

# ORGANOMETALLIC POLYMERS

Edited by

Charles E. Carraher, Jr.

John E. Sheats

Charles U. Pittman, Jr.

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*ACADEMIC PRESS RAPID MANUSCRIPT REPRODUCTION*

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**Academic Press**

New York San Francisco London 1978

A Subsidiary of Harcourt Brace Jovanovich, Publishers

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**ACADEMIC PRESS, INC.**  
111 Fifth Avenue, New York, New York 10003

*United Kingdom Edition published by*  
**ACADEMIC PRESS, INC. (LONDON) LTD.**  
24/28 Oval Road, London NW1 7DX

**Library of Congress Cataloging in Publication Data**

Symposium on Organometallic Polymers. New Orleans,  
1977.  
Organometallic polymers.

The symposium took place during the national  
meeting of the American Chemical Society in  
New Orleans, La., 1977.

1. Polymers and polymerization—Congresses.
2. Organometallic compounds—Congresses.
- I. Carraher, Charles E. II. Sheats, John E.
- III. Pittman, Charles U. IV. American  
Chemical Society. V. Title.

QD380.S93 1977

547'.8427

77-20108

ISBN 0-12-160850-6

**PRINTED IN THE UNITED STATES OF AMERICA**

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## PREFACE

Organometallic Polymers is a volume designed to cover a wide range of topics related to organometallic polymers: their synthesis, characterization, and potential applications. For the purpose of this volume we have defined an organometallic polymer as one in which the metal-containing portion is either incorporated as an integral part of the polymer or is bound to the polymer structure by covalent bonds. Some of the materials such as the phosphonitriles and sulfur nitride polymers might be classed as inorganic rather than organometallic polymers, but are included because of their close relationship to the other types of polymers discussed.

The chapters in this volume were written by the speakers at the three-day Symposium on Organometallic Polymers, held at the National Meeting of the American Chemical Society in New Orleans, on March 20–23, 1977. The authors are recognized experts within their areas of research. Most are American but some contributions from abroad have been included. There is a mix of industrial and academic authors and a mixture of basic, theoretical, and applied research topics. The volume is divided into seven sections: vinyl polymerization of organometallic monomers, condensation polymerization of organometallic monomers, polymer-bound catalysts, applications of organotin polymers, recent developments in organosilicon polymers, phosphonitrile and sulfur nitride polymers, and coordination polymers. Each section includes one or more summary or review papers, which covers progress in the field, and includes several other papers presenting various aspects of the topic. Of the polymeric materials described only two classes, the organosilicons and the polymer-bound chromocene catalysts, have widespread commercial uses. Other materials, such as the organotin polymers, the phosphonitriles, and some of the hydroformylation catalysts, seem certain to be used widely within a few years. The others at present remain laboratory curiosities and subjects of an increasing amount of research. Potential applications include use as adhesives, antifouling paint, bacteriacides, biopolymers, catalysts, conductors, controlled-release agents, fibers, flame

retardants, fungicides, haptens, implants in living tissue, paints, photo sensitizers, photostabilizers, photoresists, semiconductors, and stereospecific catalysts. Instrumental techniques for characterizing materials such as Mössbauer spectroscopy, photoacoustic spectroscopy, torsional braid analysis, thallium NMR, and X-ray crystallography are described. Considering the enormous impact the plastics and polymers formed from carbon, hydrogen, nitrogen, oxygen, silicon, and the halogens have already had on society, much more awaits the inclusion of the rest of the periodic table. In this volume polymers containing 26 other elements are described. Another symposium on the same topic is planned for 1980. We hope to have many more exciting results in the field by then.

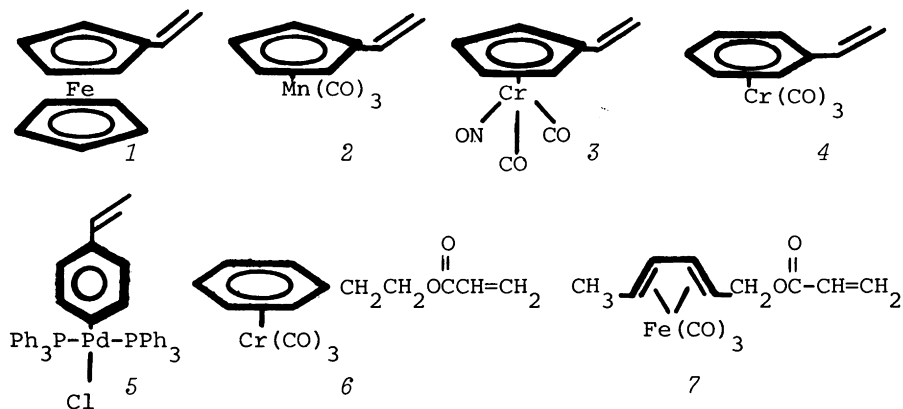
VINYL POLYMERIZATION OF ORGANOMETALLIC  
MONOMERS CONTAINING TRANSITION METALS

Charles U. Pittman, Jr.  
Department of Chemistry, University of Alabama

*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)  $\eta^6$ -(2-phenylethyl acrylate)tricarbonylchromium 6 (8), and  $\eta^4$ -(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

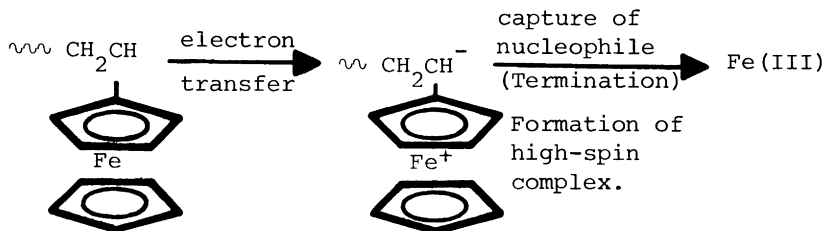




Arimoto and Haven in 1955 (10). For the next decade this area was virtually neglected in comparison with the vast attention given to organometallic condensation polymers. In this chapter, a brief review of the status of vinylorganometallic polymerizations will be given.

## II. HOMOPOLYMERIZATION.

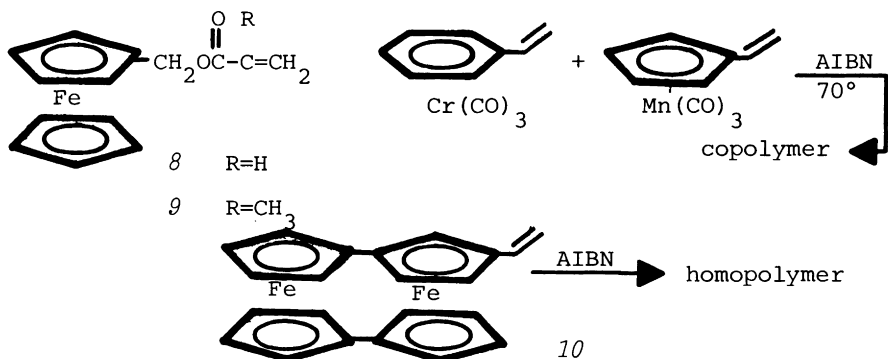
Vinylferrocene has been more thoroughly studied than any other organometallic monomer (2,3,11). Homopolymerization has been carried out using radical (2,3,11), cationic (12), and Ziegler-Natta initiators (13). Peroxides oxidize ferrocene. Using AIBN, solution polymerizations result in low molecular weights, 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 ( $C_m = 8 \times 10^{-3}$  versus  $6 \times 10^{-5}$  for styrene at  $60^\circ$ ) (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  $0.14 \text{ mm sec}^{-1}$  that was not due to either ferrocene or ferrocenium groups. In dioxane, the usual half order dependence in monomer (bimolecular termination) was observed (11).

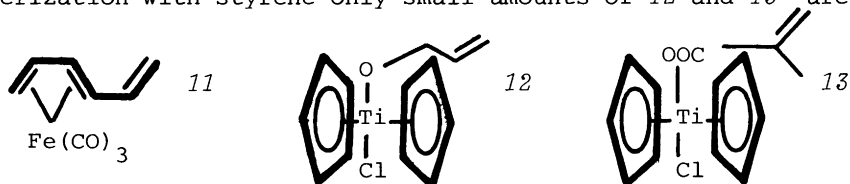
A high chain transfer constant to polymer in polyvinylferrocene polymerizations leads to chain branching. As the molecular weight increases, the resulting polyvinylferrocene becomes increasingly branched. Thus, vinylferrocene exhibits an unusual homopolymerization behavior which may be attributed to 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



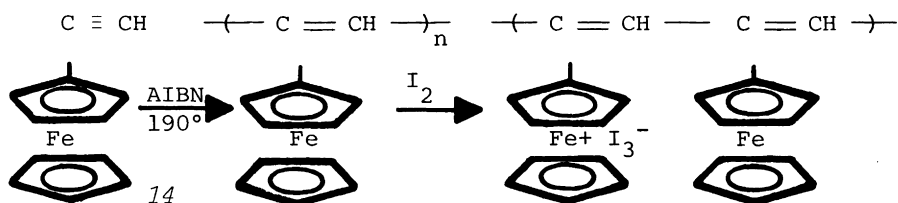
currently available. Because transition metals can far more readily undergo ionization than carbon, the potential for electron transfer mechanisms to complicate polymerization mechanisms is high.

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 have 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 polysalts were semiconducting (26).



### 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:

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

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

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