Organometallic Polymers. X. Solution Polymerization of 2-Ferrocenylethyl Acrylate and 2-Ferrocenylethyl Methacrylate

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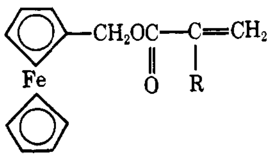
ABSTRACT: Two new ferrocene containing monomers, 2-ferrocenylethyl acrylate (IIa) (FEA) and 2-ferrocenylethyl methacrylate (IIb) (FEMA), were synthesized starting from *N,N*-dimethylaminomethylferrocene. These monomers were readily homopolymerized in benzene solution between 60 and 90° using AIBN initiation. The polymerizations are first order in monomer concentration and half-order in AIBN concentration, indicating that a normal first-order radical chain polymerization mechanism is operative. The energy of activation for polymerization of FEA in benzene is 21.7 kcal/mol between 60 and 72° while that for FEMA is 18.6 kcal/mol between 58 and 72°. 1-Ferrocenylethyl acrylate (III) was also prepared, but this monomer was substantially decomposed to vinylferrocene in competition with polymerization. Homopolymers of FEA and FEMA were characterized by infrared spectroscopy, gel permeation chromatography, vapor pressure osmometry, and viscosity measurements. Poly(2-ferrocenylethyl acrylate) was converted to its electron-transfer polymer salt upon treatment with *o*-chloranil and dichlorodicyanoquinone. Each molecule of quinone incorporated into the polymer structure was reduced to its anion. The copolymerization of FEA and FEMA with several organic monomers is described in the accompanying paper.

During the last decade the field of organometallic chemistry has matured into one of the most active research areas in all of chemistry.[4] In spite of this area's prodigious growth, the incorporation of organometallic compounds into polymers has not been extensively accomplished, despite the diversity of properties which organometallic compounds have to offer. This is especially true when one examines the polymer chemistry of transition metal organometallic compounds. Only ferrocene, of all the known organometallic compounds, has been incorporated into a wide variety of polymers,[5] and even with ferrocene derivatives, addition polymerization has been largely neglected. One exception is vinylferrocene, which has been homopolymerized by cationic and free radical addition routes by Arimoto and Haven,[6] Cassidy,[7] Baldwin and Johnson,[8] and Pittman.[9f,g]

As part of a large program[9] to prepare and characterize transition metal containing organic polymers, we had previously[9f,h] prepared and solution polymerized (initiated by AIBN) ferrocenylmethyl acrylate (Ia) and ferrocenylmethyl methacrylate (Ib). The polymerization kinetics,[9e] viscosity–molecular weight relations,[9f] and copolymerization relative reactivity ratios (r_1 and r_2)[9h] with styrene, methyl acrylate, methyl methacrylate, and vinyl acetate were obtained. These results are summarized in Table I. Upon examining the r_1 and r_2 values, it is clear that Ia and b are less reactive than methyl acrylate and methyl methacrylate, respectively. Since the ferrocene nucleus is an efficient quencher of photochemically generated triplet states[10,11] and has a large uv absorption[12,13] and low toxicity, the development of more reactive acrylate derivatives of ferrocene for copolymerization was undertaken. A more reactive monomer could be more conveniently incorporated into copolymer and terpolymer coatings to give enhanced stability to ultraviolet degradation.[14] Furthermore, the polymers previously prepared from Ia and b might be sensitive to $A_{AL}1$ ester hydrolysis in acidic media due to the extraordinary stability of α ferrocenyl carbonium ion.[13,15] By moving the position of attachment of the



Ia, R = H
b, R = CH_3

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[2] This work was taken from the Master's Thesis of R. L. Voges, University of Alabama, 1970.

[3] Undergraduate research work–study participant.

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[5] C. U. Pittman, Jr., *J. Paint Technol.*, **39**, 585 (1967); H. Valot, *Double Liaison* (*France*), **130**, 775 (1966); E. W. Neuse in "Advances in Macromolecular Chemistry," W. M. Pasika, Ed., Academic Press, New York, N. Y., 1968; T. P. Vishnyakova, *Usp. Khim.*, **36**, 2136, (1967).

[6] F. S. Arimoto and A. C. Haven, Jr., *J. Amer. Chem. Soc.*, **77**, 6295 (1955); A. C. Haven, Jr., U. S. Patent 2,821,512 (Jan 28, 1958).

[7] Y. H. Chen, M. Fernandez-Refojo, and H. G. Cassidy, *J. Polym. Sci., Part A-1*, **40**, 433 (1959).

[8] M. G. Baldwin and K. E. Johnson, *ibid., Part A-1*, **5**, 2091 (1967).

[9] For previous papers in this series, see (a) C. U. Pittman, Jr., *J. Polym. Sci., Part A-1*, **5**, 2927 (1967); (b) C. U. Pittman, Jr., *ibid.*, **6**, 1687 (1968); (c) C. U. Pittman, Jr., *Polym. Lett.*, **6**, 19 (1968); (d) C. U. Pittman, Jr., and J. A. Eikenberry, *J. Alabama Acad. Sci.*, **38** (1968); (e) C. U. Pittman, Jr., J. C. Lai, and D. Vanderpool, *Macromolecules*, **3**, 105 (1970); (f) C. U. Pittman, Jr., J. C. Lai, D. P. Vanderpool, M. Good, and R. Prados, *ibid.*, **3**, 746 (1970); (g) J. C. Lai, T. Rounsefell, and C. U. Pittman, Jr., *ibid.*, **4**, 155 (1971).

[10] J. H. Richards, *J. Paint Technol.*, **39**, 569 (1967).

[11] A. J. Fry, R. S. H. Lui, and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 4781 (1966).

[12] R. G. Schmitt and R. C. Hirt, Air Force WADC Technical Reports 59-354, 60-704, 61-298 (available from the Defense Documentation Center, Alexandria, Va.).

[13] M. Rosenblum, "Chemistry of the Iron Group Metallocenes," Part 1, Wiley, New York, N. Y., 1965.

[14] Compounds such as 2-hydroxybenzoylferrocene and 2,4-dihydroxybenzoylferrocene have been found to be very efficient uv stabilizers in a variety of polymeric systems. See R. G. Schmitt and R. C. Hirt, *J. Polym. Sci.*, **45**, 35 (1960).

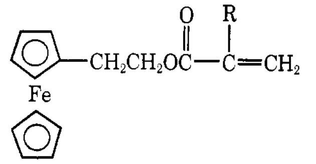
[15] M. Cais, *Organometal. Chem. Rev.*, **1**, 435 (1966); T. G. Traylor and I. C. Ware, *J. Amer. Chem. Soc.*, **89**, 2304 (1967); C. U. Pittman, Jr., *Tetrahedron Lett.*, 3619 (1967).

Table I
Polymerization Studies of Ia and Ib

Monomer	$E_{act.}$, kcal/mol	Values of $[\eta] = K\bar{M}_n^a$ in benzene: K	a	M_2(styrene) r_1	r_2	M_2(methyl acrylate) r_1	r_2	M_2(MMA) r_1	r_2	M_2(vinyl acetate) r_1	r_2
Ia	18.7	6.84×10^{-3}	0.75	0.02	2.3	0.14	4.46	0.08	2.9	1.44	0.46
Ib	32.7	2.78×10^{-2}	0.58	0.03	3.7	0.08	0.82	0.12	3.27	1.52	0.20

acrylate function to a location further removed from the ferrocene nucleus, any steric effect of the large ferrocene moiety on acrylate addition polymerization should be reduced. Simultaneously, this would also decrease sensitivity to acid-catalyzed hydrolysis.

For these reasons we synthesized 2-ferrocenylethyl acrylate (IIa) (FEA) and 2-ferrocenylethyl methacrylate (IIb) (FEMA) and studied their free radical initiated homopolymerization in benzene solutions. In addition, 1-ferrocenylethyl acrylate



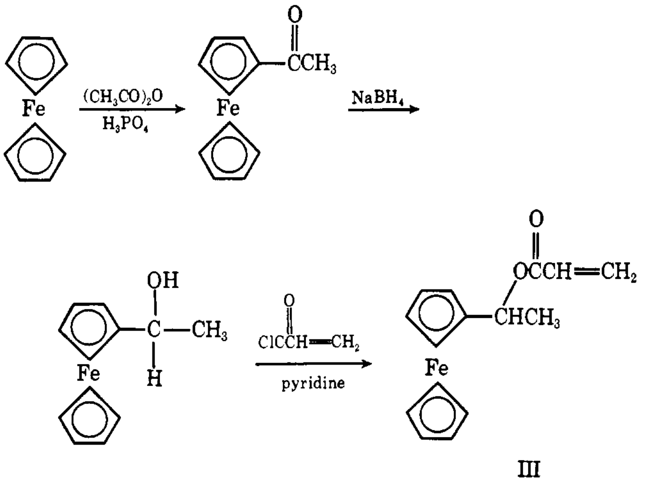
IIa, R = H
b, R = CH_3

(III) was prepared in order to compare its rate of polymerization to that of FEA. In the following paper, we present a study of the copolymerization of monomers IIa and b.

Results

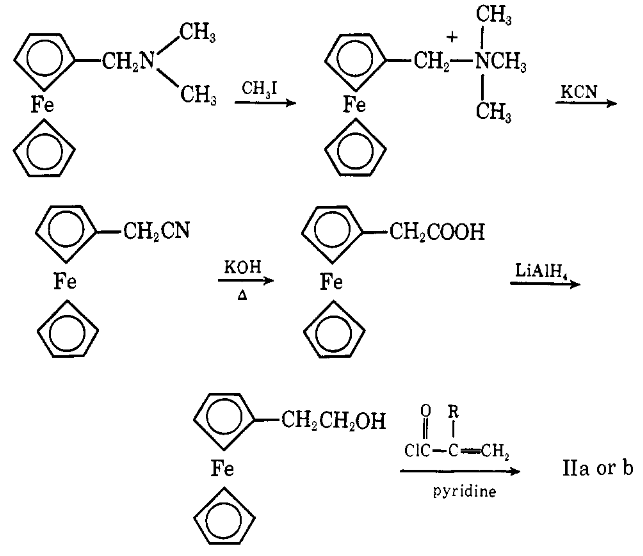
The preparation of 1-ferrocenylethyl acrylate (III) is outlined in Scheme I. Acetylferrocene was prepared by the

Scheme I



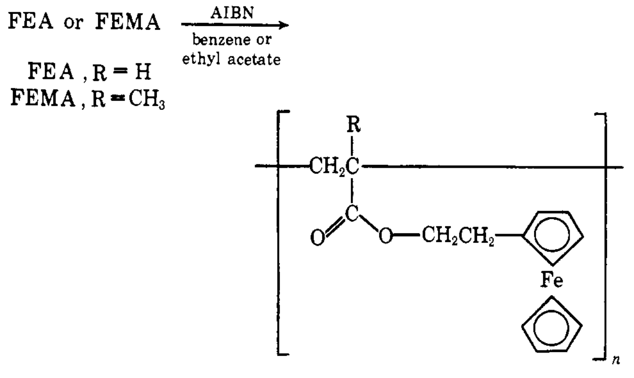
method of Graham[16] and reduced to 1-ferrocenylethanol by sodium borohydride. 1-Ferrocenylethanol was then esterified with acrylyl chloride in ether–pyridine. The synthesis of a (FEA) and b (FEMA) is outlined in Scheme II. *N,N*-Dimethylaminomethylferrocene was converted to its methiodide salt which was treated with potassium cyanide to give ferrocenylacetonitrile. This nitrile was hydrolyzed to ferrocenylacetic acid upon refluxing with potassium hydroxide in ethanol–water. Ferrocenylacetic acid was reduced to 2-ferrocenylethanol with lithium aluminum hydride, and this alcohol was esterified in ether–pyridine with acrylyl chloride to give FEA or methylacrylyl chloride to give FEMA. The details of the syntheses are presented in the Experimental Section.

Scheme II



Homopolymerization of FEA and FEMA. The monomers FEA and FEMA were readily polymerized using AIBN initiation in degassed benzene solutions. A detailed description of the polymerizations is presented in the Experimental Section. Sample homopolymerizations are listed in Tables II and III. By using high ratios of FEA or FEMA to benzene, it was possible to obtain high yields of homopolymers reproducibly. The polymers were light yellow-brown to orange-brown solids which could be cast into rather brittle films. The molecular weights were determined by vapor pressure osmometry and gel permeation chromatography. These results are summarized in Tables II and III. Elemental analyses of poly(FEA) and poly(FEMA) are summarized in Table IV. Representative gel permeation chromatograms are shown in Figures 1 and 2.

The infrared spectra of FEA and FEMA polymers were



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[16] P. J. Graham, *J. Amer. Chem. Soc.*, **79**, 3416 (1957).

TABLE II
FEA HOMOPOLYMERIZATIONS[a]

Polym no.	FEA used, g	AIBN, used, g	Benzene used, ml	Temp, °C	Time, hr	Yield, g	Yield, %	$\bar{M}_n$	$\bar{M}_w$	[η], ml/g
1	2.293	0.0460	20	70	23	0.54	23.55	26,800	69,000	8.3
2	10.076	0.1056	5	70	90	8.71	86.44	35,950	35,950	11.2
3	2.000	0.0200	10[b]	60	10	0.63	31.50	14,700	36,000	5.9

[a] No benzene-insoluble fractions were formed. [b] Polymerized in 10 ml of ethyl acetate.

TABLE III
FEMA HOMOPOLYMERIZATIONS

Polym no.	FEMA used, g	AIBN used, g	Benzene used, ml	Temp, °C	Time, hr	Yield, g: Benzene soluble	Yield, g: Benzene insoluble	Yield, %	$\bar{M}_n$[a]	$\bar{M}_w$[a]	[η], ml/g
1	2.385	0.0164	20	70	8	0.98		41.08	82,300	290,000	19.6
2	2.087	0.0230	10	70	6	1.55		74.26	63,700	166,000	14.0
3	2.385	0.0460	20	75	8	1.32		55.34	35,200	109,000	9.1
4	8.000	0.0800	6	80	12	3.12	4.02	89.00	24,800	65,000	7.2
5	5.000	0.0500	10	56	12	0.34	3.73	81.40	40,000	120,000	9.7
6	3.000	0.0300	10[b]	70	12	1.26	1.34	86.67	20,900	49,700	6.4

[a] Measured on benzene-soluble fraction. [b] Polymerized in 10 ml of ethyl acetate.

virtually identical with the spectra of the monomers except the C=C stretching absorption was totally absent, as expected. All the polymers exhibited characteristic absorptions of monosubstituted ferrocene at approximately 1000 and 1100 cm^{-1}. The ester carbonyl stretch at about 1735 cm^{-1} was intense as were the cyclopentadienyl rings' C–H out-of-plane deformations at 815 cm^{-1}. The polymers also exhibited prominent ether oxygen stretching bands at 1165 cm^{-1}, poly(FEA) and 1150 cm^{-1}, poly(FEMA).

In general, polymers which have a large amount of secondary valence bonding have high glass-transition temperatures. A ferrocene nucleus is thought to increase sharply the cohesive energy density in polyacrylates.[9f] For example, differential scanning calorimeter thermograms have been interpreted to favor the very high glass-transition temperatures of 197–210° for poly(ferrocenylmethyl acrylate) and 185–195° for poly(ferrocenylmethyl methacrylates). Thermograms of the poly(ferrocenylethyl acrylates) and poly(ferrocenylethyl methacrylates), prepared in this study, show sharp breaks at 157 and 209°, respectively. No such breaks are found before or after to above 240° and the polymers do not melt at these temperatures. If these transitions are glass transitions, this would parallel the results found earlier[9f] and provide more evidence that the ferrocene nucleus has a remarkable effect in increasing the T_g of polyacrylates.

Attempts to homopolymerize 1-ferrocenylethyl acrylate (III) were unsuccessful because of monomer degradation at the temperatures of polymerization (70–90°). Only traces of a grey polymeric material insoluble in benzene were formed. However, after quenching in petroleum ether (bp 30–60°), a monomeric material was recovered after filtering and evaporating the petroleum ether with a rotary evaporator. Thin layer chromatography on Mallinckrodt Silic AR TLC-7G with benzene solvent revealed vinylferrocene constituted most of this fraction. Infrared analysis of the residue also revealed a band at 1720 cm^{-1}, which showed that some unreacted acrylate remained. Thus, under these mild conditions (70–90° in benzene) elimination competes effectively with polymerization. The polymerization of III would be expected to be slower than that of Ia or IIa, but due to elimination of acrylic acid no polymerization rate could be approximated. Some representative polymerization attempts are summarized in Table V.

TABLE IV
ELEMENTAL ANALYSES OF FEA AND FEMA HOMOPOLYMERS

Polymer	% Fe	% C	% H
Poly(FEA-2)	18.95	62.99	6.05
Poly(FEA-3)	19.23	63.14	5.89
Calcd	19.66	63.42	5.68
Poly(FEMA-1)	18.31	64.25	5.91
Poly(FEMA-4)	18.13	64.55	6.08
Calcd	18.73	64.45	6.08

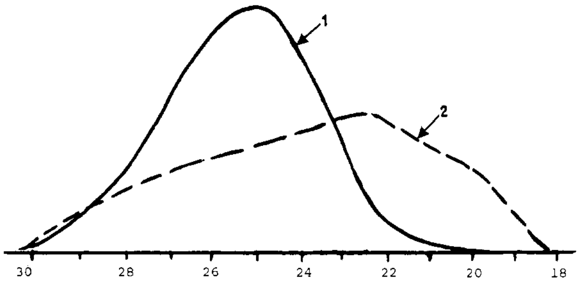

Figure 1. Gel permeation chromatograms of FEA polymers.

Kinetics of FEA and FEMA Polymerizations. The homopolymerization kinetics were studied by dilatometry. The polymerizations were first order in monomer concentra-

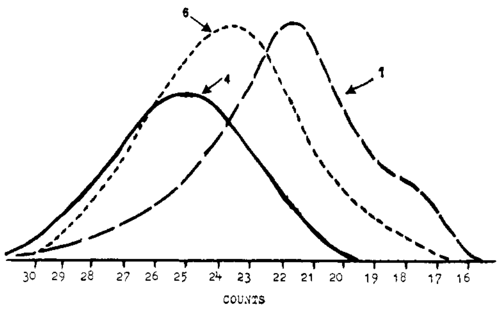

Figure 2. Gel permeation chromatograms of FEMA polymers.

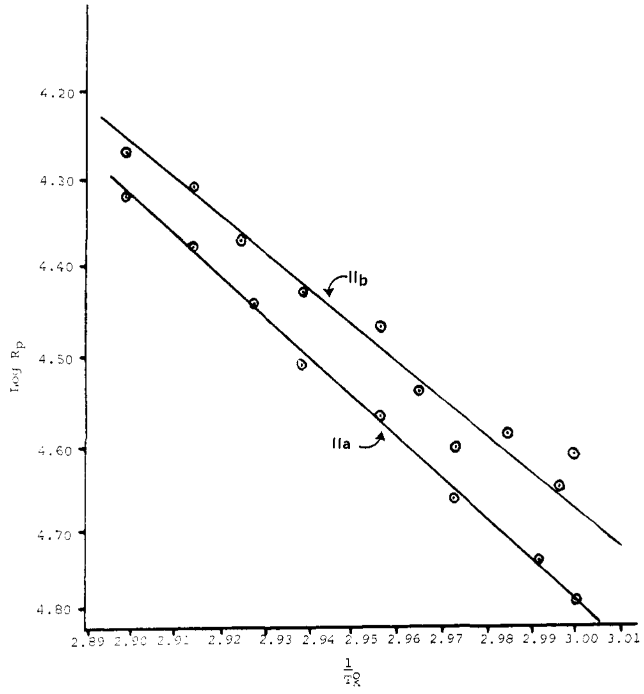

Figure 3. Arrhenius plots of the homopolymerizations of IIa and IIb at temperatures between 58 and 72°.

tion and half order in AIBN concentration for FEA and FEMA homopolymerizations. A small but steady increase in the reaction order with increasing monomer concentration occurred with FEA at monomer concentrations above 0.3 *M*. However, even at concentrations above 0.8 *M*, the order in monomer did not exceed 1.2. The kinetic data are summarized in Tables VI–IX. The activation energies for the homopolymerizations of FEA and FEMA, obtained from Arrhenius plots (see Figure 3), were 21.7 and 18.6 kcal/mol, respectively. These values were assigned from a least-squares fit of the data in the Arrhenius plot. These values may be compared to the values previously reported[9e,f] for ferrocenylmethyl acrylate (Ia) and methacrylate (Ib) of 18.7 and 32.7 kcal/mol, respectively. The overall polymerization rates of FEA and FEMA were significantly faster than those of Ia and Ib. Thus, the ferrocenyl group seems to be exerting a steric effect in Ia and Ib which slows down their rate of polymerization relative to FEA and FEMA. Patra has reported an activation energy of 12.82 kcal/mol for the AIBN-initiated homopolymerization of benzyl acrylate.[17]

Viscosity–Molecular Weight Correlations. The intrinsic viscosities of poly(2-ferrocenylethyl acrylate) and poly(2-ferrocenylethyl methacrylate) were measured in benzene (see Experimental Section) and were correlated by the Mark–Houwink[18] equation $[\eta] = K\bar{M}_v^a$. The correlations were made for both the $\bar{M}_n$ and $\bar{M}_w$ molecular weights although for polydisperse polymers the $\bar{M}_v$ used in the Mark–Houwink equation is usually closer to $\bar{M}_w$. Since the samples used in these correlations are unfractionated and of rather broad molecular weight distributions, the success of these correlations may be fortuitous, and the values of *K* and *a* reported in Table X should be considered preliminary. The Mark–Houwink plot of the viscosity–molecular weight data for poly(FEMA) is shown in Figure 4.

Poly(FEA–quinone)salts. Upon treating benzene solu-

Table V
Attempted Polymerization of 1-Ferrocenylethyl Acrylate

Monomer used, g	AIBN used, g	Benzene used, ml	Temp, °C	Time, hr	Polymer yield, g
0.5303	0.0073	5	80	120	0
9.4618	0.1000	10	70	144	0
1.4000	0.0000	5	80	48	0
2.3942	0.0250	10	90	120	0

Table VI
Kinetics of FEA Homopolymerization. Dependence of R_p on Initiator Concentration at 70° when [FEA] = 0.400 mol/l.

Run no.	[AIBN], mol/l.	$R_p \times 10^5$, mol/l. sec	$R_p \times 10^4$/[FEA][AIBN]$^{1/2}$
1	0.0050	2.13	7.53
2	0.0075	2.69	7.78
3	0.0096	3.11	7.63
4	0.0120	3.97	9.05
5	0.0142	4.16	8.72
6	0.0188	4.93	9.00
7	0.0263	5.51	8.50

Table VII
Kinetics of FEA Homopolymerization. Dependence of R_p on FEA Concentration at 70° when [AIBN] = 0.0142 mol/l.

Run no.	[FEA], mol/l.	$R_p \times 10^5$, mol/l. sec	$R_p \times 10^4$/[AIBN]$^{1/2}$[FEA]
8	0.812	9.05	9.40
9	0.550	6.11	9.33
10	0.400	4.16	8.74
11	0.300	2.70	7.56
12	0.200	1.54	6.47
13	0.200	1.48	6.21
14	0.100	0.78	6.37

Table VIII
Kinetics of FEMA Homopolymerization. Dependence of R_p on Initiator Concentration at 60° when [FEMA] = 0.400 mol/l.

Run no.	AIBN, mol/l.	$R_p \times 10^5$, mol/l. sec	$R_p \times 10^4$/[FEMA][AIBN]$^{1/2}$
1	0.0050	1.19	4.20
2	0.0096	1.82	4.65
3	0.0120	2.14	4.88
4	0.0142	2.42	5.12
5	0.0188	2.56	4.68
6	0.0234	3.11	5.08

Table IX
Kinetics of FEMA Homopolymerization. Dependence of R_p on FEMA Concentration at 60° when [AIBN] = 0.0142 mol/l.

Run no.	FEMA, mol/l.	$R_p \times 10^5$, mol/l. sec	$R_p \times 10^4$/[AIBN]$^{1/2}$[FEMA]
7	0.700	3.61	4.37
8	0.540	2.93	4.60
9	0.480	2.57	4.53
4	0.400	2.42	5.13
10	0.300	1.59	4.49
11	0.200	0.92	3.92

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(17) S. K. Patra and D. Mangaraj, *Makromol. Chem.*, 3, 168 (1968).

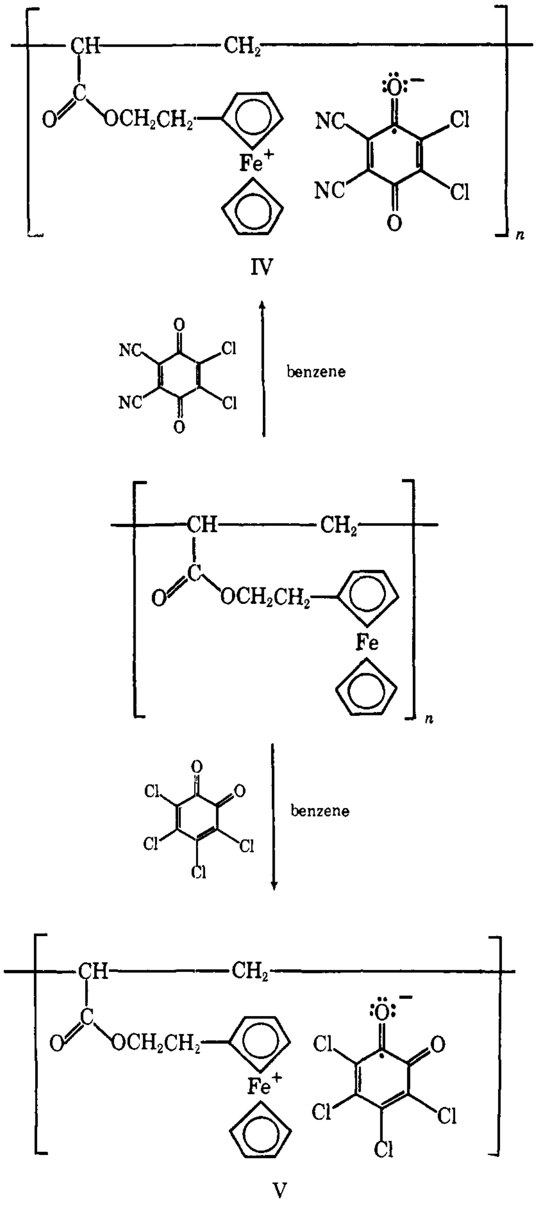
(18) H. Mark, *Z. Elektrochem.*, **40**, 413 (1934); R. Houwink, *J. Prakt. Chem.*, **157**, 14 (1940).

TABLE X
MARK-HOUWINK CONSTANTS FOR HOMOPOLYMERS OF FEA AND FEMA[a]

Polymer of	M	$K \times 10^3$	a
IIa	$\bar{M}_n$	4.68	0.70
	$\bar{M}_w$	3.16	0.50
IIb	$\bar{M}_n$	3.12	0.76
	$\bar{M}_w$	2.19	0.64

[a] [η] is given in ml/g.

tions of poly(2-ferrocenylethyl acrylate) with benzene solutions of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) or *o*-chloranil (*o*-CA), black poly(ferricinium salts) were formed (details given in Experimental Section). Both IV and V were infusable up to 365°. The number of moles of quinone incorporated into the polymers per mole of monomer was determined by elemental analysis. Since the polysalts precipitate from benzene solution, complete oxidation of each ferrocene nucleus does not necessarily occur. However, upon mixing either DDQ or *o*-CA in a 1:1 mole ratio with the polymer in benzene, almost complete oxidation occurred. Under these conditions, the resulting polysalts had a FEA/*o*-CA ratio of 1.09/1.00 and a FEA/DDQ ratio of 1.15/1.00. For every mole of quinone that was incorporated, 1 mol of ferrocene was oxidized to ferricinium. All the quinone found in the polysalts was in the form of its anion. This same result previously had been exhaustively demonstrated for polymers of Ia and Ib upon treatment with *o*-CA and DDQ.[9f] Combining infrared, ultraviolet, and Mössbauer spectroscopy with elemental analysis, it was clearly shown that each mole of incorporated quinone had oxidized 1 mol of ferrocene.[9f] Thus, in this work, only the infrared spectra were needed to confirm this result.



IV

V

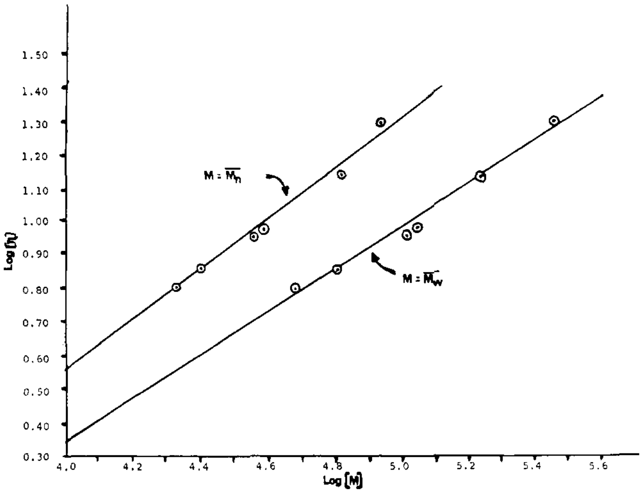


Figure 4. Viscosity-molecular weight relation for poly(2-ferrocenylethyl methacrylate).

DDQ and *o*-CA both exhibit strong carbonyl absorptions, at 1680 and 1640 cm^{-1}, respectively. This carbonyl stretching frequency is drastically lowered when the quinones are reduced to their radical ions. Brandon[19] reported the carbonyl band of DDQ had shifted to 1580-1600 cm^{-1} in the ferricinium$^+$ DDQ$^-$ salt, a result we verified.[9f] Iida[20] showed that the 1686-cm^{-1} stretching frequency of *p*-chloranil was lowered to 1524 cm^{-1} in its potassium salt. Finally, Pittman, *et al.*,[9f] demonstrated that in polymer salts of poly(ferrocenylmethyl acrylate) the carbonyl absorption of DDQ$^-$ occurred at 1570 cm^{-1} while that of *o*-CA$^-$ was found at 1585 cm^{-1}. Thus, a large lowering of the carbonyl stretching frequency was found in all these systems. In this work, the poly(FEA) salts showed a similar lowering of the quinone carbonyl stretching frequencies. The DDQ$^-$ carbonyl band was found at 1570 cm^{-1} while the *o*-CA$^-$ carbonyl band came at 1575 cm^{-1}. More importantly, no residual absorption at 1680 or 1640 cm^{-1}, due to unreduced quinone, was found.

The nitrile stretching frequency of DDQ occurs at 2230 cm^{-1} but upon reduction to DDQ$^-$ this frequency is lowered. For example, Pittman,[9f] *et al.*, observed this band at 2213 cm^{-1} in the DDQ polysalts of poly(ferrocenylmethyl acrylate). In the poly(FEA-DDQ)salts, obtained in this work, the nitrile band was found at 2210 cm^{-1} and no trace of absorption at 2230 cm^{-1} was found. Thus, all the quinone incorporated into the polysalt is in its reduced form. The polysalts also exhibited very powerful absorption between 840-850 cm^{-1} due to the cyclopentadienyl C-H out-of-plane bending frequency. Normally, in unoxidized ferrocene derivatives, this band is found at 810-830 cm^{-1}.[21] However,

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(19) R. L. Brandon, J. H. Osiecki, and A. Ottenberg, *J. Org. Chem.*, 31, 1214 (1966).

(20) Y. Iida, *Bull. Chem. Soc. Jap.*, 43, 345 (1970).

(21) I. Pavlik and V. Plechacek, *Collect. Czech. Chem. Commun.*, 31, 2083 (1966).

Spilners has reported this band to shift to 850–870 cm^{-1} in ferricinium tetrachloroferrate.[22]

Experimental Section

Monomer Synthesis. Acetylferrocene. Acetylferrocene was prepared in 80-g quantities from acetic anhydride and ferrocene by the method reported by Graham.[16] The product was sublimed and twice recrystallized from heptane to give a 61% yield (mp 85–86°, lit.[16] 85–86°). Key infrared bands observed were 3100, 2930–2850, 1735, 1370, 1340, 1107, 1045, 1028, 1005, 927, 815, and 725 cm^{-1}.

1-Ferrocenylethanol. 1-Ferrocenylethanol was prepared in 60-g quantities by the sodium borohydride reduction of acetylferrocene in methanol as reported by Hauser.[23,24] An 87% yield of 1-ferrocenylethanol (mp 74–75°, lit.[6] 73–75°) was obtained after recrystallization from ether–petroleum ether. Key infrared bands observed were 3110, 2930–2820, 1720, 1473, 1375, 1340, 1290, 1268, 1220, 1134, 1070, 1050, 1040, 1027, 1018, 948, 835, 770, and 764 cm^{-1}.

Preparation of 1-Ferrocenylethyl Acrylate. 1-Ferrocenylethanol, 30 g (0.13 mol), was dissolved in 1000 ml of anhydrous ether. The solution was cooled in an ice bath and 14.4 ml (0.182 mol) of pyridine was added with constant stirring. A solution of 14.3 ml (0.180 mol) of acrylyl chloride, in 15 ml of ether, was added dropwise to the rapidly stirring solution. Immediately, a white precipitate of pyridine hydrochloride precipitated out. The reaction was allowed to continue for 4 hr, after which time the solution was diluted with 500 ml of ether and filtered. The filtrate was then washed five times with $NaHCO_3$–H_2O, NaCl–H_2O, dried over sodium sulfate, and filtered. Solvent was removed *via* a rotary evaporator, leaving a yellow powder. The residual powder, recrystallized from hexane, gave 24.3 g (65.7%) of the product: mp 40–42°; ir (KBr) 3110, 2980–2860, 1720, 1625, 1635, 1470, 1420, 1280, 1200, 1115, 1048, 1033, 850, 825 cm^{-1}; nmr (CCl_4) δ 4.04 (s, 5, unsubstituted cyclopentadienyl ring), 4.02 (t, 2, J = 1.5 Hz, substituted ring), 4.18 (t, 2, J = 1.5 Hz, substituted ring), 1.51 (d, 3, J = 6.5 Hz, CH_3), 1.34 (q, 1, J = 6.5 Hz, H), 5.59–6.43 (ABC pattern, 3, vinyl hydrogens). *Anal.* Calcd: C, 63.41; H, 5.68; Fe, 19.66. Found: C, 63.26; H, 5.84; Fe, 18.99. It was found that the analysis for iron was often slightly low. This was also noted by Lai[25] in the analysis of similar ferrocene compounds. Thin layer chromatography (tlc) of 1-ferrocenylethyl acrylate on Mallinckrodt Silic AR TLC-7G with benzene solvent revealed a single spot of 1-ferrocenylethyl acrylate upon developing over iodine, indicating no precursor impurities.

Preparation of 2-Ferrocenylethyl Acrylate (FEA) and 2-Ferrocenylethyl Methacrylate (FEMA). The monomers FEA and FEMA were prepared in the following manner.

Methylation of *N,N*-Dimethylaminomethylferrocene. The methiodide salt of the title compound was prepared in 300–400-g quantities in yields of better than 90% by the method of Hauser.[23] The salt was washed with ether and obtained as yellow crystals which decomposed on heating at 248–249°, lit.[23] 248–250°.

Preparation of Ferrocenylacetonitrile. The preparation of ferrocenylacetonitrile, hydrolysis to ferrocenylacetic acid, and reduction to ferrocenylethyl alcohol are similar to the procedures reported by Hauser.[24]

A solution of 303 g (0.79 mol) of the methiodide of *N,N*-dimethylaminomethylferrocene and 305 g (4.7 mol) of potassium cyanide in 2400 ml of water was brought to reflux. At the end of 8 hr, the mixture was cooled and extracted four times with 1000 ml of ether, fresh ether being used for each extraction in a separatory funnel. The ethereal solution (in 500-ml aliquots) was washed five times with 1000 ml of water and the organic layer dried over Na_2SO_4. The ether was then removed with a rotary evaporator, leaving 130.7 g (83.5%) of the yellow nitrile. After recrystallization from hexane, the nitrile [mp 81–82°, lit.[24] 76–79°; ir (KBr) 3110, 2980, 2860, 2260, 1675, 1630, 1610, 1305, 1260, 1325, 1173, 1112, 1045, 1033, 1008, 908, 872, 838, 831, 819, 745, 725 cm^{-1}] was used as rapidly as possible because the nitrile darkens on standing.

Hydrolysis of Ferrocenylacetonitrile to Ferrocenylacetic Acid. A suspension of 130.7 g (0.58 mol) of ferrocenylacetonitrile in 2500 ml of water was added to a solution of 328 g (5.85 mol) of KOH in 2500 ml of water. The reaction was then brought to reflux and left to react overnight. Ethanol was then removed with a rotary evaporator to bring the volume to approximately 700 ml. Sufficient water was then added to redissolve the precipitated material which had fallen out, and acidification of the alkaline solution with 85% phosphoric acid gave golden crystals (131 g) of ferrocenylacetic acid which were collected by filtration and dried (mp 152–153°, lit.[24] 152–156°). The yield was 86%.

Preparation of 2-Ferrocenylethyl Alcohol. Ferrocenylacetic acid, 43.7 g (0.18 mol), was placed into a Soxhlet extractor over 7 g (5.43 mol) of $LiAlH_4$ in 800 ml of anhydrous ether. The $LiAlH_4$ ether suspension was brought to reflux. The refluxing was continued until all the acid had dissolved (48 hr), coloring the contents of the flask yellow-orange. The contents of the flask were then cooled in an ice bath and then treated slowly with water and 700 ml of 20% (aqueous) hydrochloric acid. The organic layer was separated and washed twice with a 5% NaOH–water solution and water and dried over sodium sulfate. Removal of the ether under vacuum left a red viscous oil which, when dissolved in warm 30–60° petroleum ether and cooled in ice, yielded 32.2 g (78%) of orange crystals (mp 40–41°, lit.[24] 41–42°) when recrystallized from 30–60° petroleum ether: ir (KBr) 3100, 2930–2850, 1375, 1340, 1111, 1045, 1030, 1005, 938, 830, 724 cm^{-1}; nmr (CCl_4) δ 4.00 (s, 5, unsubstituted cyclopentadienyl ring), 3.98 (t, 2, substituted ring), 3.95 (t, 2, J = 1.5 Hz, substituted ring), 3.57 (t, 2, J = 7.0 Hz, CH_2), 2.47 (t, 2, J = 7.0 Hz, $-OCH_2$), and 2.32 (s, 1, OH).

(a) 2-Ferrocenylethyl Acrylate. 2-Ferrocenylethyl alcohol, 64 g (0.278 mol), was dissolved in 3000 ml of anhydrous ether. Pyridine, 29 ml (0.362 mol), was then added. Acrylyl chloride, 29 ml (0.339 mol), in 30 ml of ether was then added dropwise from the pressure-equalizing funnel over a period of 1 hr. A precipitate of pyridine hydrochloride formed immediately as each drop hit the rapidly swirling solution. The reaction was continued 4 hr after which time 800 ml of ether was added and the solution filtered to remove the precipitated pyridine hydrochloride. The precipitate was washed with anhydrous ether until no yellow tinge was evident in the ether. The combined filtrate was then washed five times with 500 ml of $NaHCO_3$–H_2O, NaCl–H_2O, and water, dried over sodium sulfate, and filtered. The ether was then evaporated with a rotary evaporator, leaving a red-brown viscous oil. Yellow crystals (39.7 g, 62%) of 2-ferrocenylethyl acrylate (FEA) were obtained upon recrystallization from 30–60° petroleum ether at 0°: mp 19–21°; ir (KBr) 3110, 2980–2860, 1730, 1635, 1625, 1410, 1295, 1270, 1190, 1105, 1050, 995, 980, 805 cm^{-1}; nmr (CCl_4) δ 4.01 (s, 5, unsubstituted ring), 3.98 (t, 2, J = 1.5 Hz, substituted ring), 3.95 (t, 2, J = 1.5 Hz, substituted ring), 4.19 (t, 2, J = 7.5 Hz, CH_2), 2.60 (t, 2, J = 7.5 Hz, CH_2), 5.64–6.43 (ABC pattern, 3, vinyl hydrogens). *Anal.* Calcd: C, 63.41; H, 5.68; Fe, 19.66. Found: C, 63.28; H, 5.81; Fe, 19.97.

(b) 2-Ferrocenylethyl Methacrylate (FEMA). 2-Ferrocenylethyl alcohol, 80 g (0.348 mol), was esterified with methacrylyl chloride, 47 ml (0.487 mol), using pyridine, 42 ml (0.523 mol), in the same manner as described above in the FEA synthesis. After an identical work-up procedure a solid residue was obtained, which when recrystallized from 30–60° petroleum ether yielded 84.5 g (81%) of FEMA (mp 43–44°). *Anal.* Calcd: C, 64.45; H, 6.08; Fe, 18.73. Found: C, 63.99; H, 6.13; Fe, 18.31.

Even though the iron analysis was slightly low, thin layer chromatography of FEMA on Mallinckrodt Silica AR TLC-7G with benzene revealed a single spot upon developing over iodine, indicating no precursor impurities: ir (KBr) 3110, 2980–2860, 1720, 1640, 1460 1405, 1390, 1380, 1320, 1295, 1160, 1105, 1040, 1010, 995, 980, 940, 810 cm^{-1}; nmr (CCl_4) δ 3.99 (s, 5, unsubstituted ring hydrogens), 3.98 (t, 2, J = 1.5 Hz, substituted ring hydrogens), 4.20 (t, 2, J = 7 Hz, $-OCH_2-$), 2.63 (t, 2, J = 7 Hz, CH_2), 1.92 (s, 3, CH_3), 5.36 and 6.17 (s, 2, vinyl hydrogens).

Homopolymerization of Transition Metal Organometallic Mono-

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mers. Polymerization was carried out in either freshly distilled benzene (from P_2O_5) or freshly distilled ethyl acetate. Azobisisobutyronitrile (AIBN) was used as the free radical initiator. Commercial AIBN was recrystallized three times from methanol before use (mp 102–103°). Monomers were stored at −15° in the dark before use and were freshly prepared before use.

Fischer–Porter aerosol compatability tubes, equipped with valves, were used for polymerization runs. Weighed amounts of monomer, solvent, and initiator were charged to the tubes; the tubes were sealed and then degassed at 10^{-3} mm by three alternate freeze–thaw cycles. Liquid nitrogen was used as the freezing medium. After degassing, the tubes were placed in a Haake constant-temperature bath (Model 1280-3, ±0.01°) for a specified time. After removal from the bath, the polymer was precipitated in a rapidly swirling large excess of 30–60° petroleum ether. The polymer solution was diluted with more solvent when necessary so that fine particles of polymer precipitated rather than large chunks. This process was repeated three times to ensure that all monomers and other contaminants had been washed from the polymer. After the last precipitation, the polymer was filtered and dried in a vacuum desiccator. Some gelation during polymerization of FEMA occurred, resulting in a polymer fraction insoluble in benzene.

Infrared Spectra of Homopolymers. The infrared spectra were obtained in KBr pellets on a Perkin-Elmer Model 237 spectrometer.

Homopolymers of FEA. No C=C stretching at 1625 cm^{-1} was found in any of the homopolymers of IIa. Key ir bands were observed at 3090, 2970–2860, 1735, 1455, 1400, 1260, 1230, 1165, 1108, 1041, 1023, 1000, 815, and 479 cm^{-1}.

Homopolymers of FEMA. No C=C stretching at 1625 cm^{-1} was observed. Key ir bands were observed at 3090, 2970–2860, 1735, 1470, 1400, 1265, 1245, 1150, 1105, 1038, 1020, 998, 815, and 479 cm^{-1}.

Kinetic Studies of Homopolymerization of Ferrocenylethyl Acrylate and Ferrocenylethyl Methacrylate. The rates of polymerization (R_p) of IIa and IIb with respect to initiator concentration and monomer concentration were determined by dilatometry. The procedure used was similar to that described by Baldwin.[12] Weighed amounts of monomer, initiator, and solvent were placed in a glass bulb which was then attached to the dilatometer by means of metal springs and a ground glass joint.

A mercury reservoir was located directly below the dilatometer. The sample was frozen and then degassed at 10^{-3} mm in three alternate cycles. After the third degassing, the dilatometer was inverted and the mercury allowed to flow up to the frozen monomer and fill the dilatometer. The monomer solution was allowed to thaw and the apparatus was placed in a constant-temperature bath (+0.01°). After temperature equilibrium was reached (about 5 min), the rate of shrinkage of the solution due to polymerization was measured by following the rate at which the mercury column dropped. The number of moles which had polymerized was found by dividing the ΔV values by the molar volume contraction constant, ΔV/mol. Plots of the log of monomer concentration *vs.* time gave a straight line for each run, and the rate of polymerization was calculated from $R_p = 2.303$(slope). The ΔV/mol values were calculated from the differences in specific volumes between monomer and polymer, found from pycnometer measurements. ΔV/mol for IIa was 20.5 ml/mol and for IIb was 28.9 ml/mol (Table XI).

Plots of $-\log R_p$ *vs.* $1/T_K$° for IIa and IIb homopolymerizations gave straight lines when drawn by the method of least squares. The energy of activation for FEA between 60 and 72° was 21.7 kcal/mol and the activation energy for FEMA was 18.6 kcal/mol between 58 and 72°.

Gel Permeation Chromatography. A Waters Associates Model 200 gel permeation chromatograph was used to determine the $\bar{M}_n$, $\bar{M}_w$, and overall molecular weight distributions of the polymers. The polymers were chromatographed in tetrahydrofuran, and the chromatograms were analyzed in the standard fashion advocated by Cazes[26] using points every half-count.[27] The chromatograms were not first corrected for gaussian instrumental spreading as advocated by Tung[28] because this correction is not important in polymers with broad molecular weight distributions, and it only becomes important with increasingly narrow polymer fractions.[28]

TABLE XI
SUMMARY OF ENERGY OF ACTIVATION RUNS FOR HOMOPOLYMERIZATION OF IIa AND IIb[a]

Temp, °C	$R_p \times 10^5$, mol/l. sec	
	IIb	IIa
58	1.630	
60	2.421	1.610
63	2.460	2.134
65	3.394	2.659
67	3.739	3.036
70	5.000	4.158
72	5.356	4.785

[a] [IIa or IIb] = 0.400 *M*, [AIBN] = 0.0140 *M*.

As an absolute standard, the values of $\bar{M}_n$ were first determined by vapor pressure osmometry. This value of $\bar{M}_n$ was then used to assign the value of $\bar{M}_n$ at the position in the chromatogram which was the number-average chain length ($\bar{A}_n$). In this way a *Q* factor was determined, equal to $\bar{M}_n/\bar{A}_n$. Once *Q* had been obtained on several samples of the polymer, a *Q* value for that polymer was established as the average of those obtained, and this value was used in calculations of $\bar{M}_w$ and the overall molecular weight distribution. Homopolymers of FEA had an average *Q* value of 92 while those of FEMA exhibited an average *Q* of 93.5.

Viscosity Measurements. Viscosity measurements were made with a Cannon–Ubbelohde semimicro dilution viscometer (50L631) at 30 ± 0.01° and were run in benzene. Tables II and III summarize the molecular weight and intrinsic viscosity data.

Preparation of Poly(electron transfer)salts of Poly(2-ferrocenylethyl acrylate). Preparation of Poly(FEA–chloranil)salt. Poly(FEA), 0.2500 g (0.88 mmol), of FEA units was dissolved in 20 ml of dry benzene and added to 0.2165 g (0.88 mmol) of *o*-chloranil in 20 ml of dry benzene while stirring at room temperature. The solution turned a dark brown color as the precipitate formed and was allowed to stand overnight. The solution was then filtered and the precipitate washed with benzene until the benzene was colorless. After drying under vacuum, 0.21 g (45.2%) of the poly(FEA–chloranil)salt was obtained. The precipitate did not melt at 360°.

Anal. Found: C, 48.67; H, 3.67; Fe, 10.81. This corresponds to a FEA–chloranil mole ratio of 1.09:1.00. Ir showed 3100, 2990–2865, 1740, 1575, 1440, 1370, 1245, 1162, 1101, 996, 968, 845, 798, 775, and 714 cm^{-1}.

Preparation of Poly(FEA–DDQ)salt. Poly(FEA), 0.2500 g (0.88 mmol of FEA units), was dissolved in 20 ml of dry benzene and mixed with 0.0999 g (0.88 mmol) of DDQ in 20 ml of dry benzene while rapidly stirring the solution. A black precipitate was immediately precipitated. After stirring 30 min, the black solution was filtered and the precipitate washed with benzene until the washings were colorless. After drying under vacuum, 0.21 g (93.2%) of the poly(FEA–DDQ)salt was collected. The salt did not melt at 360°. *Anal.* Found: C, 54.46; H, 3.91; Fe, 11.39. This corresponds to a FEA–DDQ mole ratio of 1.15:1.00. Ir showed 3100, 2990, 2865, 2210, 1735, 1570, 1465, 1380, 1230, 1187, 1158, 1043, 1000, 875, 845, 773, and 700 cm^{-1}.

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