Ferrocene-containing Polymers. IV. Polymeric Ethers as Intermediates in the Self-condensation of Ferrocenyl Carbinols

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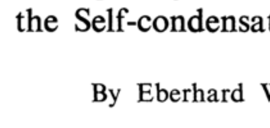
(Received September 26, 1964)

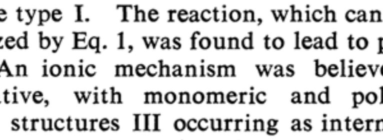
A previous paper[1] described the acid-catalyzed polycondensation of ferrocenyl carbinols of the type I. The reaction, which can be summarized by Eq. 1, was found to lead to polymers II.[2] An ionic mechanism was believed to be operative, with monomeric and polymeric[2] ether structures III occurring as intermediates. Monomers IIIa and IIIb were intercepted; however, under the experimental conditions chosen, no polymeric ethers IIId—f could be isolated.

In the present study, using carbinol Ic,[3] polycondensation reactions were conducted as before, but under milder experimental conditions, i. e., at lower temperatures and shorter reaction times in the presence of catalytic amounts of mineral acids or, less advantageously, organic acids.[4] The reaction could thus be controlled so as to give the postulated polymeric ether IIIf in addition to the monomeric main product IIIc.

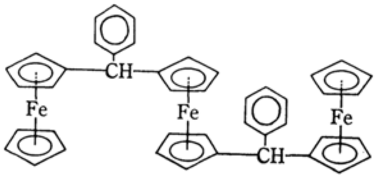


(1)

Ia, $R=H$ IIa, $R=H$
b, $R=CH_3$ b, $R=CH_3$
c, $R=C_6H_5$ c, $R=C_6H_5$



IIIa, $R=H$; R′, R″=H
b, $R=CH_3$; R′, R″=H
c, $R=C_6H_5$; R′, R″=H
d, $R=H$; R′, R″=residual polymer chain
e, $R=CH_3$; R′, R″=residual polymer chain
f, $R=C_6H_5$; R′, R″=residual polymer chain



IV

In a typical run, catalyzed by hydrochloric acid, Ic was heated under nitrogen for 15 min. at 95°C. After the catalyst had been removed by water extraction, the melt was separated into a major portion containing monomeric constituents and two small fractions of low-molecular-weight polymeric material. The polymeric fractions, obtained in a total yield of 4.0%, showed number-average molecular weights and analytical data[13] as listed in the first two lines of Table I. The findings are well in accord with the calculated composition of ether IIIf.

From the monomeric portion essentially consisting of ether IIIc, the latter was isolated by chromatography in a 83% yield[5] as a mixture of two diastereomers,[6] which were separated by fractional crystallization from hexane. The analytical data for both isomers are given in the last two lines of Table I. The less soluble species, constituting nearly 75% of the total IIIc, melted at 136—138°C and exhibited proton magnetic resonance signals at τ 2.72 (ten phenyl protons; singlet, broadening to the high-field side), 5.08 (two methine protons; singlet) and at 6.09 (18 ferrocene protons; singlet, broadening to the low- and high-field sides). The second, slightly

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

[2] The notation of the left-hand substituent in II (and also of R′ and R″ in III) was discussed earlier (Ref. 1).

[3] The bulkier R allows for more enhanced manifestation of compositional changes.

[4] Strong organic acids such as oxalic and *p*-toluenesulfonic acid, while giving similar results as mineral acids (if applied in somewhat higher concentrations), were frequently found to be partially incorporated into the polymer through esterification.

[5] 92% after 5 min. at 85°C. No IIIf isolated in this case.

[6] The possibility of polymorphism for the two species is ruled out by the difference in their high-resolution NMR spectra and the absence of heat-of-transition peaks in the differential thermogram. Only heat-of-fusion endotherms were shown at 110—112°C and 134—136°C, respectively. (DTA thermograms recorded by Mr. R. P. Colburn at a heating rate of 10°C/min. in argon, using a du Pont model 900 differential thermal analyzer). See also Ref. 8.

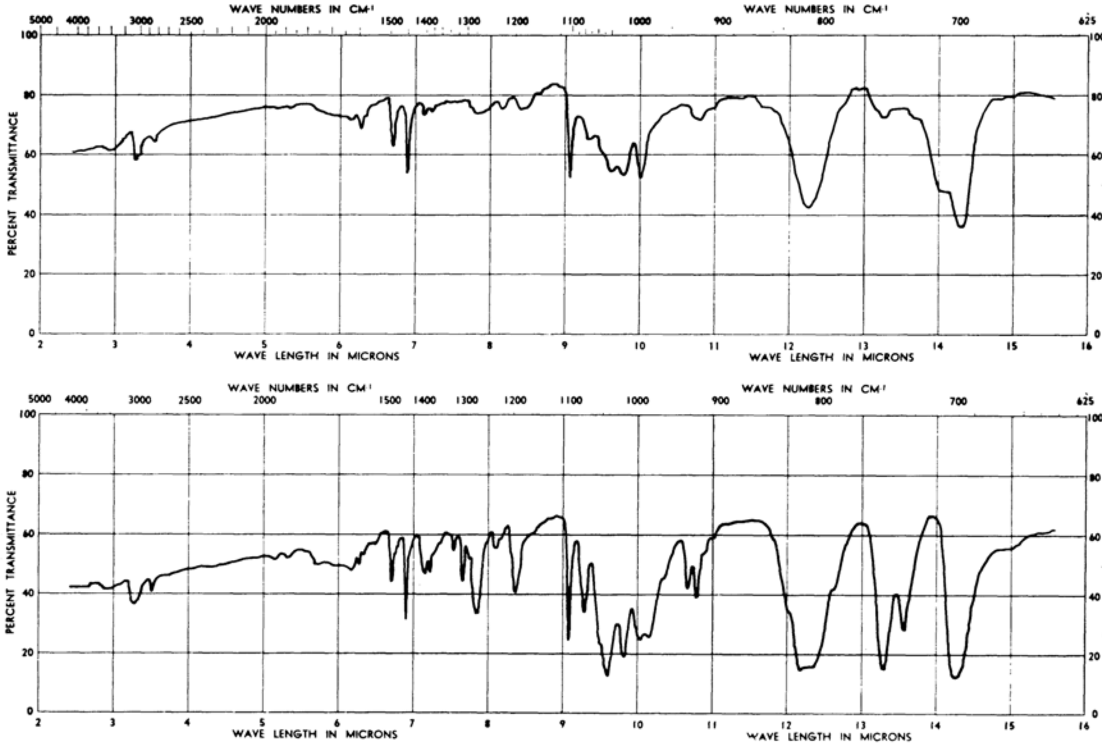

Fig. 1. Infrared spectra (KBr pellet) of:
Monomeric ether IIIc (lower curve)
Polymeric ether IIIf (upper curve)

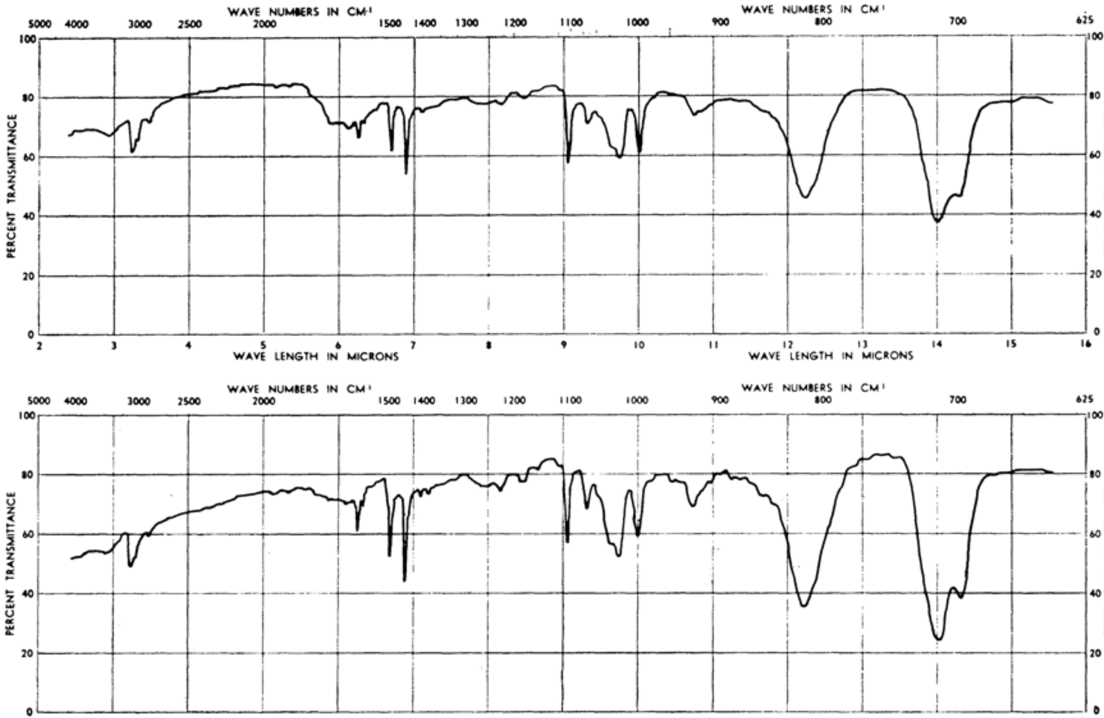

Fig. 2. Infrared spectra (KBr pellet) of:
Polymer IIc obtained by self-condensation of Ic (lower curve)
Polymer IIc obtained by post-condensation of IIIf (upper curve)

more soluble isomer,[7] melting at 111—113°C, gave NMR signals in the region τ 2.6—2.8 (ten phenyl protons; essentially a doublet structure with peaks at 2.68 and 2.76), at 4.95 and 5.08 (two methine protons; two peaks of an equal intensity), and in the region 5.9—6.2 (18 ferrocene protons; complex multiplet with two predominant peaks at 6.10 and 6.17).[8] The infrared spectra of both diastereomers IIIc, recorded on the solid compounds, were nearly identical. The spectrum of the higher melting isomer[9] is given in the lower curve of Fig. 1. Both species showed strong ether absorption at 7.85 and 9.60 μ and exhibited the typical intensity enhancement of the methine C–H stretching mode at 3.49 μ. Also strongly enhanced were the phenyl band at 8.40 μ and the 9.5-μ ferrocene band. In the skeletal range 10.7—11.0 μ, absorption was noticed at 10.80 μ. A characteristic, strong doublet appeared in the 13.5-μ region[10]; similarly intense was the phenyl δ_{C-H} band at 14.25 μ.

These spectroscopic correlations for monomeric IIIc served to corroborate the structural assignment of polymeric IIIf. The infrared spectrum of IIIf (Fig. 1, upper curve), besides showing the essential bands of the oxygen-free polymer IIc[1] presented in Fig. 2 for comparison (lower curve), exhibited low-intensity ether bands at 7.85 and 9.60 μ, the latter partially overlapping the 9.65-μ ferrocene band. Additional absorption appeared at 10.80 μ and in the 13.3-μ region, coupled with enhancement of the aforementioned bands at 3.49, 8.39 and 9.5 μ. The high intensity of the C–H deformation band at 14.25 μ, superimposing upon the analogous absorption shown in the 14.0—14.3-μ region by IIc, gave rise to a highly characteristic doublet pattern, with the high-wavelength peak dominating in intensity.

Further support of structure IIIf resulted from NMR data. The phenyl proton resonances appeared as a broad, poorly-resolved doublet, with a high-field peak near τ 2.82 corresponding to the signals of oxygen-free IIc (τ 2.86) or model compounds phenyldiferrocenylmethane[11] (τ 2.88) and 1, 1′-bis(phenylferrocenylmethyl)-ferrocene[12] (IV, τ 2.80), and a somewhat stronger low-field signal centered at τ 2.72 corresponding to the more deshielded signal average of isomers IIIc. Two separate methine resonances were shown; the weak high-field signal near τ 5.6 corresponds to the broad resonance at 5.5—5.7 in IIc and to the singlets at τ 5.40 in phenyldiferrocenylmethane and 5.49 in IV, whereas the more intense low-field peak at 5.03 is the counterpart to the average methine proton signal of IIIc. For a more quantitative evaluation of the relative intensities, IIIf was fractionally precipitated so as to give a subfraction with $M_n=830$, i. e., roughly composed of the trinuclear homologs (analytical data[13] given in third line of Table I). The integrated intensities of the phenyl/methine/ferrocenyl protons for this fraction were in the expected 15 : 3 : 26 ratio. The low-field/high-field phenyl proton ratio was ~1.4. Similarly, the low-field/high-field methine proton ratio was found to be ~1.3. Both ratios are lower than required for IIIf, suggesting contamination by IIc. The presence of IIc is not unexpected in view of the various competing propagation steps[1] operative even under the mild condensation conditions applied. Accordingly, enhanced proportions of IIc, coupled with higher M_n and increased yields

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[7] N. Weliky and E. J. Gould (*J. Am. Chem. Soc.*, **79**, 2742 (1957)) assigned structure IIIc to a compound with m. p. 52—56°C obtained by treating Ic with PBr_3. These workers also mentioned an unidentified by-product melting at 110—112°C. While under present experimental conditions the former substance was not isolated, the latter compound is probably identical with our isomer IIIc, m. p. 111—113°C.

[8] Assuming diastereoisomerism for both species IIIc, the three staggered conformations of the *d, l*-form will each give rise to a singlet signal in the methine proton region due to pair-wise equivalence of the two methine protons. At temperatures sufficiently high to ensure rapid interconversion and equal population of the conformers, one may thus expect a single time-average proton signal to occur in the mentioned region. For the meso-form, in contrast, the same temperature conditions will lead to two gauche conformers, each with two non-equivalent methine protons, which, hence, may give a doublet signal due to different shielding, and a trans conformer with two equivalent methine protons, exhibiting a singlet resonance. On this basis, it would appear tempting to assign the meso structure to the lower melting isomer. Such conclusion, however, would rest on the unproven and questionable assumption that the temperatute chosen for measurement (ambient) be high enough to preclude the occurrence of preferred conformations (e. g., trans with respect to methine H), and, hence, would have to be borne out by a study of the temperature function of the methine proton shifts.

[9] The isomer with m. p. 111—113°C exhibited additional weak absorption at 11.60 μ, but failed to show the small peak at 7.65 μ. Both compounds gave identical spectra in CS_2 solution.

[10] Also shown by the corresponding ethers with H or CH_3 in lieu of C_6H_5.

[11] Prepared by condensation of ferrocene with benzaldehyde (E. W. Neuse and D. S. Trifan, Abstr. of papers presented at 148th National Meeting, A. C. S., September 1964, p. 5 S.); identical in infrared spectrum and elemental composition with the compound described by Weliky and Gould (Ref. 7; infrared spectrum kindly furnished by Dr. Weliky).

[12] Prepared by Mrs. E. Carter in this laboratory; m. p. 190—193°C (sealed cap.). Found: C, 71.49; H, 5.38; Fe, 22.60, M_n, 720. Calcd. for $C_{44}H_{38}Fe_3$ (IV; mol. wt. 734.3): C, 71.97; H, 5.22; Fe, 22.82%. %-Homoannularity, 69.2; X-ray diffractogram, Å: 4.98; 5.57—5.65 (doublet); 6.79; 4.22; 5.37; 3.95.

[13] The percent-homoannularity values (for definition and experimental determination see Ref. 1) for fractions IIIf listed in Table I and other fractions of IIIf not mentioned in this paper were consistent with those for fractions of IIc in comparable molecular weight ranges. This identity is to be expected on account of like composition and sequence distribution of the recurring units in polymer chains R′ and R′′ of ether IIIf on the one hand and in the backbone of polymer IIc on the other hand.

TABLE I

Compound	M_n[a]	Calcd., %			Found, %			Percent-homoannularity[b]
		C	H	Fe	C	H	Fe	
IIIf, First fraction m. p.[e] 125°C	1070	73.28	5.24	20.04[c]	73.43	5.14	19.48	73.1
IIIf, Second fraction m. p.[e] 100°C	680	72.46	5.31	19.85[c]	72.42	5.42	19.22	75.2
IIIf, Subfraction m. p.[e] 95°C	830	72.88	5.28	19.93[c]	73.31	5.29	19.59	76.4
IIIc, Diastereomer with m. p. 136—138°C	560	72.11	5.34	19.72[d]	71.90	5.46	19.55	—
IIIc, Diastereomer with m. p. 111—113°C	550	72.11	5.34	19.72[d]	71.92	5.54	19.68	—

a) Mean value from duplicate runs (in benzene).
b) See Ref. 13.
c) Calcd. for IIIf, with mol. wt. 1115 (first fraction), 703 (second fraction), and 840 (subfraction).
d) Calcd. for IIIc, with mol. wt. 566.
e) Upper limit of melting range.

of polymeric products, resulted from extended heating periods under otherwise unchanged experimental conditions. Consistent with this observed trend, it was possible to post-condense IIIf, resulting in the elimination of the internal ether bridge. To this end, in a series of experiments, IIIf was fused for several hours at 100—135°C in the presence of Lewis acids. In all instances, work-up in a manner which has been described[1] gave a polymer identical in composition and spectroscopic behavior with the oxygen-free product IIc prepared earlier.[1] A typical infrared spectrum is presented in the upper curve of Fig. 2.

The described isolation of IIIf and its post-condensation to the polymer IIc devoid of an ether bridge corroborate the mechanistic inferences set forth in an earlier paper[1] regarding the intermediary role of polymeric ethers in polycondensations of ferrocenyl carbinols.

Experimental[14]

Ferrocenylphenylcarbinol (Ic) was prepared by the sodium borohydride reduction of benzoylferrocene in a manner which has been described earlier[1]; two recrystallizations from hexane gave m.p. 79—81°C. Alcoa-grade F-20 activated alumina was used for chromatography.

Polycondensation of Ic.—In an exemplifying experiment, a mixture of 5.0 g. (0.0171 mol.) of carbinol Ic and 0.025 g. of hydrogen chloride (as 1.0 N aqueous hydrochloric acid) was heated for 15 min. at 95°C. A slow stream of nitrogen was passed over the melt during this operation. The vigorously-stirred homogeneous mixture solidified after about 10 min., blocking the stirrer. Extraction of the pulverized melt with water for catalyst removal was followed by fractional extraction with cold hexane. The final residue least soluble in hexane, no longer containing low-molecular ethers or the starting material, was taken up in benzene. Freeze-drying of the concentrated solution furnished a first fraction of IIIf as an orange-brown resin, which was then vacuum-dried for 7 days at 45°C; melting range, 100—125°C. The yield was 0.09 g. (1.9%). A second, lower-molecular fraction of IIIf deposited in a resinous form upon concentration of the combined initial hexane extracts. After the monomer had been removed by hexane trituration, the product, 0.10 g. (2.1%), melted at 80—100°C. For both fractions, M_n and analytical data are collected in Table I.

The supernatant hexane solution, combined with the hexane washings from the trituration of the first fraction IIIf and concentrated to ca. 150 ml., was chromatographed on alumina, using hexane as the eluent. From the lower, major band,[15] 4.02 g. (83.0%) of crude ether IIIc was obtained; melting

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14) Melting points uncorrected. Carbon-hydrogen analyses by G. I. Robertson, Jr., Florham Park, N. J. Number-average molecular weights determined by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., in benzene solution on a Mechrolab model 301A vapor pressure osmometer; values rounded off to nearest 10. X-Ray diffractograms recorded on Norelco X-ray Diffractometer, using vanadium-filtered $K\alpha$ chromium radiation; only six strongest peaks (interplanar spacings d) within 2θ range 10—35° listed in decreasing order of intensity (mean error at $2\theta = 20°, \pm 0.04$ Å). Proton magnetic resonance spectra recorded over a sweep width of 500 c.p.s. in carbon tetrachloride solution on Varian Associates model A-60 NMR spectrometer operating at 60 mc./sec. (tetramethylsilane used as internal standard with $\tau = 10.00$ p. p. m.).

Infrared spectra taken on Baird-Atomic spectrophotometer, model NK-1 equipped with rock salt optics. Quantitative measurements (%-homoannularity. Ref. 1) conducted in spectrograde carbon disulfide, employing a cell-thickness of 0.05 cm. We are indebted to Messrs. W. M. Rade and R. L. Harvey for scanning the X-ray diffractograms and infrared spectra. Dr. S. Manatt, Jet Propulsion Laboratory, Pasadena, Calif., kindly obtained the NMR spectra.

15) Beside trace amounts of IIIf and Ic, benzoylferrocene (0.1%; m. p. 104—106°C) was isolated from the chromatogram, probably formed by oxidation of Ic on the column as repeatedly observed while purifying this carbinol. From an additional, slightly lower band, light yellow and very narrow, 1.9 mg. of an unidentified yellow, infusible crystalline compound were isolated; X-ray diffractogram, Å : 4.87; 5.62; 5.84; 8.49; 4.57; 4.08.

range, 80—125°C; M_n, 550.

Found: C, 72.15; H, 5.52; Fe, 19.76. Calcd. for $C_{34}H_{30}Fe_2O$ (IIIc; mol. wt. 566.3): C, 72.11; H, 5.34; Fe, 19.72%.

By fractional crystallization from hexane, the crude isomer mixture was separated into the two diastereomers. This tedious operation was facilitated by the X-ray diffractometric characterization of individual fractions. The less-soluble isomer crystallized as large orange prisms melting at 136—138°C (DTA endotherm,[6] sharp peak at 134—136°C); X-ray diffractogram, Å: 5.70; 6.64; 4.92; 5.43; 4.43; 5.17. The more soluble isomer, melting at 111—113°C (sharp DTA endotherm[6] at 110—112°C), was collected as small, orange-yellow crystal clusters; X-ray diffractogram, Å: 6.05; 4.83; 5.22; 5.34; 5.73; 4.69. The M_n values and elemental analytical findings for both diastereomers are listed in Table I. The two isomers were obtained in a weight ratio of approximately 3 : 1 (high-melting to low-melting species).

A 70 mg. portion of the second fraction of IIIf listed in Table I was subfractionated from a hexane solution by incremental volume reduction, using a rotating evaporator (environmental water bath maintained at 30±2°C). The four resinous deposits obtained successively were dried in vacuo for 7 days at 45°C. The major cut, 45 mg., showed the melting range of 80—95°C. M_n and analytical data are given in Table I (center line). The iron analyses were performed on material recovered from the M_n determination, which in turn had previously been recovered from NMR and infrared work.

Results similar to those described above, except for lower yields in IIIc, were obtained in condensation reactions catalyzed by 0.5% sulfuric acid (as 1.0 N sulfuric acid; 0.4 hr. heating at 100°C), 2.0% oxalic acid (2 hr. at 110°C) or 1.8% *p*-toluenesulfonic acid (2 hr. at 100°C). In the last-named two cases employing organic acids, these catalysts were partially incorporated into the polymeric reaction products, as is indicated by the elemental analyses and the appearance of ester absorption bands in the infrared spectra. Other experiments were performed in the presence of hydrochloric acid; they were similar to those which have been described but were conducted over extended heating periods. Here, the original polymer fractions isolated exhibited higher M_n values (total yields up to ~30%), and their infrared spectra increasingly resembled, but never became quite superimposable with, those of IIc. For instance, heating for one hour at the started temperature gave a polymer, melting range 100—130°C, M_n 1360, in a total yield of 9.7%.

Found: C, 73.91; H, 5.30; Fe, 20.09. Calcd. for IIIf (for IIc in parentheses): C, 73.51 (74.48); H, 5.23 (5.15); Fe, 20.11% (20.37%).

Post-Condensation of IIIf. — A typical fraction of IIIf (0.225 g.) prepared from Ic by sulfuric acid catalysis (M_n, 990. Found: C, 73.01; H, 5.28; Fe, 19.88%), was ground together with 0.011 g. of anhydrous zinc chloride[16] and fused for 1.0 hr. at 120°C in a test-tube under a blanket of dry nitrogen. The melt, liquid in the initial stage, finally became highly viscous and "stringy" and solidified on cooling. The mass was ground and extracted with water to remove the catalyst and was then worked up in a manner described in an earlier paper[1] to give two polymer fractions. The major fraction (0.105 g.), a yellow-tan solid, had a melting range of 150—180°C (partial melting); M_n, 2020.

Found: C, 74.43; H, 5.22; Fe, 20.20. Calcd. for IIc: C, 74.48; H, 5.15; Fe, 20.37%.

The infrared spectrum is presented in Fig. 2 (upper curve). The somewhat smaller second fraction, 0.070 g., a yellow solid, gave M_n 880. Found: C, 74.16; H, 5.09%. The infrared spectrum, while essentially superimposable with that of the first fraction, showed shoulders at 7.85, 9.60 and near 13.3 μ, indicating the presence of an ether bridge in a very low concentration. When the heating period in this experiment was extended to 2.0 hr., ether absorption vanished completely in both fractions.

Summary

The acid-catalyzed polycondensation of ferrocenylphenylcarbinol Ic under controlled, mild reaction conditions gives rise to the formation of low-molecular, ferrocene-containing polymeric ethers, to which, on the basis of elemental analysis, infrared and NMR spectroscopic data, the structure IIIf is assigned. Monomeric ether IIIc is isolated in addition under these conditions. In the presence of Lewis acids at elevated temperatures, ethers IIIf continue to react, with the elimination of the ether bridge, to give polymers identical with the previously reported oxygen-free compounds IIc, which were obtained directly from Ic under more rigorous conditions. In the previous work, polymers IIIf containing an ether group were postulated as intermediates but were not isolated. The observed formation of such polymers under the present experimental conditions, coupled with their successful post-condensation to IIc, is thus in accord with the earlier mechanistic implications.

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[16] Comparable results obtained in post-condensation reactions catalyzed by anhydrous aluminum chloride (4% by wt. of IIIf), but large portion (—10% by wt. of IIIf) of insoluble, crosslinked polymer and decomposition products isolated in addition.