. Winkler and H. Winkler, *J. Am. Chem. Soc.*, **88**, 964, 969 (1966).

(8) (a) F. L. Hedberg and H. Rosenberg, *Tetrahedron Lett.*, 4011 (1969); *J. Am. Chem. Soc.*, **95**, 870 (1973); (b) D. W. Slocum, R. L. Marchal, and W. E. Jones, *Chem. Commun.*, 967 (1974).

(9) (a) J. W. Huffman, L. H. Keith, and R. L. Asbury, *J. Org. Chem.*, **30**, 1600 (1965); (b) J. W. Huffman and J. F. Cope, *ibid.*, **36**, 4068 (1971).

(10) A lessened propensity of the cyclopentadienyl ring toward ferrocyne formation, relative to a benzenoid system, was predicted by Huffman et al.[9a] on the basis of its electron-rich nature and the difficulty of constructing a formal triple bond in a five-membered ring system. This is indeed consistent with the behavior of analogous five-membered heteroaromatics, which, because of increased ring strain, show appreciable resistance to hetaryne formation.[10a,b] (a) T. Kauffmann, *Angew. Chem.*, **83**, 21 (1971); (b) M. G. Reinecke and H. W. Adickes, *J. Am. Chem. Soc.*, **90**, 511 (1968).

(11) H. Shechter and J. F. Helling, *J. Org. Chem.*, **26**, 1034 (1961).

(12) Carried out in collaboration with R. O. Gohdes of this laboratory.

(13) See, for example, H. O. House, Proceeding of the R. A. Welch Foundation Conference on Chemical Research, XVII, 1974, Chapter 4; G. H. Posner, *Org. React.*, **19**, 1 (1972); **22**, 253 (1975).

(14) P. Tomboulian, D. Amick, S. Beare, K. Dumke, D. Hart, R. Hites, A. Metzger, and R. Nowak, *J. Org. Chem.*, **38**, 322 (1973); G. Köbrich and A. Baumann, *Angew. Chem., Int. Ed. Engl.*, **12**, 856 (1973); A. Maercker and J. Troesch, *J. Organomet. Chem.*, **102**, C1 (1975); and references cited in these papers.

(15) Poly(ferrocenylenes) of previous investigations[2,5,16] were found to contain [0.0]ferrocenophane (bisfulvalenediiron) in variable proportions resulting from Cu- or Co-assisted internal cyclization of dinuclear intermediates.

(16) L. Bednarik, R. O. Gohdes, and E. W. Neuse, *Transition Met. Chem.*, **2**, 212 (1977).

(17) The magnetic properties of poly(ferrocenylenes) and other ferrocene-containing polymers have been reviewed.[17a] (a) E. W. Neuse, *Adv. Macromol. Chem.*, **1**, 1 (1968); E. W. Neuse and H. Rosenberg, "Metallocene Polymers", Marcel Dekker, New York, 1970.

(18) E. C. Ashby and J. J. Lin, *J. Org. Chem.*, **42**, 2805 (1977). Although organocuprates with $Li/Cu > 2$ are unknown, such cuprates may well exist in mixtures possessing high relative organolithium contents.

(19) A. Sekiya and N. Ishikawa, *J. Organomet. Chem.*, **125**, 281 (1977).

(20) H. Watanabe, I. Motoyama, and K. Hata, *Bull. Chem. Soc. Jpn.*, **39**, 790 (1966).

(21) (a) E. R. Lippincott and R. D. Nelson, *Spectrochim. Acta*, **10**, 307 (1958). (b) J. S. Bodenheimer and W. Low, *Spectrochim. Acta, Part A*, **29**, 1733 (1973).

(22) (a) E. W. Neuse and R. K. Crossland, *J. Organomet. Chem.*, **7**, 344 (1967); (b) E. W. Neuse, *ibid.*, **40**, 387 (1972); (c) E. W. Neuse and R. K. Crossland, *ibid.*, **43**, 385 (1972); (d) J. G. Spilners and J. P. Pellegrini, Jr., *J. Org. Chem.*, **30**, 3800 (1965); (e) T. Izumi and A. Kasahara, *Bull. Chem. Soc. Jpn.*, **48**, 1955 (1975).

(23) (a) R. T. Bailey and E. R. Lippincott, *Spectrochim. Acta*, **21**, 389 (1965); (b) J. N. Willis, Jr., M. T. Ryan, F. L. Hedberg, and H. Rosenberg, *Spectrochim. Acta, Part A*, **24**, 1561 (1968).

(24) M. Rosenblum, PhD. Thesis, Harvard, 1953.

(25) D. Steele and D. H. Whiffen, *Trans. Faraday Soc.*, **55**, 369 (1959).

(26) 1,4-Diferrocenylcyclopenta-1,3-diene gives peaks at 3.40 and 6.38 ppm, and 1-ferrocenylcyclopentene resonates at 1.8–2.6 and 5.8 ppm (in $CDCl_3$).

(27) In accord with the absence of substitution reactions involving the solvents, we were unable to detect alkylated or alkoxylated ferrocenes in the mass spectra of oligomeric material, e.g., fractions III and IV.

(28) 1,2-Terferrocenyl gives distinctly reduced extinction coefficients and maxima blue shifted by some 5 nm relative to the 1,1′ isomer.[22b]

(29) S. I. Goldberg and J. G. Breland, *J. Org. Chem.*, **36**, 1499 (1971); P. V. Roling and M. D. Rausch, *J. Organomet. Chem.*, **141**, 195 (1977).

(30) The 1,3-trimer, 1,3-diferrocenylferrocene,[22c] likewise resonates near 4.4 ppm, and so probably do higher homologues containing a 1,3-disubstituted ferrocene group as could have arisen from a 1,3,1′-trilithioferrocene. Although some 1–2% of trilithiated ferrocene has been found to be present in the lithiation mixture under our experimental conditions, the absence of resonances near 4.4 ppm in the crude trimer (and also in the crude tetramer) fractions suggests the contents of such trilithiated intermediate to be too small to bring about any detectable degree of incorporation of 1,3-disubstituted groups (or 1,3,1′-trisubstituted branch point units) into the polymer chain.

(31) The tetra-, penta-, and hexameric homologues of **3** are too poorly soluble[20] to permit their isolation by the conventional fractionating precipitation techniques. For this reason they were removed from the crude polycondensation product mixture by extraction and crystallization operations (fractions III) as detailed in the Experimental Section and hence were essentially absent in the material subfractionated.

Sulfonation of a Polypentenamer and Preparation of Its Hydrogenated Derivatives

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ABSTRACT: Polypentenamer has been sulfonated using a 1:1 complex of sulfur trioxide and triethyl phosphate in chloroform. A range of polymers containing from 1.9 to 19.1 mol % sulfonate groups was prepared by this reagent and isolated in the form of sodium salts. These materials are initially free from covalent cross-links but cross-linking occurs with aging unless the polymers are stabilized with a free-radical scavenger such as hydroquinone. The unsaturated bonds in these materials can be removed by hydrogenation with *p*-toluenesulfonyl hydrazide. The hydrogenated derivatives are crystalline and no longer require a stabilizer to inhibit cross-linking. Both the unsaturated and hydrogenated polymers are hydrophilic.

The chemical modification of a polypentenamer by hydrogenation,[1] hydroformylation,[2] the addition of thioglycolate side groups,[3] and phosphorylation[4] has been previously reported from this laboratory. The objective of these studies has been the preparation of polymer derivatives containing side groups of differing chemical nature and concentration but with identical chain backbones. It has thus been necessary to carry out the reactions under conditions which preclude backbone modification by scission or cross-linking. The present work has been concerned with sulfonating polypentenamer using a 1:1 complex of sulfur trioxide and triethyl phosphate and isolating the resulting product in the form of the sodium salt. The residual double bonds in the sulfonated polypentenamer can be subsequently hydrogenated, as was previously done with the other derivatives, to yield a crystalline polyethylene derivative.

While the preparation of sulfonated polymers is an area where much effort has been directed,[5-9] the preparation of a stable, highly unsaturated, highly sulfonated polymer free from covalent cross-links has not been previously reported. Even for polymers with fully saturated backbones, sulfonation reactions generally lead to the formation of some covalent cross-links,[10,11] quite often in the form of sulfone linkages.[5,10] The reagents used in sulfonation reactions can, in most cases, be regarded as sulfur trioxide based compounds or complexes, with the reactivity of the SO_3 being regulated by the nature of the reagent.[12]

In recent years, complexes of sulfur trioxide with trialkyl phosphate having SO_3 to trialkyl phosphate ratios ranging from 2:1 to 4:1 have permitted the preparation of sulfo-

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0024-9297/79/2212-0195$01.00/0