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## Polyethynylferrocene

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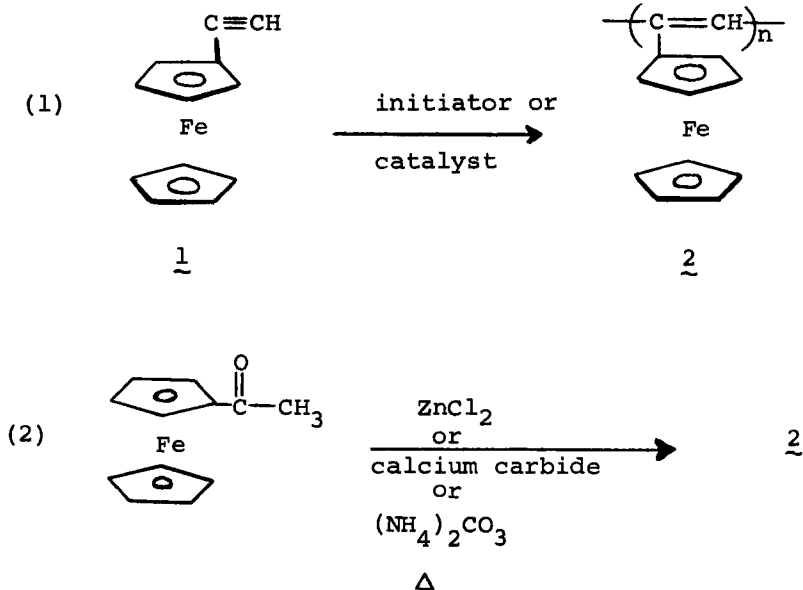
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### ABSTRACT

The completely conjugated polymer, polyethynylferrocene, was prepared by heating ethynylferrocene with catalytic amounts of azobisisobutyronitrile to 180–240° under nitrogen in bulk. Cyclotrimerization competes with polymerization under these conditions. Pure low molecular weight polyethynylferrocene was isolated and characterized by IR and NMR spectroscopy and by a gel permeation chromatography. The pure polymer exhibits a conductivity of  $2 \times 10^{-14} \Omega^{-1} \text{cm}^{-1}$ . Attempts to prepare polyethynylferrocene by heating acetylferrocene in molten zinc chloride were, contrary to literature reports, unsuccessful. A polymer containing hydroxyl and keto groups was obtained, and extensive degradation of the ferrocene groups occurred. The general reaction scheme is discussed. It includes cleavage of cyclopentadienyl rings from ferrocene and the incorporation of cyclopentane rings into the polymer structure.

## INTRODUCTION

Polyethynylferrocene, 2, has been reported by several research groups recently [1-6]. Simionescu [1, 2] obtained 2 by heating ethynylferrocene, 1, with initiators such as benzoyl peroxide, lauroyl peroxide, triisopropylboron, and bistrisphenylphosphine nickel halides. Low molecular weight 2 was formed. Using a Ziegler catalyst system,  $\text{Al(isobut)}_3\text{-VO(acac)}_2$ , failed to give any polymer. Kunitake et al. [3] and Sokolov [4] did obtain 2 using the Ziegler catalyst systems  $\text{AlEt}_3\text{-Ti(OBu)}_4$  and  $\text{Al(isoBu)}_2\text{-TiCl}_4$ , respectively, and Kunitake obtained 1,3,5-triferrocenylbenzene and its 1,2,4-isomer as by-products. Curiously, Kunitake [3] failed to obtain polymer 2 using azobisisobutyronitrile (i.e., AIBN) initiation. Paushkin and co-workers claimed that polyethynylferrocene could be obtained from the polycondensation of acetylferrocene in molten, anhydrous  $\text{ZnCl}_2$  [5] or by reaction with calcium carbide or ammonium carbonate [6] (Eq. 2). Attempts to thermally convert 1 to 2 without initiator led only to mixtures of the cyclotrimers [7].



As part of our program to prepare completely conjugated organo-metallic polymers with mixed-valence states for semiconductor studies [8], we needed to prepare large amounts of pure polyethynylferrocene. Since acetylferrocene is commercially available, the rather unlikely method of Paushkin [5, 6] was attractive, particularly in view of the far greater difficulty in obtaining 1 [9]. Thus we reinvestigated this approach and demonstrated the  $\text{ZnCl}_2$  polycondensation reaction did not give 2. However, by heating with AIBN (180 to 240°C) in bulk, good yields of 2 could be obtained from 1.

The synthetic details and structural proofs are presented in this paper.

## RESULTS AND DISCUSSION

### Polycondensations in $\text{ZnCl}_2$

Pure acetylferrocene was reacted with anhydrous  $\text{ZnCl}_2$  in several ways. Preheating to 100°C under  $\text{N}_2$  in the presence of small amounts of diglyme followed by heating in a sealed tube to 200°C for up to 5 hr gave a hard, reddish material. The crude material was ferromagnetic, indicating some iron had been freed. IR studies of fractions, purified by reprecipitation, showed hydroxyl groups ( $3500$  to  $3400\text{ cm}^{-1}$ ), aliphatic carbon-hydrogen moieties ( $2960\text{ cm}^{-1}$ ), and carbonyl groups ( $1665\text{ cm}^{-1}$ ) were all present in abundance. These samples were no longer ferromagnetic. Analyses confirmed the presence of oxygen (from 3.5 to 5.0% in all fractions), and the NMR spectrum of all soluble fractions exhibited peaks at  $\delta \sim 4.0$  (broad, m, ferrocene ring protons),  $\delta \sim 2.1$  (broad, methyl or methylene groups adjacent to a carbonyl carbon),  $\delta \sim 1.6$  (broad, m) and  $\delta \sim 0.4$  to 1 (broad, aliphatic C-H). Thus it is quite clear that the polymer product was not polyethynylferrocene, but a more complex structure. Gel permeation chromatography (GPC) of the fractions showed that broad distribution, branched materials had formed ( $\bar{M}_n$  from 10,000 to 30,000 and  $\bar{M}_w/\bar{M}_n = 5$  to 12).

Several reactions were performed without a cosolvent. Acetylferrocene was melted into anhydrous  $\text{ZnCl}_2$  in Pyrex tubes after thorough deoxygenation. After an initial period at 100°C, the samples were heated to temperatures from 145 to 200°C for 20 to 50 hr. In each case the product polymers were separated into THF soluble and insoluble fractions. The insoluble polymers exhibited IR spectra similar to those discussed above, confirming the presence of hydroxyl, keto, and aliphatic C-H functions. The soluble fractions exhibited

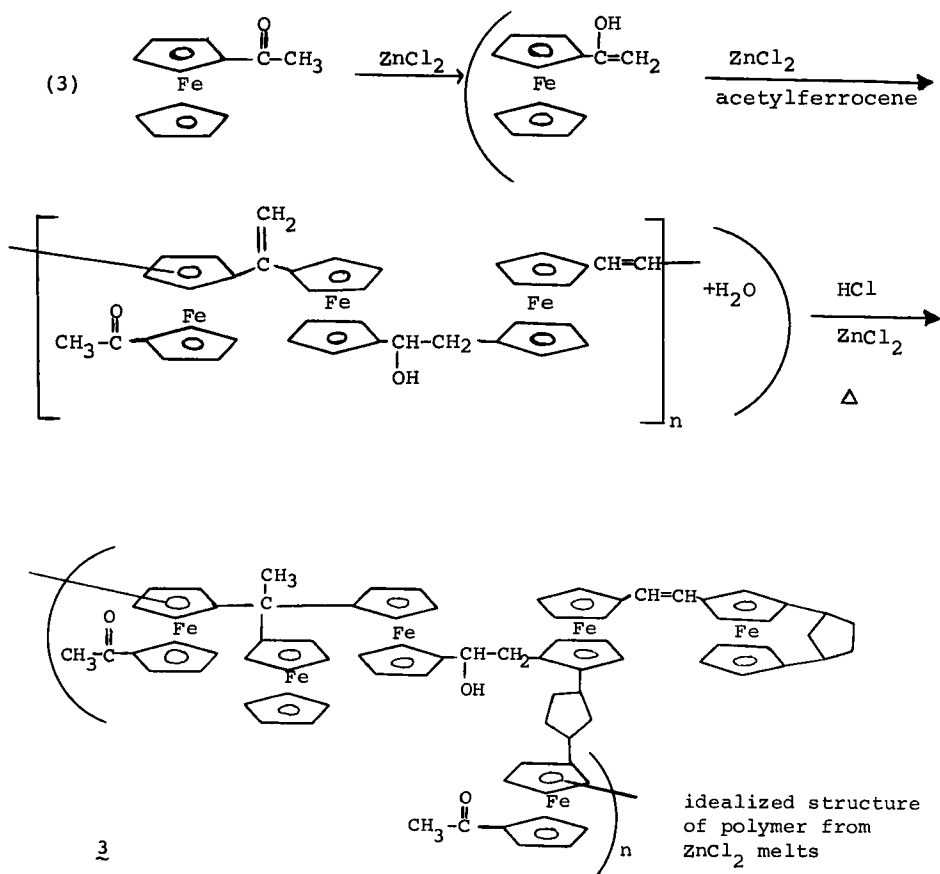
lower hydroxyl content, but analyses still found from 3.5 to 5% oxygen. After 50 hr at 145°C the soluble fractions exhibited  $\bar{M}_n = 3500$  to 6000.

As the temperature was raised or the reaction time increased, the iron content of the polymers decreased. Simultaneously, the carbon content increased and the intensity of the aliphatic C-H stretching bands increased.

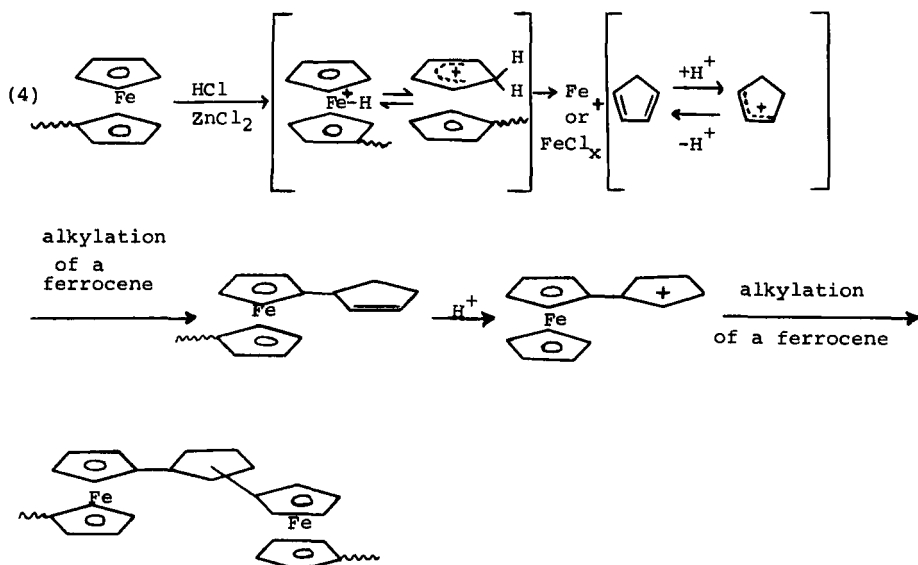
Based on our previous studies of the condensation polymerizations of ferrocene with dichlorophenylphosphine [10] and the extensive melt studies of Neuse [11, 12], the spectral, analytical, and molecular weight data are readily accommodated. Initial condensations via Friedel Crafts reactions generate a low molecular weight material containing unreacted acetyl groups, hydroxyl groups, as well as unsaturated sites in the polymer backbone. Increasing the reaction time or temperature promotes dehydration which, in turn, generates HCl in the  $ZnCl_2$  medium. The HCl- $ZnCl_2$  media is a strong acid, and dehydration to  $\alpha$ -ferrocenyl carbonium ions, enol formation, and ferrocene protonation are all increasingly promoted. Thus further alkylative polymerization and branching occurs. Furthermore, cleavage of cyclopentadienyl rings from iron is a consequence of the protonation of ferrocene in this media [10-13]. Once cleaved, the cyclopentadiene ring is in equilibrium with its corresponding cyclopentadienyl cation which can, in turn, alkylate another ferrocene ring. This gives a ferrocenylcyclopentene, which on protonation gives a ferrocenylcyclopentyl cation that inter- or intramolecularly alkylates the ferrocene moiety. Thus saturated cyclopentane units build up along the polymer chain, causing an increased carbon and decreased iron content (see Eqs. 3 and 4). Sample reactions are given in the experimental section.

### Polymerization of Ethynylferrocene 1

Low molecular weight polyethynylferrocene, **2**, was readily prepared by heating **1** with a catalytic amount of AIBN (0.4 to 3% by weight) in bulk under  $N_2$ . The best yields were obtained at temperatures from 190 to 240°C. Cyclotrimerization competes with polymerization. At temperatures above 215°C an increasingly higher percentage of the polymer generated is insoluble due to some cross-linking, presumably via a polyrecombination process [12]. Attempts to prepare **2** in benzene solutions with AIBN initiation resulted in a small amount of cyclotrimerization and very small amounts of polymer. Benzoyl peroxide also gives **2**, but a much lower yield of soluble polymer is obtained under comparable conditions.  $RhCl_2$  was a poor catalyst for synthesis of **2**. Table 1 summarizes some representative polymerizations.



Polyethynylferrocene was repeatedly precipitated from benzene solutions by methanol. The polymer appeared to be free of saturated aliphatic groups upon NMR and IR examination; no hydroxyl or keto groups were present, and the elemental analysis was that expected for pure 2 (see experimental section). The deep black polymer was stable to air in the solid phase, but when benzene or THF solutions were exposed to air, oxygen was incorporated into the polymer. The pure polymer, after reduction by ascorbic acid to insure no ferrocenium sites were present, exhibited a conductivity of  $2 \times 10^{-14} \Omega^{-1} \text{cm}^{-1}$ . This is four powers of ten less than that reported by Paushkin [5, 6] for the polymers he isolated from  $\text{ZnCl}_2$  melt system. Without doubt, his measurements were performed on



a polymer with a structure analogous to 3 containing Fe or iron salts as impurities.

In conclusion, it is clear that Paushkin's polymers did not have the idealized structure 2. Pure 2 is an entirely different material than the polycondensation products of acetylferrocene obtained in  $ZnCl_2$  systems.

## EXPERIMENTAL

Melting points were not corrected. IR spectra were obtained on a Beckman IR-33, NMR spectra on a Hitachi-Perkin Elmer R-20, and gel permeation chromatograms on a Waters Associates GPC-ALC-Model 301 equipped with 16 ft of styragel columns, calibrated with polystyrene standards. Ethynylferrocene was prepared from acetylferrocene as reported [9] and purified both by column chromatography over neutral alumina and sublimation mp 55 to 56°C (Ref. 9, 52 to 53.5°C and Ref. 14, 55 to 56°C). AIBN was twice recrystallized from methanol mp 102 to 103°C (Ref. 15, 102°C) and benzoyl peroxide from chloroform-methanol mp 106.5 to 107°C (Ref. 16, 107°C).

### Example Preparation of Polyethynylferrocene from 1 Using AIBN Initiation (Run 7, Table 1)

Ethynylferrocene (1 g, 14.3 mmoles) and AIBN (0.01 g, 0.047 mmole) were ground together into a powder, placed in a Pyrex tube, deoxygenated by three evacuation-N<sub>2</sub> repressurization cycles, and preheated to 60 to 65°C to melt the components into a solution. The reaction was placed in a constant temperature bath at 195°C for 6 hr. Following rapid cooling, the reaction mixture was dissolved into hot benzene (50 ml) under nitrogen. When an insoluble polymer was present it was filtered, extracted, dried, and collected.

The benzene solution was concentrated and the polymer was precipitated by dropwise addition to methanol. About 0.5% of 2, 6-di-*t*-butyl-*p*-cresol was added to the methanol in order to prevent any air oxidation. The precipitated polymer was reprecipitated in a similar fashion and dried in vacuo. The methanol solution was concentrated, and any unreacted **1** as well as the 1, 2, 4- and 1, 3, 5-triferrocenylbenzenes were isolated by chromatography over alumina. Polymer **2** was isolated in 84% yield (0.84 g). Column chromatography of the methanol residue over alumina, as previously reported [17], gave an 11% yield of 1, 2, 4-triferrocenylbenzene (87%) and 1, 3, 5-triferrocenylbenzene (13%) which gave IR and NMR spectra identical with the spectra of authentic samples [17].

Polymer **2** was characterized by NMR (CS<sub>2</sub>)  $\delta$  6.8 ~ 7.8 (broad, 1, vinyl hydrogen), 3.7 ~ 4.6 (broad, 9, cyclopentadienyl ring hydrogens), no other peaks detected; IR (KBr), 3070 (m, Cp C-H str.), 2940 to 2970 (vw, end group or impurity aliphatic C-H str.), 1600(m), 1480(w), 1435(w), 1410(m), 1385(w), 1250(w), 1101(s), 1052(m), 1022(m), 1000(s), 920(w), 882(m), 810(s), and 675(s) cm<sup>-1</sup>. The 1000 and 1101 cm<sup>-1</sup> band combination is characteristic of unsubstituted cyclopentadienyl rings of ferrocene [18]. GPC (THF) showed  $\bar{M}_n = 1800$ ,  $\bar{M}_w/\bar{M}_n = 1.7$

Analysis: Calculated for (C<sub>12</sub>H<sub>10</sub>Fe)<sub>n</sub>: C 68.61, H 4.81, Fe 26.58, Found: C 68.65, H 5.01, Fe 26.44.

### Polymerization of Ethynylferrocene Using Benzoyl Peroxide

The procedure was the same as that described above for the AIBN-initiated reactions. The IR spectra of polymers of this reaction matched that obtained above.



TABLE I. Polymerization of Ethynylferrocene<sup>a</sup>

Ethynylferrocene (mmole)	Initiator		Temperature (°C)	Time (hr)	Yield <sup>b</sup>		$\bar{M}_n^c$
	Compound	Wt %			% Polymer	% Cyclotrimers	
4.76	AIBN	1.3	140	12	0	0	-
4.76	AIBN	1.7	160	18	3	7	-
4.76	AIBN	1.0	170	18	19	34	2500
4.76	AIBN	1.9	180	1	26	47	2600
4.76	AIBN	0.9	190	18	49	16	1900
9.50	AIBN	1.0	195	6	70	d	2300
14.3	AIBN	1.5	195	6	84	11	1800
23.8	AIBN	1.5	195	6	57	26	1700
28.6	AIBN	1.5	195	6	78	d	1800
47.6	AIBN	3.0	195	6	79	8	1800
24.1	AIBN	2.0	205	6	81 <sup>e</sup>	3	2700
23.7	AIBN	1.7	215	6	85 <sup>f</sup>	0	2300
20.3	AIBN	1.5	225	6	82	0	2600
15.0	AIBN	1.5	240	4	88 <sup>g</sup>	0	2400
10.0	BP	1.5	170	24	12	d	1300

10.2	BP	1.5	180	6	13	d	1300
10.1	BP	1.0	195	6	17	d	1500
9.7	BP	0.4	220	12	58 <sup>h</sup>	-	1700
9.8	BP <sup>i</sup>	0.5	220	24	0	-	
4.90	RhCl <sub>2</sub> <sup>j</sup>	1.0	60	48	7	0	2220

<sup>a</sup>All polymerizations were carried out in bulk under N<sub>2</sub> unless stated otherwise.

<sup>b</sup>Based on the ethynylferrocene charged.

<sup>c</sup>Based on GPC measurements where  $Q = 85$ . This  $Q$  value was obtained from a single polymer sample on which  $[\eta]$  and vapor pressure osmometry as well as GPC measurements were made.

Since the range of molecular weights is small, this method is probably accurate to  $\pm 10\%$ .

<sup>d</sup>The amount of cyclotrimers formed was not measured.

<sup>e</sup>About 20% of the polymer was insoluble in benzene or THF.

<sup>f</sup>About 40% of the polymer was insoluble in benzene or THF.

<sup>g</sup>About 60% of the polymer was insoluble in benzene or THF.

<sup>h</sup>About 75% of the polymer was insoluble in benzene or THF.

<sup>i</sup>Run in 5 ml of xylene.

<sup>j</sup>Run in ethanol.

### Polymerization of Ethynylferrocene Catalyzed by $\text{RhCl}_2$

Ethynylferrocene (1.00 g, 4.76 mmoles) and  $\text{RhCl}_2$  (0.01 g, 1% by weight) were dissolved in freshly distilled dry ethanol. After several freeze-thaw degassing cycles the reaction tube was filled with  $\text{N}_2$  and the tube was heated to 60°C for 48 hr. The ethanol was removed in vacuo, the residue dissolved in benzene, filtered, and the polymer precipitated into hexane to give 0.072 g of polymer with an IR almost identical to that described above.

### Polycondensation of Acetylferrocene in Molten $\text{ZnCl}_2$

Acetylferrocene (5.0 g, 21.9 mmoles) and anhydrous zinc chloride (0.8 g, 5.8 mmoles) were mixed under  $\text{N}_2$  in a glass tube. The tube was evacuated, sealed, and placed in a constant temperature bath at 200°C for 3 hr. On cooling, the contents were extracted with benzene (100 ml), washed with very dilute hydrochloric acid, water, and dried ( $\text{Na}_2\text{SO}_4$ ). The organic suspension (a portion of the product was insoluble) was filtered, concentrated, and precipitated into 1600 ml of 30 to 60°C petroleum ether. The insoluble portion was ferromagnetic, but the soluble portion (14%) was not. The soluble polymer exhibited a  $\overline{M}_n = 13,000$ ,  $\overline{M}_w = 25,000$  (GPC); IR (nujol) 3500 to 3400  $\text{cm}^{-1}$  (m) hydroxyl groups, (KBr) 3060 (m), 2960 (s), 1665 (s) carbonyl groups, 1585, 1460, 1365, 1280, 1245, 1110, 1060, 1030, 1005, and 820 (s, Cp-ring out-of-plane hydrogen deformations)  $\text{cm}^{-1}$ .

Analysis: Found: C, 71.32%; H, 5.61%; O, 4.31%; Fe, 15.92%.

Lowering the temperature progressively to about 150°C resulted in a similar soluble polymer. For example, initial heating of a sample of acetylferrocene (40 g, 0.175 mole) and anhydrous zinc chloride (2.0 g, 0.015 mole) to 100°C for 2 hr followed by 50 hr at 148°C gave a dark brown solid. The solid was partially dissolved and suspended in THF, and precipitated into methanol (400 ml) and 5% HCl (200 ml). The HCl washings removed metal salts. Exhaustive extraction with THF followed by precipitation into 30 to 60°C petroleum ether gave a 4% yield of a polymer ( $\overline{M}_n = 8000$ ) with an IR spectrum identical to that reported above. Analyses of the soluble portion showed C, 72.48%; H, 5.78%; O, 4.93%; Fe, 15.58%. Iron oxide was identified in the insoluble material along with a highly branched ferrocene containing material.

The mole ratio of acetylferrocene to zinc chloride was varied from 12 to 0.3 and the temperature from 140 to 200°C. In no case was a

polymer resembling 2 obtained. In all cases hydroxyl, carbonyl, and aliphatic hydrocarbon functions were found in the polymer. At equal reaction times and charge ratios, a decrease in the %Fe was noted as the temperature increased. Similarly, the %C increased. This is indicative of more extensive ferrocene cleavage. All samples analyzed for at least 3% oxygen. The yields were small and erratic.

#### Polycondensation of Acetylferrocene in ZnCl<sub>2</sub> with Added Diglyme

Acetylferrocene (5.0 g, 21.9 mmoles), zinc chloride (4.5 g, 32.9 mmoles), and dry diglyme (10 ml) were heated slowly to 100°C in a sealed tube under N<sub>2</sub>. The reaction mixture was then heated to 200°C for 5 hr giving a hard fused reddish mass. The product was extracted with hot benzene, and the benzene layer was concentrated and added to diethyl ether (100 ml) to precipitate the extracted polymer. Two further reprecipitation steps gave 0.91 g (18%) polymer exhibiting an IR spectrum identical to that reported above (hydroxyl, carbonyl, aliphatic hydrocarbon, and ferrocene moieties all present). The NMR spectrum (pyridine)  $\delta$  3.8 to 4.5 (broad m, ferrocene ring hydrogens),  $\delta$  2.1 (broad, C-H adjacent to carbonyl),  $\delta$  1.6 (broad m),  $\delta$  ~ 0.4 to 1 (broad m, aliphatic CH) further confirmed the structure. The polymer exhibited  $\bar{M}_n = 24,000$ ,  $\bar{M}_w/\bar{M}_n = 9$  (GPC), suggesting a highly branched structure, and analyses found 4.13% O and 15.47% Fe. The insoluble product contained a cross-linked polymer similar to that of the soluble polymer (via IR), metal salts (Zn and Fe both detected), and oxides of iron.

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