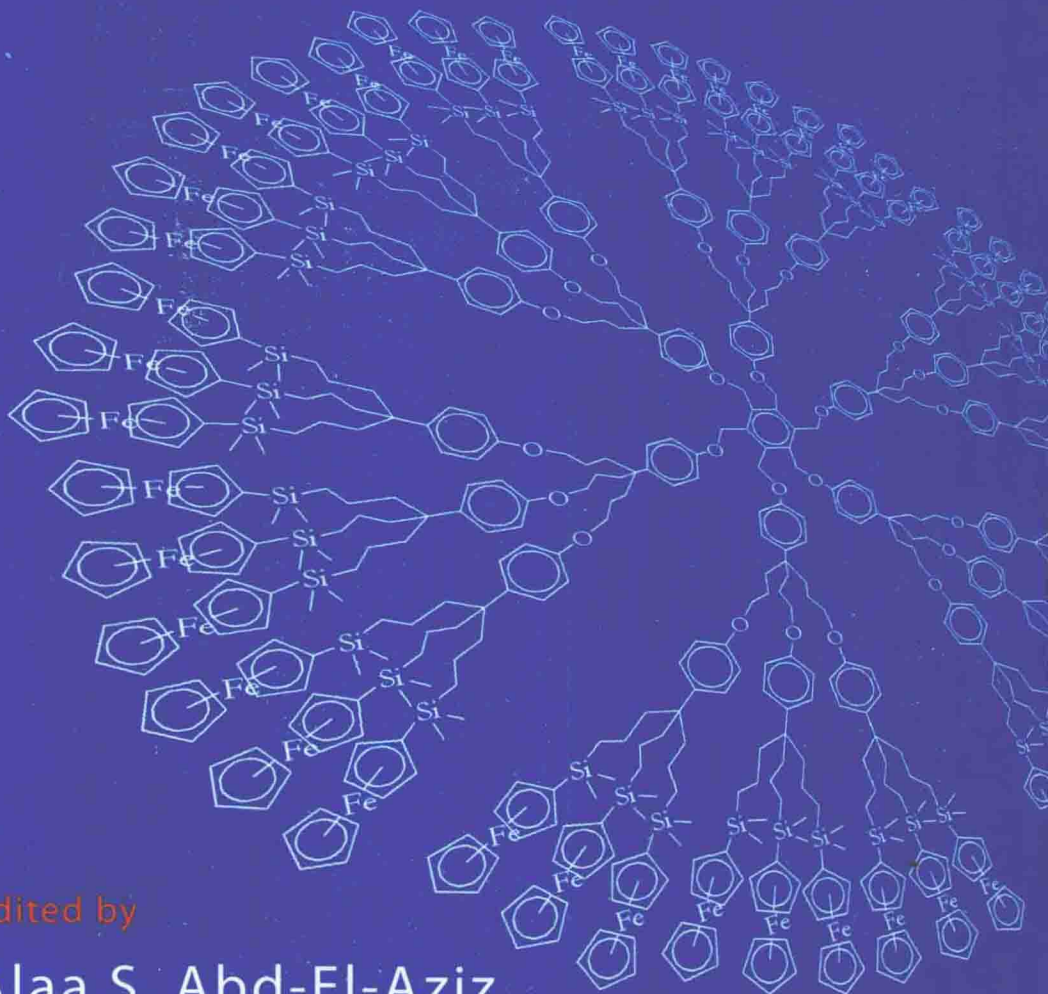# Frontiers in Transition Metal-Containing
POLYMERS

Edited by

Alaa S. Abd-El-Aziz
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FRONTIERS IN TRANSITION METAL-CONTAINING POLYMERS

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◼◼◼◼◼ PREFACE

Many of the interesting properties and functions of solid-state and biological materials can be attributed to the presence of metallic elements. Examples include magnetic materials used in data storage, superconductors, electrochromic materials, and catalysts including metalloenzymes. Following the rapid emergence of synthetic organic polymers in the first part of the twentieth century, the exciting possibilities for the development of new, easily processed materials via the incorporation of metal atoms into synthetic polymer chains intrigued scientists. Although the first metal-containing polymer, poly(vinylferrocene), was reported as early as 1955, the synthetic difficulties associated with the creation of macromolecular chains possessing metal atoms as key structural components were significant deterrents to rapid progress in the field until the last decade. Characterization during the early stages was also a key problem, and this led to the assignment of many structures without the type of convincing evidence by techniques such as NMR that would be deemed absolutely necessary today.

Many factors have contributed to the rapid and substantial recent emergence of the metallopolymer area as one of the most exciting in the whole advanced materials field. First, since the 1990's, many of the obstacles to the preparation of high molecular weight and soluble materials have been overcome through creative new synthetic approaches. Second, the recent ready access to soluble and stable well-characterized high molecular weight metallopolymers in usable quantities has allowed detailed studies of their properties and applications by polymer materials scientists and their wide variety of state-of-the-art characterization tools. This has been critical to the emergence of metallopolymers as *functional* materials. And third, the recent discovery of controlled or "living" polymerization routes to metallopolymers, which allow molecular weights to be controlled, narrow molecular weight distributions to be obtained, and block copolymers to be prepared, have provided a substantial impetus to the area. Block copolymers, for example, self-assemble in thin films or block selective solvents to form nanostructured materials with phase-separated nanodomains and micellar aggregates, respectively. Self-assembly of metal-containing block copolymers thereby provides access to metal-rich nano-structures with a variety of potential applications in nanoscience, such as in nanoparticle catalysis and nanopatterning.

The book aims to survey recent research at the frontiers of the subject and to achieve this we have been fortunate to be able to assemble an exceptional group of contributors.

Chapter 1, written by Pittmann and Carraher, two of the early pioneers of the metallopolymer field, surveys the developments in the area in the 1960s and 1970s when metallopolymers were almost unknown. Chapter 2, by Abd-El-Aziz and Shipman, surveys the recent progress in the synthetic metallopolymer field. Chapter 3, by Rider and Manners, covers the recently emerging field of block copolymers with transition metal atoms in the main chain of at least one of the blocks. Synthetic routes to metal-containing block copolymers and applications in the field of

nanoscience are described. In Chapter 4, MacLachlan covers the exciting area of π-conjugated metallopolymers and demonstrates useful properties of π-conjugated organic macromolecules that can be supplemented further by the presence of metal centers. In Chapter 5, Chan and Cheng cover the important field of metal coordination polymers and their applications in nanofabrication and include within the survey block copolymers with metals coordinated to side group substituents. The important field of rigid rod polymers containing metal atoms in the main chain—polymetallynes—is reviewed by Wong and Ho in Chapter 6. These materials have attracted much recent attention with substantial synthetic expansion and their investigation as, for example, liquid crystals, photoconductors, and photoluminescent materials (triplet emitters). Chapter 7, by Tyler, covers the intriguing field of polymers containing metal–metal bonds, which are of interest as photodegradable materials and have many other potential uses. Chapter 8, by Harvey, covers the expanding field of metallopolymers with diphosphine and diisocyanide linkers, which are of interest as a result of their photoluminescent properties and have potential in many other areas, such as liquid crystals and ceramic precursors. The redox properties of metallopolymers are covered by Nishihara in Chapter 9, which describes materials which exhibit conductivity and photoconductivity, ferromagnetic spin coupling, and electro-, photo-, and thermochromism as a consequence of the mixed valence states and unpaired electrons on the metal centers. An overview of the field of metallodendrimers and their broad applications as catalysts, luminescent materials, and sensors is provided by Hwang and Newkome in Chapter 10. Redox-active metallodendritic iron complexes and their use in design, catalysis, and molecular recognition is the special focus of Chapter 11, by Astruc. The emerging field that involves combining metallopolymers with biopolymers to prepare new functional bioconjugates is represented in Chapter 12, by Mahmoud and Kraatz, and in Chapter 13, by Shionoya. Chapter 12 describes conjugates of peptides and metallopolymers with a particular emphasis on ferrocene systems (which are currently by far the most well-developed), and Chapter 13 focuses on metal arrays based on nucleic acid and peptides.

Clearly, metal-containing polymers represent an important emerging field. We look forward to further rapid progress in the next decade.

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■ CONTENTS

Organometallic Polymers: The Early Days

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I. INTRODUCTION

Historically, polymers only contained the elements C, H, N, O, S, Cl, Br, and occasionally P. The pioneering studies of Rochow in the 1940s on polysiloxanes,[1,2] followed by the rapid development of polysiloxanes by industry in the 1960s, expanded that list of elements to Si. Subsequently, marine antifouling coatings incorporated tin into polymeric systems, through the —$OSnBu_3$ function for the most part. However, the vast majority of elements had not found their way into polymers. Since more than 40 metals exist and many have several available oxidation states, sporadic efforts were made in the 1940s, 1950s, and 1960s to introduce metals into repeating units of polymers through the use of coordination chemistry.[3,4,5] The U.S. Air Force sponsored a large effort to find thermally stable polymers during World War II and after that centered on metal chelation reactions, but useful materials did not emerge. Low molecular weight, intractable, and uncharacterizable materials were the rule. Insolubility was a problem. Some superb scientists, including Carl Marvel[6] and John Bailar[7] were prominent in this difficult effort. Since the mid-1950s, metal coordination polymers have become a large field and recent reviews are now available.[8,9,10]

Organometallic polymers, in contrast to coordination polymers, have metal-to-carbon bonds. They are the topic of this chapter. Three seminal events provided the foundation for the field of organometallic polymers to develop. The landmark discovery of ferrocene by Kealy and Pauson in 1951 marked the first organometallic compound.[11] This was quickly followed by the full elucidation of its structure and an understanding of its reactivity by Wilkinson, Rosenblum, Whiting, and Woodward.[12,13] This history was celebrated in a 2001 feature article in *Chemical and Engineering News*.[14] Finally, the first polymerization of an organometallic compound was reported by Arimoto and Haven at Dupont Co. in 1955.[15,16] Vinylferrocene **1**

was synthesized from its acetyl derivative and subjected to homopolymerization in the presence of radical initiators.[15,16] Details of the characterization never appeared and this report seemed to attract little early attention. A special edition of the *Journal of Inorganic and Organometallic Polymers and Materials* appeared in March 2005 to celebrate the 50th anniversary of this milestone.[17] It was only in the 1960s that organometallic polymers seemed to come alive. Early contributors included Neuse and Rosenberg in the United States[18] and Korshak and Sosin in Russia,[19] the latter signaling active Soviet interest in extending the scope of organometallic chemistry into polymers. In the United States much of the early activity came from the groups of Carraher and Pittman. A review of ferrocene condensation polymers in 1967 covered the work of others.[20]
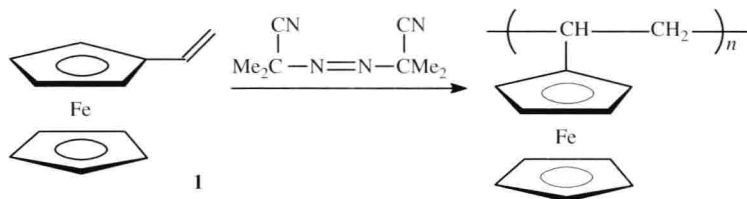

The early work in Pittman's group predominantly employed vinyl addition polymerizations while that of Carraher featured condensation polymerizations. Thus, this chapter has been divided accordingly. However, both groups had a similar vision, that of increasing the numbers of elements that could usefully appear in polymers. As he began his lectures, Carraher often jokingly stated that their efforts were all about increasing the periodic table for polymer chemists. Pittman's laboratory featured a banner with a hypothetical dream structure of a single polymer containing every transition metal. These musings simply emphasized to students, and anyone else who would listen, the opportunities that lay unexplored in the mid-to-late 1960s.

In the late 1960s and early 1970s great progress was achieved in both labs due to the application of instrumentation that, by today's standards, were primitive. At the University of Alabama, Pittman conducted kinetic studies using dilatometry,[21,22] accurate but tedious. Soluble polymers were examined by membrane osmometry and vapor-pressure osmometry to obtain absolute values and Q factors for calibrating gel permeation chromatography.[23] Gel permeation chromatography (GPC) was employed with 16 foot-long GPC column banks.[23] Next, intrinsic viscosity studies were employed when the Universal calibration method was developed by Benoit.[24] Light scattering instrumentation was primitive and difficult to use since many polymers had molecular weights that were not above 50,000 to 60,000. Nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy assisted the work. The use of Mössbauer spectroscopy for the analysis of iron-containing polymers and particularly mixed valence state polymers with ferrocene and ferricinium was employed by Pittman, Good, et al.[25,26] Carraher's group brought the use of high-resolution mass spectrometry (HR-EI-MS)[27] and matrix-assisted laser desorption ionization to organometallic polymers.[28] These and other methods led to publications of reasonably well-characterized organometallic polymers and foreshadowed the huge variety of sophisticated instrumental techniques being regularly employed today to characterize a staggering array of metal-containing polymer structures.

Pittman's introduction to organometallic chemistry occurred while he was a young officer on active duty at the U.S. Army's Solid Rocket Propulsion Laboratory in Redstone Arsenal, Alabama, in 1966. *n*-Butylferrocene was being used as a burning-rate catalyst for $NaClO_4$/ Al/organic binder-based solid propellants. Fast-burning propellants were needed for fast

acceleration, especially for portions of the Nike Zeus missile defense system. However, *n*-butylferrocene, which was the iron-containing catalyst of choice for this purpose, frequently phase separated from the binder when rockets were stored for long periods in the heat. Thus, Pittman began to synthesize ferrocene-containing polymers to prevent phase separation and to elucidate the mechanism by which iron catalyzed propellant combustion.[27,28] Thus, a variety of successful and unsuccessful polymerizations (polycondensations and addition polymerizations) were performed,[29,30] many of which could only appear in the security classified (ICRPG) literature. Without any polymer training (or misgivings), Pittman plunged into this field and continued efforts in this direction upon his arrival at the University of Alabama in 1967. His group set out to (1) synthesize new monomers, (2) develop well-characterized organometallic polymers, and (3) to uncover the basic physical–organic chemistry controlling the vinyl addition polymerization of example organometallic monomers.

Since the Arimoto/Haven report of vinylferrocene polymerization was not detailed, this monomer was made and both its homopolymerization and its copolymerization were studied with a variety of organic comonomers such as styrene, methylacrylate, maleic anhydride, acrylonitrile, methyl methacrylate, *N*-vinylpyrolidone, vinyl acetate, and so on.[31–38] The polymers were as well characterized as possible, and copolymer compositions were obtained versus feed mole ratios.
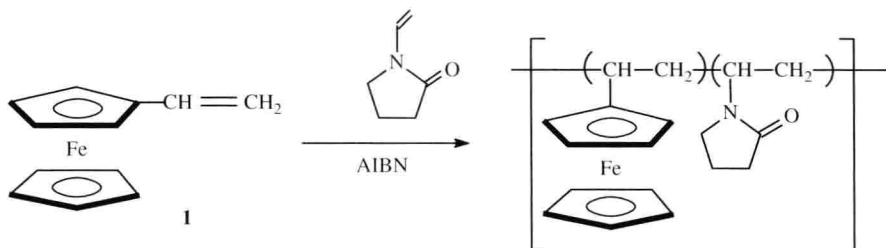
Studies of the homopolymerization kinetics that we carried out were curious and appeared to be greater than half-order in initiator and the polymerizations were sluggish under radical initiated conditions. The reason for this was cleared up by the excellent and precise homopolymerization kinetic studies of George and Hayes, who clearly demonstrated the rate was essentially first order in both initiator and monomer.[39,40,41] What could cause such a rate law? Could the iron center (formally Fe(II)) contribute? Was a redox reaction involved that would be essentially impossible for organic monomers like styrene? The observed rate law: $r = k[M]^{1.1}[I]^{1.1}$ stands in sharp contrast to the normal half-order in initiator concentration found in most vinyl addition polymerizations. Apparently, first-order chain termination had occurred rather than classic bimolecular termination. Indeed, the iron atom was playing a key role.

Internal electron transfer from iron to the radical center generated an anionic chain end, which was quickly quenched, bringing an end to chain growth (see Scheme 1.2). Thus, more initiator had to be consumed to begin a new chain. The lesson was clear: While vinylferrocene was styrene-like, the presence of the metal atom could complicate matters and it must be considered. Suddenly, the reason for our early observations of low homopolymer molecular weights,[31,37] and the lack of increase in molecular weight with a decrease in initiator concentration made sense. The polymer chain self-terminated. Furthermore, the more rapid copolymerizations that led to higher molecular-weight polymers made sense. The internal electron transfer that quenched the growing chain occurred far less often because it was not competitive with addition of the

comonomer (e.g., k_{12} was faster than internal termination). While molecular weights were impacted, the effect was less pronounced.
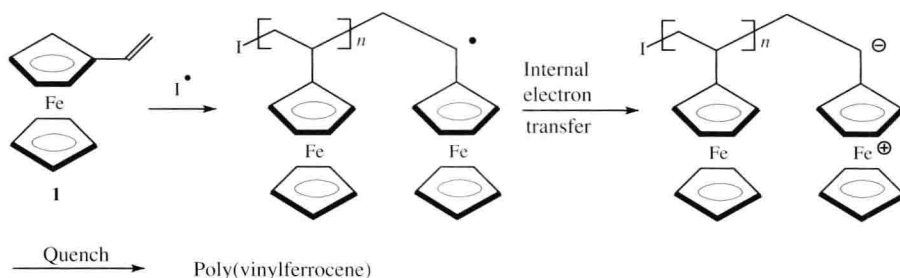
In these early years, nobody had a way to predict the composition of copolymers containing vinylferrocene or any other vinyl organometallic monomer. A better understanding of the reactivity was needed. A major effort to classify vinylferrocene copolymerization reactivity (and that of many other organometallic monomers) within the Alfrey–Price Qe scheme was begun.[42,43] This scheme, reminiscent of the Hammett $\sigma\rho$ approach. It classifies monomers according to two parameters: Q, a resonance parameter, and e, related to the vinyl group's polarity. If the Q and e values of both comonomers are known, the copolymerization reactivity ratios, r_1 and r_2, can be calculated. This allows the use of the integrated form of the copolymer equation[44,45] to calculate the composition of the copolymer at any conversion from any M_1/M_2 starting composition.

The expressions relating Q and e to the reactivity ratios are:

$$r_1 = (Q_1/Q_2)\,\text{exp-}e_1\,(e_1 - e_2)$$

$$r_1 = (Q_1/Q_2)\,\text{exp-}e_2\,(e_2 - e_1)$$

$$r_1\,r_2 = \text{exp-}(e_1 - e_2)^2$$

where the subnumbers 1 and 2 refer to monomer M_1 and M_2 in the copolymerization.

To avoid electron transfer/quenching termination, the propagating radical center was moved away from and out of conjugation with the iron. Acrylic monomers **2** and **3** were soon made, and characterized.[25,32] They underwent "normal" radical addition polymerization kinetics: $r = k[M]^1\,[I]^{1/2}$ and higher molecular weights were achieved. The radical center, no longer adjacent to the cyclopentadienyl (Cp) ring, was far enough away from the iron atom to avoid electron transfer from iron. The ferrocene moieties in these polymers were, however, easily oxidized by the addition of strongly electron-attracting quinones such as 2,3-dichloro-5, 6-dicyanobenzoquinone (DDQ). Similar oxidations occurred with poly(vinylferrocene) to generate systems where all, or a portion of, the ferrocene groups in the polymers were converted to ferricenium units (see **4** and **5**). This work eventually led us to prepare a variety of designed mixed oxidation state systems. Mössbauer spectroscopy was developed as a superb analytical tool to define the oxidation stoichiometry with the assistance of Mary Good, then at Louisiana State University in New Orleans.[25,32]

The Q and e values for monomers are particularly valuable because, at a glance, they classify structure/reactivity features of monomers in a useful way that chemists can grasp. For example, monomers with a high resonance stability have larger Q values, while electron-rich

2

3

DDQ

4

More
DDQ

5
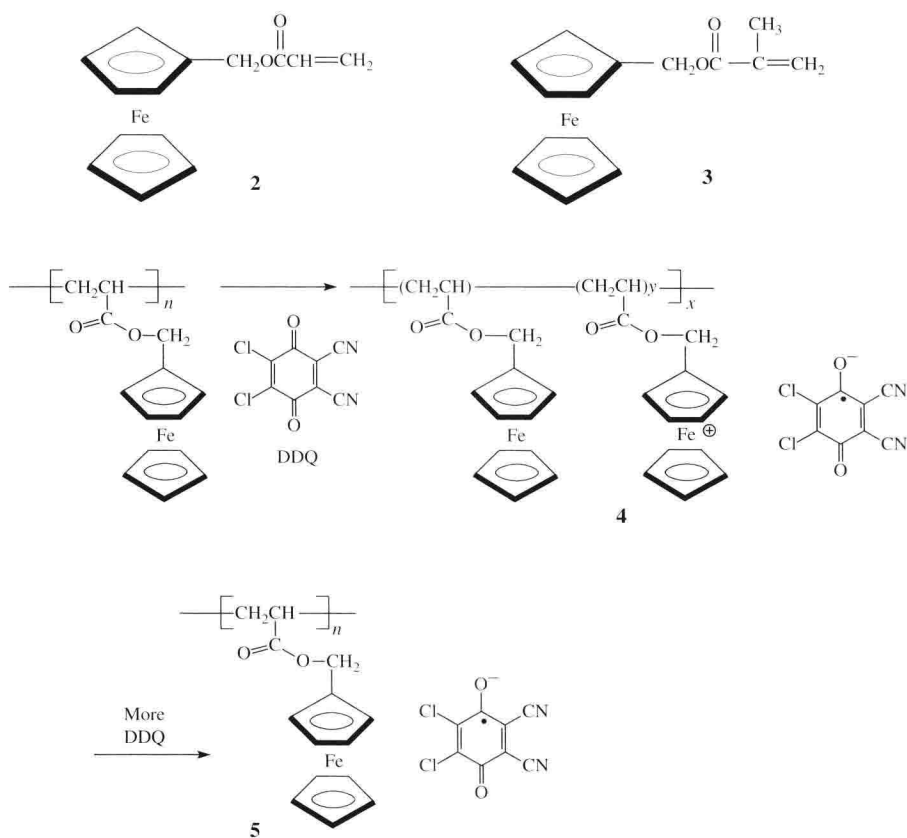
monomers have negative values of e and electron-poor monomers have a positive value of e. In the first application of physical organic approaches to organometallic polymers, the Q and e values of many organometallic monomers were determined by obtaining the relative reactivity ratios of organometallic monomers with numerous common organic monomers in over a decade of work. This established that vinylferrocene and all the other cyclopentadienyl metal monomers are extremely electron rich and have high resonance stabilization[46,47] (see Table 1.1). Many new copolymer systems were characterized and a general understanding of these addition polymerizations emerged during this program. This effort was augmented by studies of mixed oxidation state metal-containing polymers.[48]

The great stability of the ferrocenylmethyl cation suggested that the polymers of **2** and **3** would be susceptible to hydrolytic instability in polar ionizing solvents. Therefore, their 2-ferrocenylethyl analogs **6** and **7** were synthesized, homopolymerized, and their polymerization rate laws were established.[49] The copolymerizations of all four acrylates **2**, **3**, **6**, and **7**, with a large variety of common organic monomers, were established and the reactivity ratios were obtained.[33,36,49,50] The ferrocene moiety sharply increased the glass transition temperature of acrylate and methacrylate polymers.[51] The homopolymer examples are listed in Table 1.2. Apparently, ferrocene's high molecular weight and steric bulk strongly retard segmental motion, much like an anchor attached to a jump rope. Likewise, poly(vinylferrocene) exhibits a $T_g = 184$–$194°C$ far above that of its nonorganometallic analog polystyrene.

TABLE 1.1   Alfrey Price Q, e Values For Selected Vinylcyclopentadienyl Metal-Containing Monomers Versus Common Organic Monomers

Monomer	Q	e
Vinylferrocene, **1**	1.03	−2.1
η^5-(Vinylcyclopentadienyl)tricarbonylmanganese, **8**	1.1	−1.99
η^5-(Vinylcyclopentadienyl)dicarbonylnitrosylchromium, **10**	3.1	−1.98
η^5-(Vinylcyclopentadienyl)dicarbonylnitrosylmolybdenum, **11**	3.1	−1.98
η^5-(Vinylcyclopentadienyl)tricarbonylmethyltungsten, **13**	1.66	−1.98
η^5-(Vinylcyclopentadienyl)dicarbonyliridium, **12**	4.1	−2.08
Styrene	1.00	−0.80
Propene	0.002	−0.78
Maleic anhydride	0.23	+2.25

Source: Reference 46.

6, R = H
7, R = CH$_3$
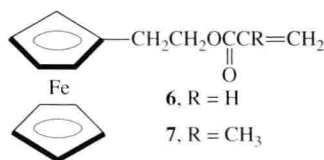
TABLE 1.2   Glass Transition Temperatures, T_g, of Acrylic Ferrocene Polymers [30]

Polymer	T_g (°C)
Poly(methyl acrylate)	3
Poly(ferrocenylmethyl acrylate)	197–210
Poly(2-ferrocenylethyl acrylate)	157
Poly(methyl methacrylate)	57–68
Poly(ferrocenylmethyl methacrylate)	185–195
Poly(2-ferrocenylethyl methacrylate)	209

Source: Reference 30.

A. η^5-Cyclopentadienylmetal and η^6-Phenylmetal Carbonyl Monomers

The chemistry of organometallic metal carbonyl compounds exploded in the early 1960s. With the advent of compounds like η^5-(cyclopentadienyl)manganesetricarbonyl and many other related species, the obvious questions became, could the vinyl derivatives of these compounds function like styrene? Would addition polymerizations be possible, or would the metal atom interfere? Would carbonyl groups and other substituents modify the reactivity of such monomers and how might they compare with vinylferrocene? Where might such monomers lie on the Q, e scheme? These were key questions we sought to answer. A vigorous program was mounted to prepare a variety of metal carbonyl-containing monomers, study their homopolymerizations, their polymerization kinetics, and their copolymerizations with common organic monomers. The structures of several of these monomers (**8–32**), references to their preparation, and where available, polymerizations and their Q and e values, are displayed in Scheme 1.1.

Mn(CO)₃
8
Q = 1.1
e = 1.99
Ref. 38, 46, 47, 52−55,
58, 66, 72

Mn(CO)₃
9
Ref. 55

Cr(CO)₂NO
10
Q = 3.1
e = −1.98
Ref. 46, 55−58,
63, 64, 72

Mo(CO)₂NO
11
Q = 3.1
e = −1.97
Ref. 46, 47,
54, 57

Ir(CO)₂
12
Q = 4.1
e = −2.08
Ref. 46, 47,
54, 57

W(CO)₃CH₃
13
Q = 1.66
e = −1.98
Ref. 58−62

W(CO)₂NO
14
Ref. 54, 57

Co(CO)₂
15
Ref. 54, 57

CuPEt₃
16
Ref. 54, 57

Rh(CO)₂
17
Ref. 54, 57

18
Ref. 54, 57, 58, 59

Cr(CO)₃
19
Ref. 66, 67, 72

Cr(CO)₃
20
Ref. 65, 66, 68, 72

Cr(CO)₃
21
Ref. 69, 72

Cr(CO)₃
22
Ref. 73

Fe(CO)₃
23
Ref. 70, 71, 72

Mo(CO)₂NO
24
Ref. 54, 57, 58

W(CO)₂NO
25
Ref. 54, 57, 58

Ir(CO)₂
26
Ref. 46, 57, 58

Co(CO)₂
27
Ref. 46, 57, 58

CuPEt₃
28
Ref. 46, 57, 58

Rh(CO)₂
29
Ref. 46, 58

Sn
30
Ref. 46

(OC)₃Co—Co(CO)₃
Co
(CO)₃
31
Ref. 46

W(CO)₃CH₃
32
Ref. 59

Scheme 1.1

B. η⁵-(Cyclopentadienyl)tricarbonylmanganese, 8

We synthesized **8**[52,53,55] and its methyl analogs, **9**,[54] in a manner similar to that of vinylferrocene, **2**. Freidel Crafts acylation proceeds readily on η⁵-(cyclopentadienyl)tricarbonylmanganese due to the aromatic nature of the cyclopentadienyl ring when complexed to the metal. Sodium borohydride reduction of the acetyl derivative and dehydration over KHSO₄ at 180–190°C generated **8**. The η⁵-(methylcyclopentadienyl)tricarbonylmanganese precursor of **9**, was available at low cost in the late 1960s from Ethyl Corporation, since it was being used as an experimental cetane additive to gasoline. The high-temperature dehydration leading to **8** was somewhat surprising in view of an earlier report by Kozikowski and Cais[74] that a thermal decomposition residue was formed during the KHSO₄-catalyzed dehydration.

The radical-initiated copolymerization of **8** was demonstrated with styrene, methyl methacrylate, acrylonitrile, and vinyl acetate, in benzene or ethyl acetate using azobisisobutyronitrile (AIBN) as the initiator.[52a] Copolymerizations of **8** with N-pyrrolidone generated water-soluble materials.[52b,c] Molecular weights and the Mark Houwink K and a values were defined.[38] Monomer **8**, like vinylferrocene, proved to be extraordinarily electron-rich, exhibiting an e value of −1.99 and a larger resonance parameter ($Q = 1.1$) than styrene (0.80).[52a] Upon heating the N-vinyl-2-pyrrolidone copolymers of **8** to 260°C under nitrogen, gas evolution (CO) and weight loss occurred. The products became increasingly insoluble with time. Water-soluble copolymers from N-vinyl-2-pyrrolidone with excellent film adhesion to glass surface.[52b,c]

Copolymers of **8** and vinylferrocene, containing two different transition metals as shown in **33**, were readily prepared by radical addition polymerization.
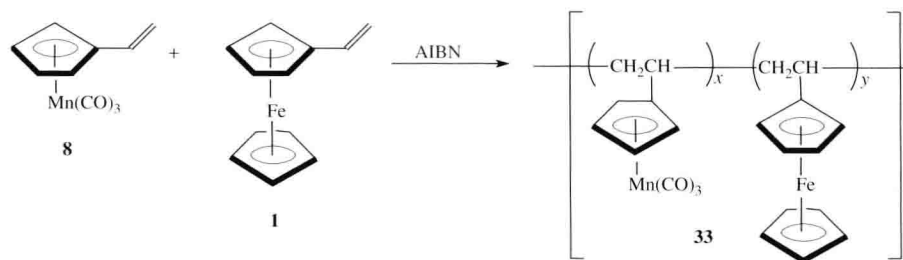
Would the tricarbonyl manganese function in monomer **8** prevent homopolymerization, or undergo electron transfer from manganese to the propagating radical center? Homopolymerization kinetic studies in benzene, benzonitrile, and acetone demonstrated that the effect of manganese was different than that of iron in **1**. The rate law was three halves order in the concentration of monomer **8** and half-order in initiator concentration.[53]

$$r = k\,[M]^{1.5}\,[I]^{0.5}$$

Molecular weight measurements confirmed that the degree of polymerization followed the relationship: $DP = [k_p/(2\,f'\,k_t k_d)^{0.5}][[M]/[I]]^{0.5}$, which is predicted by this rate law. The measured rate law is consistent with a very low initiation efficiency, where $f' = f\,[M]$.

We demonstrated that the observed rate law was not due to rapid initiator decomposition catalyzed by **8**. Instead, low initiation efficiency is a fundamental property of **8**, along with its very electron-rich vinyl group and its ability to provide a significant resonance interaction to the chain radical α to the ring.