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Ferrocene-containing Polymers. VIII. Polycondensation of *N*, *N*-Dimethylaminomethylferrocene with Ferrocene

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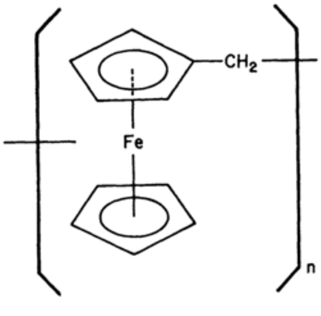
Based on previous investigations involving the self-condensation of the ferrocenyl Mannich base, *N*, *N*-dimethylaminomethylferrocene (I), the present paper describes the co-condensation of this Mannich base with ferrocene. The reactions are conducted in the melt phase in the presence of a $ZnCl_2$/HCl catalyst system. The resulting polymeric products are soluble and partially fusible and have number-average molecular weights in the 500—4000 range (unfractionated). The polymers, exhibiting the idealized structure III, are closely related to the products of self-condensation (II), with recurring units composed of ferrocenylene and methylene groups and homoannular substitution predominating along the chain. Due to the presence of ferrocene, however, an additional termination step is introduced into the overall reaction, leading to a reduced degree of polymerization. The considerable excess over the stoichiometric amount of ferrocene required to achieve this competitive termination and concomitant decrease in M_n suggests that pronounced inductive and hyperconjugative effects are operative in the ferrocenylene-methylene system, resulting in activation of the methylene-substituted ring. The isolation of the lowest homolog possible, diferrocenylmethane, lends further support to the proposed structure of the recurring unit. Spectroscopic evidence obtained on subfractionated material suggests the substitution pattern along the chain to be essentially the same as in the earlier described homocondensation polymers, which is consistent with the assumption of essentially like propagation mechanisms in both cases. A small degree of branching is also inferred from spectroscopic data.

In a previous publication,[1] the $ZnCl_2$/HCl-catalyzed formation of ferrocene-containing polymers from the ferrocenyl Mannich base, *N*, *N*-dimethylaminomethylferrocene (I), was described. The products of condensation were shown essentially to be composed of ferrocenylene-methylene recurring units, and the overall polymer structure was depicted, somewhat idealized, by the novolac-type formula II. Each polymer molecule was believed to contain a double-bridged segment resulting from termination steps through self-substitution on the penultimate ferrocenylene group of the growing chain, much as proposed[2] for the identical polycondensation product of hydroxymethylferrocene. In continuation of these earlier efforts, the present paper describes work on the polycondensation of the Mannich base in the presence of ferrocene, in which case essentially the same propagation sequence, but a different termination step, may be expected, leading to polymer III rather than II.

Results and Discussion

As in the case of homocondensation of I, the co-condensation of this Mannich base with ferrocene, summarized in Eq. 1, will proceed in several steps, the first of these[1] being the formation of adduct IV. By stepwise ionization, with V occurring as successor species,[3] complex IV will generate the metallocarbonium ion VIa (or VIb from polyhomologs of IV and V in an advanced stage of the condensation). For ions VI, the same three reaction steps can be visualized as in the homocondensation of I. These steps involve: (1) nuclear substitution of monomeric and polymeric complexes of the types IV and V (growth



II

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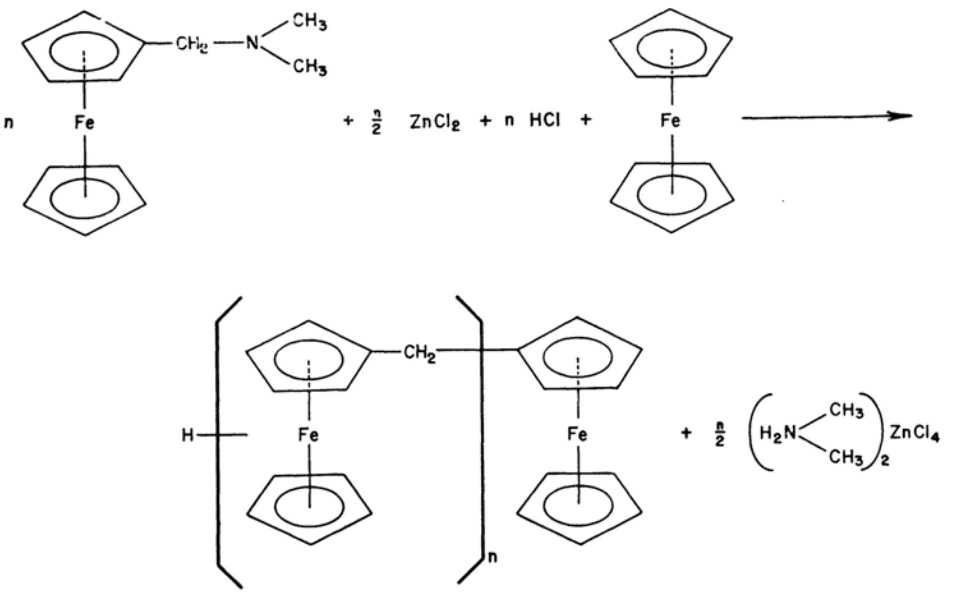
[1] E. W. Neuse and E. Quo, *J. Polymer Sci.*, **A3**, 1499 (1965).

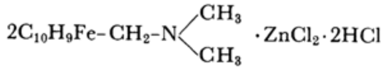
[2] E. W. Neuse and D. S. Trifan, *J. Am. Chem. Soc.*, **85**, 1952 (1963).

[3] E. W. Neuse and E. Quo, *Nature*, **205**, 494 (1965).



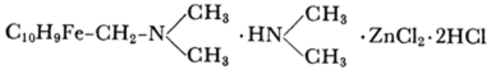
(1)

III



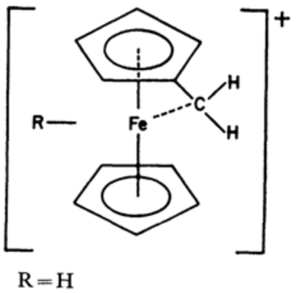
$$2C_{10}H_9Fe\text{-}CH_2\text{-}N\begin{matrix}CH_3\\CH_3\end{matrix}\cdot ZnCl_2\cdot 2HCl$$

IV



$$C_{10}H_9Fe\text{-}CH_2\text{-}N\begin{matrix}CH_3\\CH_3\end{matrix}\cdot HN\begin{matrix}CH_3\\CH_3\end{matrix}\cdot ZnCl_2\cdot 2HCl$$

V



VIa, R=H
VIb, R=Residual polymer chain

step); (2) self-substitution on penultimate ferrocene nucleus with resulting formation of a double-bridged segment as part of a nitrogen-free polymer chain (termination step); (3) nuclear substitution of nitrogen-free polymer (growth step). In addition to these three reaction steps involved in the homocondensation of the Mannich base, nuclear substitution of ferrocene may now occur as an alternate termination step (4) competing with the self-substitution reaction (2). To what extent the self-substitution step in this largely diffusion-controlled process can be suppressed as a terminating reaction in favor of (4) will largely depend on both the ferrocene concentration in the melt and the difference in reactivity between the ferrocene molecule and the substituted ferrocenyl or ferrocenylene units. Prevalence of steps (1) through (3) over (4) may be predicted as a result of inductive and hyperconjugative[4-8] activation of the substituted ferrocene rings. Therefore, in order to enforce a reaction course according to Eq. 1 by suppressing the other three reaction steps in favor of (4), it would appear necessary to employ the ferrocene co-reactant in concentrations considerably higher than required by the stoichiometry of Eq. 1.

The experimental results of a series of co-condensations confirmed these expectations. When heated with various amounts of ferrocene in the presence of zinc chloride and hydrogen chloride (or zinc chloride and water, thus generating hydrogen chloride by hydrolysis) under conditions similar to those applied in homocondensations,[1] the Mannich base readily underwent condensation to give polymers in 75—85% yield. By combining extraction, precipitation and sublimation steps, the polymer was separated in each case from unreacted ferrocene, zinc salts and traces of crosslinked polymer, to be finally collected in two crude fractions of different average molecular weights. The first fraction consisted of polymeric material, whereas the second fraction, usually somewhat

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4) K. Rinehart, Jr., K. L. Motz and S. Moon, *J. Am. Chem. Soc.*, **79**, 2749 (1957).

5) M. Rosenblum and R. B. Woodward, ibid., **80**, 5443 (1958).

6) M. Rosenblum, ibid., **81**, 4530 (1959).

7) M. Rosenblum and W. G. Howells, ibid., **84**, 1167 (1962).

8) K. L. Rinehart, Jr., D. E. Bublitz and D. H. Gustafson, ibid., **85**, 970 (1963).

TABLE I

Expt. No.	Concentrations of reactants, mol.						Temp. °C	Time hr.	Total yield of crude polymer,a) %	HCl introduced as
	I	Hydrochloride of I	Ferrocene	$ZnCl_2$	HCl	H_2O				
1	1.0	—	0.2	0.5	1.0	3.305	165	7.5	82.6	Hydrochloric acid
2	1.0	—	0.33	0.55	1.0	3.305	170	7	82.9	Hydrochloric acid
3	1.0	—	0.5	0.5	1.0	3.305	170	8	85.8	Hydrochloric acid
4	—	1.0	0.5	0.5	—	—	170	6	78.8	Hydrochloride of I
5	1.0	—	1.0	0.55	1.0	3.305	165	12	77.5	Hydrochloric acid
6b)	1.0	—	2.0	0.5	1.0	3.305	170	7	80.6	Hydrochloric acid
7	1.0	—	0.25	1.0	—	1.0	170	6	87.2	$ZnCl_2$ (hydrolysis)
8	1.0	—	0.5	1.0	—	1.0	160	8	78.8	$ZnCl_2$ (hydrolysis)
9	1.0	—	1.0	1.1	—	1.1	170	11	80.9	$ZnCl_2$ (hydrolysis)
10b)	1.0	—	2.5	1.0	—	1.0	155	9	88.5	$ZnCl_2$ (hydrolysis)

a) Combined yield of 1st and 2nd fraction, in % of theory.
b) Dioxane used as solvent.

TABLE II

Expt. No.	Fractiona)	M_n	M. p. °Cb)	Yield %	Anal. Calcd. for III			Anal. Found		
					C, %	H, %	Fe, %	C, %	H, %	Fe,c) %
1	1st	3650	155	69.6	66.60	5.10	28.30	67.01	5.13	27.34
	2nd	850	85	13.0	66.24	5.16	28.60	66.34	5.31	28.38
2	1st	2970	140	67.5	66.58	5.11	28.31	66.51	5.20	27.58
	2nd	790	95	15.4	66.21	5.17	28.62	66.41	5.39	28.29
3	1st	2590	125	74.6	66.56	5.11	28.33	66.69	5.32	27.82
	2nd	660	90	11.2	66.10	5.18	28.72	66.30	5.24	29.10
4	1st	2790	135	68.0	66.57	5.11	28.32	66.84	5.19	27.97
	2nd	740	80	10.8	65.17	5.17	28.66	66.09	5.29	28.83
5	1st	2310	120	61.2	66.54	5.12	28.34	66.80	5.25	27.76
	2nd	620	110	16.3	66.06	5.19	28.75	65.96	5.26	28.66
6	1st	2440	125	24.7	66.55	5.12	28.33	66.39	5.37	27.49
	2nd	560	100	55.9	66.02	5.19	28.79	66.10	5.32	28.49
7	1st	3700	135	77.3	66.60	5.10	28.30	66.79	5.26	27.83
	2nd	820	80	9.9	66.22	5.17	28.61	66.39	5.14	28.23
8	1st	2330	130	65.4	66.54	5.12	28.34	66.59	5.45	27.84
	2nd	720	90	13.4	66.15	5.18	28.67	65.83	5.24	28.53
9	1st	2550	125	52.2	66.56	5.11	28.33	66.07	5.13	28.02
	2nd	550	95	28.7	65.97	5.20	28.83	65.75	5.40	29.17
10	1st	1980	115	22.9	66.51	5.12	28.37	66.45	5.24	28.11
	2nd	490	100	65.9	65.89	5.22	28.89	65.58	5.31	29.10

a) First and second fractions; see text.
b) Upper limiting value of melting range.
c) Up to 0.8% low for higher-molecular compounds.

smaller, contained essentially oligomeric constituents. The reactions are illustrated by 10 examples9) summarized in Table I, and the pertaining analytical data are compiled in Table II.

The analytical results recorded confirm the anticipated structure III.10) Furthermore, the effect of the ferrocene co-reactant on the average degree of polymerization is demonstrated by a

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9) For comparison, several polycondensations were conducted with aluminum chloride as catalyst, applying experimental conditions similar to those summarized in Table I for zinc chloride. In a typical run employing Mannich base and $AlCl_3$ in a 2 : 1 molar ratio, polycondensation occurred even in the absence of additional catalyst components such as HCl or H_2O. However, due to unusually strong crosslinking and decomposition effects even at the comparatively low temperature applied (150°C), the reaction had to be terminated at an incomplete stage, and the yield in linear polymer barely approached 40%. These discouraging results prompted the abandonment of $AlCl_3$ as the Lewis acid component in these condensations.

10) Undoubtedly, the first fractions from experiments employing a high Mannich base/ferrocene ratio contain some polymer II formed via the self-substitution step (2). However, this cannot be borne out by chemical analysis since in the molecular weight ranges concerned the differences in elemental composition are too small to be analytically discernible, as becomes evident from a comparison of the calculated analytical data in Table II with those for the homocondensation product II recorded earlier1) (Calcd. for II: C, 66.71; H, 5.09; Fe, 28.20%).

comparison of the M_n and yield values, lowest molecular weights being obtained at highest ferrocene concentrations. The data also show the enhanced susceptibility of the substituted, as compared to the unsubstituted, ferrocene moiety toward electrophilic attack. This can readily be seen in such experiments as Nos. 5, 6, 9 and 10, in which the yields in oligomeric III ($n \approx 2$) were markedly lower than would have been expected for comparable ring activation of substituted and unsubstituted ferrocene units.

Employing standard fractionation procedures, several typical polymer batches were separated into subfractions of enhanced monodispersity. These subfractions had molecular weights (M_n) ranging from about 400 to 11000 and showed elemental analyses in the same good agreement with structure III as noted above for the unsubfractionated products. An X-ray diffraction study revealed crystallinity only for fractions with $M_n <$ 700. This lack of crystallinity in fractions with constituents containing four or more ferrocene nuclei is not surprising in view of assumed branching (see below) and random distribution of the 1, 2-, 1, 3- and 1, 1′-disubstituted recurring units. The lowest subfraction isolated, after chromatographic purification, proved to be identical in m. p., M_n and elemental composition with the known[11,12] diferrocenylmethane (III, $n=1$), whose structure was confirmed by percent homoannularity value[2] (96.9) and NMR spectrum, the latter showing singlets due to ferrocene (18 protons) and methylene (two protons) resonances at τ 6.09 and 6.70, respectively.[13] This unambiguous identification of the lowest homolog as diferrocenylmethane is well in support of the structural assignment III to the presently discussed polymer.

The infrared spectra (KBr pellet) of polymer III showed the bands characteristic of the ferrocenylene-methylene unit as discussed elsewhere.[2] The spectra of high-molecular fractions were practically superimposable with those of polymer II prepared either from *N, N*-dimethylaminomethylferrocene[1] or from hydroxymethylferrocene.[2] This spectroscopic identity is predictable, since the effect, if any, of a double-bridged segment in homopolymer II on the absorption pattern of the ferrocenylene-methylene units is probably too small to be detectable, with interfering absorption of other origin appearing in all characteristic regions, notably in that at 10.6—11.0μ. The occurrence of the typical medium-intensity band near 7.8 μ not only in higher molecular fractions, but even in the lowest, solely monosubstituted member (diferrocenylmethane), prohibits utilization of this peak in distinguishing 1, 3- from 1, 2-disubstituted ferrocene derivatives as suggested by Nesmeyanov.[18] (Cf., in this connection, Rosenblum and Howells.[7]) By the same reasoning, the band in the 10.8—10.9μ range exhibited by diferrocenylmethane and all higher molecular fractions cannot be utilized for this distinction.[4,6,8,19]) In going from low- to high-molecular fractions, the two bands near 9 and 10μ indicative of the presence of unsubstituted ferrocene rings[19] were attenuated in intensity. At the same time, an intensity decrease of the ring-breathing absorption near 7.1μ became apparent; while observed with other homoannularly substituted ferrocene derivatives made available for this comparison, this band failed to occur, or at best appeared very weakly, in a great number of heteroannular compounds investigated and may, therefore, be utilized in suitable cases as corroborative evidence for the presence of unsubstituted rings. The weak band at 10.60μ originally ascribed to a CH_2 rocking mode[2] was found to be exhibited in nearly unchanged intensity by all fractions except the lowest member, thus indicating a different origin; possibly, the band is associated with a 1, 3-disubstitution scheme[4,6] on ferrocene.

The majority of subfractions of III with $M_n <$ 5000 showed a defined melting behavior. This is in contrast to the predominantly infusible (when fractionated) polymer II; various degrees of monodispersity and branching possibly acount for this inconsistency. The m. p.-M_n relationship depicted in Fig. 1 may, within the molecular weight range from about 1000 to 4000, be employed for useful characterization purposes, as was done

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[11] K. Schlögl and A. Mohar, *Monatsh. Chem.*, **92**, 219 (1961).

[12] P. L. Pauson and W. E. Watts, *J. Chem. Soc.*, **1962**, 3880.

[13] The compound was converted by selenium dioxide treatment to the known[11,14–17] diferrocenylketone, for which additional structural proof resulted from its weak-coupling A_2X_2-type NMR spectrum exhibiting, in the expected area ratio, a singlet at τ 5.83 (unsubstituted ring protons) and two apparent triplet signals centered at 5.02 and 5.51 (strongly deshielded $\alpha-\beta$ protons) with practically identical " ortho " and cross-ring coupling constants ($J_{\alpha\beta} \approx J_{\alpha\beta'} \approx 2.0$ c.p.s.). These detailed analytical efforts on diferrocenylmethane appeared to be in order in view of some disagreement in the literature as to the identity of this compound. While both Schlögl's[11] and Pauson's[12] groups reported melting points in the 143—149°C range, Rinehart and co-workers, in an earlier communication,[14] assigned the diferrocenylmethane structure to a compound with m. p. 124—125°C. The analytical and spectroscopic data presented above, coupled with the oxidation to the ketone, substantiate the present assignment in accord with Schlögl's and Pauson's findings.

[14] K. L. Rinehart, Jr., A. F. Ellis, C. J. Michejda and P. A. Kittle, *J. Am. Chem. Soc.*, **82**, 4112 (1960).

[15] S. I. Goldberg, *J. Org. Chem.*, **25**, 482 (1960).

[16] M. D. Rausch, E. O. Fischer and H. Grubert, *J. Am. Chem. Soc.*, **82**, 76 (1960).

[17] K. L. Rinehart, Jr., P. A. Kittle and A. F. Ellise, ibid., **82**, 2082 (1960).

[18] A. N. Nesmeyanov, L. A. Kasitsyna, B. V. Lokshin and V. D. Vilchevskaya, *Dokl. Akad. Nauk SSSR*, **125**, 1037 (1959).

[19] M. Rosenblum, Ph. D. Thesis, Harvard University, 1953.

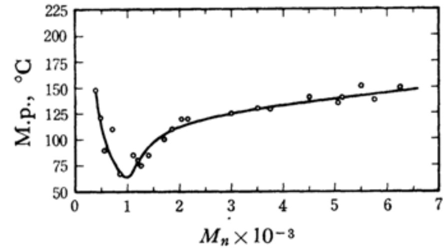

Fig. 1. Melting point, m. p., vs. number-average molecular weight, M_n, for polymer III.

earlier in related cases.2,20) For further characterization, again using subfractionated samples, the correlation

$$[\eta]=1.1\times10^{-3}M^{0.38}$$

between intrinsic viscosity, $[\eta]$, and molecular weight was determined by standard procedures. The low value of the exponent points to more globular than rod-like shape of the polymer molecules, as was similarly inferred1) for polymer II. This behavior suggests a slightly branched structure, for which corroborative spectroscopic evidence results from the downward trend1) of the percent homoannularity-molecular weight curve plotted in Fig. 2 for 15 subfractions. This curve, furthermore, demonstrates a slight prevalence of homoannular over heteroannular bonding along the polymer backbone, as is predictable on electronic grounds.1,2,4-8,21) It is of interest to note the complete coincidence of the curve in Fig. 2 with the corresponding plot1) for polymer II reproduced here for comparison, supporting the earlier assumption in this paper of an identical propagation sequence (with resulting identical substitution orientation) for both polymers II and III.

In order to arrive at a quantitative value of the degree of intralinear homoannular bonding, i. e., that proportion of homoannular bonding which is restricted to links of the backbone, a monodisperse, trinuclear fraction composed of the isomeric bis(ferrocenylmethyl)ferrocenes (III, $n=2$) was isolated by chromatography from the hexane-soluble portions of the polymer, thus offering the possibility to study the substitution orientation in III unaffected by the occurrence of side-chains. Monodispersity of this fraction and absence of components other than isomers III, $n=2$, was demonstrated22) by molecular weight determinations, elemental analyses and NMR spectra (ferrocene/methylene proton signals in the expected 26 : 4 area ratio) on subfractions obtained by repeated crystallization.23) Determination of the percent-homoannularity of this trinuclear fraction gave a value of 86.5 (average of results from three parallel chromatographic runs). From this figure, one may calculate a 59.6% content of homoannular compounds (combined 1, 2- and 1, 3-bis(ferrocenylmethyl)ferrocene) in the trinuclear isomer mixture and, hence, approximately so, of ferrocenylene units bonded homoannularly into the polymer backbone.

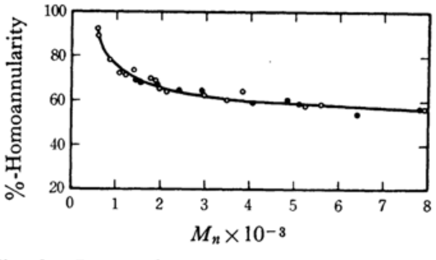

Fig. 2. Percent-homoannularity vs. number-average molecular weight, M_n, for:
Poloymer III (open circles)
Polymer II (filled-in circles)

Work on the separation of the trinuclear mixture into its components (the heteroannular compound was recently described12)) is in progress and will be reported elsewhere.24)

Experimental

Materials and Analytical Procedures. — Solvents were reagent grade; for chromatographic purposes, they were fractionated on a spinning-band column. Starting materials and other chemicals were obtained commercially or prepared and purified as described.1,2) Elemental and instrumental analyses were performed as in the earlier work.1) The solvents used for NMR and M_n determinations were, respectively, carbon

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20) E. W. Neuse and D. S. Trifan, Abstr. Papers presented at 148th National Meeting, Am. Chem. Soc., September, 1964, p. 5S.

21) R. A. Benkeser, Y. Nagai and J. Hooz, *J. Am. Chem. Soc.*, **86**, 3742 (1964). Among the two possible homoannular dispositions, steric effects are likely to lead predominantly to 1, 3-substituted units.

22) In addition, similar analyses of the preceding and subsequent chromatographic bands showed these to be devoid of isomers III, $n=2$, thus attesting to the quantitative collection of these isomers in the trinuclear fraction under consideration.

23) The conventional process of fractional precipitation and crystallization, resting on the different solubility behavior of the components, could obviously not be utilized for this separation of a monodisperse fraction, since strict dependence of the solubility on the chain-length would be expected only for those polyhomologous series in which all members are composed of identical recurring units. In contrast, with polymers composed, as in the present case, of isomeric recurring units differing in the relative position of the two substituting methylene groups, a different fractionation behavior is predictable in the low-molecular range insofar as the different solubility of isomeric oligomers possessing equal molecular weight would invariably result in the distribution of such isomers over several fractions, which hence would no longer be strictly monodisperse.

24) This effort has since been reported: E. W. Neuse, E. Quo, and W. G. Howells, *J. Org. Chcm.*, **30**, 4071 (1965).

tetrachloride (deuteriochloroform for diferrocenylketone) and benzene; viscosities were measured in benzene.

Polycondensation Reactions: Formation of III.—Employing the equipment and general technique described in an earlier paper,[2] the mixtures of Mannich base I and ferrocene with the catalyst system were heated in the molar ratios and under the experimental conditions summarized in Table I. While the catalyst system in runs No. 1—3, 5 and 6 was anhydrous zinc chloride and concentrated aqueous hydrochloric acid, zinc chloride and water were used in Nos. 7—10, thus generating hydrochloric acid by hydrolysis.[1] In run No. 4, hydrochloric acid was introduced as the hydrochloride of I, with no water added to the system. From the reaction products, extraction with warm water removed catalyst residues and dimethylammonium tetrachlorozincate, as well as unreacted complexes IV and V. The crude polymer III was then reprecipitated from benzene[25] solution by excess 2-propanol. The solid precipitate, designated as first fraction, was washed with methanol and was dried for 10 days at 50°C in vacuo. The mother-liquor, combined with the alcoholic washings, was concentrated on a rotating evaporator to remove the major portion of benzene and was poured into excess water. The resinous precipitate was taken up in benzene, filtered and the solution evaporated to dryness. The orange-brown solid remaining after removal of admixed ferrocene by vacuum sublimation, composed of oligomeric material, was designated as second fraction. The analytical data for both fractions are collected in Table II. The first (higher-molecular) fractions dissolved readily in benzene, dioxane and chloroform; the second (oligomeric) fractions, in addition, showed enhanced solubility in aliphatic alcohols, ketones and hydrocarbons.

Subfractionation of polydisperse polymer (combined first and second fractions) by conventional precipitation procedures at 25 ± 1°C, using benzene as solvent, resulted in separation of fractions possessing enhanced monodispersity. The precipitant was 2-propanol which was diluted increasingly with water as the fractionation proceeded. The total number of subfractions obtained in each series was 15—20; the last 8 of these, with molecular weights below 1000, were collected by stepwise concentrating the mother-liquor at 30°C in a rotating evaporator for benzene removal and allowing the solution to stand for 12 hr. at 25 ± 1°C. The products gave analytical results comparable to those for the unsubfractionated polymers. For example, the highest subfraction isolated analyzed as follows: C, 66.83; H, 5.17; Fe, 27.49%; M_n, 11200 (Calcd. for III: C, 66.68; H, 5.09; Fe, 28.23%), while for a typical oligomeric subfraction the findings were: C, 65.77; H, 5.20; Fe, 29.02%; M_n, 690 (Calcd. for III: C, 66.12; H, 5.18; Fe, 28.70%).

Chromatographic Oligomer Separation.—For the chromatographic separation of dinuclear and trinuclear III, low-molecular fractions were extracted with cyclohexane, thus taking up only compounds with M_n essentially below 1000—1100. In a typical run, employing 2.0 g. of the second fraction from experiment No. 5 (Table II), a cyclohexane solution (20 ml.) was prepared, from which 0.19 g. of higher-molecular III (Found: C, 66.70; H, 5.23; Fe, 28.10%; M_n, 1840) was separated by filtration. The filtrate was chromatographed under light protection on Alcoa grade F-20 alumina partially deactivated by 12 hr. exposure to air of 40% r.h., using hexane as eluent. After elution of traces of ferrocene not previously removed by sublimation, there was eluted a second band containing 0.63 g. of diferrocenylmethane, m. p. 147—149°C (from 2-propanol). X-Ray diffractogram, Å: 5.05, 5.69, 4.88, 6.13, 4.21, 4.27. Upon fusing at 160°C and re-cooling, the compound crystallized in a different system (X-ray diffractogram, Å: 5.18, 5.88, 5.66, 4.81, 4.58, 4.45); this modification was occasionally found intermixed with the stable form crystallizing from 2-propanol. A third modification crystallized from hexane (X-ray diffractogram, Å: 4.80, 5.09, 9.60, 4.20). All modifications showed the same melting point and analytical data (Found: C, 65.67; H, 5.27; Fe, 28.86%; mol. wt. 370. Calcd. for $C_{21}H_{20}Fe_2$: C, 65.67; H, 5.25; Fe, 29.08%; mol. wt. 384). By treatment with selenium(IV) oxide in refluxing benzene (10 hr.), the compound was oxidized in 48% yield to diferrocenylketone, reddish needles, m. p. 206—210°C (sealed; lit.[16,17]: 204°C, 210—211°C).

Elution of a third orange band gave 0.53 g. of the crude trinuclear isomer mixture (III, $n=2$), melting range 100—145°C. Found: C, 66.20; H, 5.08; Fe, 28.66%; mol. wt. 550. Calcd. for $C_{32}H_{30}Fe_3$: C, 66.02; H, 5.19; Fe, 28.78%; mol. wt. 582; percent-homoannularity, 88.1 (the average of three values on fractions obtained in parallel chromatographic runs was 86.5). All subfractions obtained from this fraction by extended fractional crystallization, while varying in melting points, showed analytical and molecular weight data in the same ranges.

Two higher bands of the chromatogram gave only brittle, X-ray amorphous resins, from which no subfractions with $M_n<750$ were isolable by reprecipitation or crystallization.

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[25] In several parallel runs, peroxide-free dioxane was employed in lieu of benzene as solvent in the precipitation operation. Owing to the excellent water compatibility of this solvent, the second fractions could in these cases be isolated as tack-free solids, thus facilitating their work-up. This modification offered advantages in those reactions that gave predominantly oligomeric compounds and was, therefore, employed in condensations Nos. 6 and 10 (Table I). In general, however, use of benzene was preferred because of enhanced purity of the polymer fractions collected.