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Ferrocene-containing Polymers. IX. Polycondensation of Ferrocene with Formaldehyde[1]

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The Lewis acid-catalyzed polycondensation of ferrocene with formaldehyde or its dimethylacetal gives rise to the formation of soluble, novolac-type polymers comprising ferrocenylene units interlinked by methylene bridges. In contrast to earlier work performed by other investigators in liquid hydrogen fluoride or sulfuric acid media, where only non-polymeric products were described, propagation is accomplished in the present case by condensing the reactants in a closed system in bulk at temperatures up to 170°C. The resulting polymers, with M_n values up to 4000 (unfractionated), are shown by elemental and spectroscopic analyses and viscometric data to be essentially identical with the previously reported polycondensation products of *N*, *N*-dimethylaminomethylferrocene with ferrocene. Infrared spectroscopy shows the intralinear substitution to be predominantly homoannular, which is expected as a result of the electronic effects exercised by the methylene substituent. Under appropriate conditions, additional methylene groups can be incorporated into the polymer, giving rise to double-bridged segments and inter-chain bridging. Strongly crosslinked polymers are obtained if excess aldehydic reactant is employed at temperatures in the 170—185°C range.

It has been shown in a recent paper[2] that ferrocene can be polycondensed with benzaldehyde in the melt phase to give polymers essentially conforming to structure I. This smooth generation of I from ferrocene and benzaldehyde suggested utilization of the same synthetic procedure for the preparation of the analogous, novolac-type polymer II obtained earlier[3] by polycondensation of *N*, *N*-dimethylaminomethylferrocene with ferrocene. However, all attempts in the previous work[2] to prepare this polymer by the direct condensation of ferrocene with formaldehyde (*s*-trioxane, paraformaldehyde, dimethoxymethane) failed. Neither in bulk nor in solution, employing various aliphatic or aromatic hydrocarbon solvents, could defined polymeric products be isolated.

It has now been found that under appropriate conditions, using a closed system, polycondensation of ferrocene with formaldehyde in its various forms can be enforced. This reaction, which is described in the present paper, leads to polymeric reaction products and is, thus, in contrast to ferrocene-formaldehyde condensations performed by other workers[4-8] in liquid hydrogen fluoride or sulfuric acid media, where only monomeric reaction products were reported.[8a]

Results

The polycondensation of ferrocene with formaldehyde leading to polymer II may be expressed by the summarizing Eq. 1.

When ferrocene was heated in sealed tubes with *s*-trioxane or paraformaldehyde in the presence of Lewis acids, polycondensation according to Eq. 1 was indeed observed. However, under all conditions of temperature, time, and catalyst type and concentration employed, polymer yields were generally low (25—50%) owing to side-reactions involving self-polymerization of the aldehyde and crosslinking. In contrast, good results were obtained by using the dimethyl acetal of formaldehyde, dimethoxymethane (formal). This

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[1] The work presented herein, briefly summarized in a recent note (*Nature*, **204**, 179 (1964)), was conducted by the Douglas Aircraft Company under company-sponsored research and development funds. The assistance of Messrs. R. C. Baird and R. J. Dimarzo in performing the iron analyses and scanning the infrared spectra is gratefully acknowledged. The authors are also indebted to Mr. C. A. Seil for many stimulating discussions on this subject.

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[3] E. W. Neuse and K. Koda, This Bulletin, **39**, 1502 (1966).

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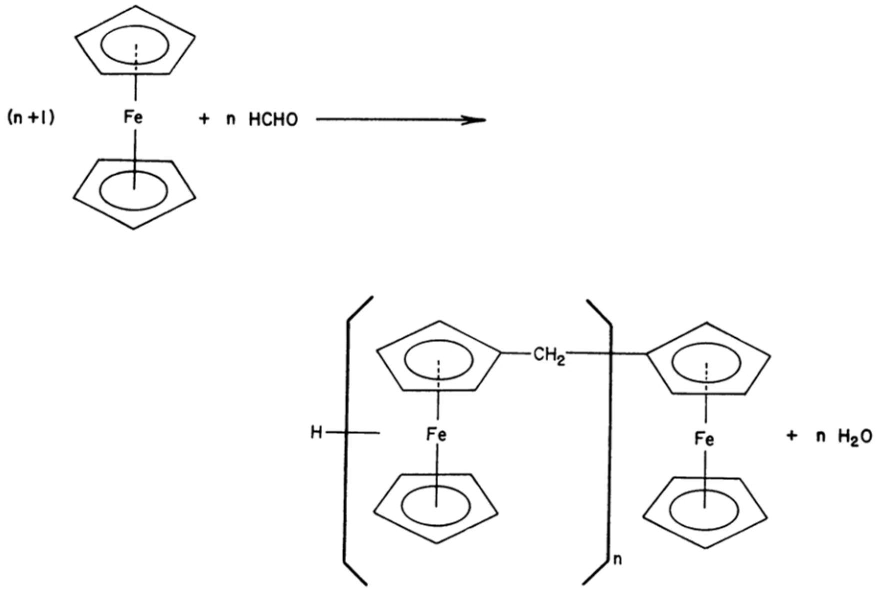
[7] K. L. Rinehart, Jr., C. J. Michejda and P. A. Kittle, *J. Am. Chem. Soc.*, **81**, 3162 (1959).

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

[8a] While this manuscript was in print, we became aware of a note by H. Valot, *Compt. rend.*, **258**, 5870 (1964), describing the isolation of polymers under conditions of sulfuric acid condensation.



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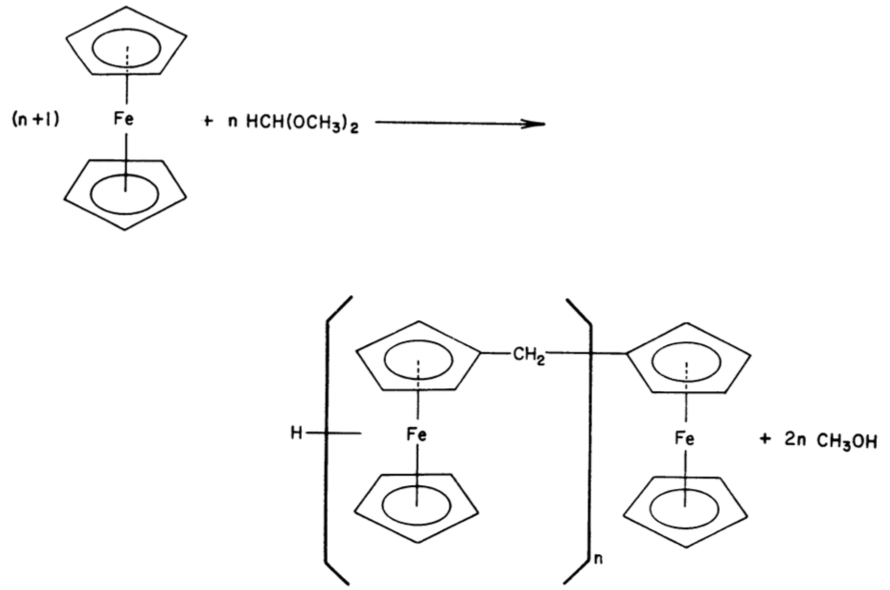

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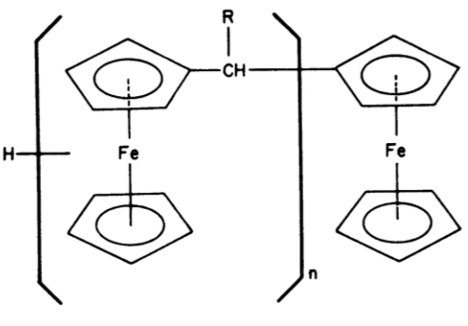

I, $R=C_6H_5$

II, $R=H$

compound was therefore employed as the aldehyde-furnishing reactant throughout the present work, and the summarized polycondensation course may accordingly be depicted by Eq. 2.

The reactions (8—12 hr., 150—170°C) were carried out in sealed tubes or high-pressure autoclaves, using zinc chloride as catalyst in concentrations ranging from 3 to 20% by wt. of ferrocene. Under such conditions, and at equimolar or near-equimolar ratios of the reactants, overall conversions were generally in the 55—70% range. At temperatures substantially lower than 150°C, only oligomers were isolable in low yields, whereas temperatures markedly higher than 170°C led to

TABLE I

Expt. No.	Molar ratio Ferrocene/Acetal	Catalyst type and concentration,[a] %		Temp. °C	Time hr.	Total crude yield of soluble condensation products,[b] %	Yield of insoluble matter[a] %
		$ZnCl_2$	$AlCl_3$				
1	1 : 0.8	5	—	170	10	53.7	< 1
2	1 : 1.0	5	—	170	9	59.5	< 1
3	1 : 1.0	10	—	170	6	64.4	< 1
4	1 : 1.2	5	—	170	9	60.9	< 1
5	1 : 1.4	5	—	165	10	66.2	< 2
6	1 : 1.7	10	—	130	5	46.9	10.4
7	1 : 1.0	5	—	180	12	72.9	< 2
8	1 : 1.0	—	10	170	3	27.0	68.3
9[c]	1 : 2.0[d]	10	—	170	6	80.4	6.1
10[c]	1 : 0.64[e]	10	—	170	10	84.8	2.2

a) By wt. of ferrocene (of starting material in Nos. 9, 10).
b) Combined yields of first and second fractions.
c) Post-condensation of oligomer.
d) Molar ration oligomeric II (M_n 780)/acetal.
e) Molar ration oligomeric II (M_n 260)/acetal.

TABLE II

Expt. No.	Fraction[a]	M_n	M.p.[b] °C	Yield %	Calcd. for II C, %	Calcd. for II H, %	Calcd. for II Fe, %	Found C, %	Found H, %	Found Fe, %
1	1st	860	70	19.8	66.24	5.16	28.60	66.27	5.10	28.51
	2nd	590	95	33.9	66.02	5.19	28.79	65.86	5.07	28.69
2	1st	1320	110	20.3	66.41	5.13	28.46	66.63	5.30	28.14
	2nd	650	90	39.2	66.10	5.18	28.72	66.23	5.25	28.47
3	1st	1570	110	29.0	66.45	5.13	28.42	66.19	5.23	28.37
	2nd	590	85	35.4	66.02	5.19	28.79	66.49	5.42	28.19
4	1st	2190	130	40.5	66.52	5.12	28.36	66.33	5.19	28.06
	2nd	500	105	20.4	65.90	5.21	28.89	66.43	5.42	28.52
5	1st	2250	125	42.7	66.53	5.12	28.35	66.63	5.16	28.08
	2nd	630	85	23.5	66.07	5.18	28.75	66.14	5.46	28.10
6	1st	2140	120	27.9	66.52	5.12	28.36	66.28	5.18	28.29
	2nd	670	90	19.0	66.10	5.18	28.72	66.22	5.19	28.60
7	1st	2370	120	51.7	67.25[c]	5.01[c]	27.74[c]	67.46	5.29	27.58
	2nd	510	100	21.2	65.92	5.21	28.87	66.50	5.50	28.63
8	1st	3900	155[d]	20.9	66.61	5.10	28.29	66.50	5.38	26.88
	2nd	980	60	6.1	66.30	5.15	28.55	66.06	5.38	27.70
9	1st	1870	140[e]	61.6	66.49	5.12	—	66.33	5.11	—
	2nd	810	65	18.8	66.22	5.17	28.61	66.41	5.36	28.21
10	1st	1130	90	58.1	66.35	5.14	28.51	66.08	5.25	—
	2nd	540	90	26.7	66.96	5.21	28.83	66.58	5.37	28.53

a) First and second fractions; see text.
b) Upper limiting value of melting range.
c) Calculated for polymer with four additional methylene groups per molecule (see text).
d) Sintering only.
e) Very large range, indicating wide molecular weight distribution.

polymers with compositions deviating from the desired structure II.

Table I summarizes the reaction conditions and resulting polymer yields for a number of typical experiments. The reactions listed were performed in an autoclave to establish conditions more suitable for large-scale preparations. For small-scale condensations conducted in ampoules, correspondingly shortened reaction times sufficed. The reaction products were worked up by earlier described procedures[3)] and were collected as two fractions: a first fraction composed of higher-molecular polymer and a second fraction containing oligomeric condensation products. All pertinent analytical data for the two fractions are compiled in Table II.

An inspection of the first three experiments listed, in which no excess aldehyde was employed, clearly shows the agreement in elemental composition of the condensation products with the anticipated structure II. Due to the presence of unreacted starting materials in the equilibrium ultimately attained, this agreement is evident even for the reaction products of such condensations (Nos. 4, 5, and especially 6) in which the acetal was employed in excess over the equimolar amount at temperatures low enough to prevent entire utilization of this reactant.

With temperatures in these reactions further increased, however, the products of polycondensation showed changes in composition distinctly detectable by elemental analysis. This is demonstrated, for instance, in experiment No. 7, in which the temperature was raised to 180°C; after 12 hr. of total heating time, the resulting polymer was found to contain as many as four $-CH_2-$ bridges⁹⁾ per molecule (M_n 2370) in excess over the number required for structure II.

For comparison, a reaction employing aluminum chloride as catalyst is included in the tables as No. 8; again, the ratio of the reactants was equimolar. The drastic increase in insoluble matter at the expense of soluble polymer resulting from crosslinking and partial destruction of the ferrocene molecule is clearly demonstrated by the analytical and yield data presented. In view of earlier communications[10-15] describing the reaction of ferrocene with aluminum chloride in chlorohydrocarbon solution, the observed effects of this Lewis acid under the presently applied conditions are not unexpected. Both Rosenberg[10,11] and Nesmeyanov[12-14] with their co-workers have shown such ferrocene derivatives to contain cyclopentyl and cyclopentenyl groups stemming from partial ferrocene cleavage. If a similar cleavage and ensuing cyclopentenyl substitution is assumed in the present case,[16] the observed crosslinking reactions might in part be explicable in terms of a polymerization mechanism involving double bonds of the cyclopentenyl rings. The major portion of crosslinks, however, was probably formed by inter-chain bridging through methylene groups as will be discussed below in detail.

On a combined polymer batch composed of fractions consistent in elemental composition with structure II, a subfractionation by precipitation and crystallization was performed as described loc. cit.[3] for the Mannich base-ferrocene polycondensation product. The 16 subfractions collected showed M_n values up to 10000 and corresponded in composition to II much as did the parent material. Chromatography of the final, lowest-molecular subfraction gave a compound shown to be identical in melting point and X-ray diffractogram with diferrocenylmethane (II, $n=1$).[3,8,17] These findings confirm the compositional identity of the present polymer with the earlier product[3] derived from *N*, *N*-dimethylaminomethylferrocene. Corroborative evidence for this identity arose from spectroscopic data, the infrared spectra recorded on comparable subfractions of both products being strictly superimposable. In addition, the viscosity-molecular weight correlation[3,18] for both products was found to be the same within experimental error, as was the relationship between intensity of the 9 μ infrared band (in terms of percent-homoannularity[2,3,19]) and number-average molecular weight depicted by the curve in Fig. 1. The coincidence of the plots in the latter case attests to the essentially identical branching pattern and substitution orientation along the polymer backbone. The trend of the graph in Fig. 1, predominantly homoannular in the oligomeric range and gradually approaching a minimum value of the percent-homoannularity, suggests[2,19] an increase in the degree of branching with rising molecular weight, this branching preferentially occurring on those ferrocene rings that are not part of the chain proper.

Figure 2 represents a plot of melting point (upper limit of melting range) against M_n, determined again

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9) Incorporation of additional methylene bridges was accompanied by competing crosslink formation if, under heating conditions similar to those above, acetal concentrations substantially higher than equimolar were applied. Thus, at an acetal/ferrocene molar ratio of 1.4 and a heating time of 14 hr. at 185°C, crosslinked polymer amounted to a total of 53.7% (by wt. of ferrocene), with soluble polymer simultaneously collected in 33.2% yield. With 100% molar excess of the acetal (acetal/ferrocene ratio=2), even at only three hours heating time at 170°C, the yield in soluble polymer decreased to 17%, while the major portion of condensation product was isolated as crosslinked matter. In each of these cases, both the crosslinked product and the corresponding soluble polymer portion were of practically the same elemental composition. Also their infrared spectra were practically identical except that slightly enhanced methylene bands were exhibited by the crosslinked compound. From this observation, a close structural relationship between the soluble polymers and their crosslinked counterparts must be inferred, with the latter types differing in their structural build-up from the former merely by the existence of inter-chain methylene bridges.

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11) S. G. Cottis and H. Rosenberg, *J. Polymer Sci.*, **2B**, 295 (1964).

12) A. N. Nesmeyanov and N. S. Kochetkova, *Dokl. Akad. Nauk SSSR*, **126**, 307 (1959).

13) A. N. Nesmeyanov, N. S. Kochetkova and R. B. Materikova, ibid., **136**, 1096 (1960).

14) A. N. Nesmeyanov, N. S. Kochetkova, P. V. Petrovsky and E. I. Fedin, ibid., **152**, 875 (1963).

15) S. I. Goldberg, *J. Am. Chem. Soc.*, **84**, 3022 (1962).

16) Evidence for such reaction coures not only in $AlCl_3$-catalyzed condensations, but even in the conventional cases employing $ZnCl_2$, rests on the broad, albeit weak proton signals occasionally observed near τ 8 in the NMR spectra of oligomeric fractions.

17) K. Schlögl and A. Mohar, *Monatsh. Chem.*, **92**, 219 (1961).

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

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

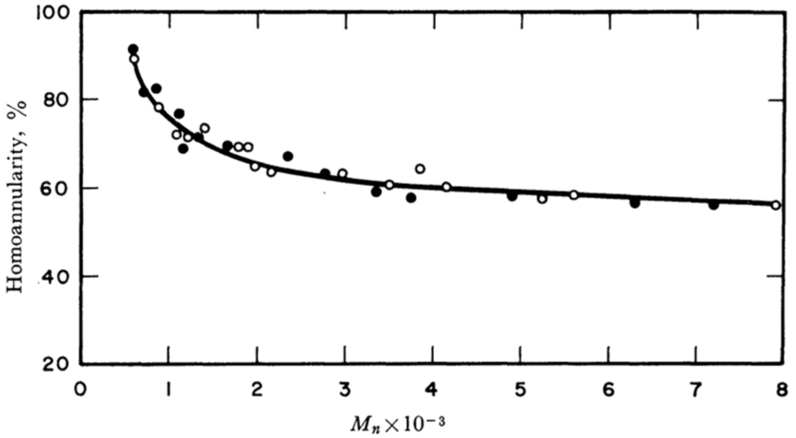

Fig. 1. Percent-homoannularity vs. number-average molecular weight for polymer II prepared by co-condensation of ferrocene with:
Formaldehyde (filled-in circles);
N, *N*-Dimethylaminomethylferrocene (open circles).

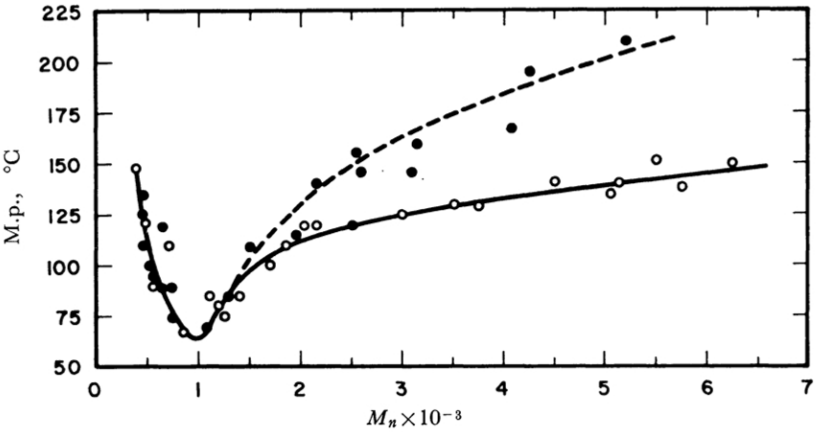

Fig. 2. Melting point vs. number-average molecular weight for polymer II prepared by co-condensation of ferrocene with:
Formaldehyde (dashed line, filled-in circles);
N, *N*-Dimethylaminomethylferrocene (solid line, open circles).

on subfractionated samples. As expected, the curve passes through a minimum in the oligomer range. In the M_n range above ~1500, it ascends more steeply than does the corresponding curve replotted for the Mannich base-ferrocene polycondensation product,³⁾ pointing to some structural differences to be discussed below.

Discussion

If, in the reaction of ferrocene with formaldehyde or its dimethyl acetal, one assumes the intermediary occurrence of hydroxymethylferrocene or its methyl ether, methoxymethylferrocene, much as in the analogous case of ferrocene-benzaldehyde condensation,²⁾ the various propagation and termination steps comprised by the summarizing Eqs. 1 and 2 may be visualized as follows:

The primary step is the Lewis acid-catalyzed generation of ferrocenylcarbinyl cations from hydroxymethyl- or methoxymethylferrocene. For these cations, in principle, the same four reaction steps are available as in the self-condensation of ferrocenyl carbinols discussed at greater length elsewhere.¹⁹⁾ However, because of the low instantaneous concentrations of the hydroxymethyl- or methoxymethylferrocene intermediate expected under the experimental conditions (their further reaction proceeding at a rate considerably higher than their rate of formation²⁾), the first two of these reaction steps, interaction with oxygen-containing species, will be irrelevant as compared to the third step, nuclear substitution of oxygen-free species. The latter step comprises the primary reaction of the cation with free ferrocene present initially in large excess over carbinol, ether or polynuclear species. The arising dinuclear derivative, diferrocenylmethane (II, $n=1$), will now compete with ferrocene for further nuclear attack by the carbinyl cation, thus resulting in trinuclear and, as propagation proceeds, in polynuclear II. In this propagation step, the effects of the methylene group on the position of the entering ferrocenylmethyl substituent will be much the same as those operative in the analogous Mannich base - ferrocene polycondensation,(3) an assumption which is borne out by the coinciding percent-homoannularity - M_n plots for the two polymer series (Fig. 1). In addition to the prevalent propagation step involving electrophilic attack by the ferrocenylcarbinyl cation on ferrocene and the oligomeric and polymeric homologs of II, primary reaction of aldehyde or acetal with ferrocene units of II to give methylol- or methoxymethyl-substituted II must be expected in an advanced stage of the condensation. The cations generated therefrom may react intramolecularly, i. e., in a terminating self-substitution reaction (step 4 in the earlier quoted paper(19); cf. restrictions discussed therein), resulting in double-bridged segments.(18) Competing with this self-substitution, they may also react intermolecularly, i. e., by attack on a different polymer molecule. If both the cationic site and the ferrocene unit attacked are in terminal position, as expected to be the predominant case during an early stage of the reaction, the result will be linear chain extension. In an advanced stage, with increasing probability of cationic site and/or attacked ferrocene unit being in an internal position, side-chain or crosslink formation will result. The occurrence of side-chain and inter-chain methylene bridging as a result of the latter reaction course must be expected accordingly in all higher-molecular fractions and is manifested experimentally in both the aforementioned trend of the curve in Fig. 1 and the higher ordinate values (in the M_n range beyond $\sim$1500) of the curve in Fig. 2 (filled-in circles) as compared to the corresponding plot (open circles) for the Mannich base-derived polymer. Such side-chain and inter-chain methylene bridge formation will become progressively important as excess aldehydic reactant is employed at elevated temperatures. The increased amounts of crosslinked polymer isolated in such typical experiments mentioned initially in which molar acetal/ferrocene ratios of 1.4—2.0 were employed at temperatures ranging from 170 to 180°C bear out this expectation.(20)

Considering the low average molecular weight range, notably of the second fractions, attained under the conditions of our closed-system experiments, it was of interest to investigate the possibility of post-condensing these low-molecular-weight products with aldehydic reactant. Such post-condensation would be expected to proceed as pointed out above, viz. through formation of methylol- or methoxymethyl-substituted II, followed by nuclear attack of the cations arising therefrom on a different polymer chain, thus resulting in distinctly increased molecular weights. In a series of experiments employing fractions of polymer II with M_n in the low 300—800 range the feasibility of such post-condensation could indeed be demonstrated. Again, the zinc chloride-catalyzed reactions were conducted in a closed-system under conditions similar to those applied in the primary condensations, formaldehyde being employed as its dimethyl acetal in concentrations ranging from 0.5 to 2 mol. per mol. of oligomer employed. A typical experiment is summarized as No. 9 in Table I. The analytical data collected for the reaction product in Table II show that the starting material, a fairly monodisperse fraction with M_n 780, was largely converted to higher-molecular polymer still exhibiting the elemental composition of II. These results suggested the direct utilization, without prior removal of the unreacted ferrocene, of the very low-molecular, crude second fractions obtained in experiments of the types listed as Nos. 1 through 7 in Table I. The post-condensation of such fractions, with concomitant partial consumption of the admixed ferrocene, is demonstrated by experiment No. 10. By circumventing the time-consuming removal of ferrocene by sublimation from the remainder of oligomers in the second fractions, the possibility of such post-condensations of ferrocene-containing oligomer batches may add to the economy of the closed-system condensations here described.

Experimental

Materials and Analytical Procedures.—*s*-Trioxane, paraformaldehyde and formal (dimethoxymethane) were used as received from commercial sources. Zinc chloride, ferrocene and solvents, all commercial products, were purified as described.(18,19) Procedures for elemental and instrumental analyses have also been presented earlier.(3,18)

Polycondensation Reactions.—The experiment described below, summarized as No. 4 in Tables I and II, exemplifies the conventional syntheses in which

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20) While the products arising from branching and single-bridge crosslinking reactions cannot be distinguished by elemental analysis from linear II, the self-substitution products (and also those structures arising from multiple inter-chain bridging), possessing additional methylene groups, deviate in composition from II and thus lend themselves to analytical characterization, provided the number of such methylene groups additionally incorporated is large enough to exceed the experimental error limits of analysis. As a typical example of products which elemental analyses show to contain double-bridged segments, i. e., CH_2 bridges in excess over the number required for structure II, the experiment listed as No. 7 in Table I was mentioned above.

the aldehydic component was employed as the acetal.[21] The reactor was a stainless steel-lined, high-pressure autoclave of 1 l. capacity, equipped with mechanical stirrer, thermometer well and thermocouple, bleeding valve, and a special safety head (rupture disc tested to 3500 psi). The vessel was flushed with dry nitrogen and was charged with the mixture of 372.1g. (2.0 mol.) of ferrocene and 18.6 g. of anhydrous zinc chloride previously ground together in a dry-box. Upon the addition of 183.0 g. (2.4 mol.) of dimethoxymethane pre-cooled to 0°C, the sealed autoclave was heated with stirring for 9 hr. at 170±2°C. The reaction product was thoroughly digested and washed with water and, after drying, was reprecipitated from benzene solution (280 ml.) by 2-propanol (4 l.). Reprecipitation in the same manner gave a yellow solid which was washed with 2-propanol and vacuum-dried for 10 days at 60°C. This portion of polymer II, 159.6 g. (40.5% yield), is listed as lst fraction in Table II. From the combined and concentrated mother-liquors and washings, a mixture of oligomeric II and ferrocene was precipitated by excess water. From the dried product, ferrocene was removed by vacuum sublimation (81.7 g. recovered). The orange-yellow residual solid, 79.0 g. (20.4% yield), is listed in Table II as 2nd fraction. In a parallel experiment, 65.0 g. of the crude second precipitate still containing the admixed ferrocene was chromatographed in the manner described in detail loc. cit.[3] to give 32.40 g. of ferrocene, m. p. 173—176°C; 14.65 g. of diferrocenylmethane, m. p. 143—146°C; and 5.86 g. of crude trinuclear isomer mixture, melting range 95—145°C.

Subfractionation of II was accomplished by fractional precipitation and crystallization as discussed previously,[3] employing a polymer batch containing portions of the first and second fractions stemming from runs No. 4 and 5. The 16 subfractions collected, with M_n values ranging from 410 to 9850, gave elemental analyses consistent with II and showed the same infrared spectroscopic and solubility behavior as did the analogous fractions of the Mannich base - ferrocene polymer.[3] Some of these fractions were used for the viscometric measurements and the plots in Figs. 1 and 2.

For analytical rather than preparative purposes, several condensations were conducted using glass ampoules or stainless steel tubes in lieu of the high-capacity autoclave. Batch sizes for glass-tube reactions ranged from 5 to 30 g., whereas the steel tubes allowed for 50—200 g. batches. The solid components were well ground together in a dry-box and were placed in the tubes inserted into a dry ice - acetone bath. Upon addition of the liquid acetal (when using the solid paraformaldehyde or trioxane, all components were directly mixed and charged into the tube), the tube contents were frozen and degassed in the conventional manner. The re-cooled tubes were then flushed with dry nitrogen, sealed and heated in a thermo-regulated aluminum block, and the reaction products were worked up as described. These products showed no essential deviations in elemental composition from the corresponding polymers prepared in autoclave reactions.

Post-condensation of Oligomeric II with Formaldehyde.—The experiment described here, listed as No. 10 in Table I, may illustrate the post-condensations of low-molecular II. The well-ground mixture of 40.0 g. of anhydrous zinc chloride and 400.0 g. (1.563 mol.) of oligomeric II still containing ferrocene (M_n 260) was placed in the nitrogen-flushed autoclave. Upon the addition of 76.09 g. (1.0 mol.). of pre-cooled dimethoxymethane, the vessel was closed and heated at 170±2°C for 10 hr. with stirring as described. The reaction product was worked up in the conventional manner. The first and second fractions obtained in yields of 240.6 g. (58.1%) and 109.3 g. (26.7%) respectively, showed the melting point and analytical data collected in Table II.

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21) Experiments employing formaldehyde in its solid, polymeric form (paraformaldehyde, *s*-trioxane) rather than as its acetal were conducted in the same manner as described above, except that the pulverized aldehyde was immediately ground together with ferrocene and catalyst. In these reactions, large amounts of insolubles were formed, and the polymers, obtained in yields up to 50%, showed elemental compositions less satisfactory than in the ferrocene-formal condensations tabulated. A typical reaction product (6 hr., 170°C, 10% ZnCl$_2$, equimolar ratio ferrocene/trioxane) analyzed as follows: C, 67.50; H, 5.23, Fe, 25.99%; M_n, 1960 (calcd. for II: C, 66.51; H, 5.12; Fe, 28.37%).