Organometallic Polymers. XI. Copolymerization of 2-Ferrocenylethyl Acrylate and Methacrylate with Styrene, Vinyl Acetate, Methyl Acrylate, and Methyl Methacrylate

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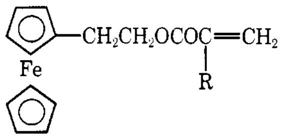
ABSTRACT: Two novel ferrocene containing monomers, 2-ferrocenylethyl acrylate (Ia) (FEA) and 2-ferrocenylethyl methacrylate (Ib) (FEMA), the preparations of which were presented in the preceding paper, have been copolymerized with styrene, vinyl acetate, methyl acrylate, and methyl methacrylate. The copolymerizations were carried out at 60–70° in degassed benzene solutions and were initiated by azobisisobutyronitrile (AIBN). Homogeneous copolymers were formed in each case. The relative reactivity ratios of each of these monomer pairs were determined, where M_1 is the monomer containing the ferrocene nucleus. The reactivity ratios were: FEA–styrene $r_1 = 0.41$, $r_2 = 1.06$; FEA–vinyl acetate $r_1 = 3.4$, $r_2 = 0.07$; FEA–methyl acrylate $r_1 = 0.76$, $r_2 = 0.69$; FEMA–styrene $r_1 = 0.08$, $r_2 = 0.58$; FEMA–vinyl acetate $r_1 = 8.79$, $r_2 = 0.06$; FEMA-methyl methacrylate $r_1 = 0.20$, $r_2 = 0.65$. Both FEA and FEMA proved to be more reactive monomers in these copolymerizations than ferrocenylmethyl acrylate (IIa) and methacrylate had been.

In the preceding paper[4] the preparation and homopolymerization of 2-ferrocenylethyl acrylate (Ia) (FEA) and 2-ferrocenylethyl methacrylate (Ib) (FEMA) were described. It was demonstrated that the AIBN-initiated solution homopolymerizations of Ia and b were faster than those of ferrocenylmethyl acrylate and methacrylate (IIa and b) (FMA and FMMA), respectively.[5] Since there are no obviously large electronic factors which account for this pronounced rate difference, a steric effect was invoked to explain these results. It was felt that the increased homopolymerization rates of FEA and FEMA suggested that these monomers would be more rapidly copolymerized with vinyl monomers than IIa and b. The AIBN-initiated copolymerization of IIa and b with styrene, methyl acrylate, methyl methacrylate, and vinyl acetate, including their relative reactivity ratios, were reported recently by Pittman, *et al.*[6] Thus, these values were available to compare with the relative reactivity ratios determined in this work.



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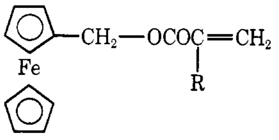

II

a, R = H
b, R = CH_3

Reports of the addition polymerization of transition metal containing organic monomers are rare[5,7] and addition copolymerizations of this class of monomers are even rarer.[6,8] Thus, there is a need to develop model organometallic monomers which may easily be copolymerized with vinyl monomers in order to begin to explore just what unusual properties transition metals may bring to the resulting plastic systems.

Experimental Section

Copolymerizations. The details of the synthesis and purification of FEA and FEMA are given in the preceding paper[4] and will not be repeated here. Styrene, vinyl acetate, methyl acrylate, and methyl methacrylate were washed with 5% aqueous sodium hydroxide, then with 10% aqueous sodium chloride, dried over anhydrous calcium chloride, and distilled under reduced pressure shortly before use. Only center cuts from these distillations were used in the copolymerizations. Benzene was distilled from P_2O_5, and commercial AIBN was recrystallized three times from methanol (102–103° with decomposition).

The monomers and AIBN were weighed on an analytical balance and dissolved in benzene. These solutions were delivered into Fischer–Porter aerosol compatability tubes from a buret. The tubes were equipped with a valve and the solutions were degassed at 10^{-2}–10^{-3} mm by three alternate freeze–thaw cycles. After degassing, the tubes were placed in a constant-temperature bath (±0.01°). After the polymerization period, the benzene–copolymer solution was added dropwise to rapidly stirring petroleum ether (bp 30–60°) to precipitate the copolymer. The copolymers were filtered and reprecipitated in this fashion two more times to ensure purification. The copolymers were then dried at 60° in a vacuum drying oven for 24 hr and weighed. The copolymer composition was then determined by analysis for per cent Fe.[9] The copolymer structure was confirmed by infrared spectroscopy, and gel permeation chromatography verified that the copolymers were homogeneous.

The infrared spectra were taken in KBr using a Perkin-Elmer Model 237 spectrometer and exhibited key bands as follows: FEA–styrene copolymer 3100, 2940–2860, 1735, 1490, 1460, 1255, 1160, 1108, 1040, 1025, 1000, 815, 755, 695, and 475 cm^{-1}; FEA–methyl acrylate copolymer 3100, 2960–2860, 1735, 1440, 1390, 1255, 1165, 1108, 1040, 1023, 1000, 815, and 478 cm^{-1}; FEA–vinyl acetate copolymer 3100, 2960–2860, 1735, 1440, 1385, 1245, 1165, 1108,

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(2) The work presented here constitutes a portion of the Master's thesis of R. L. Voges, University of Alabama, 1970.

(3) Undergraduate work-study research participant, 1969–1970.

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

(5) (a) C. U. Pittman, Jr., J. C. Lai, and D. P. Vanderpool, *ibid.*, **3**, 105 (1970); (b) C. U. Pittman, Jr., J. C. Lai, D. P. Vanderpool, M. Good, and R. Prados, Preprints of Papers of the Division of Organic Coatings and Plastics, presented at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, p 72; *Macromolecules*, **3**, 746 (1970).

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

(7) See, for example, F. S. Arimoto and A. C. Haven, Jr., *J. Amer. Chem. Soc.*, **77**, 6295 (1955); Y. H. Chen, M. F. Refojo, and H. G. Cassidy, *J. Polym. Sci.*, **40**, 433 (1959).

(8) (a) M. G. Baldwin and K. E. Johnson, *ibid., Part A-1*, **5**, 2901 (1967); (b) C. U. Pittman, Jr., *Polym. Lett.*, **6**, 19 (1968); (c) *J. Polym. Sci., Part A-1*, **9**, 651 (1971).

(9) Improved Fe analyses were obtained using combustion under pure oxygen.

1040, 1023, 1000, 815, and 478 cm^{-1}; FEMA-styrene copolymer 3100, 2960–2860, 1730, 1480, 1460, 1265, 1140, 1108, 1040, 1020, 1000, 812, 750, 695, 672, and 475 cm^{-1}; FEMA-methyl methacrylate copolymer 3100, 2990–2860, 1735, 1470, 1390, 1255, 1160, 1108, 1045, 1025, 1000, 815, 745, and 475 cm^{-1}; FEMA-vinyl acetate copolymer 3100, 2980–2820, 1730, 1460, 1385, 1245, 1160, 1108, 1040, 1023, 1000, 815, 685, and 478 cm^{-1}.

Determination of Relative Reactivity Ratios. The relative reactivity ratios were determined by employing the integrated form of the copolymer equation (eq 1) first obtained by Mayo and Lewis.[10] $M_1{}^0$ and $M_2{}^0$ are the initial molar concentrations of the

$$\log\frac{M_1}{M_2} = \frac{r_2}{1-r_2}\log\frac{M_1M_2{}^0}{M_1{}^0M_2} = \frac{1-r_1r_2}{(1-r_2)(1-r_1)}\times$$

$$\log\frac{(r_1-1)\dfrac{M_2}{M_1}-r_2+1}{(r_1-1)\dfrac{M_2{}^0}{M_1{}^0}-r_2+1} \qquad (1)$$

two monomers and M_1 and M_2 are their molar concentrations when the polymerization is terminated.

By substituting $p = (1 - r_1)/(1 - r_2)$, eq 1 is transformed into

$$r_2 = \frac{\log (M_2{}^0/M_2) - (1/p)\times \log\,[(1-p)(M_1/M_2)/(1-p)(M_1{}^0/M_2{}^0)]}{\log (M_1{}^0/M_1) + \log\,[(1-p)(M_1/M_2)/(1-p)(M_1{}^0/M_2{}^0)]} \qquad (2)$$

This equation is suitable for any per cent conversion. However, working with the equation in this form would be exceedingly tedious. Montgomery and Fry[11] recently published a computer program to utilize this equation efficiently and furnished a copy to us. This program was converted to Fortran IV for use on the IBM 360 Model 50 computer. For each monomer pair that was studied, a series of copolymerizations at two different initial monomer concentration ratios ($[M_1{}^0]/[M_2{}^0]$) were carried out to various degrees of conversion. For each initial $[M_1{}^0]/[M_1{}^0]$ ratio, a plot of the copolymer composition (in weight per cent of M$_1$) *vs.* per cent conversion was made. Thus, two such curves for each copolymerization were obtained. By selecting any two points (one from each plot) and feeding these data to the computer program, unique r_1 and r_2 values are obtained. A single 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. Instead of using only one set of two points, a series of 12–16 sets of such data points (one from each of the two $M_1{}^0/M_2{}^0$ ratio runs) was used in each determination of r_1 and r_2. This gives a range of r_1 and r_2 values which are then systematically fed into a second computer program which reconstructs a composition–conversion curve for any given r_1, r_2 pair. The regenerated curve was then determined which best fits the experimental points. The values of r_1 and r_2 which resulted in the curve having this best fit were then assigned as the relative reactivity ratios for the copolymerization.

The reason for using points from composition *vs.* conversion curves of different $M_1{}^0/M_2{}^0$ ratios deserves brief comment. 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% for suitably accurate values of r_1 and r_2. Since our experimental data are not nearly that good, we choose to use one point from each of two such curves. This permits a much lower experimental accuracy necessary to obtain acceptable r_1, r_2 values.

Table I gives a series of r_1, r_2 values obtained from various combinations of experimental points in the FEA–styrene copolymerizations.

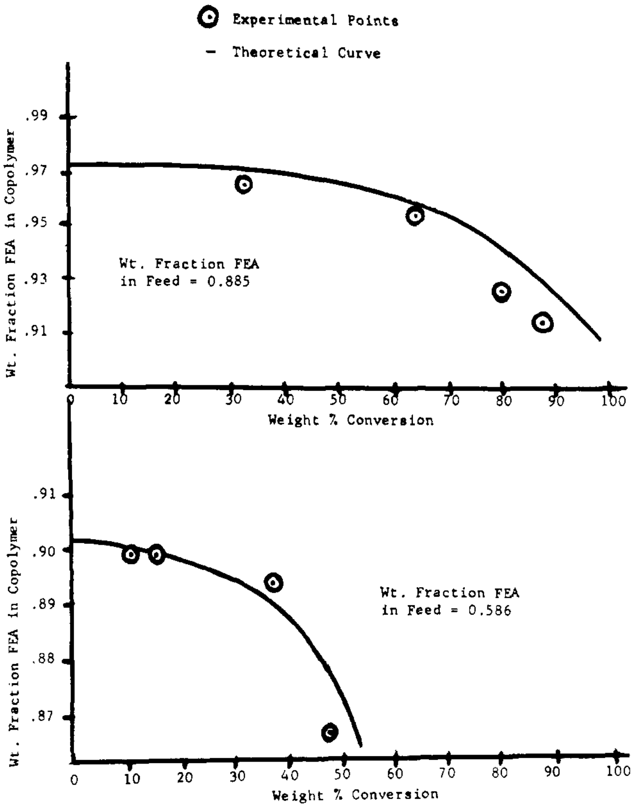

Figure 1. Composition–conversion curve for FEA–vinyl acetate copolymerization.

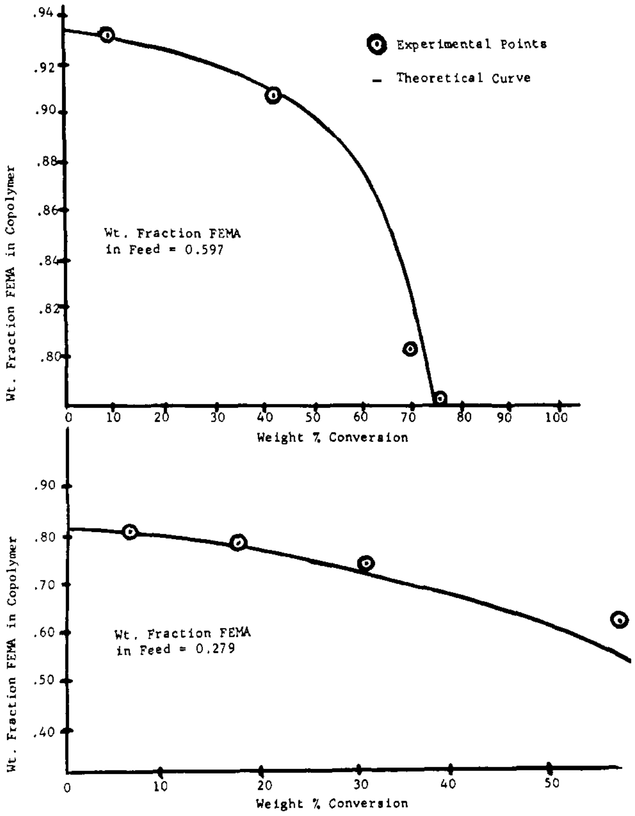

Figure 2. Composition–conversion curve for FEMA–vinyl acetate copolymerization.

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[10] F. R. Mayo and F. M. Lewis, *J. Amer. Chem. Soc.*, **66**, 1594 (1944).

[11] D. R. Montgomery and C. E. Fry, *J. Polym. Sci., Part C*, No. 25, 59 (1968).

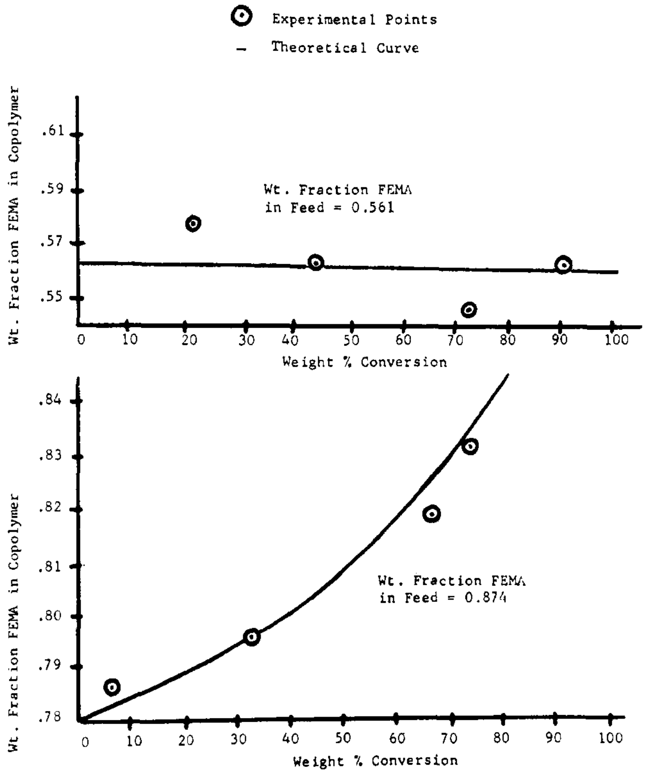

Figure 3. Composition–conversion curve for FEMA–methyl methacrylate copolymerization.

Results

The solution copolymerizations of FEA and FEMA with vinyl monomers proceeded smoothly at temperatures between 60 and 70°. The copolymers were demonstrated to be homogeneous by gel permeation chromatography. Only single-peak chromatograms were obtained. Thus, true copolymerization occurred. These copolymerizations are represented in Scheme I. Summaries of all copolymeriza-

SCHEME I

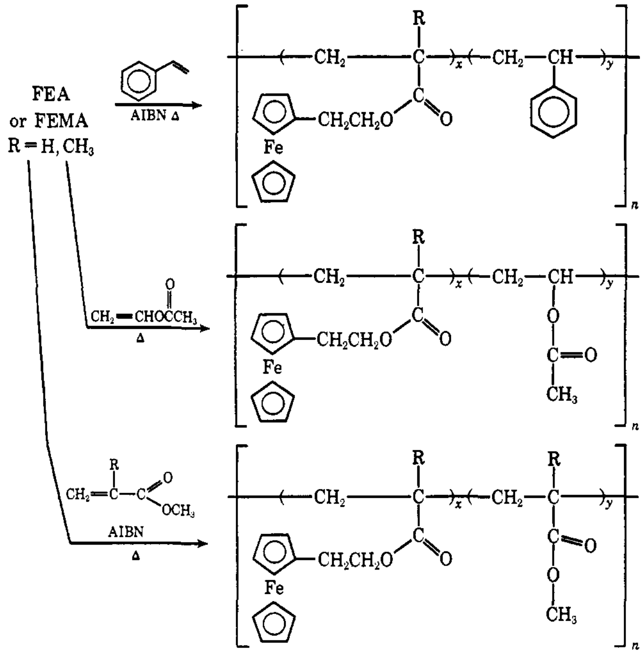

TABLE I
DETERMINATION OF RELATIVE REACTIVITY RATIOS FOR FEA–STYRENE COPOLYMERIZATION

Combination no.	r_1	r_2
1-7	0.412	1.124
1-5	0.334	1.079
1-4	0.378	1.104
1-3	0.272	1.042
8-7	0.404	1.082
8-5	0.326	1.034
8-4	0.367	1.059
8-3	0.374	1.063
6-7	0.547	1.030
6-5	0.534	1.022
6-4	0.540	1.026

TABLE II
COPOLYMERIZATION OF FEA WITH STYRENE AT 70°

Run no.	FEA in feed, g	Styrene in feed, g	AIBN in feed, g	Benzene in feed, ml	Reaction time, hr	Yield, g	% Fe in copolym	Conversion, %	Wt fraction in copolymer FEA/styrene
1	2.5000	2.1393	0.0096	10	7.5	1.0185	9.37	21.9	0.477/0.523
2	2.5000	2.1393	0.0096	10	20.0	1.7166	8.35	37.0	0.425/0.575
3	4.0000	0.6303	0.0066	10	15.0	2.0423	15.49	74.1	0.518/0.482
4	4,0000	0.6303	0.0066	10	1.5	0.3797	15.36	49.4	0.493/0.507
5	5.0000	0.6303	0.0066	10	6.4	1.3923	15.46	44.2	0.778/0.212
6	2.5000	2.1393	0.0096	10	69.5	3.4411	10.18	8.2	0.781/0.219
7	4.0000	0.6303	0.0066	10	30.0	2.5418	16.04	30.1	0.786/0.214
8	2.5000	2.1393	0.0096	10	35.1	2.2952	9.69	55.0	0.816/0.184

TABLE III
COPOLYMERIZATION OF FEA WITH VINYL ACETATE AT 60°

Run no.	FEA in feed, g	Vinyl acetate in feed, g	AIBN in feed, g	Benzene in feed, ml	Reaction time, hr	Yield, g	% Fe	Conversion, %	Wt fraction in copolymer FEA/vinyl acetate
1	2.5000	1.7677	0.0096	10	8.3	2.0228	17.00	47.4	0.865/0.135
2	2.5000	1.7677	0.0096	10	4.0	1.6002	17.58	37.5	0.894/0.106
3	2.0000	0.2600	0.0033	8	11.5	0.7096	18.29	14.5	0.898/0.007
4	2.5000	1.7677	0.0096	10	1.75	0.6188	18.33	10.8	0.899/0.101
5	2.0000	0.2600	0.0033	8	48.0	1.9029	17.96	31.4	0.996/0.034
6	1.2500	0.8839	0.0048	5	1.2	0.2304	17.68	87.3	0.914/0.086
7	2.0000	0.2600	0.0033	8	30.0	1.4508	18.77	64.2	0.955/0.045
8	2.0000	0.2600	0.0033	8	41.5	1.7944	18.23	79.4	0.927/0.073

TABLE IV
COPOLYMERIZATION OF FEA WITH METHYL ACRYLATE AT 60°

Run no.	FEA in feed, g	Methyl acrylate in feed, g	AIBN in feed, g	Benzene in feed, ml	Reaction time, hr	Yield, g	% Fe	Conversion, %	Wt fraction in copolymer FEA/methyl acrylate
1	2.5000	1.7677	0.0096	10	4.0	1.2334	12.30	28.9	0.626/0.374
2	1.2500	0.8839	0.0048	10	18.0	1.7348	11.80	81.3	0.600/0.400
3	2.0000	0.2600	0.0033	10	24.0	1.2904	17.72	46.7	0.617/0.383
4	2.5000	1.7677	0.0096	10	8.0	1.9930	12.13	77.0	0.609/0.391
5	2.0000	0.2600	0.0033	10	30.1	1.6633	17.31	57.1	0.902/0.098
6	2.0000	0.2600	0.0033	10	9.5	0.4181	17.21	73.6	0.881/0.119
7	1.2500	0.8839	0.0048	10	16.2	1.6430	11.96	18.5	0.876/0.124
8	2.0000	0.2600	0.0096	9	22.0	1.9097	16.61	84.5	0.845/0.155

TABLE V
COPOLYMERIZATION OF FEMA WITH STYRENE AT 70°

Run no.	FEMA in feed, g	Styrene in feed, g	AIBN in feed, g	Benzene in feed, ml	Reaction time, hr	Yield, g	% Fe	Conversion, %	Wt fraction in copolymer FEMA/styrene
1	2.5000	2.0421	0.0092	25	8.25	0.2607	10.43	5.74	0.557/0.443
2	2.5000	2.0421	0.0092	10	10.0	1.5974	10.40	35.2	0.555/0.445
3	2.5000	2.0421	0.0092	10	27.0	2.6934	10.18	59.3	0.547/0.453
4	2.5000	2.0421	0.0092	10	52.0	3.1384	10.28	69.1	0.544/0.456
5	4.0000	0.5980	0.0062	13	7.5	1.5428	14.23	31.6	0.757/0.243
6	4.0000	0.5980	0.0062	13	11.25	1.8162	14.18	39.5	0.760/0.240
7	4.0000	0.5980	0.0062	13	16.0	2.2714	14.29	49.4	0.763/0.237
8	4.0000	0.5980	0.0062	13	22.0	2.6714	14.65	58.1	0.782/0.218

TABLE VI
COPOLYMERIZATION OF FEMA WITH VINYL ACETATE AT 60°

Run no.	FEMA in feed, g	Vinyl acetate in feed, g	AIBN in feed, g	Benzene in feed, ml	Reaction time, hr	Yield, g	% Fe	Conversion, %	Wt fraction in copolymer FEMA/vinyl acetate
1	2.5000	1.6851	0.0092	10	16.5	2.8969	15.05	6.2	0.808/0.192
2	1.5000	3.8745	0.0064	10	1.75	0.3348	12.95	58.6	0.630/0.370
3	1.5000	3.8745	0.0064	10	20.5	3.1499	13.88	17.1	0.780/0.220
4	1.5000	3.8745	0.0064	10	5.2	0.9210	14.61	30.2	0.733/0.267
5	2.5000	1.6851	0.0092	10	19.0	3.1584	14.62	69.2	0.803/0.197
6	1.2500	0.8426	0.0043	8	1.5	0.1722	17.47	75.5	0.781/0.219
7	1.2500	0.8426	0.0043	8	7.5	0.8721	17.02	8.2	0.933/0.067
8	1.5000	3.8745	0.0064	8	9.5	1.6209	13.72	41.7	0.909/0.091

TABLE VII
COPOLYMERIZATION OF FEMA WITH METHYL METHACRYLATE AT 60°

Run no.	FEMA in feed, g	Methyl methacrylate in feed, g	AIBN in feed, g	Benzene in feed, ml	Reaction time, hr	Yield, g	% Fe	Conversion, %	Wt fraction in copolymer FEMA/methyl methacrylate
1	2.5000	1.9591	0.0092	10	3.5	0.9150	10.84	20.5	0.579/0.421
2	2.5000	1.9591	0.0092	10	10.0	3.2181	10.21	72.2	0.545/0.455
3	2.5000	1.9591	0.0092	10	11.1	4.0199	10.52	90.2	0.562/0.438
4	2.5000	1.9591	0.0092	10	7.75	2.1190	10.54	47.5	0.563/0.437
5	4.0000	0.5754	0.0062	10	5.25	3.3464	15.59	73.1	0.832/0.168
6	4.0000	0.5754	0.0062	10	7.5	3.0242	15.32	66.1	0.818/0.182
7	2.0000	0.2877	0.0031	10	3.75	0.3456	14.76	15.1	0.788/0.212
8	2.0000	0.2877	0.0031	10	5.25	0.7506	14.91	32.8	0.796/0.204

TABLE VIII
SUMMARY OF REACTIVITY RATIOS FOR FEA AND FEMA, AND COMPARISON WITH THOSE OF FMA AND FMMA[a]

M_1	M_2	r_1	r_2	M_1	M_2	r_1	r_2
FEA	Styrene	0.408 ± 0.138	1.060 ± 0.051	FMA	Styrene	0.02 ± 0.01	2.3 ± 0.3
FEA	Methyl acrylate	0.760 ± 0.027	0.687 ± 0.043	FMA	Methyl acrylate	0.14 ± 0.02	4.46 ± 0.2
FEA	Vinyl acetate	3.430 ± 0.313	0.074 ± 0.094	FMA	Vinyl acetate	1.44 ± 0.38	0.460 ± 0.08
FEMA	Styrene	0.084 ± 0.018	0.582 ± 0.010	FMMA	Styrene	0.03 ± 0.02	3.7 ± 0.2
FEMA	Methyl methacrylate	0.203 ± 0.035	0.646 ± 0.014	FMMA	Methyl methacrylate	0.124 ± 0.020	3.27 ± 0.06
FEMA	Vinyl acetate	8.791 ± 0.231	0.058 ± 0.003	FMMA	Vinyl acetate	1.52 ± 0.50	0.20 ± 0.10

[a] The r_1, r_2 values for FMA and FMMA were taken from ref 8c.

Table IX

Reactivity Ratios of Methyl Acrylate–Styrene, Methyl Acrylate–Vinyl Acetate, Methyl Methacrylate–Styrene, and Methyl Methacrylate–Vinyl Acetate

M_1	M_2	r_1	r_2
Methyl acrylate	Styrene[a]	0.18 ± 0.02	0.75 ± 0.07
Methyl acrylate	Vinyl acetate[b]	9.00 ± 2.50	0.10 ± 0.10
Methyl methacrylate	Styrene[a]	0.460 ± 0.026	0.520 ± 0.026
Methyl methacrylate	Vinyl acetate[c]	20.0 ± 3.0	0.015

[a] F. M. Lewis, C. Walling, W. Cummings, E. R. Briggs, and F. R. Mayo, *J. Amer. Chem. Soc.*, **70**, 1519 (1948). [b] F. R. Mayo, F. K. Lewis, and C. Walling, *ibid.*, **70**, 1529 (1948). [c] F. R. Mayo, C. Walling, F. M. Lewis, and W. F. Hulse, *ibid.*, **70**, 1523 (1948).

tions and the resulting copolymer compositions are given in Tables II–VII. The relative reactivity ratios are summarized in Table VIII and compared with those of FMA and FMMA. Table IX lists relative reactivity ratios for methyl acrylate and methyl methacrylate for comparison with the reactivity ratios of FEA and FEMA.

A close examination of the relative reactivity ratios summarized in Table VIII clearly demonstrates FEA and FEMA are more reactive monomers than FMA and FMMA. When copolymerized with a common comonomer, FEA always has the larger value of r_1 and a smaller value of r_2. Thus, FEA· (FEMA·) adds more readily to FEA (FEMA), in comparison to its addition to M_2, than does FMA or FMMA. Also $M_2\cdot$ adds more readily to FEA (FEMA) relative to M_2 than it does to FMA or FMMA. By including the extra methylene group between the ferrocene and acrylate functions the copolymerizability has been increased. In fact, FEA appears somewhat more reactive than methyl acrylate, while methyl methacrylate seems somewhat more reactive than FEMA (see Table IX). Clearly, FEA and FEMA are suitable acrylate monomers for a wide range of copolymerizations.

Figures 1–3 show the experimental composition–conversion data obtained in FEA–vinyl acetate, FEMA–vinyl acetate, and FEMA–methyl methacrylate copolymerizations. In addition, the theoretical composition–conversion curve for the values of r_1 and r_2 listed in Table VIII is included in these figures to illustrate the fit given by the "best" r_1, r_2 values with the experimental results. It is significant that the r_1, r_2 values chosen gave good fits of the composition–conversion data at both M_1^0/M_2^0 ratios used.

An evaluation of the properties of copolymers of FEA, FEMA, FMA, and FMMA, as well as extended studies of the scope of their copolymerization behavior are in progress and will be reported later.

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Organometallic Polymers. XIII. Addition Polymerization and Copolymerization of π-(Benzyl acrylate)chromium Tricarbonyl

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ABSTRACT: A novel metal carbonyl containing monomer, π-(benzyl acrylate)chromium tricarbonyl (BAC), has been synthesized and both homopolymerized and copolymerized using azobisisobutyrontrile (AIBN) initiation in solution. The reaction of chromium hexacarbonyl with benzyl alcohol gave π-(benzyl alcohol)chromium tricarbonyl which was esterified using acrylyl chloride in ether–pyridine. BAC is the first well-defined monomer of the chromium carbonyls which has been polymerized. Soluble homopolymers having $\bar{M}_n$ as high as 60,000 were prepared and the values of K and a in the Mark–Houwink equation, $[\eta] = KM^a$, were $K = 3.95 \times 10^{-3}$, $a = 0.82$ when $M = \bar{M}_n$. The relative reactivity ratios of BAC (M_1) copolymerizations with styrene ($r_1 = 0.10$, $r_2 = 0.34$) and methyl acrylate ($r_1 = 0.56$, $r_2 = 0.63$) were obtained, and the copolymers were demonstrated to be homogeneous by gel permeation chromatography. From gel permeation chromatography studies a Q factor of 94 was assigned to BAC. Kinetic studies of BAC homopolymerization by dilatometry were not successful because bubble formation in the dilatometer occurred at low polymer conversions. BAC was copolymerized with 2-ferrocenylethyl acrylate to give a polyacrylate containing both chromium and iron.

The addition polymerization and copolymerization of transition metal containing monomers has not yet been extensively studied. Several recent reviews of organometallic polymer chemistry attest to this.[4] Furthermore,

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