

Organometallic Polymers. XXIV. Radical-Initiated Copolymerization of Ferrocenylmethyl Acrylate and Methacrylate with Acrylonitrile, Maleic Anhydride, and *N*-Vinyl-2-pyrrolidone

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Synopsis

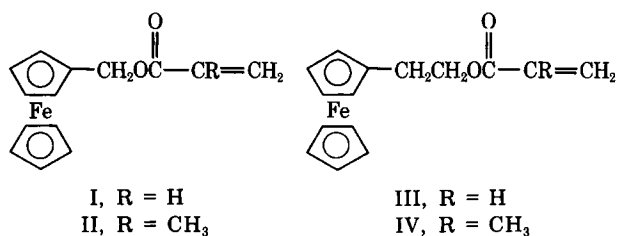
Ferrocenylmethyl acrylate (I) and ferrocenylmethyl methacrylate (II) have been readily copolymerized with maleic anhydride in benzene-ethyl acetate solutions. Similarly, II has been copolymerized with both acrylonitrile and *N*-vinyl-2-pyrrolidone in benzene solutions to give higher molecular weight copolymers in high yields. In all cases azobisisobutyronitrile has been the initiator. Based on e values obtained, the metal carbonyl substituent acts as an electron-withdrawing group. Over a wide range of comonomers (*N*-vinyl-2-pyrrolidone, styrene, vinyl acetate, methyl acrylate, acrylonitrile, and maleic anhydride) I and II exhibit r_1 values lower than (and r_2 values higher than) similar copolymerizations with methyl acrylate or methyl methacrylate. Furthermore, the Q values found for I (0.03-0.11) and II (0.08-0.18) are smaller than those for methyl acrylate (0.46) and methyl methacrylate (0.74). Thus, I and II are less reactive than expected, presumably due to steric effects.

INTRODUCTION

The synthesis of organometallic polymers¹⁻⁴ and studies of their novel properties^{1,5,6} have recently accelerated in scope. The radical-initiated addition homo- and copolymerization of a variety of organometallic vinyl monomers, such as vinylferrocene,⁷ styrenetricarbonylchromium,⁸ vinylcyclopentadienylmanganese tricarbonyl,^{1,9} and π -(benzyl acrylate)chromium tricarbonyl,¹⁰ have now been well established. Recently we have reported extensive radical-initiated copolymerization studies of ferrocenylmethyl acrylate, I,¹¹ its methacrylate, II,¹¹ and both ferrocenylethyl acrylate III^{12,13} and its methacrylate, IV.^{12,13} The relative reactivity ratios and Q - e schemes were examined for these monomers.

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This paper reports the copolymerization of I with maleic anhydride and the copolymerization of II with acrylonitrile, maleic anhydride, and *N*-vinylpyrrolidone. It completes the program which was undertaken to define the reactivity of these monomers in radical-initiated solution copolymerizations.¹¹ Monomers I and II were previously shown to behave quite differently from III and IV in copolymerizations. The reactivities of III and IV were shown to more closely resemble methyl acrylate and methyl methacrylate, respectively, than do I and II.¹¹⁻¹³ Since the ferrocene moiety is very large, steric effects were invoked to rationalize this difference in reactivity patterns. This approach seemed logical since electronic effects, which the ferrocene moiety might exert, should be insulated from the vinyl function in all monomers I-IV.

RESULTS

Ferrocenylmethyl acrylate (I) and methacrylate (II) have been synthesized and copolymerized by the method previously reported.¹¹ Copolymerizations were carried out under nitrogen in deoxygenated benzene solutions except where the comonomer was maleic anhydride where solubility limitations required the use of a 1:1 v/v solution of benzene and ethyl acetate. Each copolymer was purified by three reprecipitations from benzene (or benzene-ethyl acetate) into petroleum ether (bp 30-60°C) and dried at 60°C/10⁻²-10⁻³ mm Hg for 24 hr.

High yields of copolymers could be obtained when either I or II was copolymerized with acrylonitrile or *N*-vinylpyrrolidone. Conversely, low copolymer yields were usually obtained when maleic anhydride was used as the comonomer except when II was present in high mole per cent in the feed. Tables I-IV contain a representative series of the copolymerizations carried out for each monomer I and II. Furthermore, these tables list those copolymerizations which were used in the reactivity ratio calculations. A brief, but representative series, of copolymer viscosities and molecular weights is reported in Table V.

The reactivity ratios were determined by the method advocated by Tidwell and Mortimer.^{14,15} First, from eight to twelve copolymerizations were carried out at two widely separated $[M_1^0]/[M_2^0]$ ratios. The composition-conversion data from these runs were used to calculate crude values of r_1 and r_2 . From the crude r_1 and r_2 values, two optimum $[M_1^0]/[M_2^0]$ starting ratios were then calculated.^{14,15} Next, several copolymerizations were carried out at each of these optimized $[M_1^0]/[M_2^0]$ ratios, and

TABLE I
Representative Copolymerizations of Ferrocenylmethyl Methacrylate (M_1) and Acrylonitrile (M_2) at 80°C in Benzene Solutions*

Polymer	M_1 charged, g	M_1 charged, mole-%	AIBN, g	Reaction time, hr	Copolymer yield, %	M_1 in copolymer mole-%
1	1.99	70	0.0215	20.0	85.5	75.9
2	1.99	70	0.215	1.0	40.3	76.6
3	1.99	70	0.0215	.25	29.6	82.1
4	0.85	30	0.0122	20.0	57.0	45.3
5	0.85	30	0.0122	2.0	54.5	42.9
6	3.10	54.5	0.0358	0.33	18.8	58.4
7	3.10	54.5	0.0358	0.33	16.1	55.1
8	3.10	54.5	0.0358	0.33	16.2	56.3
9	3.10	54.5	0.0358	0.33	15.6	54.3
10	1.11	13.0	0.0249	1.0	15.6	34.5
11	1.11	13.0	0.0249	1.1	16.7	37.4
12	1.11	13.0	0.0249	1.2	20.2	32.8

* In every case 10 ml of benzene was employed. Only representative runs are summarized.

TABLE II
Representative Copolymerizations of Ferrocenylmethyl Methacrylate (M_1) and *N*-Vinyl-2-pyrrolidone (M_2) at 80°C in
1:1 (v/v) Benzene-Ethyl Acetate Solutions^a

Polymer	M_1 charged, g	M_1 charged, mole-%	AIBN, g	Reaction time, hr	Copolymer yield, %	M_1 in copolymer, mole-%
1	1.99	70	0.0232	2.0	78.5	88.6
2	1.99	70	0.0232	2.0	78.6	85.5
3	1.99	70	0.0232	0.25	12.3	85.4
4	1.99	70	0.0232	0.75	38.2	83.4
5	0.85	30	0.0163	2.0	67.0	56.5
6	0.85	30	0.0163	0.75	25.8	67.5
7	0.35	2.5	0.0577	1.0	90.9	2.2
8	0.36	2.5	0.0577	0.75	61.1	4.1
9	0.36	2.5	0.0577	0.17	33.0	13.5
10	0.14	2.5	0.0231	0.25	20.8	11.5
11	0.14	2.5	0.0231	0.30	32.5	12.2

^a In every run, 10 ml of benzene was used. Only a representative set of runs have been listed.

TABLE III
Representative Copolymerizations of Ferrocenylmethyl Methacrylate (M_1) and Maleic Anhydride (M_2) at 80°C in Benzene Solutions^a

Polymer	M_1 charged, g	M_1 charged, mole-%	AIBN, g	Reaction time, hr	Copolymer yield, %	M_1 of copolymer, mole-%
1	1.99	70	0.0228	5.0	76.4	64.5
2	1.99	70	0.0228	3.0	68.0	63.0
3	1.99	70	0.0228	1.0	44.3	62.5
4	1.99	70	0.0228	0.33	19.0	64.4
5	0.85	30	0.0154	18.0	17.2	48.9
6	0.85	30	0.0154	3.0	11.4	48.5
7	2.59	91	0.0267	0.42	30.5	82.6
8	2.59	91	0.0267	0.33	28.3	80.6
9	2.59	91	0.0267	0.33	29.3	80.7
10	0.14	2.5	0.0205	23.0	7.9	6.1
11	0.14	2.5	0.0205	46.0	15.8	14.3
12	0.28	2.5	0.0410	46.0	13.9	14.9

^a Runs 1-11 employed 5 ml of benzene and 5 ml of ethyl acetate. In run 12, 7.5 ml of each solvent was used.

TABLE IV
Representative Copolymerizations of Ferrocenylmethyl Acrylate (M_1) and Maleic Anhydride (M_2) at 80° in
1:1 (v/v) Benzene-Ethyl Acetate Solutions^a

Polymer	M_1 charged, g	M_1 charged, mole-%	AIBN, g	Reaction time, hr	Copolymer yield, %	M_1 in copolymer, mole-%
1	1.89	70	0.0218	16	23.1	75.2
2	1.89	70	0.0218	4	11.0	69.4
3	0.95	70	0.0109	62	58.6	79.0
4	0.81	30	0.0150	4	6.8	25.2
5	0.41	30	0.0080	62	26.7	41.3
6	0.14	2.5	0.0205	57	11.5	9.0
7	0.14	2.5	0.0205	42	10.8	8.4
8	0.14	2.5	0.0205	23	4.3	17.5
9	0.27	2.5	0.0410	42	3.8	17.1

^a In runs 1-8, 5 ml of benzene and 5 ml of ethyl acetate were used. In run 9, 7.5 ml of each solvent was employed.

TABLE V
Molecular Weight and Viscosity Determinations for a Representative Series of Copolymers of Ferrocenylmethyl
Acrylate and Ferrocenylmethyl Methacrylate

Copolymer ^a	M ₁ in copolymer, mole-%	$[\eta]$, dl/g ^b	$\bar{M}_n^{c,d}$	$\bar{M}_w^{c,d}$	\bar{M}_w/\bar{M}_n	T_g , °C ^e
FMMA-AN-6	58.4	0.17	24,600	113,500	5.5	—
FMMA-AN-12	32.8	0.15	6,000	24,700	4.1	—
FMMA-MAH-12	14.9	0.30	30,000	174,000	5.8	137
FMMA-MAH-9	80.7	f	f	f	f	—
FMMA-VP-1	88.6	0.20	6,600	90,000	13	130
FMMA-VP-11	12.2	0.17	g	g	g	168
FMA-MAH-3	79.0	0.012	2,800	7,050	2.5	—
FMA-MAH-7	8.4	0.014	3,500 ^{a,h}	g	g	125

^a Copolymer numbers refer to those in Tables I-IV; FMMA = ferrocenylmethyl methacrylate, FMA = ferrocenylmethyl acrylate, AN = acrylonitrile, MAH = maleic anhydride, and VP = N-vinyl-2-pyrrolidone.
^b In tetrahydrofuran at 30°C.

^c Determined by gel-permeation chromatography by using the universal calibration technique. The solvent was THF at 30°C and one of two banks of four styragel columns (Waters Associates) was used. One column bank resolved molecular weights from 10,000 to about 1,000,000. The other bank resolved polymers from 200 to 50,000 very efficiently. The calibration used polystyrene standards. There is no proof that the Universal Calibration is valid for each copolymer in this series. For FMA and FMMA copolymers previously reported,¹¹ vapor-pressure osmometry values of \bar{M}_n agreed reasonably well with GPC values of \bar{M}_n calculated by the universal calibration method. However, this was only checked for copolymers with \bar{M}_n < 15,000 and \bar{M}_w/\bar{M}_n < 2.5.

^d The molecular weights and viscosities of these polymers should not be directly related, since the copolymer compositions are markedly varying in this table.

^e Obtained by differential scanning calorimetry. It was not possible to define or observe glass transition temperatures on all copolymers.

^f This high molecular weight material is soluble only in hot THF.

^g These samples were acidic and would not come through the GPC column.

^h Obtained by vapor-pressure osmometry.

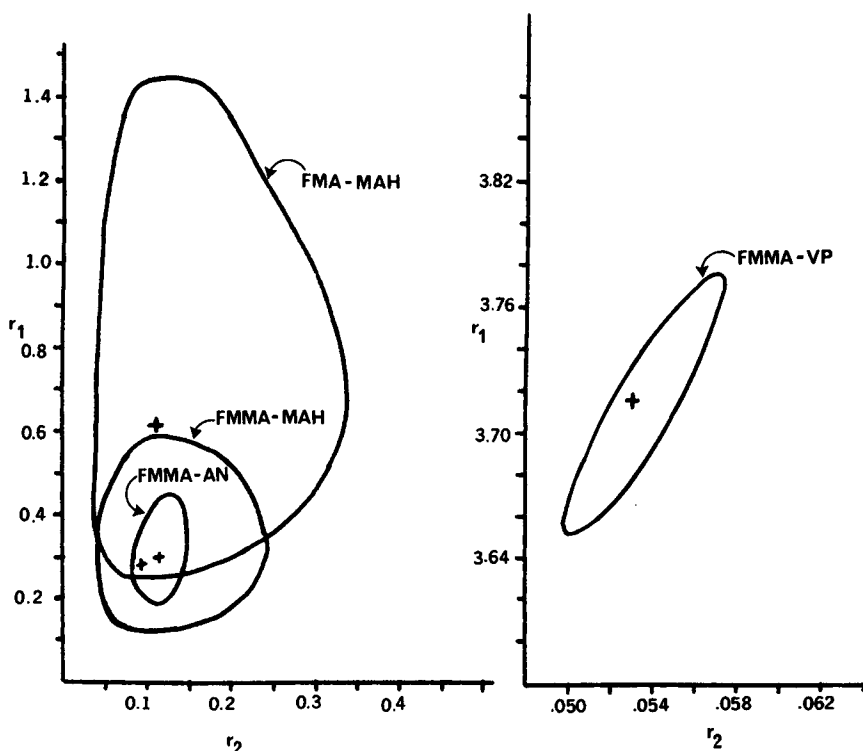


Fig. 1. 95% joint confidence limits for the relative reactivity ratios of copolymerizations of ferrocenylmethyl acrylate (FMA) and ferrocenylmethyl methacrylate (FMMA).

these latter runs were used to compute the reported r_1 and r_2 values. The computation involves a nonlinear least-squares fitting to either the differential or integrated form of the copolymer equation. These r_1 and r_2 values are summarized in Table VI along with some previous findings,¹¹ and the approximate 95% joint confidence limits [from eq. (11) of Tidwell and Mortimer¹⁴] are plotted in Figure 1. The error limits for the r_1 and r_2 values in Table VI are not listed there but can be found in Figure 1 or in the references to Table VI.¹⁶⁻²²

High yields of copolymers were obtained in copolymerizations of II with acrylonitrile, *N*-vinyl-2-pyrrolidone (yields above 90%) and maleic anhydride. Yields to 80% were obtained when the molar content of II in the feed was 70%. Yields of the copolymer of I and maleic anhydride were lower and exceeded 60% only when the molar content of I in the feed exceeded 75%. In benzene-ethyl acetate, the molecular weights of the maleic anhydride copolymers of I were much lower than those of copolymers of II with acrylonitrile or *N*-vinyl-2-pyrrolidone. Similarly, the maleic anhydride copolymerizations were slower.

Despite the very high molecular weights exhibited by some of the copolymers of II with acrylonitrile or *N*-vinyl-2-pyrrolidone, the values of

TABLE VI
Summary of the Relative Reactivity Ratios for Ferrocenylmethyl
Acrylate and Ferrocenylmethyl Methacrylate versus Those of Methyl
Acrylate and Methyl Methacrylate, with Organic Monomers

M ₁	M ₂	r ₁	r ₂	M ₁	r ₁	r ₂
FMA ^a	STY	0.02	2.3	MA ^b	0.18	0.75
FMA ^a	VA	1.44	0.46	MA ^c	9.0	0.10
FMA ^a	MA	0.14	4.46	—	—	—
FMA ^a	MMA	0.08	2.9	MA	0.56	1.73
FMA ^d	MAH	0.61	0.11 ^e	MA	2.5	0
FMMA ^d	VP	3.71	0.05	MMA	4.7	0.01
FMMA ^a	STY	0.03	3.7	MMA ^b	0.46	0.52
FMMA ^a	VA	1.52	0.20	MMA ^f	20	0.01
FMMA ^a	MMA	0.12	3.27	—	—	—
FMMA ^a	MA	0.08	0.82	MMA	1.73	0.56
FMMA ^d	AN	0.30	0.11	MMA ^h	1.20	0.15
FMMA ^d	MAH	0.28	0.10 ^e	MMA ⁱ	3.5	0.03

^a Taken from Lai et al.¹¹

^b Data of Lewis et al.¹⁸

^c Data of Mayo et al.¹⁷

^d Found in this study.

^e Finite values are calculated without considering possible copolymer composition errors resulting from finite errors in the elemental analyses. Thus, r_2 could possibly be zero. However, nonzero r_2 values for maleic anhydride (M₂) have been reported.¹⁸

^f Data of Mayo et al.¹⁹

^g Data of Bork and Coleman.²⁰

^h Data of Lewis et al.²¹

ⁱ Data of Blackley and Melville.²²

$[\eta]$ of these species suggest branching has occurred to a considerable extent. This, combined with the rather high molecular weight of monomer II, results in polymers with $\bar{M}_w > 90,000$ having intrinsic viscosities below 0.25 dl/g. Other data which suggest that branching is important are: (a) increasing the concentration of monomer results in the formation of insoluble polymers: and (b) plots of $[\eta]$ versus $\log M$ are not linear.

EXPERIMENTAL

Materials

Commercially available samples of reagent grade acrylonitrile and *N*-vinylpyrrolidone were distilled, and maleic anhydride was purified by double recrystallization before use. Ferrocenylmethyl acrylate, mp 42–43°C, and ferrocenylmethyl methacrylate, mp 52–53°C, were prepared as previously described.¹¹ They were of sufficient purity that impurities could not be detected by thin layer chromatography.

Copolymerizations

These were conducted by using the technique previously described,^{11,13} except that a temperature of 80°C was used for all studies reported here.

Molecular Weight Measurements

The universal calibration technique^{23,24} used in these studies has been thoroughly described by Grube.²⁵

Copolymer Composition

Copolymer compositions were determined by elemental analyses. The primary method used for iron analysis was x-ray fluorescence, every fifth sample being checked by atomic absorption spectroscopy. While x-ray fluorescence measurements on organometallic polymers, performed elsewhere,²⁶ have given values about 0.5% higher than either atomic absorption or gravimetric methods for iron, this did not prove to be true in this study. Both iron and nitrogen analyses were used on acrylonitrile and *N*-vinylpyrrolidone copolymers.

Infrared Spectra

The infrared spectra of the purified copolymers were run on a Perkin-Elmer model 521 spectrometer in KBr pellets and key bands are summarized below: I-maleic anhydride, 3095, 2930–2960, 1850, 1775, 1720, 1440, 1440, 1370, 1235, 1155, 1100, 1035, 996, 915, 812 cm^{-1} ; II-acrylonitrile, 3095, 2930–2980, 2240, 1715, 1620, 1440, 1405, 1375, 1265, 1237, 1140, 1100, 1035, 1023, 996, 915, 815, 755 cm^{-1} ; II-*N*-vinyl-2-pyrrolidone, 3090, 2930–2980, 1715, 1675, 1440, 1455, 1415, 1375, 1260, 1235, 1140, 110, 1035, 1020, 995, 935, 910, 810, 750 cm^{-1} ; II-maleic anhydride, 3100, 2860–2980, 1780, 1720, 1620, 1460, 1440, 1407, 1380, 1255, 1240, 1140, 1100, 1055, 1040, 1025, 998, 940, 920, 815, 753, 715 cm^{-1} .

DISCUSSION

Both ferrocenylmethyl acrylate and ferrocenylmethyl methacrylate are less reactive monomers than are methyl acrylate and methyl methacrylate, respectively. This is clearly pointed out in Table VI, where the r_1 values of the ferrocene-containing monomers are consistently lower than those of methyl acrylate (or methacrylate). Similarly, the r_2 values for copolymerizations of I or II are larger than those of methyl acrylate or methyl methacrylate, respectively. From copolymerizations with styrene, the value of Q for I is 0.11 (versus 0.46 for methyl acrylate) and Q for II is 0.08 (versus 0.74 for methyl methacrylate). Similarly, in copolymerizations with maleic anhydride and methyl acrylate, Q for I was found to be 0.05 and 0.18, respectively, while Q for II was found to be 0.03 and 0.12, respectively, in copolymerizations with maleic anhydride and methyl methacrylate.

Monomer I and II, like methyl acrylate (and methacrylate) are electron-withdrawing monomers. This is indicated by the e values determined for I of 0.96 (M_2 = styrene), 0.60 (M_2 = maleic anhydride), and 0.34 (M_2 = vinyl acetate). Similarly, II exhibits e values of 0.68 (M_2 = styrene), 0.34 (M_2 = maleic anhydride), 0.13 (M_2 = vinyl pyrrolidone). Q - e maps were constructed, but no satisfactory single values of Q and e apply to either monomers I or II over the range of monomers used here and previously.¹¹ This is not surprising in view of the rather large confidence limits associated with some of the copolymerizations. Furthermore, the small r_1 values for both I and II, relative to those of methyl acrylate (and methacrylate), suggest steric effects are intervening, and these would vary with the comonomer used.

This work constitutes, in part, work submitted for the Ph.D. degree by O. E. Ayers at the University of Alabama, University, Alabama.

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