FERROCENE-CONTAINING POLYMERS. A REINVESTIGATION OF THE POLYRECOMBINATION OF FERROCENE

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INTRODUCTION

Recently, the groups of Korshak[1,2] and Nesmeyanov[3] reported the successful synthesis of polyferrocenylenes (I) with molecular weights up to 7000*, utilizing the polyrecombination reaction previously discovered by Korshak[6,7] and demonstrated in a great number of publications[5-11]. In these reactions, *tert*-butyl peroxide was thermally decomposed at ~ 200° to give *tert*-butoxy and methyl radicals[12,13] according to eqns. (1) and (2).

$$(CH_3)_3C-O-O-C(CH_3)_3 \rightarrow 2 (CH_3)_3CO^\bullet \tag{1}$$

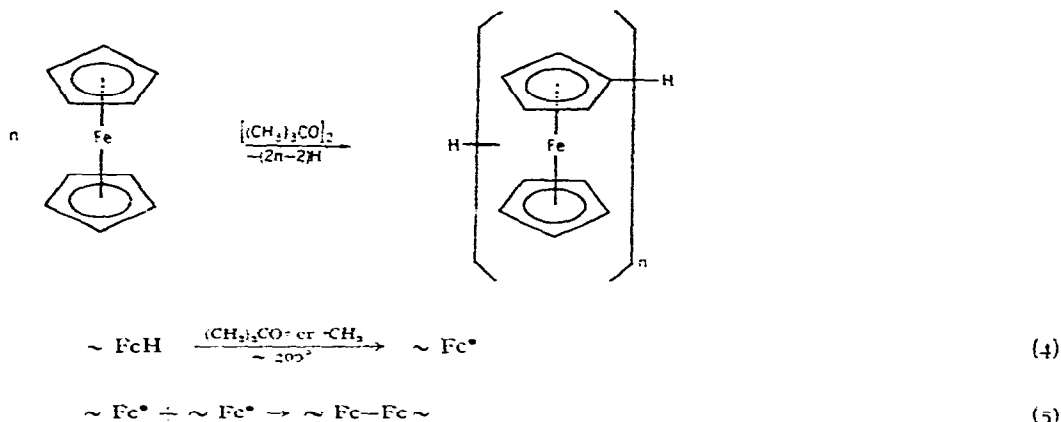$$(CH_3)_3CO^\bullet \rightarrow (CH_3)_2CO + {}^\bullet CH_3 \tag{2}$$

These radicals, by abstracting a hydrogen radical from other reactants, were converted to *tert*-butanol and methane, respectively. With ferrocene being the co-reactant, the mechanism proposed by Nesmeyanov and Korshak[3] involved the formation of ferrocenyl radicals, followed by recombination of two such radicals to give biferrocenyl. Hydrogen radical extraction from this dinuclear compound and combination of the resulting radical species with a ferrocenyl radical would then give a terferrocenyl. Further propagation, brought about by continuation of this process, would be progressively enhanced by involvement of increasingly polynuclear combination partners. For the overall polymerization process, summarized in eqn. (3), Korshak's proposed mechanism** may be depicted by eqns. (4) and (5), in which Fc

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* In a different publication[4], Korshak quotes a polyferrocenylene having the unusually high molecular weight 50,000. However, the lack of substantiating experimental data in this communication, coupled with our own contrasting experience on such products, lends little credence to Korshak's statement. See also Spilners[5] who, by a different process, obtained oligomeric polyferrocenylenes with M_n up to ~ 1500.
** Several workers have pointed out the unfeasibility of radical attack on the neutral ferrocene molecule[14-17]. At the same time, the ease of free-radical phenylation of ferricinium ion[14] (HFcH+ + Ph· → HFc–Ph + H+, where Ph = phenyl) was demonstrated[16]. The analogous reaction involving ferricinium ion and ferrocenyl radicals should correspondingly give a polynuclear ferrocene (HFcH+ + HFc· → HFc–FcH + H+). While, in the presence of the peroxide, some ferricinium will doubtlessly be formed and may well be involved in further reactions of this type, it appears unnecessary to invoke this ferrocenylation of ferricinium ion as the principal mechanism, since there is no reason to assume that the neutral ferrocene species should be less susceptible to hydrogen radical extraction by butoxy or methyl radicals than are the various benzene–aromatic systems[7,10] successfully subjected to analogous reactions at the same high temperature level.

stands for the (disubstituted) ferrocenylene ($C_{10}H_8Fe$) unit and the undulated line denotes a residual ferrocenylene polymer chain (hydrogen in the simplest case involving monomeric ferrocene).

$$\sim FcH \xrightarrow[\sim 205^\circ]{(CH_3)_3CO\cdot\ or\ \cdot CH_3} \sim Fc^\bullet \tag{4}$$

$$\sim Fc^\bullet + \sim Fc^\bullet \rightarrow \sim Fc-Fc \sim \tag{5}$$

Our general interest in ferrocene-containing polymers prompted a duplication and re-examination of the Russian work with the objective of providing a ferrocene polymer that would be devoid of non-ferrocene chain constituents and, hence, would be useful as a polynuclear model compound for comparison with other polymeric ferrocene derivatives synthesized in this laboratory.

RESULTS AND DISCUSSION

The synthetic procedure employed in the present investigation had to be worked out on the basis of the rather uninformative literature disclosures lacking detailed experimental data. As a consequence, the first attempts in this laboratory to achieve polyrecombination under a variety of conditions in open and closed systems were unsuccessful or, at best, produced trace quantities of soluble polymers. In addition, the difficulty of properly controlling the reactions frequently resulted in explosive decomposition of the peroxide with concomitant ignition of the vapors, and drastic precautions had to be taken to prevent damage or injury. The results of these early experiments suggested the following prerequisites for successful poly-recombination: (*1*) gradual addition of the peroxide to the molten ferrocene at temperatures in the 200–205° range in the absence of oxygen; (*2*) employment of a large ferrocene excess; (*3*) rapid distribution of the added peroxide in the melt to keep instantaneous butoxy radical concentrations low and, thus, minimize such side-reactions as butoxy radical recombination with formation of acetone and *tert*-butoxy-methane[2]; (*4*) speedy removal from the melt of such low-boiling by-products as *tert*-butanol and acetone, to minimize incorporation of these compounds into the polymers.

In the procedure eventually employed (see EXPERIMENTAL) these findings were taken into account, and the results with respect to polymer yields, molecular weights and elemental composition compared well with those of Korshak and Nesmeyanov. The experimental conditions for 7 typical polyrecombination reactions are

summarized in Table 1. The reactions were conducted by introducing *tert*-butyl peroxide into the ferrocene melt over the addition periods tabulated; the molar ferrocene/peroxide ratios varied in the range from about 0.3 to 0.8. Heating was terminated after completion of the peroxide addition. The reaction products were extracted with pentane to remove ferrocene and other monomeric and oligonuclear compounds. The soluble polymer portions were then extracted with benzene and were separated by precipitation with isopropanol. Molecular weight, yield and analytical data for these polymers are listed in Table 2. Small, additional portions of oligomeric products, usually no more than 5–15 % of the major polymer portions, were isolated from the mother-liquors, but were not specifically tabulated. (The yields of these oligomers are included in the total product yield figures of Table 1.)

The tabulated findings confirm the aforementioned requirements of low instantaneous butoxy radical concentration and large ferrocene excess. Thus, while optimum yields (up to ~ 27 %) were attained at ferrocene/peroxide ratios in the range 0.44–0.52, large amounts of insolubles were collected at the expense of soluble polymer in experiments conducted at reactant ratios below ~ 0.4, especially where high peroxide addition rates were employed (Nos. 6, 7). With other conditions equal, the effect of total reaction time (period of peroxide addition) on soluble polymer yields is seen in run No. 5 as compared with No. 4, slower addition rates leading to increased yields.

The most conspicuous feature of the tabulated analytical data is the marked difference between the found elemental compositions and those calculated for (I). The invariably low iron and high hydrogen percentages indicate rather high contents in non-ferrocene moieties in these recombination products much as in the equally composed polymers obtained by Korshak and others. (Only in a single instance[2] have elemental analyses been given in the literature, these data being in the same general range as reported in Table 2.) While the number of experiments conducted is too small to permit clear-cut conclusions, it appears that increased incorporation of such non-ferrocene constituents into the polymer chain results from ferrocene/peroxide ratios below 0.4.

The infrared spectra of subfractionated samples showed, in addition to the common bands of the ferrocene system, moderate absorption in the regions typical of methylene and methyl groups, with broad bands appearing in the 3.35–3.50 μ region (stretching) as well as near 6.9 and 7.3–7.4 μ (deformation). Furthermore, weak aliphatic ether absorption appeared at 9.5 μ. The spectra of lower-molecular fractions showed the aliphatic bands in enhanced resolution, exhibiting peaks at positions (3.37, 3.42, 3.49, 6.85–6.90, 7.28, 7.40 and 8.35 μ) suggestive of *tert*-butyl groups. The presence of aliphatic (methylene and methyl) groups was also indicated in the NMR spectra of low- and high-molecular fractions, broad signals appearing near τ 8.0 and 8.7.

With this spectroscopic evidence strongly suggesting the involvement of radical fragments stemming from the peroxide, it was of interest to search for defined, monomeric by-products whose identification might allow some inferences regarding the structural nature of these non-ferrocene moieties in the polyrecombination products. To this end, the pentane extracts from the crude reaction products (see above) were chromatographed on alumina. In a typical run, employing the pentane extract obtained in experiment No. 5, the band following the ferrocene zone gave a

crude biferrocenyl from which a slightly more soluble contaminant, m.p. 145–146°, was separated by repeated recrystallization. Elemental and spectroscopic analyses and comparison with an authentic sample[18] identified this compound as diferrocenylmethane (II).

A second ferrocene derivative, m.p. 76–77°, was isolated from a subsequent chromatographic band. The infrared spectrum of this compound, in its essential features, resembled that of *tert*-butylferrocene (sample kindly furnished by Dr. T. LEIGH, Imperial Chemical Industries, Ltd., Macclesfield, Cheshire, England) showing the typical stretching (3.37, 3.43 and 3.48 μ) and deformation (6.80, 7.25, 7.38, 8.10 and 8.35 μ) modes of the *tert*-butyl group. The 8.35-μ peak was superimposed by strong ether absorption, as was the 9.65-μ ferrocene band. On the basis of this spectroscopic behavior, coupled with elemental analyses and molecular weight determinations, the product was assigned structure (III) (ferrocenylmethyl *tert*-butyl ether).

This assignment was corroborated by proton magnetic resonance. The NMR spectrum showed singlets at τ 5.93 (combined ferrocene and methylene protons) and 8.76 (equivalent methyl protons) in the ratio 10.6:9.0. The strong downfield shift of the methylene proton signal, resulting from the deshielding effect exerted by the adjacent oxygen, is of the same order as that observed with other ferrocene compounds possessing an alkoxymethylene substituent, *e.g.*, bis(ferrocenylmethyl) ether. For unambiguous structural proof, (III) was synthesized independently by etherification of ferrocenylcarbinol[19] with *tert*-butanol.

In addition to (II) and (III), the chromatogram provided, in overall yields of 1–2 %, three ferrocene derivatives that were shown by elemental analyses and molecular weight determinations to be isomeric terferrocenyls (I, $n = 3$). One of these isomers, melting at 196–197°, was identified as 1,3-diferrocenylferrocene by comparison with an authentic compound prepared in an independent study[20]. While the remaining two isomers, m.p. 226–228°, and 260–265°, have not yet unambiguously been identified (*cf.* Hata[21], Nesmeyanov[22], Huffman[23]), the fact that all three isomers were isolated indicates that radical attack occurred on all three possible sites (2-, 3-, 1'-). This principal availability of both homo- and heteroannular sites for further radical attack must be considered as a factor effectively preventing unlimited linear chain growth in favor of side-chain and, ultimately, crosslink formation as indeed observed in more advanced stages of the reaction.

The formation of by-products (II) and (III) can be rationalized in terms of a mechanism involving methylferrocene as intermediate, the latter having arisen via methyl radicals. (Analogous methylation of benzene-aromatic compounds in the presence of *tert*-butyl peroxide was observed by Korshak[10].) Although we were unable to isolate this derivative, its presence was indicated by the appearance of a peak with mass number 200 in the mass spectrogram of the crude ferrocene eluted from the chromatogram. (The adsorptivity of methylferrocene on alumina being very close to that of ferrocene itself, the small quantities of this derivative in the large excess of ferrocene are likely to be eluted together with the parent compound.) Rapid extraction of an aliphatic hydrogen radical from this compound may be expected; coupling of the resultant, stabilized[24] ferrocenylcarbinyl radical with ferrocenyl or butoxy radicals will then give (II) (and (III), respectively.

The isolation of these aliphatic ferrocene derivatives as by-products permits the conclusion that the regular polyrecombination process of eqn. (3) is superimposed by

several significant side-reactions* involving the radicals (IV)–(VII) and related species as well as their corresponding polyhomologs. These radical intermediates, arising by extraction of a hydrogen radical from methylferrocene, diferrocenylmethane and, above all, such ethers as (III), may recombine with a ferrocenyl or polyferrocenylene radical, thus introducing methylene and methinyl bridges as well as ether groupings of the types $-CH_2-O-C(CH_3)_2-CH_2-$ and $-CH=O-C(CH_3)_3-$ into the polymer chains. For the products obtained one may, hence, propose a structure comprising short polyferrocenylene segments that are interlinked by aliphatic bridging groups of the mentioned types. The found elemental polymer compositions listed in Table 2, indeed, agree well with the composition calculated for a polymer chain containing, for example, one $-CH_2-O-C(CH_3)_2-CH_2-$ bridge for every three ferrocenylene units (footnote b, Table 2). The poor hydrolytic and thermal stabilities of the polymers (see EXPERIMENTAL), unexpected for a fully aromatic, conjugated system, may also be traced to such non-ferrocene chain segments.

The findings discussed in the foregoing clearly demonstrate that the polyrecombination reaction of ferrocene in the presence of *tert*-butyl peroxide cannot be utilized for the preparation of pure polyferrocenylene. Efforts directed toward the development of more suitable syntheses will be dealt with in forthcoming publications.

EXPERIMENTAL

Analytical procedures, materials

Temperatures are given in °Centigrade. Melting points, uncorrected, were taken up to 300°. Number-average molecular weights were measured in benzene solution on a Mechrolab Model 301A Vapor Pressure Osmometer,; findings were recorded as mean values from duplicate determinations and were rounded off to the nearest 10. Infrared spectra were recorded on KBr pellets, employing a Perkin–Elmer, Model 521, Spectrophotometer equipped with grating optics. Mass spectra were recorded by the Petroleum Analytical Research Corporation, Houston, Texas, at 70 ev ionizing voltage. A Varian Associates Model A-60 NMR spectrometer operating at 60 Mc/sec. was employed for recording the high-resolution proton magnetic resonance spectra; the solvent was deutero-chloroform. Chemical shifts, τ, are given in ppm relative to tetramethylsilane as internal standard. Thermogravimetric analyses were performed on a du Pont Model 900 Thermoanalyzer at a heating rate of 15°/min. All other analyses were conducted as described[25].

Ferrocene, commercially available, was purified by chromatography on alumina in hexane solution; m.p. 173–175°. *tert*-Butyl peroxide, reagent grade, was used without further purification.

Polyrecombination of ferrocene

The reaction conditions for seven typical recombination experiments are summarized in Table 1. As an example, the experiment listed as No. 1 is described below.

Dry ferrocene, 60.0 g (0.322 mole), was placed into a 100-ml round-bottom,

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* The importance of these side-reactions results from the enhanced rates at which radical species of the types (IV)–(VII) will arise from their corresponding parent compounds (despite the low concentrations of the latter), as compared to the relatively low rate of hydrogen extraction from the aromatic ferrocene or polyferrocenylene species.

I

II

III

IV

V

VI

VII
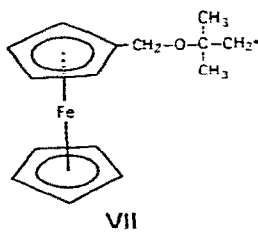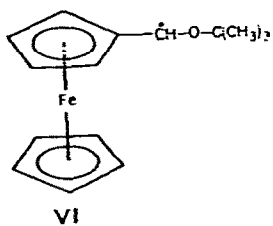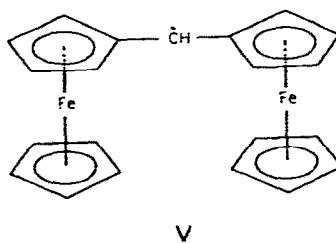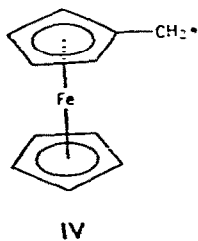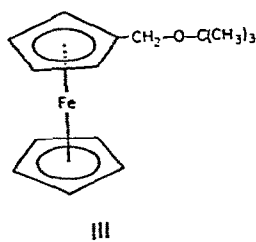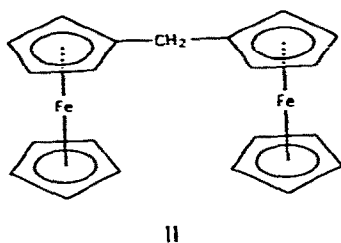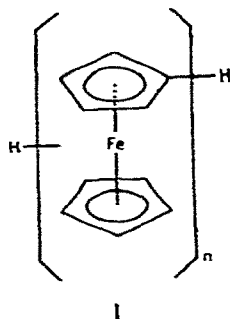
three-neck flask equipped with mechanical stirrer and equalizing dropping funnel, with the stem of the latter reaching below the surface of the charge. A distillation head, with its upper opening sealed by a glass stopper and its descending side-arm leading into a receiver flask cooled by a dry-ice bath, was fitted to the third neck. A nitrogen source was connected to the dropping funnel, and the latter was charged with 58.72 g (0.403 mole) of *tert*-butyl peroxide. After preheating the flask in an oil bath to 205° and flushing the system with nitrogen, peroxide addition was started at a rate of about 20 g per h. Throughout the addition, a steady stream of nitrogen was maintained, entering through the equalizing system of the dropping funnel and leaving through the distillation head. In this manner, the current aided in removing the low-boiling by-products, acetone and *tert*-butanol, which were collected along with some unreacted *tert*-butyl peroxide in the receiver flask and were identified by vapor phase chromatography. In this and all other instances, the major component of this distillate was found to be *tert*-butanol (50–60%), followed by *tert*-butyl peroxide (30–40%), acetone (2–5%) and other unidentified products (10–25%).

TABLE I

POLYRECOMBINATION OF FERROCENE

No.	Molar ratio ferrocene: peroxide	Rate of peroxide addition (g/h)	Total heating time[a] (h)	Temp. (°C)	Total polymer yield (%)	Insolubles (%)[b]
1	0.80	20	---	205	12.9	0.5
2	0.60	30	7.0	205	19.5	0.3
3	0.52	47	3.3	200	22.9	0.2
4	0.44	21	8.7	200	21.7	0.5
5	0.44	16	11.2	200[c]	20.8[c]	0.8[c]
6	0.39	30	7.0	200	13.2	58.0
7	0.31	28	9.0	200	9.2	69.8

[a] Period of peroxide addition for 100-g ferrocene batch. [b] By weight of ferrocene. [c] At reaction temperatures of 220 and 245°, yields in soluble polymer (insolubles in parentheses) were 20.6% (12.6%) and 9.8 (33.1%), respectively.

The reaction product was Soxhlet-extracted with pentane to remove ferrocene and oligomers. The residual reddish-brown solids were dissolved in 100 ml of benzene, and the solution, filtered from 0.08 g of dark-brown residue, was poured into vigorously stirred excess isopropanol (ca. 500 ml). The collected precipitate was washed with isopropanol and dried as before, to give 6.5 g (10.9%) of brown, powdery product. M_n value and analytical data for this first fraction are listed in the first line of Table 2. The fraction, with melting range 250–260° (sealed), showed complete solubility in dioxan, chloroform and benzene. The mother-liquor, combined with the isopropanol washings, was concentrated to one-half its original volume and was poured into excess water. Upon the addition of 5 ml of concentrated hydrochloric acid to facilitate flocculation, the suspension was briefly shaken and the precipitated solid was filtered off, thoroughly washed with water and dried as before. This second fraction, 1.20 g (2.0%), showed the melting range 110–130°; M_n, 910. (Found: C, 68.23; H, 5.55; Fe, 25.05. $C_{30}H_{42}Fe_5$ calcd.: C, 65.13; H, 4.59; Fe, 30.28%.)

The concentrated pentane extract was subjected to chromatographic separation as described below for the pentane extract of experiment No. 5, to give 40.2 g of ferrocene (67.0 % recovery), 4.0 g (6.7 %) of biferrocenyl, and *ca.* 0.8 g of other mono- and oligonuclear products.

TABLE 2

COMPOSITION OF POLYMER (I)

No.	$M_n{}^a$	Yield (%)	Anal. calcd. for $(I)^b$ (%)			Anal. found (%)		
			C	H	Fe	C	H	Fe^a
1	3850	10.9	65.23	4.43	30.33	64.40	5.19	25.69
2	5370	18.1	65.24	4.42	30.34	65.87	5.37	25.61
3	6210	21.6	65.25	4.41	30.34	64.28	5.24	25.44
4	6500	21.5	65.25	4.41	30.34	63.94	5.26	25.42
5	6150	25.6	65.25	4.41	30.34	64.27	5.33	25.77
6	8120	12.2	65.25	4.41	30.34	67.85	5.46	24.20
7	4700	7.8	65.24	4.42	30.34	67.55	5.49	24.41

^{a} Mean value from duplicate runs. ^{b} For comparison, the calculated values for a polymer segment, $C_{35}H_{34}OFe_3$, containing a $-CH_2-O-C(CH_3)_2-CH_2-$ bridging group along with three ferrocenylene units are: C, 65.87; H, 5.37; Fe, 26.25%.

Subfractionation

Several first fractions obtained from experiments that were conducted under the conditions of Nos. 3–5, Table 1, were subfractionated by reprecipitation in the conventional manner from benzene solution at 25 ± 1°. The precipitant was hexane. The products, dried for 7 days *in vacuo* at 40°, were light-brown powders (the highest members dark-brown) possessing an elemental composition essentially identical with that of the parent polymer. Generally, out of the total number of 15–20 subfractions thus obtained, the first three to five, after drying, were no longer completely soluble in benzene or dioxan. The remainder of the subfractions, still completely soluble, showed M_n values from 900 to about 10,000 and could be cast or sprayed from their solutions into brittle, transparent films. The lower members, with $M_n < 3000$, were fusible or partially fusible up to 300°.

Some of the subfractions, along with their parent polymers, were tested for hydrolytic and thermal stabilities. The former was determined by refluxing a 100-mg sample for 24 h in water and determining the percentage of product that had become insoluble in benzene after this treatment. While biferrocenyl retained complete solubility, 50–70 % insolubles were found for samples with $M_n > 2500$. The thermal stability was determined by thermogravimetric analysis in argon atmosphere. The thermograms for all samples showed incipient weight loss at about 300; the curves reached the 70-% residual weight mark near 500° and leveled off at 62–66 % residual weight in the vicinity of 600°.

By-products (III) and (IV), terferrocenyls

The chromatographic treatment of the pentane extract stemming from the various experiments listed in Table 1 is illustrated by the procedure described below, employing the pentane-soluble portion from run No. 5.

The pentane extract from an experiment with 100 g of ferrocene used as starting material was evaporated to dryness in a rotating evaporator. The residual, semi-crystalline mass was taken up in hexane and was chromatographed on 2800 g of Alcoa grade F-20 activated alumina, using hexane as eluent. From the first band eluted there was collected 43 g of crude ferrocene. The second band contained 4.5 g of crude biferrocenyl which, after several recrystallizations from heptane, melted at 236–239° (sealed); mixed m.p. with authentic product[26] undepressed. (A sample was kindly supplied by Dr. RAUSCH.) From the final biferrocenyl mother-liquors, 0.09 g of a second crystalline component, m.p. 145–146°, was isolated. The compound was identical by X-ray diffractogram and mixed m.p. with diferrocenylmethane (II) prepared by a different procedure[18]. (Found: C, 65.70; H, 5.29. $C_{21}H_{20}Fe_2$ calcd.: C, 65.67; H, 5.25 %.)

The third band of the chromatogram gave 0.11 g (0.1 %) of a poorly soluble crude terferrocenyl, which after repeated recrystallizations from hexane was obtained as fine, orange needles melting at 260–265° (sealed). (Found: C, 65.40; H, 4.87; mol. wt. mass-spectr., 554. $C_{30}H_{26}Fe_3$ calcd.: C, 65.03; H, 4.73 %; mol. wt., 554.)

The final mother-liquors of the same fraction yielded a very soluble compound which was purified by sublimation, giving 0.030 g of yellow plates, m.p. 76–77°, of ferrocenylmethyl tert-butyl ether (III). The compound was independently prepared by etherification of ferrocenylcarbinol[19]. This was accomplished by heating 0.150 g of the latter with 5 ml of tert-butanol and a drop of 0.1 N tert-butanolic HCl for 1 h on the steam bath, evaporating the solvent and subjecting the solid residue to vacuum sublimation. There was obtained 0.045 g of product (III), m.p. 72–75°; no depression on admixture with the above compound. (Found: C, 65.90; 66.18; H, 7.53, 7.40; Fe, 20.25; mol. wt., 276. $C_{15}H_{20}OFe$ calcd.: C, 66.19; H, 7.41; Fe, 20.52 %; mol. wt., 272.)

The fourth chromatographic zone was eluted in two cuts. The first cut furnished 0.54 g (0.5 %) of red-orange needles of a terferrocenyl, which after repeated crystallizations from ethanol had m.p. 226–228° (sealed). (Found: C, 65.45; H, 4.80; Fe, 30.58; mol. wt. in dibromomethane, 556. $C_{30}H_{26}Fe_3$ calcd.: C, 65.03; H, 4.73; Fe, 30.24 %; mol. wt., 554.)

From the second cut of this band, there was isolated 0.14 g (0.13 %) of a third terferrocenyl isomer. Several recrystallizations from heptane furnished a product melting at 196–197° (sealed); no depression on admixture of authentic 1,3-diferrocenyl-ferrocene[20].

ACKNOWLEDGEMENTS

SUMMARY

Earlier work by Korshak and other Russian authors on the preparation of polyferrocenylenes by the recombination reaction of ferrocene in the presence of tert-butyl peroxide has been reinvestigated. It has been demonstrated that, under

carefully controlled conditions at temperatures near 200°, ferrocene can indeed be polymerized to give soluble polymeric compounds, comparable in molecular weight range and physical properties with Korshak's products. These polymers, however, possess overall elemental compositions distinctly differing from that of polyferrocenylene. Spectroscopic and elemental analyses, corroborated by the isolation not only of biferrocenyl and terferrocenyls, but also of diferrocenylmethane and ferrocenylmethyl *tert*-butyl ether as by-products, indicate the polymer chains to be composed of small polyferrocenylene segments interlinked by methylene and aliphatic ether groups. These bridging groupings are believed to have arisen through the involvement of methyl and *tert*-butyl radicals generated by thermal decomposition of the *tert*-butyl peroxide, with methylferrocene postulated as an additional intermediate. Consistent with the presence of such non-ferrocene constituents, the polymers exhibit poor hydrolytic stability and, in thermogravimetric analysis, show a thermal stability behavior inferior to that expected for a polymeric compound strictly composed of ferrocenylene units.

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