

Free-Radical Homopolymerization and Copolymerization of Vinylferrocene

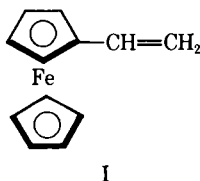
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Synopsis

The benzene solution homopolymerization of vinylferrocene, initiated by azobisisobutyronitrile, gave a series of benzene-soluble homopolymers. Thus, free-radical copolymerization studies were performed with styrene, methyl acrylate, methyl methacrylate, acrylonitrile, vinyl acetate, and isoprene in benzene. With the exception of vinyl acetate and isoprene, which did not give copolymers with vinylferrocene under these conditions, smooth production of copolymers occurred. The relative reactivity ratios, r_1 and r_2 , were obtained for vinylferrocene-styrene copolymerizations by using the curve-fitting method for the differential form of the copolymer equation, by the Fineman-Ross technique, and by computer fitting of the integrated form of the copolymer equations applied to higher conversion copolymerizations. In styrene (M_2) copolymerizations, the curve-fitting and Fineman-Ross methods both gave $r_1 = 0.08$, $r_2 = 2.50$, while the integration method gave $r_1 = 0.097$, $r_2 = 2.91$. Application of the integration method to methyl acrylate and methyl methacrylate (M_2) gave values of $r_1 = 0.82$, $r_2 = 0.63$; $r_1 = 0.52$, $r_2 = 1.22$, respectively. The curve-fitting method gave $r_1 = 0.15$, $r_2 = 0.16$ for acrylonitrile (M_2) copolymerizations. From styrene copolymerizations, vinylferrocene exhibited values of $Q = 0.145$ and $e = 0.47$.

INTRODUCTION

A number of polymers, which contain the ferrocene group, have been prepared in recent years, and have now been reviewed.¹⁻⁴ While many condensation polymers and unusual structures have been studied, the number of studies of free-radical addition polymers containing ferrocene have been few in number. Vinylferrocene(I) has been homopolymerized by cationic and free-radical routes. Arimoto and Haven^{5,6} homopoly-



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merized vinylferrocene using azobisisobutyronitrile (AIBN) initiation, but they did not extensively characterize the polymers. Cassidy et al.⁷ bulk polymerized vinylferrocene, using AIBN initiation, and obtained polyvinylferrocene with a \bar{M}_n of 48,600. Low molecular weight ($4000 > \bar{M}_n$) polyvinylferrocene was produced by cationic polymerization with $\text{BF}_3 \cdot \text{OEt}_2$, TiCl_4 , AlCl_3 , SnCl_4 , and Et_2AlCl .⁸ In that study, the cationic copolymerization with styrene incorporated styrene into the copolymer only when the styrene content in the monomer feed exceeded 90%. With $\text{BF}_3 \cdot \text{OEt}_2$ -catalyzed initiation in toluene, vinyl isobutyl ether (M_2) copolymerized with vinylferrocene (M_1) giving $r_1 = 0.01 \pm 0.1$ and $r_2 = 9.7 \pm 1.0$. Vinylferrocene has recently been copolymerized with butadiene in toluene solutions by one of us using cobaltic and manganic acetylacetonates as initiators.⁹ Radical-initiated copolymerizations with methyl acrylate, methyl methacrylate, acrylonitrile, vinyl acetate, or isoprene have not been reported.

The most extensive study of vinylferrocene homopolymerization and copolymerization previously published is the study by Baldwin and Johnson.¹⁰ The rate of AIBN-initiated solution polymerization of vinylferrocene ($k = R_p/[\text{M}][\text{I}]^{1/2} = 1.1\text{--}1.8 \times 10^{-4}$) was similar to that of styrene. This study also suggested that ferrocene was very similar to styrene in its effect on the rates of polymerization of methyl methacrylate (MMA) and ethylacrylate. While the data were not precise enough for the determination of relative reactivity ratios, rough estimates were made indicating that r_1 and r_2 ($M_1 = \text{MMA}$ and $M_2 = \text{VF}$) were both less than one and in the same range as that for MMA-styrene copolymerizations where $r_1 = 0.46$ and $r_2 = 0.52$.¹¹ Since polymers containing the ferrocene group might have interesting redox or electron-exchange properties,^{7,12,13} possibilities as charge-transfer complexed polymers,¹³⁻¹⁵ potential as semiconducting polymers,^{13,16} or ultraviolet- and γ -radiation-absorbing materials,¹⁷⁻¹⁹ we undertook this investigation of the copolymerizability of vinylferrocene with a series of commercially important organic monomers.*

EXPERIMENTAL

Materials

Vinylferrocene was prepared starting with commercial acetylferrocene (Arapahoe Chemical Company). This was reduced with NaBH_4 to hydroxyethylferrocene²¹ in ethanol solution. Hydroxyethylferrocene was dehydrated by using CuSO_4 catalysis in boiling toluene with hydroquinone inhibitor²² or by direct sublimation from an alumina-hydroxyethylferrocene powder mixture.²³ The vinylferrocene was sublimed before use, mp $46.5\text{--}47.5^\circ\text{C}$.⁵ Styrene was washed with 10% aqueous NaOH , with water, dried over anhydrous Na_2SO_4 and then distilled, with a center cut used for

* Initial reports of our work on the homopolymerization of vinylferrocene have appeared.²⁰

all polymerizations. Methyl acrylate, methyl methacrylate, acrylonitrile, vinylacetate, and isoprene were washed with 5% aqueous NaOH, water, dried over Na₂SO₄ and distilled under vacuum. Only center cuts were used. Benzene was distilled from P₂O₅ and AIBN was recrystallized from methanol (mp 102–103°C, decomposition).

Techniques

Monomers and AIBN were weighed, using an analytical balance, and dissolved into benzene. These solutions were placed in Fisher-Porter Aerosol compatibility tubes, equipped with a valve, and degassed at 10⁻³ mm by three alternate freeze-thaw cycles. After degassing, the tubes were placed in constant temperature baths controlled to $\pm 0.01^\circ\text{C}$. All copolymerizations were run at 70°C. After completion of the polymerizations, the benzene solutions were added dropwise to rapidly stirring petroleum ether or methanol to precipitate the polymer. The polymer was filtered and reprecipitated in this manner two more times to insure its purity. The polymers were then dried under vacuum and weighed. Infrared spectra were taken on a Perkin-Elmer Model 237 instrument, and the glass transition temperatures were approximated by using the differential scanning calorimetry technique on a Perkin-Elmer DSC Model 1B calorimeter. Number-average molecular weights were determined by using a Mel-Labs vapor pressure osmometer (VPO), and molecular weight distributions were measured on a Waters Model 200 gel-permeation chromatograph. The molecular weight distributions were then calculated by using the VPO-determined values of \bar{M}_n at the number-average chain length \bar{A}_n on the gel-permeation chromatogram. A Q factor of 88 was used for vinylferrocene as in previous work.²⁰ Viscosities were measured in benzene by using Cannon-Fenske viscometers.

Determination of Relative Reactivity Ratios

The relative reactivity ratios were determined by using both the differential form of the copolymer composition equation,^{24a} eq. (1), and

$$\frac{d[M_1]}{d[M_2]} = \left(\frac{[M_1]}{[M_2]} \right) \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \quad (1)$$

the integrated form of this equation²⁵ [eq. (2)].

$r_2 =$

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

where

$$P = (1 - r_1)/(1 - r_2)$$

The differential form [eq. (1)] was applied to vinylferrocene-styrene (and acrylonitrile) copolymerizations by performing a series of polymerizations to low conversions, the $[M_1^0]/[M_2^0]$ ratio being varied for the monomer pair in each run. At low conversion $d[M_1]/d[M_2]$ becomes m_1/m_2 (the monomer mole ratio found in the copolymer). In each case vinylferrocene is defined as M_1 . A plot was made of m_1 versus $[M_1^0]$ (mole fraction of M_1 in the starting solution), 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. Alternatively, the Fineman-Ross²⁶ method was applied to this data. Substituting F for $[M_1]/[M_2]$ and f for m_1/m_2 in eq. (1) and rearranging results in eq. (3), which can be rearranged, in turn, to eq. (4).

$$F/f(f-1) = r_1 F^2/f - r_2 \quad (3)$$

$$(f-1)/F = -r_2 f/F^2 + r_1 \quad (4)$$

A plot of $(F/f)(f-1)$ as the ordinate and F^2/f as the abscissa gives a straight line whose slope is r_1 and whose intercept is $-r_2$ by eq. (3). In equation (4), a plot of $(f-1)/F$ versus f/F^2 gives a slope of $-r_2$ and an intercept of r_1 . The advantage of having both forms of the equation is that in some cases one gives a better straight line than the other.

The most convenient method for determining reactivity ratios was by use of the integrated equation, eq. (2). This permitted polymerizations to higher conversions which is important with an expensive monomer such as vinylferrocene. In this technique, a series of polymerizations, to different per cent conversions, were performed at two different initial monomer concentration ratios, $[M_1^0]/[M_2^0]$. For each initial ratio, a plot of the copolymer composition (in weight per cent of M_1) versus the weight per cent conversion was constructed. One point from each of the two curves was selected, and this set of points was fed into a computer program developed by Montgomery and Fry²⁷ and adapted by us to an IBM-360-Model 50 computer by using Fortran IV. Each such data point gives r_2 as a function of P . For any set of two points there is a unique value of P that gives identical values of r_2 . The program accepts initial monomer concentrations and both polymer composition and conversion data for two points and varies P so as to rapidly converge r_2 for this data. These r_2 and P values are then used to calculate r_1 . For each copolymer, we used 16 sets of data points (one taken from each of the two curves) for each determination of r_1 and r_2 . This gives a range of r_1 and r_2 values which are then used to reconstruct new polymer composition versus conversion curves by using a second computer program.²⁷ The best values of r_1 and r_2 are those which give calculated composition versus conversion curves which most closely fit the experimental curves.

Any two data points from a single experimental composition-conversion curve could be used to get r_1 and r_2 , but this requires input experimental data accurate to an order of $\pm 0.01\%$. Our experimental data are not nearly that good. By using two appropriately different initial monomer

compositions, one point from each of the resulting composition versus conversion curves can be used with a much lower experimental accuracy necessary to obtain acceptable r_1 , r_2 values. By using 16 such sets of points we are able to cover a range in which the true r_1 and r_2 values surely lie. The best r_1 and r_2 values for our data are then chosen by picking the specific r_1 and r_2 values in this range which regenerated composition-conversion curves most closely duplicating the experimental curves.

RESULTS

Homopolymerization

The results of homopolymerizations in benzene solution are summarized in Table I. While good yields of poly(vinylferrocene) could be obtained,

TABLE I
Homopolymerization of Vinylferrocene in Benzene Solution

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

* 80% benzene-soluble and 20% benzene-insoluble.

the molecular weights were not very high. Since the range of molecular weight in these samples was not large, no meaningful correlation of $[\eta]$ with \bar{M}_n or \bar{M}_w could be obtained.

By using differential scanning calorimetry, the glass transition temperature T_g for all the polyvinylferrocene samples were found at approximately 190°C. Since the chromatograms exhibited broad curves, this value is approximate. However, compared with polystyrene's T_g of 88°C, it is clear the ferrocene nucleus sharply increases the cohesive energy in these polymers relative to a benzene ring. Polyvinylferrocene gave ultraviolet bands at 440, 323 (sh), 260, and 232 $m\mu$ with extinction coefficients of 109, 4960, 6600, and 6460, respectively.

Copolymerization

The low conversion copolymerizations of vinylferrocene with styrene and acrylonitrile are summarized in Table II and III; these data were treated by curve fitting (see Fig. 1) and by the Fineman-Ross method (see Fig. 2). Copolymerizations of vinylferrocene with styrene, methyl

TABLE II
Copolymerization of Vinylferrocene and Styrene at 70°C to Low Conversion

Vinylferrocene in Feed, mole-%	Reaction time, hr	Conversion, %	Fe in copolymer, %	Vinylferrocene in copolymer, mole-%
10.03	1.0	2.63	2.17	4.22
25.40	3.5	9.27	4.87	10.02
40.08	3.6	4.35	7.65	16.75
50.12	5.0	6.30	9.45	21.57
62.25	9.2	6.61	12.02	36.75
79.94	20.0	5.26	16.45	44.97
89.97	20.0	7.36	19.34	57.61

• The weight ratio of vinylferrocene to AIBN was always between 150 to 1000 in these studies.

acrylate, and methyl methacrylate to higher conversions are summarized in Table IV. Smooth copolymerizations took place, and the copolymers obtained gave homogeneous, single polymer gel-permeation chromatograms. The relative reactivity ratios in these copolymerizations are tabulated in Table V along with calculated Q and e values for vinylferrocene. Determinations of r_1 and r_2 by using integrated eq. (2) were performed by using 16 pairs of data points for each monomer pair. Example data for the styrene copolymerization is summarized in Table VI.

Several attempts to copolymerize vinylferrocene with vinyl acetate and isoprene were unsuccessful. Vinylferrocene, vinyl acetate, and AIBN in a mole ratio of 0.48/1/0.0124, respectively, were added to benzene (10.92 g

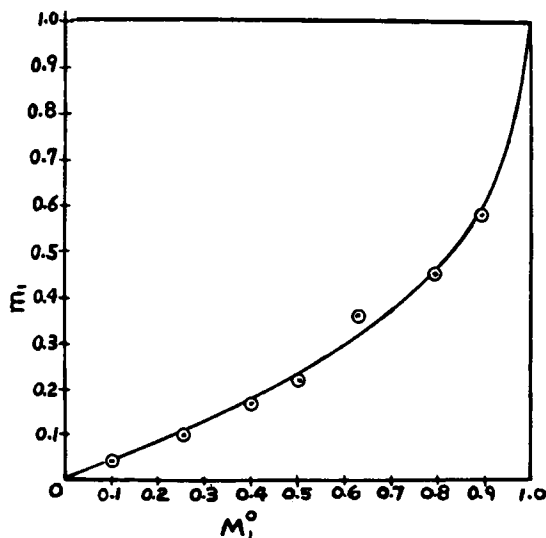


Fig. 1. Copolymerization of vinylferrocene (M_1) with styrene to low conversions: (\odot) experimental points; (—) theoretical curve generated for $r_1 = 0.08$, $r_2 = 2.50$.

TABLE III
Copolymerization of Vinylferrocene and Acrylonitrile at 70°C to Low Conversion^a

Vinylferrocene in feed, mole-%	Reaction time hr	Conversion, %	Fe in copolymer, %	Vinylferrocene in copolymer, mole-%
9.92	0.25	1.83	16.45	29.3
25.25	0.40	3.85	18.88	38.8
39.98	0.50	2.99	19.72	45.2
47.97	0.75	6.70	20.99	49.1
64.49	1.00	1.91	22.05	56.0
77.46	12.0	6.87	22.49	59.6
89.79	13.2	7.40	23.13	64.0

^a Each initiated by 0.1 mole-% AIBN.

TABLE IV
Copolymerizations of Vinylferrocene (M_1) at 70°C in Benzene Initiated by AIBN^a

No.	M_2	Weight fraction in feed, vinylferro- cene/ M_2	Reaction time, hr	Con- version, %	% Fe in Co- polymer	Weight Fraction M_1/M_2 in Copolymer
1	Styrene	0.404/0.596	3.5	9.23	4.87	0.185/0.815
2	"	"	9.0	18.71	5.06	0.192/0.808
3	"	"	15.0	22.49	5.10	0.194/0.806
4	"	"	23.0	24.91	5.12	0.195/0.805
5	"	0.780/0.220	15.0	2.61	12.82	0.487/0.513
6	"	"	24.0	8.76	12.97	0.492/0.508
7	"	"	36.0	10.66	13.02	0.495/0.505
8	"	"	38.8	21.93	13.18	0.500/0.500
1	Methyl acrylate	0.477/0.523	6.0	17.4	14.10	0.535/0.465
2	"	"	18.5	51.0	13.83	0.525/0.475
3	"	"	24.0	66.0	13.63	0.517/0.483
4	"	"	36.0	78.8	13.20	0.501/0.499
5	"	0.387/0.613	3.0	6.5	12.16	0.461/0.539
6	"	"	16.6	44.0	11.71	0.444/0.556
7	"	"	8.0	12.0	12.10	0.459/0.541
1	Methyl meth- acrylate	0.440/0.560	38.0	75.2	10.73	0.407/0.593
2	"	"	24.0	36.2	10.11	0.384/0.616
3	"	"	10.0	8.9	9.66	0.367/0.633
4	"	"	20.0	34.0	10.09	0.382/0.618
5	"	0.361/0.639	5.0	14.4	7.89	0.300/0.700
6	"	"	16.0	43.4	8.34	0.317/0.683
7 ^b	"	"	20.0	51.2	8.44	0.321/0.679

^a With 0.1 mole-% AIBN unless otherwise noted.

^b With 0.2 mole-% AIBN.

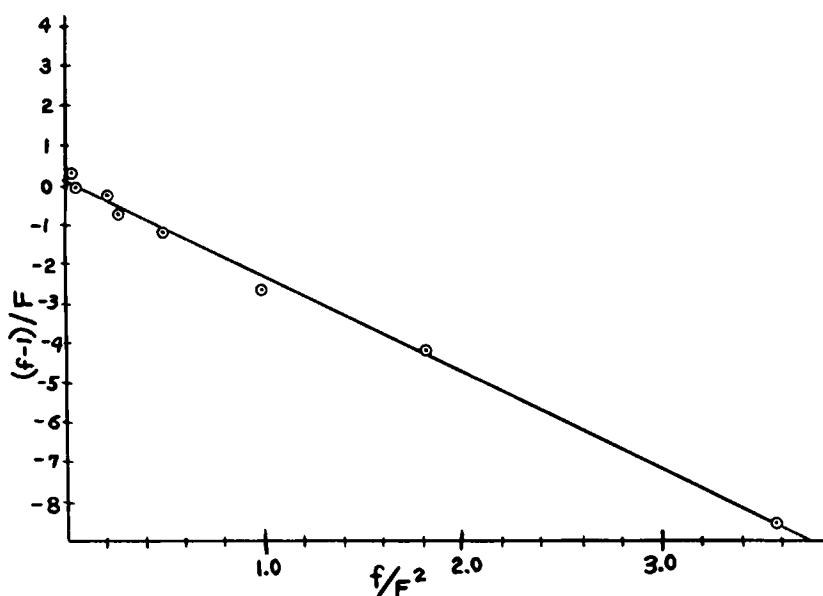


Fig. 2. Fineman-Ross plot for vinylferrocene-styrene copolymerizations.

vinylferrocene to 100 ml of solution) and polymerizations at 70°C were carried out for reaction times ranging from 47 to 144 hr. On work-up, unreacted vinylferrocene was recovered. Other unsuccessful attempts were made when the mole ratio was changed to 0.206/1/0.075. A series of unsuccessful attempts to copolymerize vinylferrocene with isoprene were

TABLE V
Relative Reactivity Ratios in Vinylferrocene Copolymerizations
at 70°C Initiated by AIBN in Benzene

M_2^a	r_1	r_2	$r_1 r_2$	Q	e
Styrene ^b	0.08 ± 0.04	2.50 ± 0.20	0.20	0.145^c	0.47^c
Styrene ^d	0.08 ± 0.02	2.50 ± 0.50	0.20		
Styrene ^e	0.097 ± 0.043	2.91 ± 0.07	0.28		
Methyl acrylate ^e	0.82 ± 0.05	0.63 ± 0.03	0.52	1.16^f	1.39^f
Methyl meth- acrylate ^e	0.52 ± 0.27	1.22 ± 0.37	0.64	0.79^g	1.07^g
Acrylonitrile ^e	0.15 ± 0.05	0.16 ± 0.05	0.024	0.05^h	0.73^h

^a Vinylferrocene is M_1 in all cases.

^b From curve-fitting technique by use of differential form of the copolymer equation.

^c Based on $Q_2 = 1.0$ and $e_2 = -0.8$ for styrene.²⁸

^d By use of the Fineman-Ross treatment.

^e Using the integrated form of the copolymer equation on copolymerizations to higher conversions.

^f Based on $Q_2 = 0.46$ and $e_2 = 0.58$ for methyl acrylate.²⁸

^g Based on $Q_2 = 0.74$ and $e_2 = 0.40$ for methyl methacrylate.^{24b,29}

^h Based on $Q_2 = 0.44$ and $e_2 = 1.2$ for acrylonitrile.^{24b}

TABLE VI
Individual Vinylferrocene-Styrene Relative Reactivity Ratios Generated from Various Combinations of Data Points from Copolymerizations at Two Different Monomer Feed Ratios by the Integrated Form of Copolymer Equation^a

Combination number ^a	r_1	r_2
1-5	0.1290	2.9171
1-6	0.1079	2.8940
1-7	0.1058	2.8917
1-8	0.0542	2.8354
2-5	0.1299	2.9233
2-6	0.1085	2.8985
2-7	0.1063	2.8960
2-8	0.0547	2.8356
3-5	0.1348	2.9567
3-6	0.1127	2.9302
3-7	0.1104	2.9274
3-8	0.0569	2.8632
4-5	0.1395	2.9888
4-6	0.1167	2.9607
4-7	0.1143	2.9577
4-8	0.0595	2.8902

^a Initial mole ratios of vinylferrocene to styrene were 0.725/1 for runs 1-4 and 0.139/1 for runs 5-8.

^b From Table III.

made at 70°C in mole ratios of 0.32/1, respectively (weight ratio 1/1 with 0.01 AIBN).

The values of Q and e for vinylferrocene (M_1) were determined from the experimental values of r_1 and r_2 , summarized in Table V, and from literature values of Q_2 and e_2 for the comonomer (see footnotes, Table V). The standard equations (5)-(7)^{24c} were used in these calculations.

$$r_1 = (Q_1/Q_2) \exp\{-e_1(e_1 - e_2)\} \quad (5)$$

$$r_2 = (Q_1/Q_2) \exp\{-e_2(e_2 - e_1)\} \quad (6)$$

$$r_1 r_2 = \exp\{-(e_1 - e_2)^2\} \quad (7)$$

A Q - e map was constructed to include all four copolymerizations.^{24d} Q_1 was plotted versus e_1 for both extremes of uncertainty of both r_1 and r_2 . The intersecting area is the region for the correct Q and e . This was done for all four copolymerizations in hopes of finding a region where Q and e would be a best fit for all copolymerizations. It was clear that no such region exists in these copolymerizations and the normal Q - e predictions do not appear to be possible with vinylferrocene.

This behavior is not unexpected for vinylferrocene. When compared to a phenyl ring, the ferrocene nucleus exhibits an extraordinary ability to stabilize adjacent positive charge.³⁰⁻³³ For example, σ^+ of p -ferrocene (determined from p -ferrocenylphenylethyl chloride solvolyses) is -0.71 and σ^+

of the α -ferrocenyl substituent is -1.4^{32} . Even in the meta position, ferrocene exhibits σ_1 of -0.88^{34} (-0.05).³⁵

Under the conditions of weaker electron demand exhibited when *p*-ferrocenylbenzoic acid dissociates, ferrocene shows a Hammett σ_p of 0.18 which is roughly equivalent to that of a methyl group.³⁴ On the other hand, available evidence indicates the ferrocenyl group destabilizes radical anions³⁶ and radical^{37,38} centers in comparison with the effect exerted by a phenyl ring. Thus, one could not expect vinylferrocene to fit neatly into the *Q-e* scheme.

Certain trends can be noted by observing the values of r_1 and r_2 reported in Table V. A growing polymer chain, ending in either styryl or a ferrocenyl radical, prefers to add to styrene as opposed to vinylferrocene. This is expected since the ferrocene nucleus does not stabilize radical centers as much as a phenyl ring. [The Q_1 value for vinylferrocene (M_1) of 0.145 in styrene copolymerizations emphasizes this low reactivity.] As the reactivity of M_2 decreases on going from styrene to methyl acrylate, r_1 increases. Now the terminal ferrocenyl radical on a propagating chain has a choice between two rather unreactive (compared to styrene) monomers: methyl acrylate or vinylferrocene. Thus, no great selectivity is exhibited, and r_1 becomes 0.82.

Methyl acrylate is an electron-withdrawing monomer compared to styrene. The transition state for a ferrocenyl radical adding to methyl acrylate could be stabilized by a polar resonance contribution which contributes more strongly than when a styryl radical adds to methyl acrylate. This follows from ferrocene's remarkable ability to supply electron density as the demand increases. However, this tendency is not so strong as to cause alternation or to cause r_1r_2 to approach zero. A ferrocenyl radical can add to methyl methacrylate, relative to vinylferrocene, more readily than it can add to methyl acrylate. This follows from the r_1 value of 0.52 (versus 0.82 for methyl acrylate). This is expected because methyl methacrylate can be attacked by many radicals more rapidly than methyl acrylate can; because the methyl group stabilizes the transition state of radical attack more than the starting materials. For instance, a styryl radical adds to methyl methacrylate and methyl acrylate at 60°C with propagation constants of 339 and 235, respectively.³⁹ The respective constants for the addition of the radical of vinyl acetate are 250,000 and 37,000.³⁹ Thus, methyl methacrylate should be attacked by ferrocenyl radicals more rapidly than methyl acrylate. The increase in r_2 going from methyl acrylate (0.63) to methyl methacrylate (1.22) in vinylferrocene copolymerizations also reflects methyl methacrylate's greater reactivity.

The vinylferrocene-acrylonitrile copolymerization shows a marked tendency to alternate. The small values of r_1 and r_2 (0.15 and 0.16, respectively) lead to an r_1r_2 product of 0.024 which is close to zero. This is evidence for a significant polar contribution to the transition state when a ferrocenyl radical adds to acrylonitrile or when the radical of acrylonitrile adds to vinylferrocene. This is in accord with the great ability of ferrocene to supply electron density towards electron deficient centers. The vinyl

group in acrylonitrile is more strongly positively polarized than is the vinyl group in methyl acrylate. With this increased positive character, the polar contribution to the transition state increases in importance until a strong tendency to alternate is reached with acrylonitrile as M_2 . Further studies with maleic anhydride as M_2 are now under way.⁴⁰

Vinylferrocene should now be considered a promising monomer for copolymerization with a wide variety of organic monomers. It should become a useful specialty additive to copolymer and terpolymer systems currently in use.

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