Macromolecules Containing Metal and Metal-Like Elements

Volume 6

Transition Metal-Containing Polymers

Edited by

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Published by John Wiley & Sons, Inc., Hoboken, New Jersey.
Published simultaneously in Canada.

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Library of Congress Cataloging-in-Publication Data:

ISBN-13 978-0-471-68445-9
ISBN-10 0-471-68445-7
ISSN 1545-438X

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

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Preface

Almost 70 of the approximately 115 elements are transition metals. These are elements with electrons successively added to their "d" or "f" subshells and have both filled and unfilled orbitals suitable for bonding. They exhibit a variety of oxidation states and bond formations, such as sigma and pi bonds or coordination bonds as are found in typical chelate structures. These characteristics are the reason that transition metal-containing macromolecules exist in a wide variety of structures including linear, two-dimensional, three-dimensional, dendrite, and assemblies. Many of these polymers are often referred to as organometallic polymers. We have, somewhat arbitrarily, separated this class from coordination polymers, which have been covered in Volumes 1, 3, and 5.

The interest in transition metal-containing polymers stems from the optical, biological, thermal, catalytic, electrical, and magnetic properties of these materials. They are candidates as essential materials for a wide variety of applications for the 21st century because of these properties. They are used in the coatings, colorants, pharmaceutical, aerospace, and communications industries. They can serve as precursors for ceramics.

This volume begins with a general review that includes an overview of the general types of polymers already synthesized. Different approaches to their synthesis and background information are included to help the reader to understand transition metal-containing macromolecules. This information provides an introduction to both Volumes 6 and 7 of this series. Activity in this important area is increasing exponentially. New materials, properties, synthetic routes, and common applications constitute the root of this rapid development.

Most polymers are useful because of their inactivity; however, metal-containing polymers are finding uses because of their chemical reactivity in diverse areas such as catalysis, photodegradation, and lithography. This volume contains reviews of each of these important areas that illustrate the possible application of metal-containing macromolecules in this important emerging area of reactive materials.

Series Preface

Most traditional macromolecules are composed of less than 10 elements (mainly C, H, N, O, S, P, C1, F), whereas metal and semi-metal-containing polymers allow properties that can be gained through the inclusion of nearly 100 additional elements. Macromolecules containing metal and metal-like elements are widespread in nature with metalloenzymes supplying a number of essential physiological functions including respiration, photosynthesis, energy transfer, and metal ion storage.

Polysiloxanes (silicones) are one of the most studied classes of polymers. They exhibit a variety of useful properties not common to non-metal-containing macromolecules. They are characterized by combinations of chemical, mechanical, electrical, and other properties that, when taken together, are not found in any other commercially available class of materials. The initial footprints on the moon were made by polysiloxanes. Polysiloxanes are currently sold as high-performance caulks, lubricants, antifoaming agents, window gaskets, O-rings, contact lens, and numerous and variable human biological implants and prosthetics, to mention just a few of their applications.

The variety of macromolecules containing metal and metal-like elements is extremely large, not only because of the large number of metallic and metalloid elements, but also because of the diversity of available oxidation states, the use of combinations of different metals, the ability to include a plethora of organic moieties, and so on. The appearance of new macromolecules containing metal and metal-like elements has been enormous since the early 1950s, with the number increasing explosively since the early 1990s. These new macromolecules represent marriages among many disciplines, including chemistry, biochemistry, materials science, engineering, biomedical science, and physics. These materials also form bridges between ceramics, organic, inorganic, natural and synthetic, alloys, and metallic materials. As a result, new materials with specially designated properties have been made as composites, single- and multiple-site catalysts, biologically active/inert materials, smart materials, nanomaterials, and materials with superior conducting, nonlinear optical, tensile strength, flame retardant, chemical inertness, superior solvent resistance, thermal stability, solvent resistant, and other properties.

There also exist a variety of syntheses, stabilities, and characteristics, which are unique to each particular material. Further, macromolecules containing metal and metal-like elements can be produced in a variety of geometries, including linear, two-dimensional, three-dimensional, dendritic, and star arrays.

In this book series, macromolecules containing metal and metal-like elements will be defined as large structures where the metal and metalloid atoms are (largely) covalently bonded into the macromolecular network within or pendant to the polymer backbone. This includes various coordination polymers where combinations of ionic, sigma-, and pi-bonding interactions are present. Organometallic macromolecules are materials that contain both organic and metal components. For the purposes of this series, we will define metal-like elements to include both the metalloids as well as materials that are metal-like in at least one important physical characteristic such as electrical conductance. Thus the term includes macromolecules containing boron, silicon, germanium, arsenic, and antimony as well as materials such as poly(sulfur nitride), conducting carbon nanotubes, polyphosphazenes, and polyacetylenes.

The metal and metalloid-containing macromolecules that are covered in this series will be essential materials for the twenty-first century. The first volume is an overview of the discovery and development of these substances. Succeeding volumes will focus on thematic reviews of areas included within the scope of metallic and metalloid-containing macromolecules.

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CHAPTER 1

Introduction

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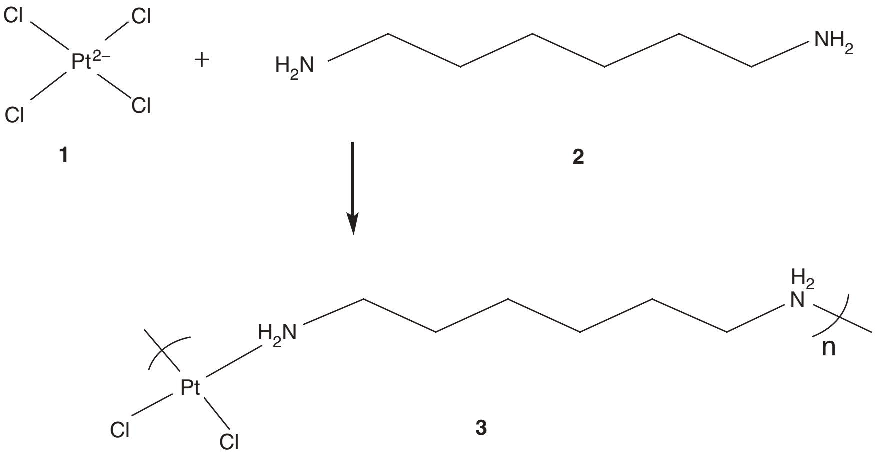
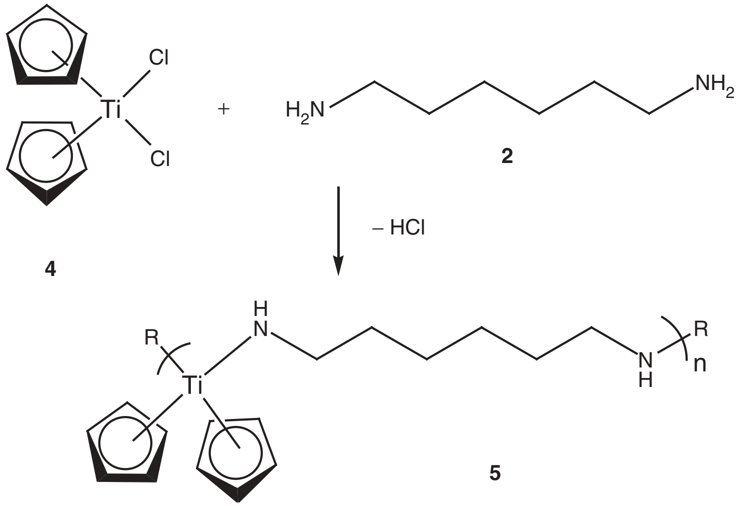
I. COVERAGE

Transition metal-containing macromolecules come in a wide variety of structures. While volume 5 of this series dealt with metal coordination polymers, in this book we focus on transition metal-containing polymers where the metal is bonded to at least one organic group through σ- and/or π-bonds. Many of the macromolecules covered in this volume are often referred to as organometallic polymers. The term *organometallic compound* refers to compounds that contain at least one metal–carbon (M–C) bond, whether the bond is σ or π or some combination of both types of bonding.[1–5]

The line that divides classical and nonclassical metal complexes, organometallic complexes, and coordination compounds is imperfect. For instance, what constitutes a coordination reaction and a condensation reaction? Piperidine is an organic compound, that can react with metal-containing sites in two different ways. If the N-proton is retained, then the reaction is a coordination reaction and the resulting product a coordination compound. In this case, the nitrogen donates its lone pair of electrons to the metal site. However, if the proton is lost, then the reaction is described as a condensation reaction with the product called a condensation product. Polymers formed from such condensation reactions are covered in this volume. Schemes 1 and 2 depict reactions that illustrate the difference between coordination and condensation reactions using 1,6-hexanediamine.[5–13]



Scheme 1 Coordination reaction between tetrachloroplatinate and 1,6-hexanediamine.

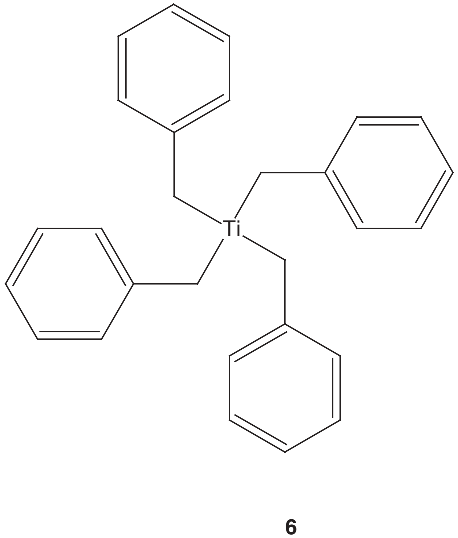


Scheme 2 Condensation reaction between titanocene dichloride and 1,6-hexanediamine.

II. GENERAL CONCEPTS

The elementary chemistry of transition metals can be understood using traditional chemistry terms. This is easily illustrated with the chemistry of titanium. Titanium, the second transition element, has an outer or valence electron configuration of $4s^2$, $3d^2$. Its most common oxidation state is $+4$, with titanium losing or sharing four electrons. While compounds with titanium in the -1, 0, $+2$, and $+3$ exist; they are easily oxidized to titanium $+4$. The energy for removal of four electrons is high, so most titanium +4 compounds are covalent rather than ionic. Ferrocene, for example, when viewed according to the 18-electron rule, has 8 valence electrons, ($4s^2 3d^6$), and each cyclopentadienyl (Cp) ion contributes 5 electrons giving a total of 10 electrons contributed by the two Cp units for a total of 18 electrons. Not all of the transition metals require the 18 electrons, some seek only 16 electrons. For titanocene dichloride, the titanium atom already has 4 electrons $4s^2 3d^2$, with each Cp contributing 5 electrons for a total of 10 electrons. Each chloride supplies 1 electron for a total of 2, giving a total of 16 electrons. Titanocene dichloride, however, has a vacant hybrid orbital; and to obtain 18 electrons, it can bind to double bonds. Deviations from the 16/18-electron rule are common in neutral bis(cyclopentadienyl) complexes. Thus Cp_2VCl_2 has 5 valence electrons derived from the vanadium atom, 10 total electrons from the two Cp groups, and 2 total electrons from the two chlorides for a total of 17 valence electrons.

The compounds of titanium will be briefly described to illustrate the behavior and structural considerations in common organometallic compounds. Organotitanium compounds have been extensively studied because of their use in the production of stereoregular polymers. Here, we will briefly focus on some organotitanium(IV) compounds. Alkyl titanium complexes can be made using bulky groups, where titanium hydride elimination is impossible. Structures **6** and **7**, are examples of two of these compounds.



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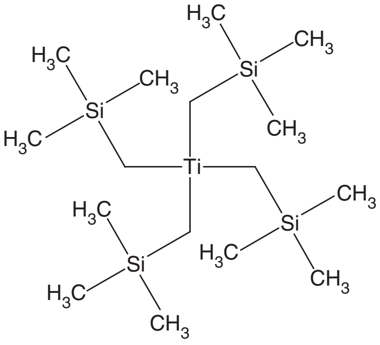

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A number of Cp derivatives of Ti exist. Titanocene dichloride exists as a distorted tetrahedron, with the planes of the Cp rings facing the titanium metal. This is unlike ferrocene and cobalticinium salts for which the metal atoms are sandwiched between the parallel Cp rings. The structure of titanocene dichloride is similar to that of many of the other π-bonded Cp structures. Numerous derivatives of the titanocene moiety exist. These derivatives consist of various substituents, including alkyl, aryl, halides, thiols, carbonyls, and ethers. There are also numerous compounds containing substituents on the ring. All of these derivatives have a distorted tetrahedral geometry about the titanium atom.

For many classical Lewis acid-base reactions, the Cp rings appear inert and condensation reactions occur with other substituents on the metal. In Figure 1, typical reactions with titanocene dichlorides that result in the formation of polymers are described.

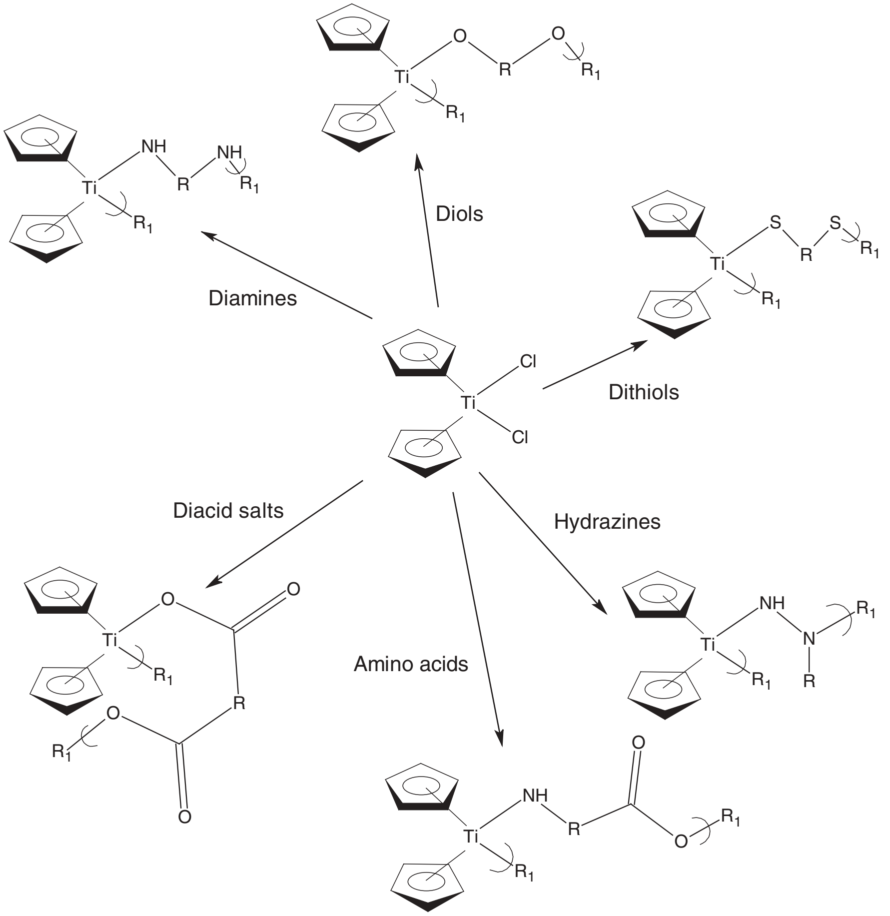
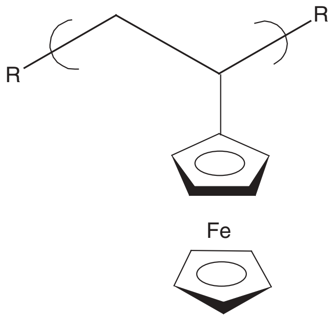


Figure 1 Synthetic pathways for the synthesis of polymers from titanocene dichloride.

III. HISTORICAL

Since the first example of a metallocene based polymer was reported in 1955 by Arimoto and Haven, just a few years after the discovery of ferrocene, there has been an ever increasing interest in the development of organometallic polymers.[14–18] This interest stems from the electrical, magnetic, optical, biological, thermal or catalytic properties that this class of polymers possess. Organometallic polymers have found applications in the coating, colorant, pharmaceutical, and aerospace industries. Organometallic polymers encompass many different classes of macromolecules. Due to the nature of the organic ligands, the metal and the type of M–C bond, a great variety of structures exist within each class. Transition metals can be either σ- or π-bonded to the carbon skeleton of the backbone or side chains. The first half of the 20th century saw many advances in organic and inorganic polymer chemistry, but it was not until the 1950s that organometallic polymers were identified as a new class of polymeric materials.[19,20]

The formation of polymetallocenes through homoannular or heteroannular substitution is not the only method for obtaining the polymers; they can also be formed by polymerization via the metal. The metallocene can be attached to the polymer chain as in poly(vinyl ferrocene) (**8**), or it can be an integral part of the polymer backbone (**9**).[19]



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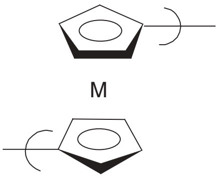

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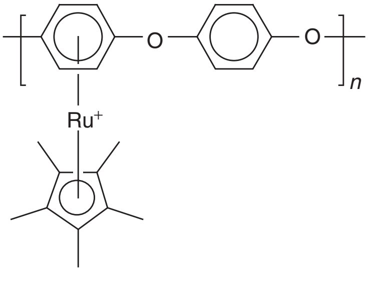
Arene cyclopentadienylmetal and arene metal carbonyl complexes are two other classes of materials that are metallocene-like in structure. The first report of the synthesis of the η^6-mesitylene–η^5-cyclopentadienyliron cation in 1957 by Coffield et al.[21] was a seminal event in this research field. However, it was the 1985 report on the polymerization of η^6-dichlorobenzene–η^5-cyclopentadienylruthenium with diphenolic compounds, forming compounds such as **10**, by Segal[22] that caused research in this area to expand.



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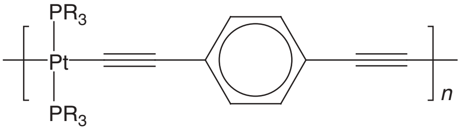
Research in poly(metal acetylides) such as structure **11**, dominates the area of transition metals σ-bonded to organic moieties.[23,24] Since the first report of these polymers in the 1970s, many researchers have described the incorporation of various types of transition metals into this class of materials. This class of organometallic polymers contains rigid-rod structures, making these polymers ideal for electrical and optical applications.



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This chapter presents an overview of the chemistry of organometallic polymers, with emphasis on recent advances in this field.

IV. POLYMERS CONTAINING BIS-(CYCLOPENTADIENYL) METAL COMPLEXES

As noted earlier, a number of cyclopentadienyl metal-containing polymers have been synthesized. In some cases, the Cp has been substituted. In general when the substitution is "organic," such as replacing the five Cp-hydrogens with methyl groups, the resulting products possess increased steric bulk; more electron-donating ablity; and have more "organic-like" properties, including greater solubility in organic solvents. The electron donating nature of the methyl group makes the resulting pentamethyl-Cp a stronger-field ligand than Cp itself. Thus $(Me_5Cp)_2Mn$ is low spin in contrast to Cp_2Mn. The visible spectra of most $(Me_5Cp)_2M$ compounds show greater splitting between the $2a_{1g}$ and $2e_{1g}$ orbitals. Physical constants related to the electron density on the metal are also generally greater for the substituted Cp complexes. This electron buildup makes the substituted-Cp compound easier to oxidize than the corresponding nonsubstituted Cp. The reduction potential is often shifted by -0.5 V for such compounds.[25] The combination of steric hindrance and a greater gap between HOMOs and LUMOs gives organic-substituted Cp-compounds greater kinetic and thermal stability relative to Cp itself.

$C_5H_5^{-1}$ is essentially an η^5 ligand donating six electrons. The general term *metallocene* is used to describe these bis(cyclopentadienyl) metal complexes. The most heavily studied metallocene is ferrocene.

In the MO treatment of ferrocene, the a_1' frontier orbital and all lower orbitals are full, but the e_1'' and all higher orbitals are empty. These frontier orbitals are considered to be neither strongly bonding nor strongly antibonding. This characteristic