It is to be noted, however, that chain folding is a widely accepted mechanism for the crystallization of synthetic high polymers[10] as well as many natural linear polymers. For these systems it is admitted that the extended chain form is unquestionably the most stable, since a fold usually represents molecular distortion and strain. However, folding is tolerated since kinetic factors control the crystallization and, as a result of this, the effect of temperature is to increase the length of chain segments between folds. This is clearly the opposite to what has been observed in our case and suggests an important influence of solvent on the phenomenon.

Polymerization of Ferrocenylmethyl Acrylate and Ferrocenylmethyl Methacrylate. Characterization of Their Polymers and Their Polymeric Ferricinium Salts. Extension to Poly(ferrocenylethylene)

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ABSTRACT: Poly(ferrocenylmethyl acrylate), poly(ferrocenylmethyl methacrylate), and poly(ferrocenylethylene) have been prepared by AIBN-catalyzed, free-radical polymerization in benzene solution. Treatment of these polymers with strongly electron attracting compounds such as tetracyanoethylene, dichlorodicyanoquinone, and *o*-chloranil leads to poly(ferricinium) salts, or polymeric charge-transfer derivatives. The characterization of these polymers was carried out by kinetic studies, infrared, nuclear magnetic resonance, ultraviolet, and Mössbauer spectroscopy, as well as gel permeation chromatography and viscosity studies. Some of these studies must be carried out before treatment with the electron acceptor. Mössbauer spectroscopy was found to be an excellent analytical technique to determine the percentage of ferrocene groups converted into ferricinium units, since iron in ferrocene groups exhibits a large quadrapole splitting (~2.4 mm/sec), while in ferricinium groups iron has a single peak. Each molecule of electron-attracting quinone in the poly(ferricinium) salts was present as its radical anion. Polysalts were prepared in which varying percentages of the ferrocene nuclei had been oxidized to ferricinium units. The homopolymerizations were first order in [monomer], half order in [AIBN], giving polymers with $\bar{M}_n = 5\text{–}36 \times 10^3$ before addition of electron acceptors. The activation energies were determined for the first-order polymerizations.

Over the past 15 years a large variety of polymers containing ferrocene has been prepared and reviewed.[2] In spite of the large number of condensation polymers and unusual polymeric structures which have been prepared, references are rare to addition polymers containing ferrocene, especially free-radical-initiated addition polymers. One of the few exceptions is vinylferrocene which has been polymerized to poly(ferrocenylethylene), a tan powder melting at 280–285°, by the use of azobisisobutyronitrile (AIBN) in bulk and in solution.[3] However, even poly(ferrocenylethylene), PFE, has not been extensively characterized. No previous polymerization of ferrocene-containing acrylates has been reported. One reason that reports of addition polymers of ferrocene (and other transition metal-containing organometallic compounds) are rare is that easy oxidation of the transition metal can occur instead of polymerization, with strongly oxidizing initiators. Ferrocene is readily oxidized to the stable ferricinium ion at a potential of -0.56 V.[4a] Free radicals, formed from initiators such as benzoyl peroxide, in some cases oxidize ferrocene instead of initiating polymerization, and cations, such as the nitronium ion, oxidize ferrocene instead of attacking the cyclopentadienyl rings electrophilically. In strong acids ferrocene is protonated at iron.[4b] Thus, in some cases normal cationic polymerization of ferrocene derivatives will be thwarted. Furthermore, initial free-radical polymerization of ferrocene derivatives can be precluded if the iron atom catalyzes either preferential decomposition of the initiator or reduces growing chain radicals.

Several factors make addition polymers of ferrocene derivatives, such as vinylferrocene and acrylates of ferrocene, of paramount interest. First, Richards[5]

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(2) C. U. Pittman, Jr., *J. Paint Technol.*, **39** (513), 585 (1967); H. Valot, *Double Liaison*, **130**, 775 (1966); M. Dub, "Compounds of the Transition Metals," Vol. 1, Springer-Verlag, Berlin, 1966; E. W. Neuse in "Advances in Macromolecular Chemistry," Vol. 1, M. W. Pasika, Ed., Academic Press, New York, N. Y., 1968; E. W. Neuse and H. Rosenberg, Ferrocene Polymers," Marcel Dekker, New York, N. Y., in press; T. P. Vishnyakova *Usp. Khim.*, **36**, 2136 (1967).

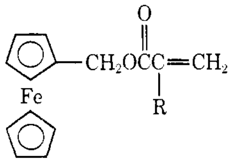
(3) F. S. Arimoto and A. C. Haven, *J. Amer. Chem. Soc.*, **77**, 6295 (1955); A. C. Haven, Jr., U. S. Patent 2,821,512 (1958); C. Y. Hua, F. Refojo, and H. G. Cassidy, *J. Polym. Sci.*, **40**, 433 (1959); M. G. Baldwin and K. E. Johnson, *ibid., Part A-1*, **5**, 2091 (1967).

(4) (a) J. A. Page and G. Wilkinson, *J. Amer. Chem. Soc.*, **74**, 6149 (1952); (b) T. J. Curphey, J. O. Santer, M. Rosenblum, and J. H. Richards, *ibid.*, **82**, 5249 (1960).

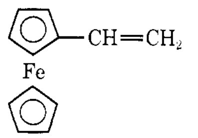
(5) J. H. Richards, *J. Paint Technol.*, **39**, (513), 569 (1967).

and Hammond[6] have demonstrated that ferrocene functions as a very efficient quencher of photochemically generated triplet states in anthracene, as well as a sensitizer in the photochemical dimerization of isoprene and the isomerization of *cis-* to *trans*-piperylene. Thus, coatings made from copolymers which include the ferrocene nucleus could exhibit special stability to many photochemical degradation reactions brought about by exposure to sunlight. This is an especially attractive possibility when one considers ferrocene's low toxicity and high absorption of ultraviolet[7] and γ[8] radiation. Also, ferrocene might serve as an internal catalyst to promote certain curing reactions. Ferrocene's easy oxidation might lead to polymers containing ferricinium units useful in special ionic adhesive roles. Polyacrylates and polymethacrylates of ferrocene derivatives are expected to exhibit very high glass-transition temperatures, T_g, due to ferrocene's high density, symmetry, and tendency to crystallize. Two of the highest T_g values previously reported for methacrylate polymers are 190–196° for poly(3,5-dimethyl-1-adamantyl methacrylate)[9] and 142° for poly(*m*-dioxane methacrylate).[10]

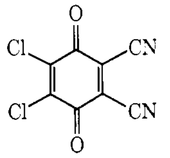
We now report the AIBN-catalyzed solution polymerization of ferrocenylmethyl acrylate (I, FMA), ferrocenylmethyl methacrylate (II, FMMA), and vinylferrocene (III), and the characterization of these polymers. Second, we report the reaction of these polymers with the strong electron attractors dichlorodicyanoquinone (IV), (DDQ), *o*-chloranil (V, *o*-CA), and tetracyanoethylene (VI, TCNE). to give polymeric ferricinium salts, and we discuss the characterization of these polymers using Mössbauer spectroscopy.



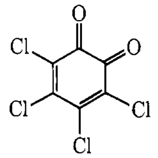
I, R = H
II, R = CH_3



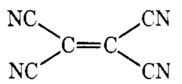
III



IV



V



VI

Experimental Section

Synthesis of Monomers. The methiodide salt of *N,N*-dimethylaminomethylferrocene was converted to hydroxymethylferrocene in 90% yield as reported previously[11] (mp 81–82°, lit.[11] mp 81–82°). Esterification of hydroxymethylferrocene in ether-pyridine at 0° with either acryloyl chloride or methacrylyl chloride gave FMA (mp 42–43° after three recrystallizations, increased suddenly to 70° after the sixth recrystallization from heptane) and FMMA (mp 52–54°) in yields of 75 and 84%, respectively. The melting points were obtained by differential scanning calorimetry because thermal polymerization begins to occur measurably at their melting points. These monomers hydrolyze easily in methanol–water systems. Key ir bands for FMA were observed at 3110, 2980–2860, 1720, 1625, 1635, 1460, 1400, 1385, 1280, 1190, 1115, 1050, 994, 955, 937, 820, and 740 cm^{-1} and for FMMA at 3108, 2980–2860, 1720, 1640, 1460, 1375, 1302, 1250, 1170, 1114, 1149, 1004, 950, and 820 cm^{-1}. Nmr spectra were in accord with the correct structures as follows: (FMA) unsubstituted cyclopentadienyl ring hydrogens 4.04 (s), substituted ring 4.00 (t) and 4.17 (t), J = 1.5 Hz, CH_2 4.85 (s), vinyl hydrogens ABC pattern 5.51–6.40; (FMMA) CH_3 1.90 (s), unsubstituted ring hydrogens 4.04 (s), substituted ring 4.01 (tr) and 4.16 (tr), J = 1.5 Hz, CH_2 4.84 (s) and nonequivalent vinyl hydrogens at 5.43 and 6.01 (s). The chemical shifts were expressed in parts per million downfield from TMS.

Anal. Calcd for FMA: C, 62.26; H, 5.22; Fe, 20.67. Found: C, 62.57; H, 5.36; Fe, 19.70. Calcd for FMMA: C, 63.42; H, 5.68; Fe, 19.66. Found: C, 64.02; H, 5.82; Fe, 19.20.

Vinylferrocene was prepared from hydroxyethylferrocene by sublimation from alumina[12] or by $CuSO_4$-catalyzed dehydration[13] and was found to be identical (ir, nmr, melting point) with authentic samples.

The explanation for the sharp increase in the melting point of FMA after many recrystallizations is not clear. Both the 42–43 and the 70° melting point samples appeared pure on both alumina and silica gel tlc plates and polymerizations of each gave, within experimental error, polymers of identical molecular weight distributions.

Solution Polymerization. Polymerizations of vinylferrocene, FMA, and FMMA were carried out in degassed benzene solutions. Weighed amounts of monomer, initiator (AIBN), and benzene (distilled from P_2O_5) were placed in Fisher–Porter aerosol compatability tubes, equipped with a valve, and degassed at 10^{-3} mm by three alternate freeze–thaw cycles. After degassing, the tubes were placed in a constant-temperature bath controlled to ±0.01°. FMA and FMMA were prepared shortly before use and stored at −15° in the dark. Upon completion of polymerization the polymer was precipitated from benzene by dropwise addition to excess petroleum ether (bp 30–60°). The polymer was filtered and redissolved in benzene and reprecipitated two more times, and then residual solvent was removed under vacuum. The polymers were solid yellow to brown materials with FMA and FMMA. The polymerizations resulted in both benzene soluble and benzene insoluble fractions. The insoluble fractions swelled in boiling benzene and in some cases actually seemed to dissolve although with great difficulty. Polymers of vinylferrocene were totally benzene soluble. AIBN was recrystallized from methanol (mp 102–103° with decomposition).

The cross-linking in the insoluble fractions of the polyacrylates probably arises from hydrogen abstraction α to ferrocene followed by branching from that point.

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(7) R. G. Schmitt and R. C. Hirt, American Cyanamid Co., Air Force WADC Technical Reports, 59-354; 60-704; 61-298 (available from the Defense Documentation Center, Alexandria, Va.).

(8) R. C. McIlhenny and S. A. Honigstein, July 1965, Air Force Report No. AF MLTR-65-294, AD 476623, Contract No. AF-33-(615)-1694.

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(11) J. K. Lindsay and C. R. Hauser, *J. Org. Chem.*, **22**, 355 (1957).

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Synthesis of Poly(ferricinium) Salts. Poly(ferrocenylethylene), PFE, poly(ferrocenylmethyl acrylate), PFMA, or poly(ferrocenylmethyl methacrylate), PFMMA, were dissolved into benzene and these solutions were treated with a benzene solution of DDQ, *o*-CA, or TCNE. With DDQ and *o*-chloranil the solutions turned black and black precipitates were immediately formed. After stirring 20–30 min at 25° the precipitate was filtered, washed with benzene and ether, and dried in a vacuum desiccator. More polar solvents such as methylene chloride, acetone, and acetonitrile were also used for these preparations. When the polymers were treated with TCNE, precipitates did not form, indicating electron transfer from ferrocene did not occur to any great extent upon initial mixing in solution. However, upon standing in solution some precipitate was formed.

Mössbauer Spectra. The Mössbauer spectra were collected in a Nuclear Data Series 2200 multichannel analyzer operated in the multiscaling mode. The preamplifier, linear amplifier, linear gate, and Mössbauer drive unit (Model 154) were obtained from Austin Science Associates. All spectra were taken at 77°K on sample sizes in the range of 38–25 mg/cm^2 with isomer shift values for the compounds being given with respect to nitroprusside. The data were refined using a conventional Lorenzian line shape fitting program and data fits were taken on two computers, an IBM 360 and a PDP-10. All values of isomer shift and quadrapole splittings were the average of two runs. The areas were obtained using Simpsons' rule as an approximation for the computer fit. The areas of the peaks were then related to the number of iron atoms in a particular environment.

Two assumptions were made in the calculations of the actual percentages of iron present in each environment (as ferrocene or as ferricinium). The first was that we were using thin absorbers. This is a valid assumption as can be seen from the small sample sizes which were used. The second assumption was that the recoil free fraction of the absorbing nuclei was the same for each species present. The recoil free fraction is dependent on several factors. One of the most important factors is the type of lattice in which the resonant nuclei are embedded. In the polysalts it would seem a good approximation to suggest both ferrocene and ferricinium units dispersed along the polymer chain should have nearly equal recoil free fractions. These assumptions permitted the use of the area under the resonance peaks to be a direct measure of the number of absorbing iron atoms in each specific environment.

Other Techniques. Infrared, ultraviolet, and nuclear magnetic resonance spectra were obtained using a Perkin-Elmer IR Model 237, a Cary 14 uv recording spectrometer, and a Varian HA-100 nmr spectrometer, respectively. The gel permeation chromatograms were obtained on a Waters Model 200 chromatograph on a bank of styragel columns calibrated in the standard fashion with narrow distribution polystyrenes. A Mel Labs vapor pressure osmometer was used to make measurements of $\bar{M}_n$ and both Cannon-Fenske and Ostwald viscometers were employed for viscosity measurements.

Kinetics. The polymerization kinetics were studied by dilatometry in constant-temperature baths held at ±0.01° using the method previously described by Baldwin.[14] The values of ΔV/mol in benzene were 17.3 ml/mol for FMA and 13.2 ml/mol for FMMA polymerizations.

Results and Discussion

TABLE I
THE ACTIVATION ENERGY FOR THE HOMOPOLYMERIZATION FMA WITH AIBN IN BENZENE FROM RATES OF POLYMERIZATION BETWEEN 50 AND 70° [a]

Temp, °C	1/°K × 10^3	$R_p \times 10^6$, mol/l. sec	$-\text{Log } R_p$
50.00	3.094	1.016	5.9031
53.00	3.066	1.382	5.8595
55.00	3.046	2.288	5.6406
55.00	3.046	2.053	5.6016
58.00	3.019	2.823	5.5493
60.00	3.002	3.220	5.4922
60.00	3.002	3.357	5.4741
63.00	2.974	3.658	5.4367
67.00	2.939	5.478	5.2614
67.00	2.939	6.064	6.2172
70.00	2.914	6.863	6.1635

[a] [AIBN] = 0 01400 mol/l.; [FMA] = 0.4000 mol/l.

TABLE II
THE ACTIVATION ENERGY FOR HOMOPOLYMERIZATION OF FMMA WITH AIBN IN BENZENE FROM RATES OF POLYMERIZATION BETWEEN 50 AND 70° [a]

Temp, °C	1/°K × 10^3	$R_p \times 10^6$ mol/l. sec	$-\text{Log } R_p$
60.00	3.002	1.146	5.9407
63.00	2.974	1.305	5.8846
65.00	2.957	2.155	5.6657
67.00	2.939	2.849	5.5454
68.00	2.930	3.601	5.4436
70.00	2.914	4.550	5.3420
70.00	2.914	4.742	5.3240
73.00	2.888	6.638	5.1780
75.00	2.871	8.710	5.0600

[a] [AIBN] = 0.1400 mol/l.; [FMMA] = 0.3998 mol/l.

Homopolymer Characterization. Kinetic Studies. Both FMA and FMMA homopolymerizations were first order in [monomer] and one-half order in [AIBN]. These kinetic data were recently reported.[15] The Arrhenius activation energy of FMA homopolymerization, between 50 and 70°, was 18.7 kcal/mol where [AIBN] = 0.01400 mol/l. and [FMA] = 0.4000 mol/l. For FMMA homopolymerization, the E_a = 32.7 kcal/mol, at the same concentrations, between 60 and 75°. These results, summarized in Tables I and II, parallel those found for methylacrylate and methymethacrylate polymerizations. The excellent straight line plots and high reproducibility found throughout the kinetic studies leave little doubt that a classic first-order radical polymerization mechanism describes the mechanism of these polymerizations. Thus, normal linear acrylate polymers are indicated for the benzene soluble fractions. The insoluble gelled fractions most probably occur by chain transfer to the "benzyl-like" methylene group followed by chain growth from this point.

Elemental Analyses. The elemental analyses were in agreement with (but do not require) the linear polymer structure. Usually the analyses of Fe were slightly low, but this appears to be a function of the method of analysis. It should also be noted that correction for end groups was not made in the calculated values. Since

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[14] M. G. Baldwin, *J. Polym. Sci., Part A-1*, **1**, 3209 (1963); M. G. Baldwin and K. W. Johnson, *ibid.*, **5**, 2091 (1967).

[15] C. U. Pittman, Jr., J. C. Lai, and D. Vanderpool, *Macromolecules*, **3**, 105, (1970).

TABLE III

Sample	Found, % C	H	Fe
PFMA 69-18	63.95	5.35	19.42
PFMA 69-24	63.62	5.57	19.60
Calcd	62.26	5.22	20.67
PFMMA 3001	64.22	5.79	17.80
PFMMA 3004	64.44	6.12	18.52
Calcd	63.42	5.68	19.66
PFE 002	67.96	5.91	24.74
PFE 003	67.90	6.24	23.53
Calcd	67.95	5.71	26.33

the monomer molecular weight is high and polymer molecular weights are reasonably low, iron values slightly lower than calculated must be expected. Representative elemental analyses are given in Table III.

Infrared Spectra. As expected for monosubstituted ferrocenes,[16] a sharp band combination at 1000 and 1100 cm^{-1} was present in all the polymers. The cyclopentadienyl rings' CH out-of-plane deformations[16] were present at about 810 cm^{-1} as were sp^2 hybridized carbon–hydrogen stretching bands above 3000 cm^{-1}.

PFMA. The polymer spectra were devoid of the C=C stretch at 1625–1635 cm^{-1} found in the monomer. An intense ester carbonyl stretch at 1738 cm^{-1} was present along with a strong broad CO stretch at 1168 cm^{-1}. Other bands were found at 3100, 2990–2865, 1470, 1460, 1385, 1270, 1248, 1109, 1043, 1030, 1004, 902, 809, and 673 cm^{-1}.

PFMMA. The polymer spectra were devoid of the monomer C=C stretch at 1640 cm^{-1}. An intense ester carbonyl appeared at 1725 cm^{-1} along with a broad CO stretch at 1162 cm^{-1}. Other bands were found at 3100, 2990–2850, 1470–1450, 1365, 1268, 1250, 1112, 1047, 1033, 1007, 920, 810, and 690 cm^{-1}.

PFE. The polymer spectra were completely devoid of the C=C stretch at 1625 cm^{-1} present in the monomer. As expected for an aliphatic ferrocene derivative, bands were found at 3095, 2860–2990, 1457, 1360, 1218, 1103, 1038, 1020, 997, 805, and 670 cm^{-1}.

Nmr Spectra. The nmr spectra of PFMA and PFMMA were obtained in chlorobenzene solvent at 125°. These spectra clearly showed both the unsubstituted and substituted cyclopentadienyl ring hydrogens and both the methyl (PFMMA) and methylene hydrogens of chain. However, serious paramagnetic broadening of all the peaks was observed. Even when small traces of ascorbic acid were added, this broadening remained. Thus, accurate area measurements and chemical shift determinations were not possible. This broadening also prevented an analysis of the relative amounts of syndiotactic, isotactic, and atactic polymer present.

Molecular Weight Distribution. Gel permeation chromatography (gpc) was used to determine the polymer molecular weight distributions. Vapor pressure osmometry provided an absolute measure of $\bar{M}_n$. This value of $\bar{M}_n$ was then used to assign the molecular weight at the number average chain length as determined from gel permeation chromatograms in tetrahydrofuran at room temperature. Thus, a Q factor was determined for each polymer by the following relation $Q = \bar{M}_n/A_n$, where A_n is the number average chain length calculated from the gpc chromatograms. Individual Q factors, determined on four PFMA polymers, varied only slightly from 89.0 to 93.6, in spite of the fact that the values of $\bar{M}_n$ varied from 6955 to 20,130 and values of $\bar{M}_w$ varied from 9960 to 82,300 (see Table IV). Thus, the average, Q = 90.8 mol wt units/Å, was selected and used to interpret all the PFMA gel chromatograms.

TABLE IV
DETERMINATION OF THE FACTOR Q FOR FMA POLYMERS

Polymer no.	$\bar{M}_n$ osmometry	$\bar{A}_n$ gpc, Å	Q	$\bar{M}_w$[a]
17A	20,130	222	90.7	82,300
18	12,100	136	89.0	22,700
24	12,550	134	93.6	26,600
25	6,955	77.4	89.9	9,960

[a] Calculated from the gpc data using Q = 90.8.

TABLE V
DETERMINATION OF THE FACTOR Q FOR FMMA POLYMERS

Polymer no.	$\bar{M}_n$ osmometry	$\bar{A}_n$ gpc, Å	Q	$\bar{M}_w$[a]
3006	8,650	91.9	94.1	16,100
1004	12,030	127	94.6	18,100
3002	15,920	177	89.9	78,400
3004	28,100	299	93.9	83,600
3001	35,500	360	98.6	211,000

[a] Calculated from gpc data using Q = 93.1.

Q factors, individually determined on five samples of PFMMA, showed a somewhat wider range of 89.9–98.6 (Table V). However, sample 3001, Q = 98.6, had a significantly broader molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 6.02) than the other four samples. More importantly, the gpc curves showed a portion of this polymer eluting at count numbers below 19.5. This portion of the polymer has a molecular weight too high to be resolved effectively by the column bank employed in these studies. Thus, a Q factor of 93.1 (the average of the first four samples) was chosen. A value of 88 was previously determined for the factor Q for PFE.[17a]

The calculation of $\bar{M}_n$ and $\bar{M}_w$ from gpc curves was carried out in the standard fashion advocated by Cazes[17b] using points every half-count,[18] and the results are summarized in Tables VI, VII, and VIII. Figures 1–3 are representative of the chromatograms obtained on homopolymer samples. It should be emphasized that the chromatograms were not first corrected for Gaussian instrumental spreading as advocated by Tung

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(16) (a) M. Rosenblum, Thesis, Harvard University, 1953; M. D. Rausch, *et al.*, *J. Amer. Chem. Soc.*, **82**, 76 (1960); (b) M. Rosenblum, "Chemistry of the Iron Group Metallocenes," Part I, Wiley, New York, N. Y., 1965, pp 37–39.

(17) (a) Determined by Mr. D. VanLandyt who is thanked for his aid in running gpc curves; (b) J. Cazes, *J. Chem. Educ.*, **43**, A567 (1966).

(18) J. E. Hazell, L. A. Prince, and H. E. Stapelfeldt, *J. Polym. Sci., Part C*, No. 21, 43 (1968).

TABLE VI
YIELDS, MOLECULAR WEIGHTS, AND INTRINSIC VISCOSITIES OF BENZENE-SOLUBLE FMA HOMOPOLYMERS

Polymer no.	$\bar{M}_n$	$\bar{M}_w$	[η], ml/g	Polymerization conditions % AIBN	Temp, °C	Time, hr	Yields Total, %[a]	Benzene soluble	Benzene insoluble
17A	20,130	82,300	12.76	0.836	90	66	56.9	70	30
18	12,100	22,700	7.59	0.703	95	66	54.7	61	39
20	5,660	9,060	4.92	0.620	80	91	37.8	72	28
21	9,200	14,500	6.48	0.657	80	250	37.3	100	
22	8,100	10,220		0.960	80	61	47.7	100	
23	14,850	35,700	7.65	1.019	90	96	68.3	100	
24	12,550	26,600	7.80	0.914	100	96	51.9	100	
25	6,955	9,960	5.31	1.038	120	96	68.6	88	12

[a] After three reprecipitations and work-up. Since samples were small the true yields are undoubtedly higher.

TABLE VII
MOLECULAR WEIGHTS AND INTRINSIC VISCOSITIES OF BENZENE-SOLUBLE FRACTIONS OF FMMA HOMOPOLYMERS

No.	$\bar{M}_n$	$\bar{M}_w$	[η], ml/g	Polymerization conditions % AIBN	Temp, °C	Time, hr	Yields Total %[a]	Benzene soluble	Benzene insoluble
1004	12,030	18,200							
3001	35,500	211,000	12,44	1.079	80	96	66.5	100	
3002	15,920	78,400	8.26	0.994	70	96	52.7	64	36
3003	28,200	160,000	10.92	0.513	80	96	71.4	100	
3004	28,100	83,600	10.50	0.499	90	72	64.7	100	
3005	6,110	9,100	4.37	0.945	100	96	58.2	60	40
3006	8,650	16,100	5.07	1.044	120	96	62.3	100	

[a] See Table VI, footnote *a*.

TABLE VIII
HOMOPOLYMERIZATION OF VINYLFERROCENE IN BENZENE SOLUTION

No.	$\bar{M}_n$	$\bar{M}_w$	[η], ml/g	Wt % AIBN	Temp, °C	Reaction time, time, hr	% yield
1	11,400	19,000	6.80	0.985	70	96	69.5
2	10,900	18,100	6.56	1.006	80	96	62.0
3	11,400	18,900	6.54	1.152	70	94.5	73.0
4	6,800	10,500	4.08	1.000	90	96	29.1
5	7,320	11,100	4.22	0.996	100	96	23.8
6	5,560	9,200	3.85	0.995	120	96	33.3
7	9,730	16,600	6.02	1.090	60	143	39.3
8	10,700	15,400	4.81	0.600	80	96	28.2[a]

[a] 80% benzene soluble and 20% benzene insoluble.

and others.[19] Thus, the distributions reported here might be slightly broader than the true values. However, this correction is not important in polymers of broad molecular weight distribution,[19] and it becomes increasingly important with increasingly narrow polymer fractions. The gpc curves demonstrated that the benzene-soluble portion of PFMA, PFMMA, and PFE polymers were homogeneous without significant cross-linking.

Viscosity–Molecular Weight Relations. The intrinsic viscosities of PFMA, PFMMA, and PFE polymers were correlated by the Mark–Houwink[20,21] equation, $[\eta] = KM^a$, where M was both $\bar{M}_n$ and $\bar{M}_w$ (Table IX). For linear rodlike polymers, the value of a should, according to Staudinger,[22] be 1. For randomly coiled molecules Kuhn[23] showed a might be as low as 0.5. The use of $\bar{M}_n$ in this equation is strictly justified only when

TABLE IX
SUMMARY OF MARK–HOUWINK CONSTANTS[a]

Polymer	*M*	*K*	*a*
PFMA	$\bar{M}_n$	6.84×10^{-3}	0.75
PFMA	$\bar{M}_w$	1.16×10^{-1}	0.42
PFMMA	$\bar{M}_n$	2.78×10^{-2}	0.58
PFMMA	$\bar{M}_w$	2.14×10^{-1}	0.34

[a] The molecular weight range of available PVF samples was too narrow to get meaningful values of *K* and *a*.

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(19) L. H. Tung and J. R. Runyon, *J. Appl. Polym. Sci.*, **13**, 775, 2397 (1969).

(20) H. Mark, *Z. Elektrochem.*, **40**, 413 (1934).

(21) R. Houwink, *J. Prakt. Chem.*, **157**, 14 (1940).

(22) H. Staudinger, "Die Hochmolekularen Organischen Verbindungen," J. Springer, Berlin, 1932, pp 28, 199.

(23) W. Kuhn, *Kolloid-Z. Z. Polym.*, **62**, 269 (1933); **68**, 2 (1934).

TABLE X
GLASS TRANSITION TEMPERATURES

Polyacrylates	T_g, °C	Polymethacrylates	T_g, °C
Methyl	3[a]	Methyl	57–68[g]
Ethyl	−23[a]	Ethyl	47[a]
n-Propyl	−51.5[a]	*n*-Propyl	33[a]
n-Butyl	−70[a]	*n*-Butyl	17[a]
n-Tetradecyl	−20[a]	*tert*-Butyl	107[b]
n-Hexadecyl	+35[a]	*n*-Octyl	−70[a]
p-Cyanophenyl	92[b]	*p*-Cyanophenyl	155[b]
Pentachlorophenyl	146[b]	*m*-Dioxane	142[h]
3,5-Dimethyl-1-adamantyl	100–106[c]	3,5-Dimethyl-1-adamantyl	190–196[c]
Ferrocenylmethyl	197–210[d]	Ferrocenylmethyl	185–195[d]
Ferrocenylethyl	157[e]	Ferrocenylethyl	209[e]
Polystyrene	90–101,[f] 81[g]	Poly(ferrocenylethylene)	184–194[d]

[a] R. H. Wiley and G. M. Brauer, *J. Polym. Sci.*, **3**, 455, 647 (1948); **4**, 351 (1949). [b] S. Krause, J. J. Gormley, N. Roman, J. A. Shetter, and W. H. Watanabe, *J. Polym. Sci., Part A*, **3**, 3573 (1965). [c] Reference 9. [d] This work. [e] Unpublished work of C. U. Pittman, Jr., and R. L. Voges. [f] B. Ke, *Polym. Rev.*, **6**, 396 (1964). [g] H. Mark and A. V. Tobolsky, "Physical Chemistry of High Polymers," Vol. II, 2nd ed, Interscience, New York, N. Y., 1950, p 347. [h] Reference 10.

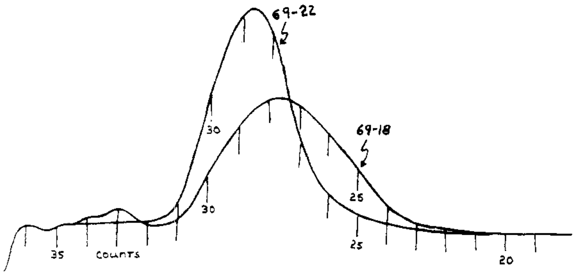

Figure 1. Gpc curves of PFMA samples.

carefully fractionated polymers are used[24] (an unavailable condition in this study). For many high polymers, viscosity average molecular weights are closer to the $\bar{M}_w$ values and where $a = 1$, $\bar{M}_n = \bar{M}_w$.[25] Since, by necessity, we used unfractionated polymers of varying $\bar{M}_w/\bar{M}_n$ ratios, the observed approximately straight-line plots of log $[\eta]$ *vs.* log $\bar{M}_n$ (or $\bar{M}_w$) were somewhat surprising. One should consider the values of a and K as preliminary. However, it is obvious that these molecules are moderately coiled in benzene. The viscosity measurements are summarized in Tables VI, VII, and VIII.

Glass Transition Temperatures. Glass transition temperatures were measured under nitrogen using the differential scanning calorimeter technique. The reported values should be understood as approximate values. The dsc curves were not always sharp and easily interpreted. The values could be approximated in all cases, and it is strikingly clear from these results that ferrocene-containing acrylate polymers and poly(ferrocenylethylene) have very high values of T_g. This indicates the ferrocene nucleus sharply increases the cohesive energy density in these polymers. The effect of the ferrocene nucleus on T_g can be compared to that of the benzene ring. Polystyrene exhibits a T_g of 81°, whereas poly(ferrocenylethylene) has a T_g of 184–194°. Poly(pentachlorophenyl acrylate), which has one of the highest T_g values of any polyacrylate (T_g = 146°), still falls short of T_g 200° for ferrocenylmethyl acrylate. Thus, ferrocene appears to be a functional group of great interest in preparing polymers with high glass-transition temperatures. The summary of our T_g measurements, with those of other polymers of interest taken from the literature, is given in Table X.

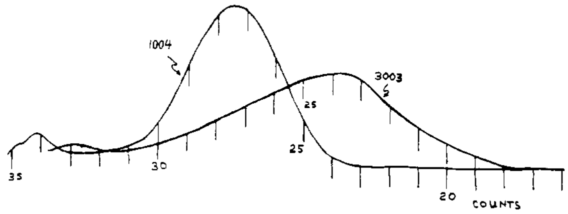

Figure 2. Gpc curves of PFMMA samples.

Characterization of the Polysalts. The polymeric complexes formed when ferrocene-containing polymers were treated with DDQ and *o*-CA were examined by ir, uv, and Mössbauer spectroscopy in addition to elemental analyses. The key questions to answer were: (1) had a polymeric charge-transfer[26] complex been formed or had the ferrocene nuclei been ionized to ferricinium units by the quinones, (2) what was the stoi-

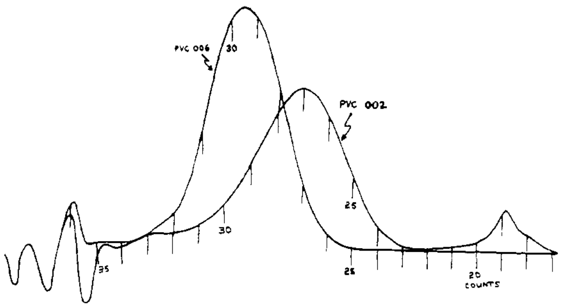

Figure 3. Gpc curves of PFE samples.

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(24) P. J. Flory, *J. Amer. Chem. Soc.*, **65**, 372 (1943).

(25) W. R. Sorenson and T. W. Campbell, "Preparative Methods of Polymer Chemistry," 2nd ed, Interscience, New York, N. Y., 1968, p 45.

(26) M. Rosenblum, R. W. Fish, and C. Bennett, *J. Amer. Chem. Soc.*, **86**, 5166 (1964).

TABLE XI
INFRARED SPECTRA OF QUINONES AND POLYSALTS[a]

	DDQ		*o*-CA
Sample	C=O stretch	-C≡N stretch	C=O stretch
Pure quinone	1680	2230	1640
PFMA	1570	2213	1585
PFMMA	1582	2205	1595
PFE	1567	2213	1599
Ferrocene	1575	2205	1601

[a] In Nujol mulls.

chiometry. Previous ir[26,27] and Mössbauer[28] studies indicated that pure ferrocene was converted to a ferricinium salt when treated with DDQ. This would suggest that the same oxidation of ferrocene might occur when our homopolymers were treated with DDQ and *o*-CA.

Infrared Studies. DDQ and *o*-CA both exhibit strong carbonyl absorption at 1680 and 1640 cm^{-1}, respectively. The carbonyl stretching frequency is drastically lowered when such quinones are converted to their radical anions.[27,29] Brandon, *et al.*,[27] reported the carbonyl band at 1580–1600 cm^{-1} in the ferricinium–DDQ salt, a result we verified. Iida[27] showed the carbonyl band at 1686 cm^{-1} in *p*-CA was lowered to 1524 cm^{-1} in its K^+CA^- salt. This corresponded to a reduction in the force constant from 9.7 to 7.3 mdyn/Å. The C=C stretch was similarly reduced from 1571 to 1540 cm^{-1} corresponding to a force constant decrease from 6.6 to 6.1 dmyn/Å or a bond length increase of 0.01 Å. A similar lowering of the quinone carbonyl stretching frequency was exhibited in PFMA–DDQ, PFMMA–DDQ, PFE–DDQ, PFMA–*o*-CA, PFMMA–*o*-CA, and PFE–*o*-CA samples (see Table XI) prepared in our work.

The C≡N stretching frequency in DDQ is 2230 cm^{-1}. In the polysalts, this stretching was found at frequencies from 15 to 25 cm^{-1} lower as expected in the anion. The polysalts also exhibited additional absorption in the 840–870-cm^{-1} region in addition to the normally powerful 810–830-cm^{-1} [30] band associated with the cyclopentadienyl C–H out-of-plane bending frequencies. This observation is consistent with Spilners' [31] recent report of a shift of ferrocene's 810–830-cm^{-1} band to the 850–870-cm^{-1} region in ferricinium chloroferrates. Thus, the polysalt ir spectra are in accord with the transfer of an electron from ferrocene to the quinone for each quinone molecule present in the polysalt. However, only a portion of the ferrocene units are oxidized.

TABLE XII
UV SPECTRA OF FERROCENE-CONTAINING
MONOMERS, POLYMERS, AND POLYSALTS

Sample	λ_{max}, mμ	ε (respectively)
FMA[a]	440, 247	111, 4,800
FMMA[a]	440, 247	140, 4,960
PFMA[b]	430, 237	105, 4,950
PFMMA[b]	430, 237	101, 4,380
PFE[b]	440, 323 (sh)	109, 4,960
	260, 232	6,660, 6,460
Ferrocene–DDQ[c]	590, 545	5,200, 4,900
	457, 345	5,500, >5,000
PFMA–DDQ[c]	550–600 (tailing and shoulder)	*d*
	460, 410	*d*
	325	*d*
PFMMA–DDQ[c]	600 (weak), 525	*d*
	405, 330	*d*
Ferrocene–*o*-CA[c,e]	600 (sh), 531	1,110; 1,310
	354, 282 (sh)	1,150
	250, 226	11,850; 15,200

[a] In acetonitrile. [b] In methylene chloride. [c] In DMF· DMF prevents accurate determination of transitions below 300 mμ. [d] Samples were not totally dissolved and do not necessarily represent the structure of the solid. Thus, extinction coefficients were not obtained. [e] Mp 146–148°.

TABLE XIII

	Found, %			Calcd moles of
Sample	C	H	Fe	ferrocene/mole of quinone
PFMA–DDQ 69-23	50.80	3.69	11.08	1.0/1
PFMMA–DDQ 3001	53.61	3.82	11.34	1.09/1
PFE–DDQ 002	54.74	3.88	14.38	1.29/1
PFMA–CA 005	47.80	4.12	12.23	1.33/1
PFMMA–CA 3001	53.54	4.43	15.34	3.07/1
PFE–CA 002	60.01	5.00	20.06	5.88/1

Ultraviolet Spectra. Ferrocene[32] has uv λ_{max} at 440 and 325 mμ (ε 91 and 52, respectively) as well as very powerful absorption below 250 mμ. The spectra of the homopolymers all exhibited similar spectra except that the 325-mμ band was masked by the tailing of a large 247-mμ band (see Table XII). It is well known that ferricinium salts absorb at about 610–630 mμ.[32–34] This band has been assigned to $^2E_{2g} \rightarrow {}^2E_{1\mu}$, which is the charge-transfer transition from the $e_{1\mu}$ bonding ligand level to the hole in the e_{2g} metal level.[34b] Our attempts to observe polysalt uv spectra were frustrated by their insolubility in most solvents. PFMA–DDQ was partially soluble in DMF as was PFMMA–DDQ. The *o*-CA salts were insoluble, even in this solvent. Thus, in the uv spectra obtained, one cannot ignore that the soluble portion is not necessarily representative of the solid. Second, in the dilute solutions used, equilibria might be set up which are not present in the solid.[26] Thus, at this time the uv spectra are of little use in quantitatively assigning structure to the polysalts. However, it is possible to state that ferricinium ion is present in these spectra from the long wavelength absorption which the ferrocene nucleus does not have. These spectra are summarized in Table XII.

Elemental Analyses. Sample analyses of polysalts are given in Table XIII. It should be noted that these

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

(28) R. L. Collins and R. Pettit, *J. Inorg. Nucl. Chem.*, **29**, 503 (1967).

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

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

(31) I. J. Spilners, *J. Organometal. Chem.*, **11**, 381 (1968).

(32) See ref 16b, pp 40–41.

(33) G. Wilkinson, M. Rosenblum, M. C. Whiting, and R. B. Woodward, *J. Amer. Chem. Soc.*, **74**, 2125 (1952).

(34) (a) S. M. Aharoni and M. H. Litt, *J. Organometal. Chem.*, **22**, 171 (1970); (b) Y. S. Sohn, D. N. Hendrickson, and H. B. Gray, *J. Amer. Chem. Soc.*, **92**, 3234 (1970).

analyses give the ratio of ferrocene to quinone which can then be compared to the Mössbauer spectra. A direct correspondence between the moles of quinone present and the amount of ferricinium ion was found.

TABLE XIV
MÖSSBAUER SPECTRA OF FERROCENE HOMOPOLYMERS[a]

Compd	I.S.,[b] mm/sec	Q.S.,[c] mm/sec
PFE	0.78	2.44
PFMA	0.78	2.42
PFMMA	0.78	2.42

[a] I.S. value relative to nitroprusside. [b] Precision is ±0.01 mm/sec. [c] Precision is ±0.02 mm/sec.

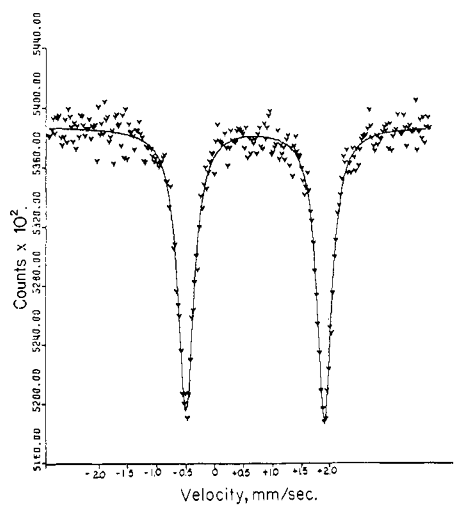

Figure 4. Mössbauer spectrum of PFE.

TABLE XV
MÖSSBAUER SPECTRA OF FERROCENE-CONTAINING POLYSALTS OF *o*-CA AND DDQ[a]

Compd	Iron present as ferrocene			Iron present as ferricinium		
	I.S.[b]	Q.S.[c]	% Fe	I.S.[b]	Q.S.[c]	% Fe
PFE-CA	0.81	2.43	75.6	0.77		24.4
PFMA-CA	0.80	2.42	41.8	0.78		58.2
PFMMA-CA	0.79	2.42	61.5	0.78		38.5
Ferrocene-DDQ				0.79		100
PFE-DDQ	0.78	2.43	53.4	0.80		46.6
PFMMA-DDQ	0.80	2.44	72.0	0.79		28.0
PFMA-DDQ	0.80	2.40	58.0	0.79	0.53	42.0

[a] I.S. values reported relative to nitroprusside. [b] Precision on all runs ±0.01 mm/sec. [c] Precision on all runs ±0.02 mm/sec.

Mössbauer Spectra. Mössbauer spectroscopy provided an ideal analytical method for analyzing the oxidation state of iron in the polysalts. In previous work, Collins and Pettit[28] had demonstrated that pure ferrocene exhibited a doublet in the Mössbauer spectrum with an isomer shift (I.S.) of +0.475 mm/sec relative to Fe metal and a large quadrapole splitting (Q.S.) of 2.400 mm/sec. However, ferricinium dichlorodicyanoquinone gave a single line spectrum (Q.S. = 0) with an I.S. of 0.466 mm/sec. Thus, ferrocene and ferricinium units have distinctly different Mössbauer spectra, and they can easily be differentiated. Furthermore, these workers[28] demonstrated that the ferrocene-tetracyanoethylene charge-transfer complex[35] exhibited a Mössbauer spectrum similar to that of ferrocene alone. This charge-transfer complex exhibited an I.S. of 0.465 mm/sec with a Q.S. of 2.397 mm/sec.

The clear distinction between ferrocene and ferricinium has also been shown in Goldanskii's studies of ferricinium bromide.[36] In this example the spectrum is a doublet, but the quadrapole splitting is extremely small compared to that of ferrocene.

The Mössbauer spectra of the ferrocene-containing homopolymers all consisted of a quadrapole doublet with I.S. and Q.S. values almost identical with ferrocene. These are summarized in Table XIV. The spectra were extremely sharp and clear as illustrated by the Mössbauer spectrum of PFE shown in Figure 4. The values reported in Tables XIV and XV are reported relative to nitroprusside, while those of Collins and Pettit are relative to Fe metal. When compared to the same standard these values agree.

The Mössbauer spectra of the DDQ and *o*-CA-containing polysalts were distinctly different from those of the pure homopolymers. The spectra of PFMA-CA (Figure 5) and PFE-DDQ (Figure 6) illustrate this point. In each case the spectra consisted of an outer doublet due to the unreacted ferrocene nucleus and a broad central line due to ferricinium ion. In one case, PFMA-DDQ, the central ferricinium band is actually a doublet with a small (0.53 mm/sec) Q.S. In order to

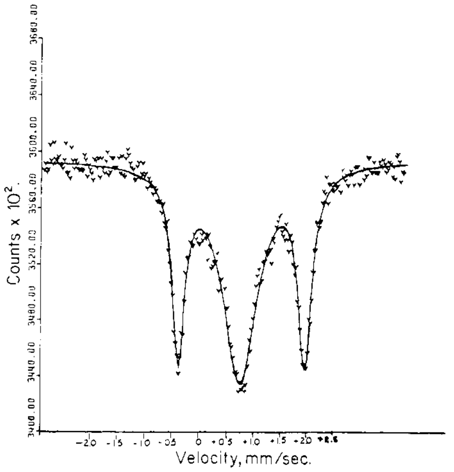

Figure 5. Mössbauer spectrum of P-FMA-CA.

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(35) E. Adman, M. Rosenblum, S. S. Sullivan, and T. N. Margulis, *ibid.*, **89**, 4540 (1967).

(36) V. I. Goldanskii and R. H. Herber, "Chemical Applications of Mössbauer Spectroscopy," Academic Press, New York, N. Y., 1968, p 29.

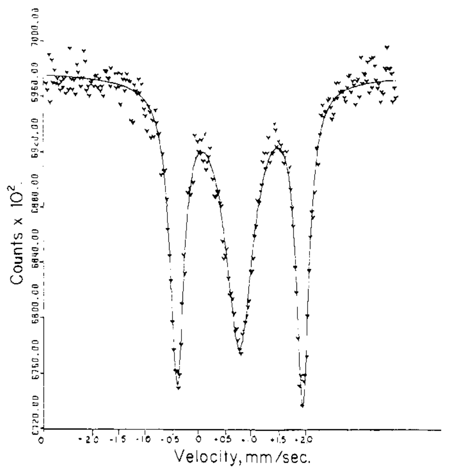
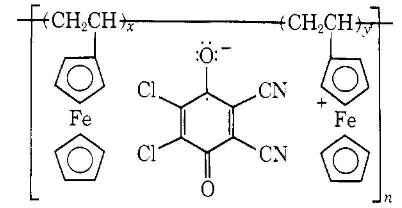


Figure 6. Mössbauer spectrum of PFE–DDQ.

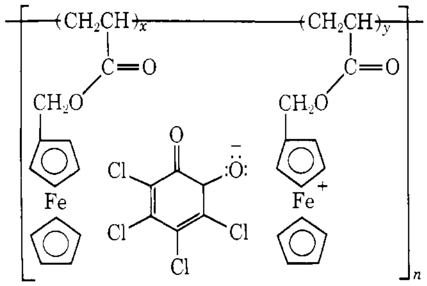
obtain a standard value, the spectrum of the ferrocene–DDQ salt was obtained. It was a singlet. A representative series of these spectra are summarized in Table XV. The areas under the peaks enable a direct measure of the amount of iron present as ferrocene or as ferricinium in the polysalt, and these are listed as percentages in Table XV. An interesting point is that the width of the central band is always twice the width of the lines of the doublet.

Mössbauer spectra of poly–TCNE complexes present a more complicated picture. Some complexes seem to change color with time and accompanying changes are noted in the infrared spectra. PFE–TCNE exhibits a three-peak Mössbauer spectrum analogous to the DDQ and CA polysalts. PFMA–TCNE exhibits a similar spectrum except the center peak is a doublet with a small Q.S. (0.66). Since ferrocene–TCNE gives a two-peak, distinct, charge-transfer type of spectrum, the PFE–TCNE and the PFMA–TCNE complexes appear to have iron present as both ferrocene and ferricinium units. However, all the spectra are not this simple. Furthermore, whether TCNE or pentacyanopropenide anions[26] are present as the counterions is not yet settled. Thus, conclusions as to the structure of the TCNE complexes must be deferred until further study.

The polysalts of DDQ and *o*-CA are clearly electron-transfer salts where each quinone is present as its radical anion with a ferricinium counterion. The amount of ferrocene converted to ferricinium corresponds to the amount of quinone incorporated. Structures VII and VIII are representative. It is possible to vary the percentage of iron present as ferrocene or as ferricinium by changing the ratio of quinone to polymer which is mixed together in solution. Alternatively, the solvent used plays a role in stoichiometry of the salt produced.



VII,
PFE-DDQ



VIII,
PFMA-*o*-CA

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