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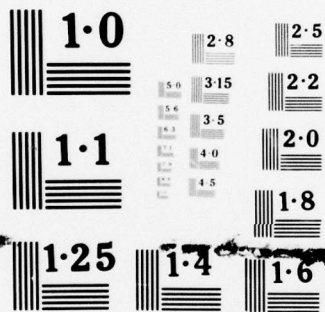
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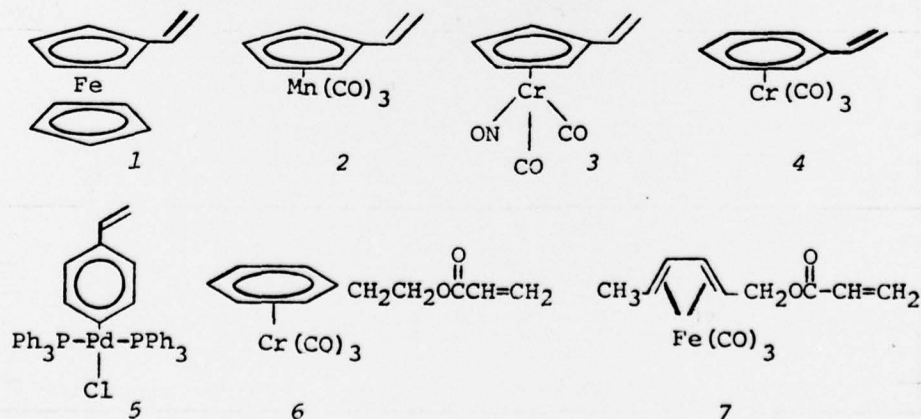
VINYL POLYMERIZATION OF ORGANOMETALLIC MONOMERS CONTAINING TRANSITION METALS

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ABSTRACT. This chapter provides a general review of the vinyl monomers, containing transition metals, which have been prepared and polymerized. The reactivity of such monomers in addition to homo- and copolymerizations is described. The *Q-e* scheme is used to semiempirically classify the vinyl reactivity of several organometallic monomers.

I. INTRODUCTION.

The effect that transition metal functions exert in vinyl polymerization of vinyl organometallic monomers has just recently undergone serious study. (1) Example transition metal-containing monomers are vinylferrocene 1, (2,3) vinylcyclopentadienyltricarbonylmanganese 2, (4) vinylcyclopentadienyldicarbonylnitrosylchromium 3, (5) styrenetricarbonylchromium 4, (6) *trans*-bis(tributylphosphine)(4-styryl)palladiumchloride 5, (7) η^6 -(2-phenylethyl acrylate)tricarbonylchromium 6, (8) and η^4 -(2,4-hexadiene-1-yl acrylate)tricarbonyliron 7. (9) The first vinyl polymerization of an organometallic derivative was the radical-initiated homopolymerization of vinylferrocene by



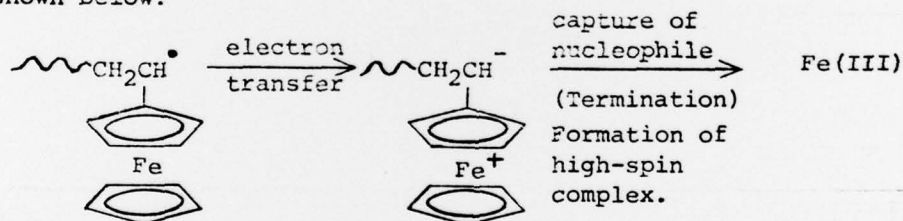
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Arimoto and Haven in 1955.(10) For the next decade this area was virtually neglected in comparison with the vast attention given to organometallic condensation polymers. In this chapter, a brief review of the status of vinylorganometallic polymerizations will be given.

II. HOMOPOLYMERIZATION.

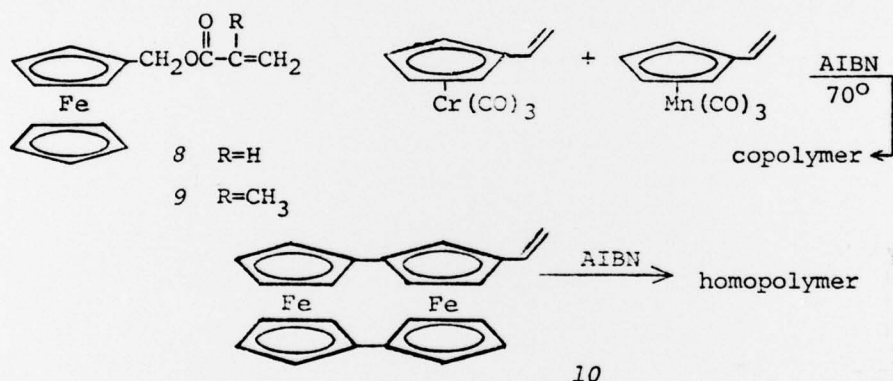
Vinylferrocene has been more thoroughly studied than any other organometallic monomer.(2,3,11) Homopolymerization has been carried out using radical,(2,3,11) cationic,(12) and Ziegler-Natta initiators.(13) Peroxides oxidize ferrocene. Using AIBN, solution polymerizations result in low molecular weights, but bulk polymerizations give higher molecular weights. Unlike most vinyl monomers, the molecular weight does not increase with a reduction in initiator concentration, but it does increase with an increase in monomer concentration.(2) This anomalous behavior was explained by showing that vinylferrocene has a high chain transfer constant ($C_m = 3 \times 10^{-3}$ versus 6×10^{-5} for styrene at 60°).(3) Furthermore, the kinetics of homopolymerization in benzene follow $r_p = k[VF][AIBN]$. This rate law requires an intramolecular termination process as shown below:



Apparently, intramolecular electron transfer from iron to the radical end occurs giving an Fe(III) end group. This behavior was subsequently supported by Mössbauer spectroscopy(11) which showed the presence of an absorption at 0.14 mm sec^{-1} that was not due to either ferrocene or ferrocenium groups. In dioxane, the usual half order dependence in monomer (bimolecular termination) was observed.(11)

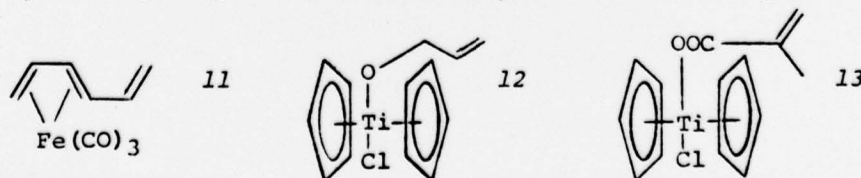
A high chain transfer constant to polymer in polyvinylferrocene polymerizations leads to chain branching. As the molecular weight increases, the resulting polyvinylferrocene becomes increasingly branched. Thus, vinylferrocene exhibits an unusual homopolymerization behavior which may be attributed to the influence of the organometallic function. This raises the question: How will other organometallic groups influence vinyl polymerizations?

Unusual kinetic behavior has been found in homopolymerization of 2.⁽¹⁴⁾ For example, in benzonitrile $r_p = k[(2)]^{3/2}[AIBN]^{1/2}$. The explanation for this result is not yet known and kinetic studies in other solvents are in progress. Acrylic monomers of ferrocene, where the ferrocenyl moiety is insulated from the reactive vinyl group, appear to follow the normal terminal model mechanism. For example, ferrocenylmethyl acrylate, 8, and ferrocenylmethyl methacrylate, 9, both exhibit a half order dependence on initiator⁽¹⁵⁾ (i.e., $r_p = K[\text{monomer}]^1[AIBN]^{1/2}$). On the other hand, styrenetricarbonylchromium, 4, will not homopolymerize at all although it readily copolymerizes.⁽⁶⁾ The reason for this is unclear. Steric arguments appear invalid because 4 readily copolymerizes with 2⁽⁶⁾, and the very bulky 3-vinylbisfulvalenediiron, 10, has been observed to homopolymerize.⁽¹⁶⁾ Monomers 5-7 each readily homopolymerize using



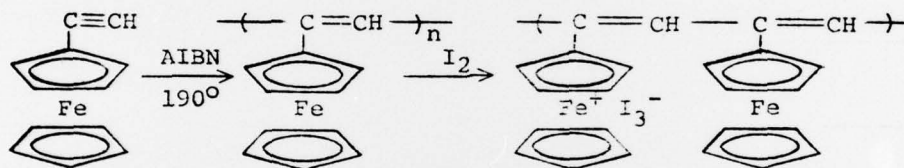
azo-initiators but no kinetic studies are currently available. Because transition metals can far more readily undergo ionization than carbon, the potential for electron transfer mechanisms to complicate polymerization mechanisms is high.

Monomer 11 has been prepared but it would not undergo radical initiated homopolymerization.⁽⁹⁾ Indeed, it would not copolymerize and it inhibited the polymerization of styrene and methyl acrylate. Presumably, the radical, resulting from chain attack at its vinyl group, is stable and does not permit chain propagation. Titanium allyl and methacrylate monomers 12 and 13 give only very low molecular weight materials using benzoyl



peroxide initiation. (17) On copolymerization with styrene only small amounts of 12 and 13 are incorporated in accord with a low reactivity and high chain transfer activity for these monomers. (18)

A surprising effort has been expended to polymerize ethynylferrocene 14. Free radical, cationic, Ziegler, and anionic initiation has been tried but in most studies the resulting polymers were poorly characterized. (19-25) Benzoyl peroxide initiation gives very short chains. (23) Using AIBN initiation at 190°, poly(ethynylferrocene) was obtained without evidence of aliphatic C-H absorptions in the ir. (24) The highly purified polymer is an insulator ($\sigma = 4 \times 10^{-14} \text{ ohm}^{-1} \text{ cm}^{-1}$) but mixed-valence polymers were prepared by partial oxidation with agents such as iodine and DDQ and these poly-salts were semiconducting. (26)



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III. COPOLYMERIZATIONS.

How do organotransition metal functions effect the reactivity of vinyl groups in cationic, radical, and anionic copolymerizations? The standard way to classify the vinyl copolymerization reactivity of organic monomers has been to obtain reactivity ratios and, using these, derive the values of Q and e of that monomer. Thus, the semiempirical Q - e scheme has been employed to classify several organometallic monomers according to the electron richness (Price's polarity term e) of the vinyl group in copolymerization reactions. Using styrene as the standard comonomer (M_2), relative reactivity ratios (r_1 and r_2) have been determined using the non-linear least squares fitting of the integral form of the copolymer equation advocated by Tidwell and Mortimer. (27) The values of Q and e for organometallic monomers were then computed from:

$$r_1 = (Q_1/Q_2) \exp(-e_1(e_1 - e_2))$$

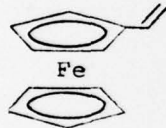
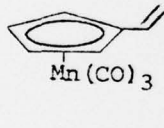
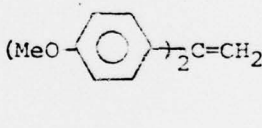
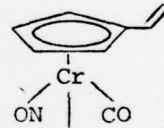
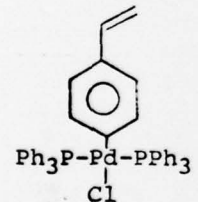
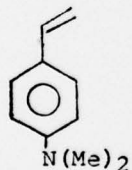
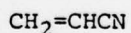
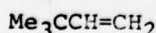
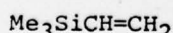
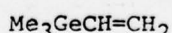
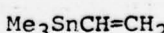
$$r_2 = (Q_2/Q_1) \exp(-e_2(e_2 - e_1))$$

$$r_1 r_2 = \exp(-(e_1 - e_2)^2)$$

Since a ferrocene moiety is an enormously stabilizing function toward adjacent positive charge, we thought the vinyl group should appear extraordinarily electron rich when under attack by radicals which are electron deficient. This turned out to be correct. An e_1 value of -2.1 was found for vinylferrocene in styrene copolymerizations. (28) How would this trend be effected if a tricarbonylmanganese group is complexed to the cyclopentadienyl ring? Will the carbonyl groups exert a strong electron withdrawing group which is felt at the vinyl group? The answer is no. (28)

The values of e_1 determined for organometallic monomers 1, 2, and 3 in styrene copolymerizations are all large negative values, emphasizing the fact that their vinyl groups are all exceeding electron rich. (28) The cyclopentadienyl ring seems to be a very strongly e^- -donating group in all cases. The para palladium function in 5 also appears to be an exceptionally

Values of e_1 for Organometallic and Standard Monomers

			
e -2.1	-1.99	-1.96	-1.9
			
e -1.62	-1.37	-0.80	+1.21
			
e -.63	-.14	+.43	+.96

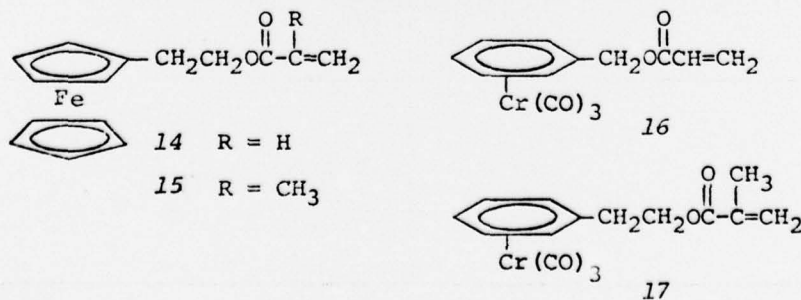
strong e^- -donator. (7) In fact, the value of e_1 for 5 is -1.62, which is significantly larger negatively than that for p-dimethylaminostyrene ($e = -1.37$). For the main group series of organometallic monomers, $R-CH=CH_2$ (where $R = Me_3C, Me_3Si, Me_3Ge, \text{ and } Me_3Sn$) the order of e values is puzzling. As one goes from carbon through tin the vinyl groups become less

electron rich.(29) It is strange that the larger and less electronegative tin atom does not appear, by the Q-e scheme, to readily release electron density in radical copolymerizations. In this series the Q values were low in every case indicating no great resonance stabilization was involved.

The systematic copolymerization and Q-e classification of vinylferrocene 1 and vinylcyclopentadienyltricarbonylmanganese 2 has now been carried out.(28) A range of comonomers was chosen to span a wide range of e_2 values from very electron rich to very electron deficient. Reactivity ratios were derived from a large number of copolymerizations (in most cases) and the values of e_1 for 1 and 2 were calculated. These values are listed in Table 1. A striking feature is that the Q-e scheme appears to break down when electron deficient comonomers are employed (i.e., acrylonitrile etc.). The break occurs after vinyl acetate. This phenomenon, similar to a sudden change of slope in a Hammett σ - ρ plot, signifies a change in mechanism.(30) Since the Q-e scheme is defined in terms of the terminal model, it is no longer appropriate to apply the scheme if this model mechanism is not operating.

A logical interpretation for the failure of the Q-e scheme to hold, when using electron deficient comonomers, invokes competition from a charge-transfer-complex model. Since monomers 1 and 2 are extremely electron rich, the formation of charge-transfer complexes with acrylonitrile, diethylfumarate, fumaronitrile or maleic anhydride is suggested. In some cases spectral evidence confirms the existence of complexes. If the charge-transfer complexes enter the propagation sequence, then the Q-e scheme would no longer have any meaning because the Q-e scheme derivation assumes the terminal copolymerization model is operating.

Acrylic monomers of ferrocene, dienetricarbonyliron, and (η^6 -phenyl)tricarbonylchromium have been synthesized and copolymerized with common organic monomers (styrene, methyl acrylate, methyl methacrylate, acrylonitrile, and vinyl acetate). These acrylic organometallic monomers include (6-9) and (14-17).



The large number of copolymerizations performed permitted the determination of the reactivity ratios for a large number of cases. These are summarized in Table 2 with references.

TABLE 1

Classification of Vinylferrocene, 1, and Vinylcyclopentadienyltricarboxylmanganese, 2, According to the Q-e Scheme

Comonomer M ₂	e ₂	Values of e ₁ from Copolymerizations	
		Vinylferrocene	Vinylcyclopentadienyltricarboxylmanganese
Vinylferrocene	-2.1	-	-2.6
Vinylcyclopentadienyltricarboxylmanganese	-1.99	-2.6	-
N-Vinylcarbazole	-1.40	-2.4	-
p-N,N-Dimethylaminostyrene	-1.37	-2.2	-1.9
1,3-Butadiene	-1.05	-1.80 ^a	-
	-1.40	-2.1	
N-Vinyl-2-Pyrrolidone	-0.90	-2.1	-2.9
Styrene	-0.80	-2.1	-1.99
Vinyl Acetate	-0.22		-1.62
Methyl Methacrylate	+0.40	-0.20 ^b	
Methyl Acrylate	+0.58	-0.32 ^b	-0.95
Acrylonitrile	+1.20	-0.81 ^{b,c}	-0.95
Dimethylfumarate	+1.25	alternating	
Fumaronitrile	+1.96	alternating	alternating
Maleic Anhydride	+2.25	-0.1 ^d	

^aA value of -1.05 was reported in reference (33), but the value of -1.80 is calculated from the same experimental points using the nonlinear least squares method and the integrated form of the copolymer equation.

^bSlightly different e₁ values are listed in the references. Values in this table were computed from data in those references as per footnote a.

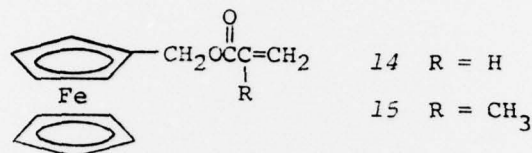
^cr₁·r₂ = 0.024, high alternation tendency.

^dr₁·r₂ = 0.003, close to alternating.

IV. CATIONIC AND ANIONIC INITIATION.

Using high vacuum-break seal techniques, we have been unable to obtain polymers 1, 2, or 3 anionically. Initiator

systems included K₂Naph, NaNaph, BuLi, LiAlH₄, PhMgBr, and EtMgBr. Since vinyl monomers are so electron rich (i.e., Q-e scheme), this behavior is not surprising. The successful anionic homo- and copolymerization of ferrocenylmethyl acrylate 14 and methacrylate 15 has been accomplished.⁽³⁹⁾ Using LiAlH₄ initiation, high molecular weights (to 7.5 x 10⁵) were achieved at narrow distributions ($\bar{M}_N/\bar{M}_W = 2.7$). Furthermore, the molec-



ular weight could be controlled by varying the monomer: initiator ratio.⁽³⁹⁾ This suggested the presence of "living polymers." Indeed, they were demonstrated by sequential monomer addition experiments and by block copolymer synthesis. Block copolymers of 14 with acrylonitrile styrene, and methyl acrylate were prepared with controlled block lengths.

TABLE 2

Summary of Reactivity Ratios of Acrylic Organometallic Monomers with Common Organic Monomers

Organometallic Monomer (M ₁)	M ₂				
	Styrene	Methyl acrylate	Methyl methacrylate	Acrylo-nitrile	Vinyl acetate
6	Solvent	EA(31)	EA(31)	EA(31)	
	°C	70°	70°	70°	
	r ₁	0.10	0.3	0.6	
	r ₂	0.50	1.0	0.2	
7	Solvent	Bz(32)	Bz(32)	Bz(32)	Bz(32)
	°C	80°	80°	80°	80°
	r ₁	0.26	0.30	0.34	2.0
	r ₂	1.81	0.74	0.74	0.05
8	Solvent	Bz(34)	Bz(34)	Bz(34)	Bz(34)
	°C	70°	70°	70°	70°
	r ₁	0.02	0.14	0.08	1.44
	r ₂	2.3	4.46	2.9	0.46
9	Solvent	Bz(34)	Bz(34)	Bz(34)	Bz(35)
	°C	70°	70°	70°	80°
	r ₁	0.03	0.08	0.12	0.30
	r ₂	3.7	0.82	3.37	0.11

-continued-

TABLE 2 (continued)

Organometallic Monomer (M_1)	M_2			
	Styrene	Methyl acrylate	Methyl methacrylate	Acrylo- lonitrile Vinyl acetate
14	Solvent	Bz(36)	Bz(36)	Bz(36)
	$^{\circ}\text{C}$	70 $^{\circ}$	60 $^{\circ}$	60 $^{\circ}$
	r_1	0.41	0.76	3.4
	r_2	1.06	0.69	0.07
15	Solvent	Bz(36)	Bz(36)	Bz(36)
	$^{\circ}\text{C}$	70 $^{\circ}$	60 $^{\circ}$	60 $^{\circ}$
	r_1	0.08	0.20	8.8
	r_2	0.58	0.55	0.06
16	Solvent	EA(37)	EA(37)	
	$^{\circ}\text{C}$	60 $^{\circ}$	70 $^{\circ}$	
	r_1	0.10	0.56	
	r_2	0.34	0.62	
17	Solvent	EA(38)	EA(36)	EA(38)
	$^{\circ}\text{C}$	70 $^{\circ}$	70 $^{\circ}$	70 $^{\circ}$
	r_1	0.04	0.90	0.07
	r_2	1.35	1.19	0.79

IV. ACKNOWLEDGEMENT.

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