Macromolecules

Volume 6, Number 1 January–February, 1973

Organometallic Polymers. XXIII.[1] Free-Radical-Initiated, Solution Copolymerization of Cyclopentadienylmanganese Tricarbonyl

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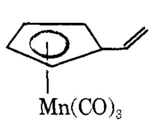
Received July 5, 1972

ABSTRACT: Vinylcyclopentadienylmanganese tricarbonyl (1) has been readily copolymerized with styrene, methyl acrylate, acrylonitrile, vinyl acetate, and vinylferrocene in benzene or ethyl acetate at 70° using azobis-(isobutyronitrile) (AIBN) initiation. A large series of copolymerizations of 1 was performed with each comonomer and polymers with relatively high molecular weight were obtained. The copolymers were characterized by vapor pressure osmometry, gel permeation chromatography, intrinsic viscosity measurements, and infrared spectroscopy. All copolymers were insulators, and they formed films which exhibited fungus resistance in accelerated growth tests. The relative reactivity ratios, r_1 and r_2, were obtained using the nonlinear least-squares optimized fitting of the integrated form of the copolymer equation according to the method of Mortimer and Tidwell. Where 1 is defined as M_1, the values of the relative reactivity ratios were as follows: for M_2 = styrene, $r_1 = 0.098$ and $r_2 = 2.50$; for M_2 = methyl acrylate, $r_1 = 0.19$ and $r_2 = 0.47$; for M_2 = acrylonitrile, $r_1 = 0.19$ and $r_2 = 0.22$; for M_2 = vinyl acetate, $r_1 = 2.35$ and $r_2 = 0.06$; for M_2 = vinylferrocene, $r_1 = 0.44$ and $r_2 = 0.49$. From these results the Q and e values were calculated for 1 ($e_1 = -1.99$, when M_2 = styrene). From the $Q - e$ studies it was apparent that 1 is a strongly electron-donating monomer. However, a separation of resonance, polar, and steric effects was impossible, and it is not certain that a linear free-energy ($Q - e$ type) relationship exists for the M_2 series used. It is clear that one cannot yet predict r_1, r_2 values for a given M_2 using r_1, r_2 and current $Q - e$ values from polymerizations with another M_2. Possible errors are discussed.

Reports of the addition polymerization and copolymerization of organometal carbonyl monomers are extremely rare in contrast to their metallocene analogs.[3] Recent books devoted to organometallic carbonyl chemistry and metalorganic polymers are devoid of reports of organometal carbonyl polymers. Rochow and Stern have reported the synthesis of polymers with the repeating unit -[R-$M(CO)_x]_n$-, where R was a fluorocarbon and M a transition metal.[4] A very brief report of the thermal polymerization of vinylcyclopentadienylmanganese tricarbonyl (1) during the dehydration of (1-hydroxyethyl)cyclopentadienylmanganese tricarbonyl over $KHSO_4$ at 170° by Cais has appeared.[5] Manuel and Berger reported that refluxing iron pentacarbonyl with polybutadiene produced a polymer containing conjugated diene-iron tricarbonyl functional groups along the chain.[6]

Our group has undertaken a major study of organometal carbonyl-containing polymers to begin the exploration of this neglected area. The novel monomer, π-(benzyl acrylate)chromium tricarbonyl (2) was homopolymerized and copolymerized with styrene and methyl acrylate.[7] Homopolymers having M_n as high as 60,000 were prepared, the Mark–Houwink relation was established, and relative reactivity ratios for the copolymerizations were established. Styrenetricarbonylchromium (3) was also prepared and copolymerized with styrene, methyl acrylate, and 1.[1b] The reaction of polystyrene with chromium hexacarbonyl in refluxing dimethoxyethane was shown to give a polystyrene with $-Cr(CO)_3$ functions complexed to the phenyl rings.[1b] Also, the novel (diene acrylate)tricarbonyliron monomer 4 has been both homo- and copolymerized.[8] Co-



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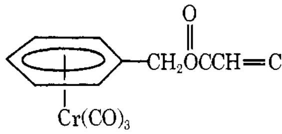

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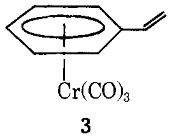

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[1] For previous papers in this series, see (a) D. O. Cowan, J. Park, C. U. Pittman, Jr., Y. Sasaki, T. K. Mukherjee, and N. A. Diamond, *J. Amer. Chem. Soc.*, 94, 5110 (1972); (b) C. U. Pittman, Jr., P. L. Grube, O. E. Ayers, S. P. McManus, M. D. Rausch, and G. A. Moser, *J. Polym. Sci., Part A-1*, 10, 379 (1972), and references therein.

[2] This work constitutes a portion of the master's dissertation of G. V. Marlin and the doctoral dissertation of T. D. Rounsefell.

[3] E. W. Neuse and H. Rosenberg, "Metallocene Polymers," Marcel Dekker, New York, N. Y., 1970.

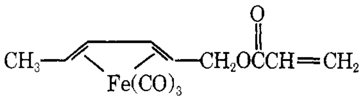
[4] E. Rochow and R. Stern, U. S. Patent 3,291,783 (1966).

[5] J. Kozikowski and M. Cais, U. S. Patent 3,290,337 (1966).

[6] M. Berger and T. A. Manuel, *J. Polym. Sci., Part A-1*, 4, 1509 (1966).

[7] C. U. Pittman, Jr., R. L. Voges, and J. Elder, *Macromolecules*, 4, 302 (1971).

[8] C. U. Pittman, Jr., O. E. Ayers, and S. P. McManus, unpublished work.



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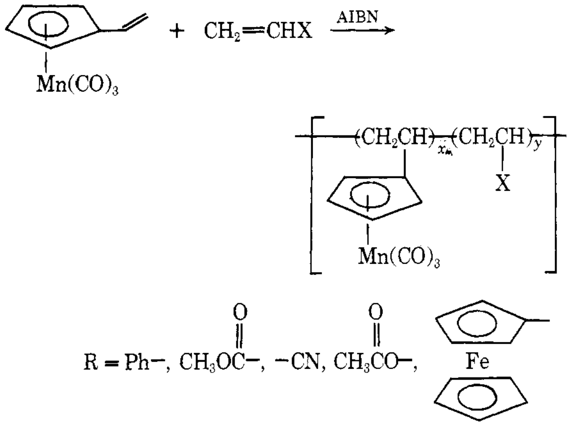
polymerization studies of 1 with both vinylferrocene and *N*-vinyl-2-pyrrolidone have now appeared[9] and initial accounts of the work reported in this paper have been briefly noted.[10,11]

Since 1 is easy to prepare,[5,10] air and moisture stable, and an analog of both styrene and vinylferrocene, it represents a transition metal carbonyl monomer of unusual opportunity for polymer chemists. Furthermore, cyclopentadienylmanganese tricarbonyl and its methyl derivative have been used (1) to deposit metal and metal carbide films on glass, ceramic, or metal surfaces;[12] and (2) as a catalyst for the oxo process,[13] suggesting interesting possibilities for polymers of 1. Thus, in this paper we report extensive studies of the copolymerization of 1 with styrene, methyl acrylate, acrylonitrile, vinyl acetate, and vinylferrocene. The relative reactivity ratios and $Q - e$ scheme for each of these copolymerizations has been completed.

Results

Vinylcyclopentadienylmanganese tricarbonyl (1)[14] was readily prepared by the aluminum chloride catalyzed acylation of cyclopentadienylmanganese tricarbonyl with acetyl chloride followed by sodium borohydride reduction and dehydration at 190° over $KHSO_4$ in the presence of hydroquinone. Monomer 1 was obtained in about 50% yield (based on $C_5H_5Mn(CO)_3$), after purification by column chromatography (silica gel), and vacuum distillation. The purity was sufficient that only 1 could be detected by tlc. Solution copolymerizations of 1 with styrene, methyl acrylate, and vinylferrocene[15] were carried out in degassed benzene. Copolymerizations with acrylonitrile and vinyl acetate were carried out in degassed ethyl acetate. All reactions were conducted at 70° under nitrogen using azobis(isobutyronitrile) (AIBN) initiation.[16] Homopolymerizations were accomplished in benzene using AIBN initiation. The homopolymer yields varied with monomer concentration and molecular weights up to 25,000 were obtained.[17] Each polymer was purified by three reprecipitations from benzene (or ethyl acetate) into petroleum ether, and the absence of monomeric impurities was established by gel permeation chromatography. Equation 1 illustrates the copolymerizations.



(1)

Copolymer yields greater than 60% could be obtained in each reaction except where vinyl acetate was 65 mol %, or more, of the initial charge. Tables I–V tabulate the experimental details of those polymerizations used to calculate the relative reactivity ratios. The relative reactivity ratios, r_1 and r_2, were calculated by the method advocated by Mortimer and Tidwell.[18] First, four to six copolymerization runs were carried out at two widely separated $[M_1^0]$ $[M_2^0]$ ratios[19] and crude estimates of r_1 and r_2 were obtained. From these values, the two optimized initial monomer concentration ratios were selected from previously computed tables.[18] Many copolymerizations were then carried out at those two ratios. This data was used to compute the "best" values of r_1 and r_2 and the approximate 95% joint confidence limits (from eq 11 of ref 18) of r_1 and r_2. Table VI lists the values of r_1, r_2, Q, and e[20] obtained for the copolymerizations of 1. The 95% joint confidence limits have been plotted in Figures 1 and 2.

Each copolymer was characterized by gel permeation chromatography, intrinsic viscosity measurements, and, where sufficient sample was available, by vapor pressure osmometry. Molecular weights ($\bar{M}_n$ and $\bar{M}_w$) and distributions were most accurately determined using the "universal calibration" gel permeation chromatography method.[21,22]

A few representative molecular weight measurements are summarized in Table VII for example copolymers. From these values it is clear that well-defined, moderately high molecular weight polymers were obtained. Increasingly higher molecular weights were obtained as (1) the amount of solvent was reduced, (2) the amount of initiator was reduced in the initial charge (but a second charge added after long polymerization times), and (3) as the temperature was lowered from 90 to 60°.[23] The copolymers gave smooth single peak GPC curves of broad molecular weight distribution. Binodal peaks were not found.

The infrared spectra of each polymer were recorded, and the spectral assignments are summarized in the Experimental Section. Nmr spectra were recorded, but the

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(9) C. U. Pittman, Jr., and P. L. Grube, *J. Polym. Sci., Part A-1*, 9, 3175 (1971).

(10) C. U. Pittman, Jr., *Chem. Tech.*, 417 (1971); C. U. Pittman, Jr., *J. Paint Technol.*, 43, 561, 29 (1971).

(11) *Chem. Eng. News*, 36 (Dec 16, 1970).

(12) J. Kozikowski, V. Norman, and T. P. Whaley, U. S. Patent 3,253,946; *Chem. Abstr.*, 65, 5168 (1966).

(13) Ethyl Corporation, British Patent, 863,277 (1961); *Chem. Abstr.*, 56, 9969*f*.

(14) A. N. Nesmeyanov, *et al.*, *Dokl. Akad. Nauk SSSR*, 154, 646 (1964); *Chem. Abstr.*, 60, 0713.

(15) J. C. Lai, T. Rounsefell, and C. U. Pittman, Jr., *J. Polym. Sci., Part A-1*, 9, 651 (1971).

(16) Attempts to use benzoyl peroxide initiation were less successful because 1 was oxidized and either 1, or its oxidation products, catalyze the decomposition of peroxide initiators. Gas evolution was noted when peroxide initiators were used.

(17) Unpublished work, C. U. Pittman, Jr., J. C. Lai, and T. D. Rounsefell.

(18) P. W. Tidwell and G. A. Mortimer, *J. Polym. Sci., Part A*, 3, 369 (1965).

(19) D. R. Montgomery and C. E. Fry, *J. Polym. Sci., Part C*, 25, 59 (1968).

(20) The values of Q and e for 1 were computed using the standard equations $r_1 = (Q_1/Q_2)\exp[-e_1(e_1 - e_2)]$ and $r_2 = (Q_2/Q_1)\exp[-e_2(e_2 - e_1)]$. For a discussion, see T. Tsuruta and K. F. O'Driscoll, "Structure and Mechanism in Vinyl Polymerization," Marcell Dekker, New York, N. Y., 1969, Chapters 1 and 2.

(21) H. Coll and D. K. Gilding, *J. Polym. Sci., Part A-2*, 8, 89 (1970).

(22) The agreement of GPC with vpo was good using a universal calibration.

(23) Each of these trends is only clearly found when $[M_1^0]:[M_2^0]$ is held constant.

Table I
Copolymerization of Vinylcyclopentadienylmanganese Tricarbonyl (M_1) and Styrene (M_2) at 70° in Benzene Solution

Polymer No.	M_1 Charged to Reaction (g)	Mol % M_1 Charged to Reaction	AIBN (g)	Vol of Benzene (ml)	Reaction Time (hr)	Copolymer Yield		Mol % of M_1 in Copolymer
						g	%	
1	2.399	34.91	0.0286	20	10.3	1.13	25.7	18.1
2	2.399	34.91	0.0286	20	5.0	0.78	17.7	18.1
3	2.278	34.91	0.0272	19	17.0	1.50	36.1	17.6
4	2.278	34.91	0.0272	19	30.0	1.63	39.2	17.8
5	2.278	34.91	0.0272	19	48.0	1.82	43.8	18.9
6	1.522	15.36	0.0271	19	4.0	0.84	15.8	7.4
7	1.522	15.36	0.0271	19	8.0	1.43	26.9	7.5
8	1.522	15.36	0.0271	19	12.0	2.00	37.6	7.6
9	1.522	15.36	0.0271	19	24.0	2.55	48.0	7.4
10	1.522	15.36	0.0271	19	48.0	2.90	54.4	8.1
11	1.802	35.40	0.0441	10	93.0	2.07	62.8	21.0
12	1.203	15.34	0.0444	10	186.0	3.13	74.4	9.0
13	1.796	35.33	0.0442	10	186.0	1.97	60.1	20.2
14	6.267	88.29	0.0339	15	8.83	1.24	18.7	66.5
15	3.146	88.39	0.0190	15	8.83	0.56	16.9	62.7
16	1.888	87.04	0.0105	15	15.0	0.20	10.0	57.9
17	3.005	90.47	0.0107	10	10.3	0.43	13.5	67.2
18	4.002	90.66	0.0135	14	10.0	0.50	12.0	64.7
19	4.007	90.74	0.0137	14	10.0	0.26	6.2	61.8
20	4.016	91.01	0.0142	14	10.0	0.35	8.4	63.6
21	4.114	44.91	0.0325	25	4.0	0.48	7.5	21.9
22	4.118	44.80	0.0320	25	4.0	0.54	8.4	21.8

Table II
Copolymerization of Vinylcyclopentadienylmanganese Tricarbonyl (M_1) and Methyl Acrylate (M_2) at 70° in Benzene Solution

Polymer No.	M_1 Charged to Reaction (g)	Mol % M_1 Charged to Reaction	AIBN (g)	Vol of Benzene (ml)	Reaction Time (hr)	Copolymer Yield		Mol % of M_1 in Copolymer
						g	%	
1	1.932	15.98	0.0283	15	70.7	4.43	77.2	7.48
2	1.932	15.98	0.0283	15	5.7	3.29	57.3	8.84
3	1.932	15.98	0.0283	15	25.5	4.06	70.9	7.61
4	1.932	15.98	0.0283	15	12.3	3.75	65.5	8.95
5	1.932	15.98	0.0283	15	3.0	2.25	39.3	10.34
6	3.754	42.38	0.0268	20	26.0	2.75	48.6	24.22
7	3.754	42.38	0.0268	20	6.0	1.65	29.2	26.57
8	3.754	42.38	0.0268	20	17.4	2.29	40.4	26.08
9	3.754	42.38	0.0268	20	74.0	2.95	52.1	25.20
10	1.548	15.98	0.0229	16	4.6	2.13	46.4	20.40
11	2.197	15.98	0.0325	22.6	3.2	2.36	36.7	21.14
12	1.693	15.98	0.0251	17.5	2.2	0.66	14.5	21.99
13	2.601	38.84	0.0310	14.4	28.5	3.19	77.1	38.50
14	2.489	38.92	0.0198	13.8	2.8	0.78	19.8	39.72
15	2.998	23.00	0.0338	23.6	1.2	1.28	19.0	29.38
16	2.004	22.99	0.0226	15.8	2.3	1.00	22.2	29.09
17	2.004	23.01	0.0225	15.8	2.3	1.04	23.1	28.88
18	2.006	23.03	0.0225	15.8	2.5	1.12	24.8	28.09
19	4.231	93.84	0.0217	15.2	3.0	0.87	20.0	85.47
20	4.424	94.10	0.0226	15.8	3.3	1.05	23.3	82.35
21	4.256	94.05	0.0218	15.2	3.0	0.81	18.6	81.35
22	4.247	94.00	0.0217	15.2	3.0	0.82	18.9	84.32

spectra were not of sufficient quality to provide monomer sequence distribution information.[24-26]

Copolymers of 1 could, in many cases, be cast into films. In general, as the mole fraction of the 1 in the copolymer increased, the films became increasingly brittle. Copolymers with a high metal content were codissolved into solutions of polystyrene and from these solutions films were cast. Copolymers of 1 with styrene and vinylferrocene are very soluble in benzene or toluene. When M_2 is polar (*i.e.*, vinyl acetate, methyl acrylate, or acrylonitrile) the benzene solubility is reduced, but common solvents such as H_4furan, ethyl acetate, and mixed solvents such as ethyl acetate–benzene can be used to make concentrated polymer solutions. All the copolymers were insoluble in

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(24) A. D. Keltoy, "Stereochemistry of Macromolecules," Vol. 3, Marcel Dekker, New York, N. Y., 1968, Chapters 1-2.

(25) K. Bacon, "Newer Methods of Polymer Characterization," Interscience, New York, N. Y., 1964.

(26) Line broadening due to viscosity and/or paramagnetic impurities was such that very high resolution was not obtained. This was true at the several temperatures tried.

Table III
Copolymerization of Vinylcyclopentadienylmanganese Tricarbonyl (M_1) and Acrylonitrile (M_2) at 70° in Ethyl Acetate Solution[a]

Polymer No.	M_1 Charged to Reaction (g)	Mol % M_1 Charged to Reaction	AIBN (g)	Vol of Ethyl Acetate (ml)	Reaction Time (hr)	Copolymer Yield g	Copolymer Yield %	Mol % of M_1 in Copolymer
1	2.000	30.00	0.0231	20.0	53.5	1.29	41.8	36.6
2	1.817	30.01	0.0210	15.0	21.0	1.17	41.7	40.1
3	1.817	30.01	0.0210	15.0	43.5	1.35	48.2	39.2
4	1.817	30.01	0.0210	15.0	24.5	0.72	25.6	33.3
5	1.338	30.02	0.0150	11.0	9.75	0.49	23.6	39.8
6	1.338	30.02	0.0150	11.0	70.0	0.93	45.0	36.8
7	2.478	29.82	0.0285	20.4	4.0	0.41	10.9	38.7
8	2.197	30.00	0.0253	18.2	170.5	0.80	23.7	60.0
9	1.900	70.00	0.0157	19.0	39.1	0.62	29.8	59.2
10	1.900	70.00	0.0157	19.0	9.3	0.33	15.9	56.6
11	1.900	70.00	0.0157	19.0	20.3	0.49	23.5	58.4
12	1.900	70.00	0.0157	19.0	72.5	0.65	31.2	58.5
13	1.900	70.00	0.0157	19.0	184.0	0.65	31.3	56.6
14	1.346	29.98	0.0311	18.8	118.3	1.72	83.2	38.2
15	2.847	69.28	0.0314	28.5	29.0	1.13	35.9	59.2
16	2.506	70.0	0.0275	25.0	43.0	1.01	36.6	57.5
17	1.858	41.30	0.0209	19	2.4	0.026	1.05	36.42
18	1.858	41.30	0.0209	19	19.9	0.204	8.3	35.51
19	1.858	41.30	0.0209	19	27.7	0.089	3.6	33.8
20	1.858	41.30	0.0209	19	45.4	0.086	3.5	26.1
21	1.857	40.91	0.0333	19	0.66	0.037	1.5	36.1
22	1.857	40.91	0.0333	19	1.3	0.084	3.4	33.9
23	1.857	40.91	0.0333	19	3.0	0.125	5.1	35.3
24	1.857	40.91	0.0333	19	14.0	0.443	17.9	36.3
25	1.857	40.91	0.0333	19	41.0	0.721	29.1	35.6
26	3.173	72.62	0.0212	19[a]	16.5	0.341	9.9	47.8
27	3.173	72.62	0.0212	19[a]	43.5	0.432	12.5	40.2
28	3.173	72.62	0.0212	19[a]	93	0.464	13.5	36.5
29	3.173	72.62	0.0212	19[a]	312	0.412	11.9	35.4

[a] Copolymerizations 26–29 were run in benzene.

Table IV
Copolymerization of Vinylcyclopentadienylmanganese Tricarbonyl (M_1) and Vinyl Acetate at 70° in Ethyl Acetate

Polymer No.	M_1 Charged to Reaction (g)	Mol % M_1 Charged to Reaction	AIBN (g)	Vol of Ethyl Acetate (ml)	Reaction Time (hr)	Copolymer Yield g	Copolymer Yield %	Mol % of M_1 in Copolymer
1	4.209	46.27	0.0293	10	4.0	1.15	19.1	73.4
2	2.058	14.81	0.0314	10	5.0	0.41	6.3	61.2
3	2.946	5.39	0.0396	15	24.5	1.18	5.3	38.9
4	6.205	36.02	0.0148	10	4.5	1.05	10.2	79.9
5	4.610	40.85	0.0214	10	4.5	0.92	12.9	83.4
6	1.006	3.04	0.0390	10	18.0	0.74	5.7	23.3
7	1.013	3.06	0.0389	10	18.0	0.65	5.0	23.3
8	4.379	28.79	0.0207	10	4.5	0.64	7.6	59.4
9	4.385	28.83	0.0192	15	4.5	0.53	6.2	61.7
10	1.116	2.43	0.0386	15	18.0	1.01	5.6	19.5
11	1.110	2.42	0.0359	15	122	0.59	3.3	19.9
12	1.112	2.42	0.0171	15	12.0	0.56	3.1	22.0
13	4.379	28.76	0.0123	15	4.5	0.42	5.0	59.9
14	1.115	2.42	0.0102	15	24.0	0.45	2.5	22.9
15	4.380	28.82	0.0100	15	4.5	0.46	5.5	61.7

hexane and isopropyl alcohol and partially soluble in cyclohexanone.

Electrical conductivity and conductivity-humidity exposure tests were carried out on several copolymers according to MIL Standard 202, Method 106.[27] All the polymers were insulators. On exposure to high humidity, the conductivity of copolymers of **1** and vinylferrocene, methyl acrylate, and styrene (with a high mol fraction of styrene) increased continuously for about 3–4 days and then leveled off. Homopolymers of **1** and styrene copolymers, containing high mol fractions of **1**, exhibited an initial increase in conductivity followed by a decrease which leveled off at 6–7 days. Table VIII summarizes a few representative results.

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(27) A standard Y test pattern, using solder plated copper conductors on a ceramic base, with a 0.08-cm gap was employed. The film thicknesses used were from 0.0026 to 0.0009 in.

Table V
Copolymerization of Vinylcyclopentadienylmanganese Tricarbonyl (M_1) and Vinylferrocene (M_2) at 70° in Benzene

Polymer No.	M_1 Charged to Reaction (g)	Mol % M_1 Charged to Reaction	AIBN (g)	Vol of Benzene (ml)	Reaction Time (hr)	Copolymer Yield g	Copolymer Yield %	Mol % of M_1 in Copolymer
1	1.141	25.82	0.0210	19	15.0	0.076	1.83	28.0
2	1.141	25.82	0.0210	19	50.0	0.746	17.9	32.7
3	1.141	25.82	0.0210	19	120.0	0.291	6.98	45.9
4	1.141	25.82	0.0210	19	237.2	0.455	10.9	27.8
5	1.172	25.95	0.0293	19	24.0	0.794	18.7	31.9
6	1.172	25.95	0.0293	19	48.0	0.929	21.8	32.7
7	1.172	25.95	0.0293	19	88.5	1.197	28.1	31.8
8	1.172	25.95	0.0293	19	185.0	1.052	24.7	32.2
9	1.172	25.95	0.0293	19	206.0	1.13	26.6	36.3
10	3.078	71.50	0.0201	19	19.8	0.408	9.7	64.4
11	3.078	71.50	0.0201	19	49.5	0.454	10.8	63.1
12	3.078	71.50	0.0201	19	119.8	0.577	13.7	63.5
13	3.078	71.50	0.0201	19	241.5	0.567	13.5	63.7
14	3.078	71.50	0.0201	19	456	0.529	12.6	64.2
15	1.099	27.85	0.0372	14.2	185	1.090	29.3	28.9
16	0.849	25.93	0.0386	11.7	165.5	0.871	28.2	31.3
17	2.647	71.53	0.0362	13.7	167.0	1.401	38.7	65.5
18	2.782	71.60	0.0381	14.5	70	1.53	40.2	64.8
19	1.641	29.33	0.0529	20.0	24.8	1.39	26.2	20.3
20	0.890	17.02	0.0489	18.5	24.4	1.06	21.7	32.0
21	0.819	17.00	0.0450	17.0	17.0	0.739	16.4	21.4
22	3.518	83.00	0.0418	15.5	47.0	1.485	35.5	78.4
23	4.157	83.01	0.0494	18.5	25.3	1.78	36.1	77.2

To study potential biological activity which monomer 1 might impart to polymer coatings, accelerated growth fungus resistance tests were made. Tests were run on each of the polymers listed in Table VIII using *Chaetomium globosum, Aspergillus niger, Aspergillus flavus,* and *Penicillium citrium* in accordance with specification MIL-I-7444B.[28] No growth was supported by any of the organometallic polymer films despite vigorous growth on viability controls.[28] Thus, the presence of monomer 1 in the polymer appears to exhibit a retarding influence on fungus growth.[29,30]

Experimental Section

Vinylcyclopentadienylmanganese Tricarbonyl. Cyclopentadienylmanganese tricarbonyl was purchased from the Ethyl Corporation and used without further purification. It was acylated as reported by Kozikowski[31] and Fischer.[32] Yellow crystals of the acetyl derivative were obtained in yields between 70 and 85% (mp 41-42°, lit. mp 41.5-42.5°).[32]

The acetyl derivative was reduced in an open beaker with a 2 molar excess of sodium borohydride in ethanol-benzene (50:50, v/v) in from 10- to 50-g quantities at 0° and room temperature. The (α-hydroxyethyl)cyclopentadienylmanganese tricarbonyl was worked up by a procedure similar to that described by Nesmeyanov[14] and isolated in yields ranging from 70 to 80%.

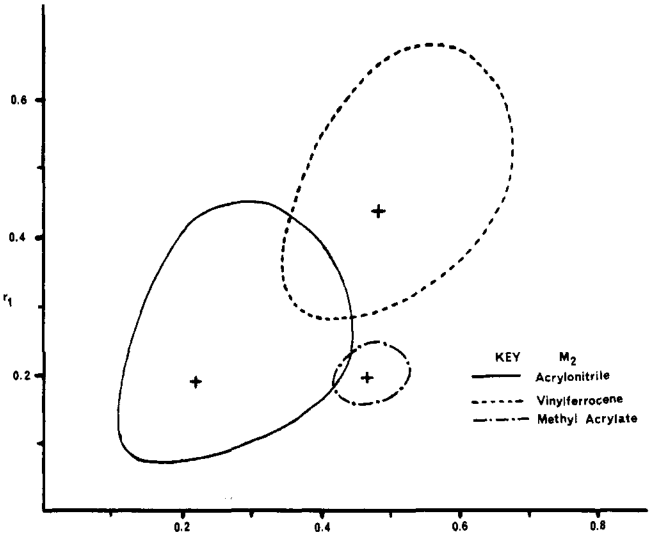

Figure 1. Approximate 95% joint confidence limits of r_1 and r_2 for copolymerizations of vinylcyclopentadienylmanganese tricarbonyl with acrylonitrile, vinylferrocene, and methyl acrylate.

The dehydration of (α-hydroxyethyl)cyclopentadienylmanganese tricarbonyl was carried out by flash distillation over $KHSO_4$ in the presence of hydroquinone at 190-200°.[14] Monomer 1 was usually isolated in yields between 65 and 80% using this method bp 64° (0.01 mm) and lit. bp 55-56° (0.005 mm).[14] In some instances much lower yields resulted, due to thermal polymerization of monomer 1 with some accompanying thermal decomposition of the resulting polymer. For monomer 1 nmr (neat) showed δ 4.55 (t, 2, J < 2 Hz, β Cp H's), 4.77 (t, 2, J < 2 Hz, α Cp H's), 5.08 (dd, 1, J_{BX} = 10 Hz, J_{AB} < 2 Hz, vinylic H_B), 5.39 (dd, 1, J_{AX} = 17 Hz, J_{AB} < 2 Hz, vinylic H_A), 6.14 (dd, 1 H, J_{AX} = 17 Hz, J_{BX} = 10, vinylic H_X), where Cp—CH_X=CH_AH_B and H_A is

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(28) In this procedure test films of polymer are applied to a ceramic substrate in the presence of a specific enriched agar, NH_4NO_3, K_2HPO_4, $MgSO_4$, and KCl culture medium. The samples are then inoculated with the spore culture (10 days old and alive). Control growth supports of paper and twine are also used in each case as viability controls. The inoculated samples are incubated 14 days at 85°F and 100% relative humidity. In every case, extensive growth took place on the paper and twine.

(29) All the usual precautions in interpreting such accelerated growth tests should be applicable here. Further studies of the fungus resistance of organometallic coatings are in progress.

(30) A preliminary report of the fungus resistance of polymers containing 1 was presented at the Fourth Symposium of the Paint Research Institute, "Mildew Induced Defacement of Organic Coatings," Warren, Ohio, March 27-28 (1972).

(31) J. Kozikowski, *J. Amer. Chem. Soc.*, 81, 2995 (1959).

(32) E. O. Fischer and K. Plesske, British Patent 864,834 (April 1961); *Chem. Abstr.*, 55, 2338 (1961).

Table VI

Relative Reactivity Ratios, r_1 and r_2 and the Computed Values of Q and e for Vinylcyclopentadienylmanganese Tricarbonyl (M_1) Copolymerizations in Solution at 70°

Monomer 2	Rel React Ratios r_1	r_2	r_1r_2	Q_1	e_1	Q_2	e_2
Styrene	0.098	2.503	0.24	1.03	−1.99	1.0[a]	−0.80[a]
Methyl acrylate	0.194	0.468	0.091	0.35	−0.95	0.42[a]	0.60[a]
Acrylonitrile	0.186	0.219	0.041	0.32	−0.59	0.60[a]	1.20[a]
Vinyl acetate	2.35	0.061	0.143	0.58	−1.62	0.026	−0.22[a]
Vinylferrocene	0.436	0.485	0.21	29.91	−3.32	1.10[b]	−2.07[b]
	0.436	0.485		4.67	−2.55	0.4[c]	−1.3[c]

[a] Values of Q_2 and e_2 were obtained (J. Brandrup and E. H. Immergat, Ed., "Polymer Handbook," Interscience Publishers, New York, N.Y., 1966). [b] Obtained from copolymerizations of vinylferrocene with styrene, see ref 15 (note ref 15 only the negative value of Q was listed for vinylferrocene. However, the positive value of 1.10, not listed, is clearly preferable in view of the great electron donating value of the ferrocene nucleus on electron demand). [c] C. Aso, T. Kunitake, and T. Nakashima, *Kogyo Kagaku Zasshi,* **72,** 1411 (1969).

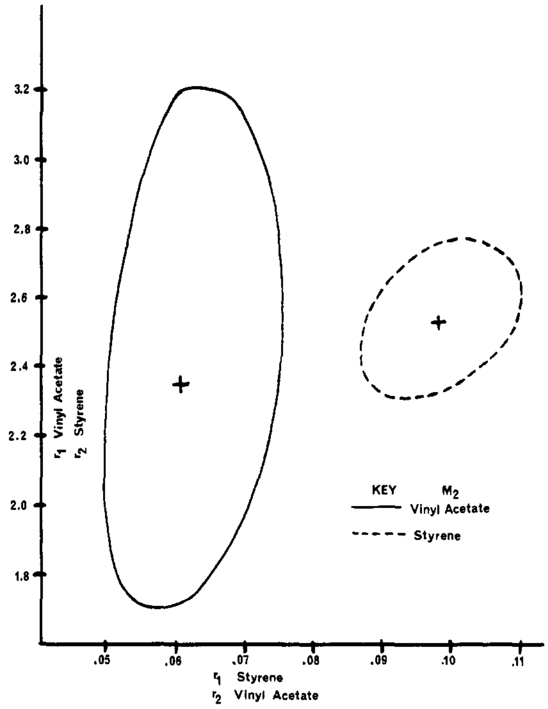

Figure 2. Approximate 95% joint confidence limits of r_1 and r_2 for copolymerizations of vinylcyclopentadienylmanganese tricarbonyl with vinyl acetate and styrene.

cis to Cp). Infrared spectra (NaCl pellet)[33] showed 3120 (ring CH str A_1), 3092 (ring CH str E_1, E_2), 3020 (vinyl CH str), 2025 vs (CO str A_1), 1930 vs (CO str E_1), 1636 (C=C str), 1487, 1405 (ring C—C str, E_2), 1302, 1251, 1069 sh, 1059 (out-of-plane CH def E_2), 1040 (out-of-plane CH def E_1), 1020 (in-plane CH def E_1), 990 and 918 s ($CH=CH_2$ def), 840 broad (out-of-plane CH def A_1 and E_1), 729, 663 s (MnCO bend, E), 622 s (MnCo bend A_1) cm.$^{-1}$

Copolymerizations and Copolymer Characterization. The copolymerizations were carried out in Fisher-Porter aerosol compatability tubes after three alternate freeze-thaw degassing cycles followed by repressurization with nitrogen. The details of the polymer work-up procedure have been described previously.[15,34] Viscosities were measured in H_4furan at 30° using Can-non-Fenske viscometers. Gel permeation chromatograms were run in H_4furan at 30 ± 0.1° on a Waters Model 301 GPC on one of two column banks. Each bank contained four styragel columns (3 ft long each). Banks A and B were composed of columns with the following exclusion limits in ångströms, respectively: bank A, 5 × 10^4 to 1.5 × 10^4, 1.5 × 10^4 to 5 × 10^3, 2 × 10^3 to 700, and 700 to 250; bank B, two each of 1.5 × 10^5 to 5 × 10^4, one each of 5 × 10^4 to 1.5 × 10^4 and 1.5 × 10^4 to 5 × 10^3. The Universal calibration method[21] was applied and the chromatogram peaks were analyzed in the standard fashion[35] using three points or more per count.[36] A Hewlett-Packard Model 302B vapor pressure osmometer using benzene as the solvent, was used to obtain the values of $\bar{M}_n$ for several polymers. These values were used to check the applicability of the Universal calibration.

Table VII

Molecular Weight and Intrinsic Viscosity Determinations for a Representative Series of Copolymers of 1

Polymer No.[a]	Mol % M_1 in Co-polymer	$[\eta]$[b] (dl/g)	$\bar{M}_n$[c]	$\bar{M}_w$[c]	$\bar{M}_w/\bar{M}_n$
VCM-STY-11	21.0	0.114	7,000	40,800	5.84
VCM-STY-23[d]	38.7	0.105	14,500	85,500	5.90
VCM-MA-13	38.5	0.089	11,800 11,126[e]	76,800	6.49
VCM-MA-20	83.2	0.063	14,100	58,300	4.13
VCM-AN-3	39.2	0.068	13,800	65,400	4.75
VCM-AN-15	59.2	0.038	12,000	22,300	1.86
VCM-VA-3	38.9	0.057	6,000	20,500	3.41
VCM-VA-4	79.9	0.145	19,700	35,000	1.78
VCM-VF-15	28.9	0.044	7,700	13,800	1.79
VCM-VF-18	64.8	0.039	9,050	15,200	1.68

[a] VCM = vinylcyclopentadienylmanganese tricarbonyl; STY = styrene; MA = methyl acrylate; AN = acrylonitrile; VA = vinyl acetate; VF = vinylferrocene. The numbers refer to those in Tables I–V. [b] In H_4furan at 30°. [c] Determined by GPC using the Universal calibration technique unless otherwise noted. [d] Not listed in Table I. [e] From vapor pressure osmometry.

The infrared spectra were run in KBr on a Perkin-Elmer Model 237 or a Beckman IR Model 33 spectrometer. Key bands are summarized for one example copolymer each as follows (in cm^{-1}).

VCM-STY. 3070 and 3040 (Cp ring CH str A_1, E_1 and E_2), 3010 (benzene ring CH str), 2910, 2840 (sp^3 CH str), 2004 vs (CO str A_1), 1918 vs (CO str E), 1598 and 1490 (benzene ring), 1454 (sp^3 CH def), 1255, 1085 and 1065 (out-of-plane CH def E_2), 1019 (in-plane CH bend E_2), 900, 829 (out-of-plane CH def A_1 and E_1, 755 and 690 (monosubstituted phenyl ring CH def), 658 and 620 (MnCO bend E and A_1).

VCM-VA. 3100 (Cp ring CH str), 2910 and 2840 (sp^3 CH str), 2005 vs (CO str A_1), 1915 vs (CO str E), 1725 (ester CO str), 1462, 1413, 1369, 1233, 1055 (out-of-plane CH def E_2), 1030 (in-plane CH bend E_1), 925 sh (in-plane ring def E_2), 900, 842 sh and 830 (out-of-plane CH def A_1 and E_1), 655 and 620 (MnCO bends E_1 and A_1).

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(33) The bands are assigned based on the spectral analysis of cyclopentadienylmanganese tricarbonyl (see I. J. Hyams, R. T. Bailey, and E. R. Lippincott, *Spectrochim. Acta, Part A,* 23, 273 (1967).

(34) J. C. Lai, T. D. Rounsefell, and C. U. Pittman, Jr., *Macromolecules,* 4, 155 (1971).

(35) J. Cazes, *J. Chem. Educ.,* 43, A567 (1966).

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

Table VIII
Humidity-Conductivity Test Results[a]

Polymer Sample	Film Cast from	Conductivity (ohm^{-1} cm^{-1})		
		Initial	3 Days	7 Days
1-homopolymer	2-Butanone	6.3×10^{-13}	6.3×10^{-9}	7.5×10^{-12}
1-vinylferrocene-8	Benzene	2.5×10^{-13}	1.7×10^{-10}	1.3×10^{-10}
1-methyl acrylate-6	Phenol	2.4×10^{-13}	6.2×10^{-10}	1.1×10^{-10}
1-styrene-10	H_4furan	3.7×10^{-12}	9.4×10^{-9}	7.1×10^{-9}
1-styrene-16	Toluene	1.1×10^{-13}	5.0×10^{-10}	1.9×10^{-12}

[a] Carried out according to MIL Standard 202, Method 106.

VCMMA. 3130 and 3045 (Cp ring CH str A_1 and E), 2995, 2970, 2920 (sp^3 CH str), 2005 vs (CO str A_1), 1930 vs (CO str E), 1725 (ester CO str), 1445, 1275 (O—C str), 1206, 1175 (-CO—O str), 1045 (in-plane CH bend E_1), 918, 845 (out-of-plane CH def A_1 and E_1), 672 and 649 (MnCO bend E).

VCMAN. 3070-3030 (Cp ring CH str), 2955, 2920 (sp^3 C—H str), 2120 (CN str), 2005 vs (CO str A_1), 1915 vs (CO str E), 1725 w, 1475, 1455, and 1420 (CH def and Cp ring C—C str E_1), 1380, 1260, 1060 (Cp CH out-of-plane def E_2), 929 (Cp CH in-plane def E_2), 860 (Cp CH out-of-plane def A_1 and E_1), 680 and 650 (MnCO bend E).

VCMVF. 3130, 3040 (Cp ring CH str), 2940, 2935 (sp^3 CH str), 2004 vs (CO str A_1), 1910 vs (CO str E), 1454, 1440, 1400, 1380 (C—H def and Cp ring C—C str E_1), 1110 (unsubstituted ferrocene Cp ring antisym ring breathing),[37] 1000 (unsubstituted ferrocene Cp ring C—H in-plane bend)[37] 1045 (sh) 1030, 918 (in-plane Cp ring def E_2) 815-837 (out-of-plane CH def A_1 and E_1 for both VCM and VF Cp rings) 678, 663 (MnCO bend E), 633 (MnCO bend A_1), 540.

Attempts to measure homo- and copolymerization kinetics, using dilatometry,[38] were not successful due to gas bubble formation in the dilatometer at low conversions. This could be due to some manganese-induced decomposition of AIBN or to a small amount of decomposition with CO evolution during the polymerization.

Discussion

Monomer reactivity ratios are instructive for consideration of the reactivity and structure of vinyl monomers in polymerization. Complete studies of these parameters for a large variety of vinyl monomers are now available.[39,40] Unfortunately, no vinyl monomers containing transition metals had been included in these previous studies. However, studies from our laboratories have now begun to fill this void. The r_1, r_2, Q, and e values for vinylferrocene,[15,41] styrenetricarbonylchromium,[1b] π-(benzyl acrylate) chromium tricarbonyl,[7] and four ferrocene-containing acrylates and methacrylates[38,42,43] have now appeared. It is interesting to compare the polymerization reactivity of vinylcyclopentadienylmanganese tricarbonyl (**1**) with some of these values.

The value of $1/r_2$ for **1** (M_1), when styrene is M_2, is 0.40. This may be compared to 0.86 when M_1 is *p*-methoxystyrene or 5.26 when M_1 is *p*-nitrostyrene.[44] Thus, it would appear that $CpMn(CO)_3$ ring fits the class of α substituents which are more electron donating than either *p*-methoxyphenyl or *p*-dimethylaminophenyl moieties. Furthermore, this value is quite close to the range of $1/r_2$ values (0.35-0.40) obtained for vinylferrocene,[15] an exceptionally good donator of charge in situations of high electron demand.[45]

The electron-donating tendency of the $CpMn(CO)_3$ group is also indicated by the high negative values of e which were obtained in this work (see Table VI). The value of e_1 obtained from styrene (M_2) copolymerizations is -1.99. This may be compared to *e* values of vinylferrocene (-2.07[18] or -1.3), *p*-methoxystyrene (-1.1), styrene (-0.8), *p*-nitrostyrene ($+0.4$), and acrylonitrile ($+1.20$). The quantity *e* represents the polar character of the monomer. One can suggest the high *e* values obtained for both ferrocene and $CpMn(CO)_3$ substituents could be due to a large amount of polarization in the transition state.[46] However, adopting this view, the variation in *e* for **1** with different monomers becomes hard to explain. The *e* value of monomer **1** changes as M_2 is varied from vinylferrocene (-3.32 to -2.55) to styrene (-1.99), vinyl acetate (-1.62), methyl acrylate (-0.95), and acrylonitrile (-0.59). Copolymerizations with the more electron donating monomers give (as seen above) the larger minus values of *e* for monomer **1**. One would expect the highly electron attracting acrylonitrile radical to induce a larger charge separation when reacting with a molecule of **1** then would a vinylferrocene or styrene radical. In order to extend the range of these studies, we are currently investigating the copolymerization of both vinylferrocene and **1** with *N*-vinylcarbazole ($e = -1.34$)[39] and maleic anhydride ($\ln r_1r_2 = 0$).

In the $Q - e$ scheme the largest tendency toward alternation results when the quantity $e_1 - e_2$ is maximized. That this is true for **1** is shown in Table VI where the greatest tendency toward alternation occurs in acrylonitrile copolymerizations. However, where the $e_1 - e_2$ values are markedly reduced, the increase in r_1r_2 is relatively small.[47]

A study of the $Q - e$ maps of all these studies gives no clearer picture other than the generalizations already outlined. To rationalize these results more clearly, three possibilities can be considered. First, errors inherent in the experimentation could lead to large discrepancies which would render obtaining precise $Q - e$ values impos-

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(37) M. Rosenblum, "Chemistry of the Iron Group Metallocenes," Part 1, Wiley-Interscience, New York, N. Y., 1965, pp 38-39.

(38) C. U. Pittman, Jr., R. L. Voges, and W. R. Jones, *Macromolecules*, 4, 291 (1971).

(39) L. J. Young, *J. Polym. Sci., Part A*, 54, 411 (1961).

(40) H. Mark, B. Immergut, E. H. Immergut, L. J. Young, and K. I. Beynon in "Copolymerization," G. E. Ham, Ed., Wiley-Interscience, New York, N. Y., 1964, p 695.

(41) C. U. Pittman, Jr., and P. L. Grube, *J. Polym. Sci., A-1*, 9, 3175 (1971).

(42) J. C. Lai, T. D. Rounsefell, and C. U. Pittman, Jr., *Macromolecules*, 4, 155 (1971).

(43) C. U. Pittman, Jr., R. L. Voges, and W. B. Jones, *Macromolecules*, 4, 298 (1971).

(44) C. Walling, D. Seymour, and K. B. Wolfstirn, *J. Amer. Chem. Soc.*, 70, 1544 (1948).

(45) The ability of the ferrocene moiety to stabilize adjacent plus charge is exceptionally sensitive to the electron demand relative to a phenyl ring. Thus, although the cyclopentadienyl ring in **1** has an $Mn(CO)_3$ group attached, its ability to stabilize radical centers may not differ very much from that of ferrocene.

(46) T. C. Schwan and C. C. Price, *J. Polym. Sci.*, 40, 457 (1959).

(47) Where the polarities of the two monomers do not differ appreciably, the product r_1r_2 is usually $\simeq 1$, where steric effects are not important.

sible. This will be discussed further later. Secondly, both the ferrocene and $CpMn(CO)_3$ moieties are very large sterically. Not only do they resemble isopropyl groups, but they have depth in a direction perpendicular to the Cp rings. Thus, they are actually far larger than *tert*-butyl groups. Systematic studies of steric effects in vinyl polymerizations have been observed by Chikanishi and Tsuruta in a series of α-substituted acrylates,[48] but that series bears little structural resemblance to monomer 1. Thus, it must be admitted that steric effects are not yet understood in metallocene and related monomers.[49] Finally, the electronic effects in metallocene and metal carbonyl-containing monomers might not operate to give linear free-energy correlations with monomers of such widely varying structure and electron demand as styrene and acrylonitrile. There is probably some truth to all three of these considerations.

A complete analysis of the experimental error inherent in these relative reactivity ratios is not necessary. Small errors in determining yields[50] or in the weighting the various experiments[51] are negligible in these studies. The most serious source of error is probably in the determination of the copolymer compositions by elemental analyses. Fairly small errors in the elemental analyses can lead to significant changes in the calculated copolymer compositions. In particular the $M_1{:}M_2$ ratio in the copolymer is sensitive when greater than 90% of one of the monomers is present. To ensure against major errors, many samples were reanalyzed by different commercial firms using atomic absorption, colorimetric, and gravimetric techniques. Agreement was ordinarily within ±0.5% between these methods. When this level of agreement was not found, the point was rejected and redone. However, recent analyses conducted on these samples by X-ray fluoresence methods have systematically differed by more than ±0.5%.[52] The confidence which may be placed in the r_1 and r_2 values given in Table VI, excluding analytical errors, is graphically portrayed in Figures 1 and 2. While the interpretation of these confidence limits is subject to the limitations discussed previously,[51] it was these limits which were used in defining the $Q - e$ maps referred to earlier.

In conclusion, the facile radical initiated solution copolymerization of monomer 1 with a series of vinyl monomers has been demonstrated. The polymers have reasonably high molecular weights, they are insulators, and they seem to exhibit interesting fungus resistant properties in films. Finally, from an analysis of the $Q - e$ scheme, 1 may be classified as an electron-donating monomer, but a clear disection of polar, resonance, and steric effects on the reactivity of 1 has not been accomplished.

Acknowledgments. This work was supported, in part, by the Petroleum Research Fund, administered by the American Chemical Society. The University of Alabama Computer Center generously provided free time to perform the computations reported herein. Dr. John Lai conducted some of the initial polymerization studies of monomer 1. We gratefully acknowledge Environmental Protection Agency Grant No. 5-P1-WP-225-02 for the support of G. V. M. from the period of Aug 22, 1971, to Aug 13, 1972, and Professor George Whittle, the principal investigator of that grant. Mr. P. L. Grube performed many of the GPC chromatograms reported here. The Paint Research Institute is thanked for a fellowship in support of the polymer film studies along with A. G. Valles, Autonetics Aerospace and Marine Products Division, North American Rockwell Corp., Anaheim, Calif. The Research Corp. is thanked for funds to purchase the gel permeation chromatograph and the vapor pressure osmometer used in this work. We are grateful to G. A. Mortimer and P. W. Tidwell for supplying us with the computer programs necessary to employ their method which we regard as the best available method for computing and analyzing relative reactivity ratios.

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(48) K. Chikanishi and T. Tsuruta, *Makromol. Chem.*, 73, 231 (1964).

(49) For example, styrenetricarbonylchromium would not homopolymerize ($k_{11} = 0$) but was readily copolymerized with both styrene and 1.[1b] Also, it has been demonstrated that the r_1 and r_2 values of ferrocenylmethyl acrylate are considerably different than those of electronically similar ferrocenylethyl acrylate and the same is true of their corresponding methacrylates.[42,43]

(50) Yield errors are not particularly important because the copolymer composition versus conversion plots do not have steep slopes in the region form 0 to 45% conversion. Furthermore, analysis of computer print-outs of these curves show errors in yields as high as ±5% would have a negligible effect on the r_1 and r_2 values.

(51) P. W. Tidwell and G. A. Mortimer, *J. Macromol. Sci., Rev. Macromol. Chem.*, C4 (2), 281 (1970).

(52) D. E. Leyden, J. C. Lennox, Jr., and C. U. Pittman, Jr., *Anal. Chim. Acta,* in press. In this technique the total percentage of the polymer accounted for by metal analyses for the VCMVF series (where both Mn and Fe analyses were obtained) was always greater than results from commercial laboratories.