Copolymerization of Ferrocenylmethyl Acrylate and Ferrocenylmethyl Methacrylate with Organic Monomers

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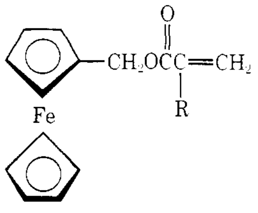
ABSTRACT: Two novel ferrocene-containing monomers, ferrocenylmethyl acrylate, Ia (FMA), and ferrocenylmethyl methacrylate, Ib (FMMA), have been synthesized. Both Ia and Ib were copolymerized with styrene, methyl acrylate, methyl methacrylate, and vinyl acetate in benzene solutions initiated by azobisisobutyronitrile (AIBN) at 70°. Homogeneous copolymers were formed in each case, and the relative reactivity ratios of each copolymerization were determined. The values of r_1 and r_2 were: FMA (monomer 1)–styrene $r_1 = 0.02$, $r_2 = 2.3$; FMMA (monomer 1)–styrene $r_1 = 0.03$, $r_2 = 3.7$; FMA–methyl acrylate $r_1 = 0.14$, $r_2 = 4.46$; FMMA–methyl acrylate $r_1 = 0.08$, $r_2 = 0.82$; FMA–mefhyl methacrylate $r_1 = 0.08$, $r_2 = 2.9$; FMMA–methyl methacrylate $r_1 = 0.12$, $r_2 = 3.27$; FMA–vinyl acetate $r_1 = 1.44$, $r_2 = 0.46$; and FMMA–vinyl acetate $r_1 = 1.52$, $r_2 = 0.20$. While both FMA and FMMA are less reactive than other acrylates and methacrylates, they can be incorporated into copolymers which might have important commercial applications.

In the past 20 years the field of organometallic chemistry has expanded at a prodigious rate and now employs a significant fraction of all research chemists.[3] However, examples of the incorporation of organometallic compounds into polymeric systems are not as widespread as one might expect. A number of polymers containing the ferrocene group have been prepared in recent years[4] due to the thermal stability, moisture stability, and air stability of this group. Vinylferrocene, for example, is one of the few organometallic monomers which has been homopolymerized by cationic and free-radical addition routes. Arimoto and Haven,[5] Cassidy,[6] Baldwin and Johnson,[7] and Pittman[8] have studied the AIBN-initiated homopolymerization of vinylferrocene, and an extensive characterization of these polymers, by osmometry, gpc, ir, uv, Mössbauer spectroscopy, and viscosity, has now been reported.[8] Only low molecular weight ($4000 > \overline{M}_n$) poly(ferrocenylethylene) was obtained by cationic initiation using $BF_3 \leftarrow Et_2O$, $TiCl_4$, $AlCl_3$, $SnCl_4$, and Et_2AlCl.[9] An extensive study of free-radical-initiated copolymerizations of vinylferrocene with styrene, methyl acrylate, methyl methacrylate, acrylonitrile, vinyl acetate, and isoprene has now appeared from our laboratory[10] as part of a continuing study of organometallic polymers.[8,11]

Beyond poly(ferrocenylethylene), few free-radical-initiated addition polymers have been prepared which contain organic monomers of transition metals. One exception is our recent report of the homopolymerization of ferrocenylmethyl acrylate, Ia (FMA), and ferrocenylmethyl methacrylate, Ib (FMMA).[11e] Both FMA and FMMA were polymerized in benzene solution using AIBN initiation.[8,11e] Extensive characterizations of these homopolymers and their poly electron-transfer complexes, formed on treatment with dichlorodicyanoquinone and *o*-chloranil, were carried out using ir, nmr, uv, and Mössbauer spectroscopy, gpc, osmometry, and viscometry. In addition, the kinetics, measured by dialatometry, demonstrated both homopolymerizations were classic first-order processes which were first order in [monomer] and half-order in [AIBN]. Other reports of transition metal containing acrylates and their polymerizations, while rare, have sporadically appeared. For example, allyloxytitanocene chloride has been homopolymerized and copolymerized with styrene and methyl methacrylate by Korshak, *et al.*[4f] Acryloyl-, furylacryloyl-, and *trans*-cinnamoylferrocene have been both homo- and copolymerized.[4g,h]



Ia, R = H
Ib, R = CH_3

Since FMA and FMMA were so readily homopolymerized in benzene solution, copolymerization studies were undertaken. The ferrocene nucleus was expected to impart some very unusual properties to copolymer systems; thus, a series of important commerical monomers was chosen for our

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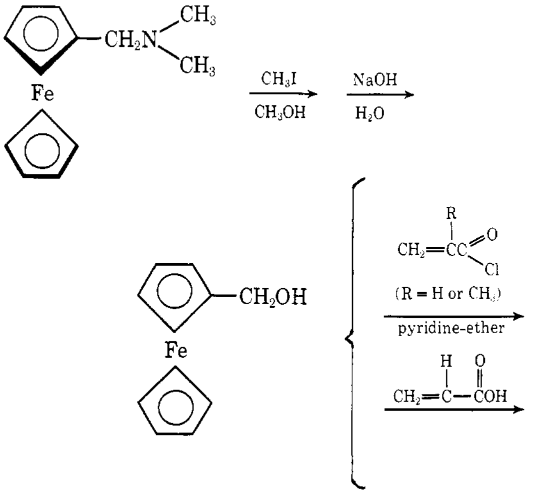
studies. Both Richards[12] and Hammond[13] have shown that ferrocene can act as an efficient quencher of photochemically generated triplet states in anthracene and as a sensitizer in both the photochemical dimerization of isoprene and the *cis*- to *trans*-piperylene isomerization. Second, ferrocene has a high absorption of ultraviolet[14] and γ[15] radiation and a low toxicity. Thus, incorporation of this nucleus into coatings might lead to enhanced stability toward photochemical degradation or special catalytic effects on curing reactions. In fact, compounds such as 2-hydroxybenzoylferrocene and 2,4-dihydroxybenzoylferrocene have been tested as uv absorbers in a variety of polymer systems[16] and found to be very efficient uv stabilizers of polymeric systems. Homopolymers of ferrocene derivatives were shown to have rather high glass-transition temperatures.[8] Finally, ferrocene is readily oxidized to the stable ferricinium ion at a potential of 0.56 V.[17] This property might protect other oxidation sensitive groups in a coating from being oxidized.

Results and Discussion

Monomers. FMA and FMMA (Ia, b) have been prepared by methylation of *N,N*-dimethylaminomethylferrocene with methyl iodide followed by hydrolysis of the quaternary ammonium salt in NaOH to hydroxymethylferrocene.[18] Esterification of this alcohol with acryloyl chloride (alternatively acrylic acid) and methacryloyl chloride gave FMA and FMMA, respectively. The details are given in the Experimental Section. The yield of FMA obtained by direct esterification of hydroxyethylferrocene (85%) was always significantly greater than that obtained using acryloyl chloride in pyridine–ether solution. Both FMA and FMMA were readily hydrolyzed in methanol–water systems, probably due to SN1 solvolysis which is a result of ferrocene's remarkable ability to stabilize an adjacent positive charge.[19] Thus, methanol–water should be avoided in workup procedures involving either these monomers or their polymers.



Ia, b

Copolymerizations. All copolymerizations were carried out at 70°, in degassed benzene solution, initiated by AIBN (see Experimental Section). In every case, the copolymers were precipitated three times into 30–60° petroleum ether to ensure their purity. Additionally, selected samples from each series were analyzed by gel permeation chromatography to prove that the polymers formed were truly homogeneous copolymers. The ferrocene-containing monomer is always defined as M_1.

Two techniques were used to determine the relative reactivity ratios. The first technique used the differential form of the copolymer equation[20] (eq 1). In this technique, a series of copolymerizations of a specific monomer pair was

$$\frac{d[M_1]}{d[M_2]} = \left(\frac{M_1}{M_2}\right)\frac{r_1M_1 + M_2}{r_2M_2 + M_1} \tag{1}$$

carried out to low conversions, varying the $[M_1^0]/[M_2^0]$ ratio for the monomer pair each run. Since $d[M_1]/d[M_2]$ becomes m_1/m_2 (the monomer ratio found in the copolymer) at very low conversions and since the monomer concentrations stay essentially constant during the polymerization, any two copolymerization runs to low conversion define an r_1 and r_2. In this study plots were made of m_1 *vs.* M_1^0 (mole fraction of monomer 1 in the starting solution) for a series of copolymerizations, and the values of r_1 and r_2 were obtained by fitting the curve generated by the best r_1, r_2 pair to the experimental curve. Best values of r_1 and r_2 are easily obtained by Fineman–Ross plots.[21]

The second method utilized the integrated form of the copolymer equation[22] (eq 2). The use of eq 2 [where $P = (1 - r_1)/(1 - r_2)$] permitted the use of copolymerizations to higher

$$r_2 = \frac{\log (M_2^0/M_2) - (1/P) \log [(1 - P)(M_1/M_2)/(1 - P)(M_1^0/M_2^0)]}{\log (M_1^0/M_1) + \log [(1 - P)(M_1/M_2)/(1 - P)(M_1^0/M_2^0)]} \tag{2}$$

conversion, which was important, due to the limited quantities of available monomers in this study. A series of copolymerizations at two different initial monomer concentration ratios ($[M_1^0]/[M_2^0]$) was carried out to a series of different conversions. For each initial $[M_1^0]/[M_2^0]$ ratio, a plot of the copolymer composition (in weight per cent of M_1) *vs.* per cent conversion was made. One point from each of these two plots was selected, and these data were fed into a computer program developed by Montgomery and Fry[23] and adapted by us to an IBM-360 Model 50 computer using Fortran IV.[24] Each such data point gives r_2 as a function of P, and for any two points there is a unique value of P that gives identical values of r_2. Thus, the program accepts initial monomer concentrations and polymer composition–conversion data for two points and varies P to rapidly converge r_2 for these data. These r_2 and P values are then used to calculate r_1. For each copolymer, we used 12–16 sets of data points (one from each of the two plots) for each determination of r_1

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TABLE I
COPOLYMERIZATION OF FMA AND STYRENE AT 70° TO LOW CONVERSIONS

Run no.	FMA in feed, g	Styrene in feed, g	AIBN in feed, g	Benzene in feed, ml	Reaction time, hr	% yield	% Fe in copolymer	Mol % FMA in copolymer
1	2.6979	9.4445	0.0168	4.00	0.50	1.1	2.59	5.55
2	2.7033	4.1865	0.0082	4.00	2.00	4.8	4.34	9.29
3	4.0488	3.6635	0.0084	9.00	3.50	4.3	6.96	16.35
4	4.3193	2.5039	0.0067	10.00	4.00	2.0	9.29	23.90
5	4.0503	1.0521	0.0047	10.50	7.00	7.1	9.97	26.39
6	6.7328	0.7763	0.0038	15.00	7.00	0.56	10.30	27.55
7	8.6398	0.8440	0.0064	20.00	12.00	5.10	12.28	36.01
8	8.1070	0.3511	0.0053	18.00	16.00	2.70	13.41	41.51
9	12.7750	0.2824	0.0082	25.00	40.00	2.50	16.13	57.75

TABLE II
COPOLYMERIZATION OF FMMA AND STYRENE AT 70° TO LOW CONVERSIONS

Run no.	FMMA in feed, g	Styrene in feed, g	AIBN in feed, g	Benzene in feed, ml	Reaction time, hr	% yield	% Fe in copolymer	Mol % FMMA in copolymer
10	4.2615	3.6470	0.0082	12.10	8.0	7.90	4.39	9.53
11	5.6820	2.0842	0.0065	15.40	12.0	4.66	7.46	18.42
12	5.2410	1.2051	0.0049	15.00	12.0	5.05	9.21	24.79
13	5.8586	0.9783	0.0049	17.00	13.0	4.45	9.50	25.70
14	4.6890	0.5952	0.0042	12.10	15.0	4.02	10.04	29.25
15	5.0230	0.4056	0.0040	17.00	16.0	3.58	11.51	34.35
16	4.9560	0.2246	0.0034	17.00	22.0	2.94	12.43	38.80

and r_2. This gives a range of r_1 and r_2 values which are then used to reconstruct a new polymer composition–conversion curve using a second computer program.[23,24] The "best" values of r_1 and r_2 are those which give calculated composition–conversion plots which most closely fit the experimental curves.

From a single experimental composition conversion curve, any two data points could be used to get r_1 and r_2. However, this requires input data accurate to an order of ±0.01%. Since our experimental data are not nearly that good, we choose to use one point each from two composition–conversion curves at different initial monomer concentration ratios. This permits a much lower experimental accuracy necessary to obtain acceptable r_1 and r_2 values.

Styrene Copolymers. Both FMA and FMMA were copolymerized to low conversions with styrene in benzene at 70°. These copolymerizations are summarized in Tables I (FMA) and II (FMMA). The m_1 *vs.* M_1^0 plot for FMMA–styrene copolymerization is shown in Figure 1, and the Fineman–Ross plots for FMA–styrene and FMMA–sytrene copolymerizations are given in Figures 2 and 3, respectively. The values of r_1 and r_2 were $r_1 = 0.02 \pm 0.01$ and $r_2 = 2.3 \pm 0.3$ for FMA copolymerizations and $r_1 = 0.03 \pm 0.02$ and $r_2 = 3.7 \pm 0.2$ for FMMA copolymerization with styrene.

Methyl Acrylate Copolymers. FMA was copolymerized with methyl acrylate to higher conversions (technique 2), while FMMA was copolymerized to low conversions (technique 1). All these runs were carried out in benzene solutions at 70° initiated by AIBN. These copolymerizations are summarized in Tables III and IV, respectively. Figure 4 shows the m_1 *vs.* M_1^0 plot for the FMMA–methyl acrylate copolymerizations. The values of r_1 and r_2 were 0.14 ± 0.02 and 4.46 ± 0.2 for FMA–methyl acrylate and 0.08 ± 0.03 and 0.82 ± 0.07 for FMMA–methyl acrylate.

Methyl Methacrylate Copolymers. Methyl methacrylate was copolymerized to low conversions with FMA (Table V, $r_1 = 0.08 \pm 0.03$ and $r_2 = 2.9 \pm 0.5$) and to higher conversions with FMMA (Table VI). The high conversion composition–conversion curves for the FMMA–methyl methacrylate copolymerizations at initial monomer weight ratios of 0.499:0.501 and 0.649:0.351 (M_1/M_2), are shown in Figure 5. The experimental points and the theoretical curve which was reconstructed from $r_1 = 0.124$ and $r_2 = 3.27$ are both illustrated. From the close fit of the regenerated curve to the experimental points at both M_1/M_2 ratios, it is obvious that these are "good" r_1 and r_2 values.

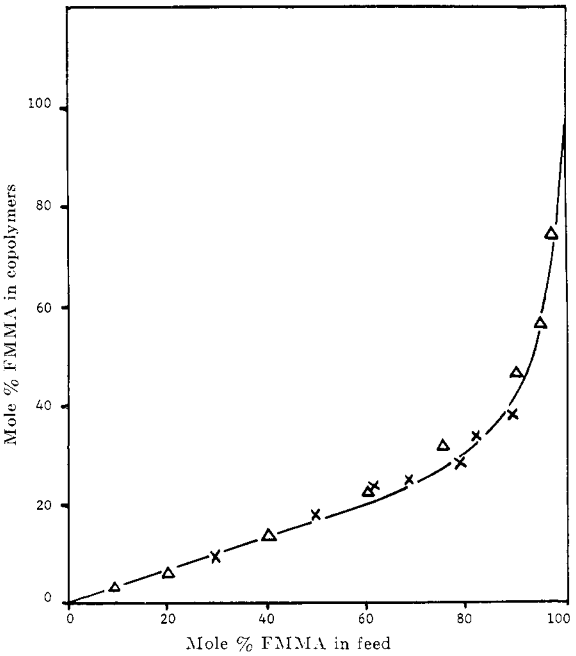

Figure 1. Composition curve for FMMA–styrene copolymerization: ×, experimental points; Δ, theoretical points based on $r_1 = 0.03$, $r_2 = 3.7$.

Table III
Copolymerization of FMA and Methyl Acrylate at 70° to High Conversions

Run no.	FMA in feed, g	MA in feed, g	AIBN in feed, g	Reaction time, hr	Yield, g	% Fe in copolymer	Conversion, %	Wt fraction in copolymer FMA/MA
17	2.337	3.363	0.0157	6.0	0.809	4.00	14.2	0.154/0.846
18	2.337	3.363	0.0157	12.0	2.195	4.40	38.5	0.169/0.831
19	2.337	3.363	0.0157	16.0	2.423	4.51	42.5	0.173/0.827
20	2.337	3.363	0.0157	20.0	2.583	4.62	45.3	0.178/0.822
21	2.337	3.363	0.0157	30.0	2.759	4.68	48.4	0.180/0.820
22	2.850	2.850	0.0143	5.0	0.143	4.71	2.5	0.181/0.819
23	2.850	2.850	0.0143	12.0	0.599	4.97	10.5	0.191/0.809
24	2.850	2.850	0.0143	24.0	0.798	5.05	14.0	0.194/0.806
25	2.850	2.850	0.0143	48.0	2.286	6.01	40.1	0.231/0.769

Table IV
Copolymerization of FMMA and Methyl Acrylate at 70° to Low Conversions

Run no.	FMMA in feed, g	ME in feed, g	AIBN in feed, g	Benzene in feed, ml	Reaction time, hr	% yield	% Fe in copolymer	Mol % FMMA in copolymer
26	2.1691	4.9281	0.0158	12.2	2.5	5.78	6.69	13.5
27	2.8226	2.2076	0.0088	9.0	3.0	1.95	10.12	24.2
28	4.0747	2.4137	0.0102	10.0	6.0	9.09	10.20	25.1
29	4.5033	1.8229	0.0093	10.0	8.0	4.38	11.06	28.0
30	4.7085	1.0408	0.0074	12.0	13.0	3.83	12.03	32.6
31	5.0225	0.5088	0.0061	14.1	18.0	3.80	15.08	43.4
32	5.4100	0.2557	0.0065	14.4	21.0	1.94	15.45	52.7

Table V
Copolymerization of FMA and Methyl Methacrylate at 70° to Low Conversion

Run no.	FMA in feed, g	MMA in feed, g	AIBN in feed, g	Benzene in feed, ml	Reaction time, hr	% yield	% Fe in copolymer	Mol % FMA in copolymer
33	2.0735	5.7074	0.0146	12.0	0.60	6.20	1.61	3.03
34	2.5116	2.4928	0.0083	14.0	1.20	4.00	4.90	10.32
35	3.8341	2.8044	0.0122	16.8	1.20	2.25	6.32	14.02
36	4.2637	1.5790	0.0083	12.0	2.00	3.85	9.04	22.34
37	4.4807	1.0808	0.0075	13.0	2.50	2.25	10.18	26.40
38	4.7560	0.5940	0.0062	12.5	6.00	1.96	11.60	32.12
39	5.1403	0.2974	0.0070	14.0	8.50	5.36	15.19	50.60
40	5.1010	0.1001	0.0070	16.0	12.00	8.85	18.14	72.54

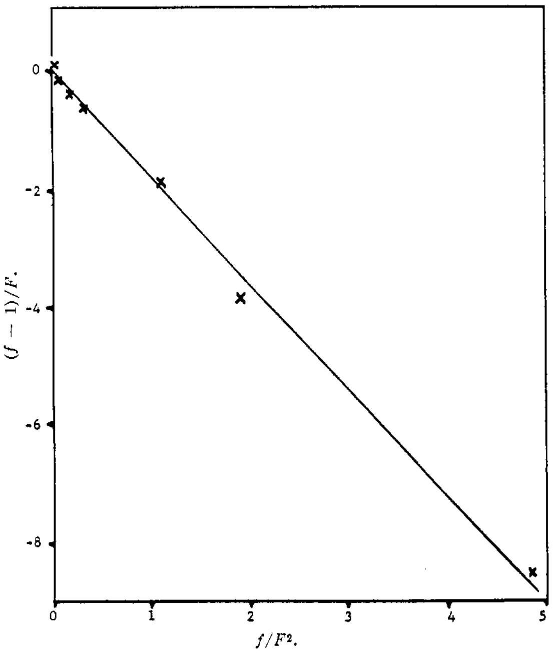

Figure 2. Fineman–Ross plot for FMA–styrene copolymerization.

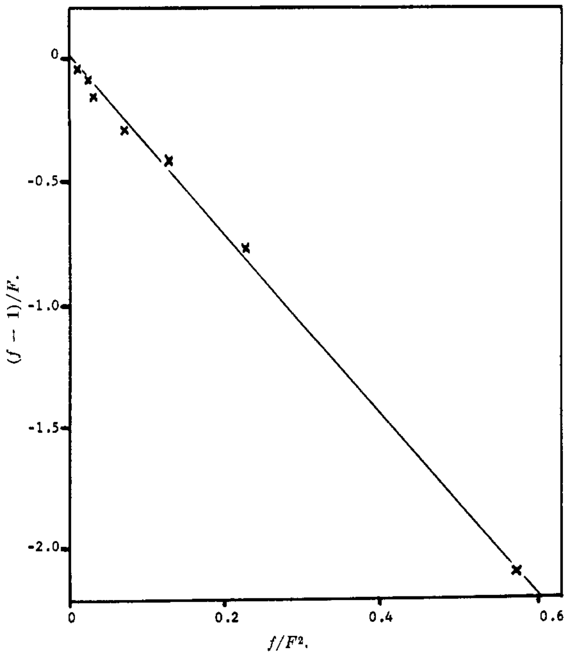

Figure 3. Fineman–Ross plot for FMMA–styrene copolymerization.

TABLE VI

COPOLYMERIZATION OF FMMA AND METHYL METHACRYLATE AT 70° TO HIGH CONVERSIONS

Run no.	FMMA in feed, g	MMA in feed, g	AIBN in feed, g	Reaction time, hr	Yield, g	% Fe in copolymer	Conversion, %	Wt fraction in copolymer FMMA/MMA
41	1.9967	2.0062	0.0088	2.00	0.2802	4.53	7.00	0.230/0.770
42	1.9967	2.0062	0.0088	5.00	0.7555	4.74	18.87	0.241/0.759
43	1.9967	2.0062	0.0088	7.00	0.8398	4.81	20.98	0.245/0.755
44	1.9967	2.0062	0.0088	9.50	1.2350	5.06	30.85	0.258/0.742
45	3.0098	1.6309	0.0098	19.70	0.1995	6.75	4.30	0.343/0.657
46	3.0098	1.6309	0.0098	39.00	0.7425	7.11	16.00	0.362/0.638
47	3.0098	1.6309	0.0098	54.00	0.9237	7.26	19.90	0.369/0.631
48	3.0098	1.6309	0.0098	69.00	1.8332	8.06	39.50	0.410/0.590

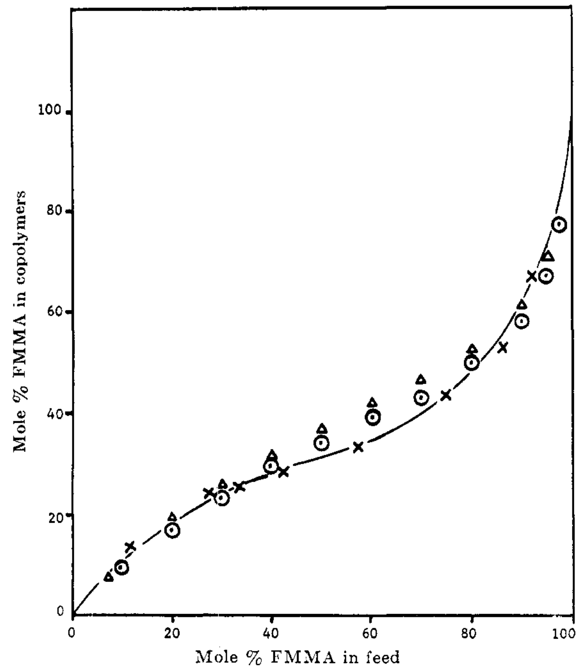

Figure 4. Composition curve for FMMA–methyl acrylate copolymerization: ×, experimental points; Δ, theoretical points based on r_1 = 0.080, r_2 = 0.818; ⊙, theoretical points based on r_1 = 0.060, r_2 = 1.00.

Vinyl Acetate Copolymers. Vinyl acetate was copolymerized with both FMA and FMMA to higher conversions (see Tables VII and VIII, respectively). The composition–conversion curves for the FMA–vinyl acetate pair are shown in Figure 6 for initial M_1/M_2 weight ratios of 0.401 : 0.599 and 0.610 : 0.390. As can be seen, one experimental point (at 8.10% conversion) is significantly removed from the computer generated curve based on r_1 = 1.44 and r_2 = 0.46, which was determined from 16 combinations of the data points. Other experiments were carried out to repeat this run at these same conditions, and the resulting points fell into the shaded circle, much closer to the regenerated curve. Using these new points to redetermine r_1 and r_2 did not change their values. This illustrates the value of performing experiments at two initial monomer concentrations. The values of r_1 and r_2 for FMMA vinyl acetate copolymerization are 1.52 ± 0.30 and 0.20 ± 0.10.

The reactivities, both of FMA and FMMA, in the copolymerizations reported in this paper were much lower than for methyl acrylate and methyl methacrylate. This is illustrated in Table IX where all the r_1, r_2, Q, and e values for FMA and FMMA are summarized. This is clearly illustrated by the small magnitude of r_1 in the FMA and FMMA copolymerizations with methyl acrylate and methyl methacrylate. In all four cases the value of r_1 was between 0.14 and 0.08. Thus, the FMA and FMMA radicals add more rapidly to methyl acrylate or to methyl methacrylate than to itself. This low reactivity is further emphasized by comparing the low r_1 values in the FMA and FMMA copolymerizations with

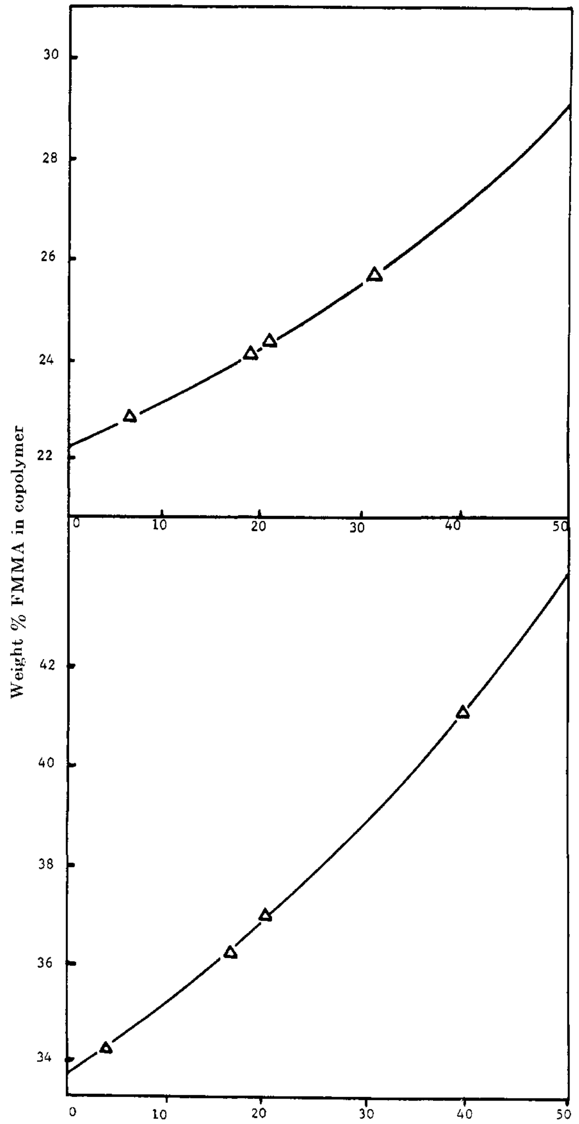

Figure 5. Composition–conversion curves for FMMA–methyl methacrylate copolymerization: Δ, experimental points; ———, theoretical curve based on r_1 = 0.124, r_2 = 3.27; initial monomer composition = 0.499:0.501 by weight (top), 0.649:0.351 by weight (bottom).

TABLE VII
COPOLYMERIZATION OF FMA AND VINYL ACETATE AT 70° TO HIGH CONVERSIONS

Run no.	FMA in feed, g	VA in feed, g	AIBN in feed, g	Reaction time, hr	Yield, g	% Fe in copolymer	Conversion, %	Wt fraction in copolymer FMA/VA
49	2.0040	2.9920	0.0381	19.5	0.405	11.87	8.10	0.574/0.426
50	2.0040	2.9920	0.0381	29.5	0.760	11.41	15.2	0.552/0.448
51	1.9040	2.8430	0.0362	49.0	1.890	10.78	39.8	0.522/0.478
52	1.6032	2.3936	0.0305	94.0	1.827	10.62	45.7	0.514/0.486
53	2.8641	1.8340	0.0365	7.0	0.489	15.15	10.4	0.733/0.267
54	2.8641	1.8340	0.0365	15.0	0.845	15.01	14.9	0.726/0.274
55	2.8641	1.8304	0.0365	36.0	1.642	14.86	35.1	0.719/0.281
56	2.8641	1.8340	0.0365	48.0	2.110	14.72	44.9	0.712/0.288
57	2.8461	1.8340	0.0365	72.0	2.368	14.55	50.4	0.704/0.296
58	1.9040	2.8430	0.0362	72.0	1.674	9.68	35.3	0.468/0.532

TABLE VIII
COPOLYMERIZATION OF FMMA AND VINYL ACETATE AT 70° TO HIGH CONVERSIONS

Run no.	FMMA in feed, g	VA in feed, g	AIBN in feed, g	Reaction time, hr	Yield, g	% Fe in copolymer	Conversion %	Wt fraction in copolymer FMMA/VA
59	2.2455	1.2014	0.0073	25.2	0.114	15.59	4.2	0.793/0.207
60	2.9938	1.6018	0.0098	40.3	0.420	16.27	9.1	0.827/0.173
61	2.9938	1.6018	0.0098	60.0	0.250	16.18	5.4	0.823/0.177
62	2.9990	4.0007	0.0186	24.0	0.150	14.29	2.1	0.727/0.273
63	2.3992	3.2006	0.0149	48.2	0.168	14.04	3.0	0.714/0.286
64	2.9990	4.0007	0.0186	65.0	0.250	13.32	3.6	0.678/0.322

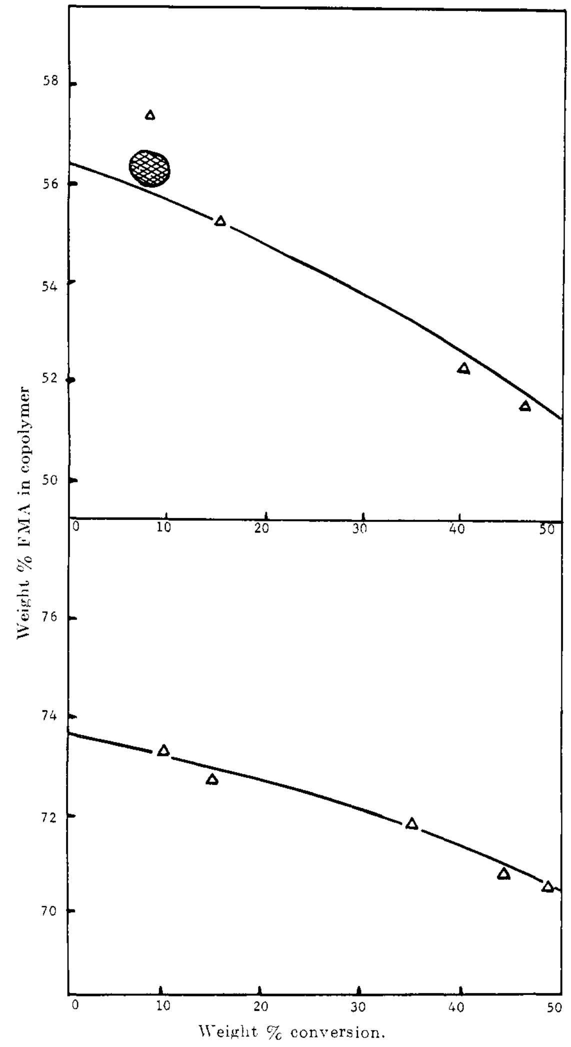

Figure 6. Composition–conversion curve for FMA–vinyl acetate: Δ, experimental points; ———, theoretical curve based on r_1 = 1.44, r_2 = 0.460; initial monomer composition = 401:599 by weight (top), 610:390 by weight (bottom).

styrene (0.02 and 0.03) to the r_1 values in the methyl acrylate (M_1) and methyl methacrylate (M_1) copolymerizations with styrene (0.18 and 0.46, respectively[25]). Both FMA and FMMA are more reactive than vinyl acetate. An FMA radical, for example, adds more rapidly to FMA (M_1) than to vinyl acetate (r_1 = 1.44) and a vinyl acetate radical adds more rapidly to FMA than to vinyl acetate (r_2 = 0.46).

The explanation for this low reactivity is not clear.[26,27] The bulky ferrocene group is far removed from the reaction center for radical attack on FMA or FMMA. However, the addition of an FMA (or FMMA) radical to a molecule of FMA (or FMMA) might be somewhat hindered, because the secondary radical center is spaced six atoms from two ferrocene ring carbons.[28] This effect might be further enhanced by crowding from other monomer units back in the growing chain. In our hands, space-filling models suggest this as a possibility but this is only speculation at this time. Since the ferrocene is insulated from the acrylate function by a methylene group, any electronic effects the ferrocene ring might exert should be negligible.

Experimental Section

Preparation of Hydroxymethylferrocene. *N,N*-Dimethylaminomethylferrocene (obtained from Arapahoe Chemical Co., Boulder, Col.) was converted to its methiodide by the method of Lindsay and Hauser.[18] This salt was then converted to hydroxymethylferrocene as previously reported.[18]

Esterification of Hydroxymethylferrocene. (a) Hydroxymethylferrocene, 10.8 g (0.05 mol), and 7.0 ml of pyridine were mixed with 300 ml of anhydrous ethyl ether with constant stirring in a three-necked 500-ml flask which was placed in an ice bath. A solution of 6.4 g (0.06 mol) of acrylyl chloride in 50 ml of ether was added dropwise *via* a pressure-equalizing funnel. Reaction was

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[25] L. J. Young, *J. Polym. Sci.*, **54**, 411 (1961); H. Mark, B. Immergut, E. H. Immergut, L. J. Young, and K. I. Beyon, "Copolymerization," G. E. Ham, Ed., Interscience, New York, N. Y., 1964, p 695.

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TABLE IX
RELATIVE REACTIVITY RATIOS AND Q AND e VALUES FOR FMA AND FMMA COPOLYMERIZATIONS[a]

M_1	M_2	r_1	r_2	Q_1	e_1
FMA	Styrene	0.02 ± 0.01	2.3 ± 0.3	0.106	0.955
FMMA	Styrene	0.03 ± 0.02	3.7 ± 0.2	0.083	0.683
FMA	Methyl acrylate	0.14 ± 0.02	4.46 ± 0.2	0.180	1.256
FMMA	Methyl acrylate	0.08 ± 0.03	0.82 ± 0.07	0.014	2.23
FMA	Methyl methacrylate	0.08 ± 0.03	2.9 ± 0.5	0.414	1.609
FMMA	Methyl methacrylate	0.12 ± 0.02	3.27 ± 0.06	0.331	1.35
FMA	Vinyl acetate	1.44 ± 0.38	0.46 ± 0.07	0.050	0.342
FMMA	Vinyl acetate	1.52 ± 0.30	0.20 ± 0.10	0.101	0.79

[a] The values of Q_2 and e_2 used in these calculations were respectively 1.0 and −0.80 for styrene,[26] 0.46 and 0.58 for methyl acrylate, 0.74 and 0.40 for methyl methacrylate,[27] and 0.028 and −0.3 for VA. The values of Q_1 and e_1 were computed from the listed r_1 and r_2 values and the respective Q_2 and e_2 values of M_2 employing the standard equations relating r_1, r_2, Q_1, Q_2, e_1, and e_2.[20]

immediate with pyridine hydrochloride precipitating out. After 2 hr, the mixture was diluted with ether, washed with aqueous sodium bicarbonate and aqueous sodium chloride, dried over sodium sulfate, and filtered. The filtrate was then concentrated to dryness by means of a rotary evaporator. The residual powder was recrystallized from hexane and yielded 7.45 g (55.5%) of FMA (mp 42–43°).

Anal. Calcd for C, 62.26; H, 5.22; Fe, 20.67. Found: C, 62.57; H, 5.36; Fe, 20.18.

Key ir bands observed were: 3110, 2980–2860, 1720, 1625, 1635, 1460, 1400, 1385, 1280, 1190, 1115, 1050, 994, 955, 937, 820, and 740 cm^{-1}.

Nmr bands observed were unsubstituted cyclopentadienyl ring hydrogens 4.04 (s); substituted ring 4.00 (tr) and 4.17 (tr), J = 1.5 Hz; CH_2 4.85 (s); and vinyl hydrogens, ABC pattern, 5.51–6.40 ppm downfield from TMS.

(b) A three-necked 0.5-l. flask equipped with condenser, nitrogen inlet, and mechanical stirrer was charged with 10.8 g (0.05 mol) of hydroxymethylferrocene, 18.0 g (0.25 m) of acrylic acid, 0.1 g of hydroquinone, 0.05 g of *p*-toluenesulfonic acid, and 300 ml of methylene chloride. The mixture was heated to reflux for 5.0 hr. After cooling, the solution was filtered and washed first with 150 ml of 20% aqueous sodium carbonate solution and then several times with distilled water and finally dried over anhydrous sodium sulfate and filtered. The filtrate was then concentrated to dryness and the residue recrystallized from hexane to give 11.4 g (85%) of FMA.

(c) Hydroxymethylferrocene, 69.0 g (0.319 mol), and 35.0 ml of pyridine (0.383 mol) were dissolved in 1500 ml of anhydrous ethyl ether with constant stirring in a three-necked 3-l. flask on an ice bath. A solution of 45.0 g (0.383 mol) of methacrylyl chloride in 400 ml of anhydrous ethyl ether was added dropwise *via* a pressure-equalizing funnel. After 2 hr of stirring at 0°, the reaction mixture was filtered and the precipitate was washed with 800 ml of anhydrous ethyl ether. The combined ethereal solution was washed with 500 ml of 20% aqueous sodium bicarbonate solution, 500 ml of 20% sodium chloride solution, and then ten more times with 500 ml of distilled water and dried over anhydrous sodium sulfate and filtered. The filtrate was then concentrated to dryness in a vacuum desiccator in the dark. The residue, recrystallized from hexane, yielded 76.0 g (85%) of FMMA (mp 52–54°).

Anal. Calcd: C, 63.42; H, 5.68; Fe, 19.66. Found: C 64.02; H, 5.82; Fe, 19.20.

Key ir bands were observed for FMMA at 3108, 2980–2860, 1720, 1640, 1460, 1375, 1302, 1250, 1170, 1114, 1149, 1004, 950, and 820 cm^{-1}. The nmr spectrum was in accord with the title compound: 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 5.43 and 6.01 (s). The chemical shifts were expressed in parts per million downfield from TMS.

Copolymerizations of FMA and FMMA with Commercial Organic Monomers. Quantities of FMA and FMMA, synthesized as described above, were prepared shortly before use. The other monomers were purchased commercially. Styrene was washed with 10% aqueous NaOH and water, dried over anhydrous Na_2SO_4, and vacuum distilled before use. A center cut was used. Methyl acrylate, methyl methacrylate, and vinyl acetate were washed with 5% aqueous NaOH solution and water, dried over anhydrous Na_2SO_4, and vacuum distilled. Benzene was distilled from P_2O_5 and AIBN was recrystallized several times from methanol (mp 102–103° dec).

Monomers and AIBN were weighed on an analytical balance and dissolved into benzene which was delivered from a buret into Fisher–Porter aerosol compatibility tubes equipped with a valve. The solutions were degassed at 10^{-3} mm by three alternate freeze–thaw cycles. After degassing, the tubes were placed in constant-temperature baths controlled to 70 ± 0.01°. (All copolymerizations were run at this temperature.) After a certain period of time, the benzene solution was added dropwise to rapidly stirring 30–60° petroleum ether to precipitate the copolymer. The copolymer was filtered and reprecipitated in this manner two more times to ensure its purity. It was then dried under vacuum and weighed and the composition was determined through an Fe elemental analysis.

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