
Macromolecules Containing Metal and Metal-Like Elements

Volume 7

Nanoscale Interactions of Metal-Containing Polymers

Edited by

Alaa S. Abd-El-Aziz

*Department of Chemistry, The University of Winnipeg, Winnipeg, Manitoba,
Canada*

Charles E. Carraher Jr.

*Department of Chemistry and Biochemistry, Florida Atlantic University,
Boca Raton, Florida, and Florida Center for Environmental Studies, Palm
Beach Gardens, Florida*

Charles U. Pittman Jr.

*Department of Chemistry, Mississippi State University, Mississippi State,
Mississippi*

Martel Zeldin

Department of Chemistry, University of Richmond, Richmond, Virginia

 **WILEY-INTERSCIENCE**

A John Wiley & Sons, Inc., Publication

**Macromolecules
Containing Metal and
Metal-Like Elements**

Volume 7

Macromolecules Containing Metal and Metal-Like Elements

Volume 7

Nanoscale Interactions of Metal-Containing Polymers

Edited by

Alaa S. Abd-El-Aziz

*Department of Chemistry, The University of Winnipeg, Winnipeg, Manitoba,
Canada*

Charles E. Carraher Jr.

*Department of Chemistry and Biochemistry, Florida Atlantic University,
Boca Raton, Florida, and Florida Center for Environmental Studies, Palm
Beach Gardens, Florida*

Charles U. Pittman Jr.

*Department of Chemistry, Mississippi State University, Mississippi State,
Mississippi*

Martel Zeldin

Department of Chemistry, University of Richmond, Richmond, Virginia

 **WILEY-INTERSCIENCE**

A John Wiley & Sons, Inc., Publication

Copyright © 2006 by John Wiley & Sons, Inc. All rights reserved

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

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, (978) 750-8400, fax (978) 750-4470, or on the web at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008, or online at <http://www.wiley.com/go/permission>.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services or for technical support, please contact our Customer Care Department within the United States at (800) 762-2974, outside the United States at (317) 572-3993 or fax (317) 572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic formats. For more information about Wiley products, visit our web site at www.wiley.com.

Library of Congress Cataloging-in-Publication Data:

ISBN-13 978-0-471-68440-4
ISBN-10 0-471-68440-6
ISSN 1545-438X

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

Contributors

Laurence Belfiore, Department of Chemical and Bioresource Engineering, Colorado State University, Ft. Collins, CO 80523

Charles Carraher, Department of Chemistry, Florida Atlantic University, Boca Raton, FL 33431 and Florida Center for Environmental Studies, Palm Beach Gardens, FL 33410

A.D. Pomogailo, Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow Region 142432, RUSSIA

Ulrich Schubert, Institute of Materials Chemistry, Vienna University of Technology, Getreidemarkt 9, A-1060 Wien, AUSTRIA

Contents

Preface	xiii
Series Preface	xv
1. Nanocluster Assemblies and Molecular Orbital Interactions in Macromolecule-Metal Complexes	1
<i>Laurence A. Belfiore and Sarah E. Fenton</i>	
I. Introduction	3
II. Methodology of Transition Metal Coordination in Polymeric Complexes	4
A. Polymeric Coordination Complexes with d-Block Salts that Exhibit an Increase in T_g	4
B. Chemical Bonding, Coordination, and Transition Metal Compatibilization	5
i. Ligand Field Stabilization Energy Description of the Enhancement in T_g for Polymeric Complexes with Transition Metals	6
ii. Energetic Ligand Field Models and the Methodology of Transition Metal Coordination	8
C. Well-Defined Low-Molecular-Weight Transition Metal Complexes that Increase T_g	9
D. Attractive Polymeric Ligands	10
E. Identifying Attractive Interactions via Hard and Soft Acids and Bases	10
F. Displacement of Weak Neutral Bases in the First-Shell Coordination Sphere by Stronger Bases	11
i. Anionic Ligands are the Last Ones that Should Be Displaced to the Second Shell	13
G. Complexes with the Same Local Symmetry Above and Below the Glass Transition	14
i. Complexes with Reduced Symmetry Above T_g	14
H. Consideration of Interelectronic Repulsion and Ligand Field Splitting When There Is Ambiguity in the d-Electron Configuration	15
III. Jørgensen's Parametric Representation of Ligand Field Splitting and Interelectronic Repulsion	18
A. Polymeric Complexes with Enhanced Glass-Transition Temperatures	19

B. Polymeric Complexes with Reduced Glass-Transition Temperatures	20
C. Other Considerations	20
IV. Pseudo-Octahedral d^8 Nickel Complexes with Poly(4-vinylpyridine)	20
A. Ligand Field Stabilization Energies	20
B. Coordination Crosslinks vs. Coordination Pendant Groups	22
C. Ligand Field Model of the Glass Transition in Macromolecule–Metal Complexes	24
D. Linear Least Squares Analysis of $\Delta(\text{LFSE})$ via the Concentration Dependence of T_g in P4VP/ Ni^{2+} Complexes, Subject to the Constraint that $\beta \leq 1$	26
V. d^6 Molybdenum Carbonyl Complexes with Poly(vinylamine) that Exhibit Reduced Symmetry Above the Glass-Transition Temperature	27
A. Experimental Results	27
B. Ligand Field Splitting Parameters for Molybdenum Hexacarbonyl	28
C. Ligand Field Stabilization for Complexes of Molybdenum Hexacarbonyl and Poly(vinylamine) in the Glassy State	29
D. Quantum Mechanical Model Parameters and Trigonal Bipyramid 5-Coordinate d^6 Complexes of Molybdenum Hexacarbonyl and Poly(vinylamine) with D_{3h} Symmetry Above T_g	29
E. Square Pyramid 5-Coordinate d^6 Complexes of Molybdenum Hexacarbonyl and Poly(vinylamine) with C_{4v} Symmetry Above T_g	31
F. Pentagonal Planar 5-Coordinate d^6 Complexes of Molybdenum Hexacarbonyl and Poly(vinylamine) with D_{5h} Symmetry Above T_g	32
G. Ligand Field Stabilization of 5-Coordinate d^6 Complexes of Molybdenum Hexacarbonyl and Poly(vinylamine) Above T_g	33
VI. Cobalt, Nickel, and Ruthenium Complexes with Poly(4-vinylpyridine) and Poly(L-histidine) that Exhibit Reduced Symmetry in the Molten State	34
A. Polymeric Coordination Complexes with d-Block Salts	34
B. Ruthenium d^6 Complexes	37
C. Cobalt d^7 Complexes	37
D. Nickel d^8 Complexes	38
E. d-Orbital Energies for Five-Coordinate Complexes above T_g	38
i. Trigonal Bipyramid d^n Complexes with D_{3h} Symmetry	38
ii. Square Pyramid d^n Complexes with C_{4v} Symmetry	39
iii. Pentagonal Planar d^n Complexes with D_{5h} Symmetry	39
F. Summary of LFSE Calculations for 5-Coordinate d^n Complexes	41

G. Stabilization of Metal d-Electrons in Mixed-Ligand Complexes	41
H. Consideration of Interelectronic Repulsion and Δ_0 When There is Ambiguity in the d-Electron Configuration for Complexes with Pseudo-Octahedral Symmetry	43
I. Correlation between T_g Enhancement and the Difference Between Ligand Field Stabilization Energies in the Glassy and Molten States	44
J. Tetrahedral Co^{2+} Complexes Below T_g and 3-Coordinate Complexes in the Molten State	46
VII. Total Energetic Requirements to Induce the Glass Transition via Consideration of the First-Shell Coordination Sphere in Transition Metal and Lanthanide Complexes	48
A. Density Functional Estimates of Metal–Ligand Bond Dissociation Energies	48
B. The Energetics of Ligand Dissociation Reactions in Model Systems; Comparison with Experimental T_g Enhancements for d-Block and f-Block Complexes	49
VIII. Summary	50
IX. Acknowledgments	51
X. References	51
2. Metal Oxide Clusters as Building Blocks for Inorganic–Organic Hybrid Polymers	55
<i>Ulrich Schubert</i>	
I. Introduction	56
II. Synthesis of Organically Modified Transition Metal Oxide Clusters	58
A. Postsynthesis Modification of Pre-Formed Metal Oxide Clusters	59
B. In Situ Modification	59
III. Synthesis and Structural Characterization of the Cluster-Reinforced Polymers	63
IV. Properties of the Cluster-Based Hybrid Polymers	67
V. Summary	69
VI. Acknowledgments	69
VII. References	70
3. Metal-Containing Polydyes	73
<i>Charles E. Carraher Jr.</i>	
I. Introduction	73
II. Group IVB–Containing Polydyes	74
III. Ruthenium-Containing Polydyes	80
IV. Hematoporphyrin-Containing Polydyes	82

V. Summary	85
VI. References	85
4. Metallopolymer Nanocomposite-Macromolecular Metallocomplexes as Precursors for Polymers, Polymer Inorganics, and Bionanocomposites	87
<i>A. D. Pomogailo</i>	
I. Introduction	89
II. General Characteristics, Classification of Nanoparticles by Size, Structural Organization, and Dimensional Phenomena	91
III. Problems of Stabilization of Metal Nanoparticles by Polymers	102
IV. Basic Considerations of the Combinations of Macromolecules and Metals	108
V. Typical Formation Processes and the Structure of Nanometric Metal Particles in Polymers	113
A. Technique of the Atomic Metal Evaporation	113
B. Preparation of Polymer-Immobilized Nanoparticles by Plasma Polymerization	117
C. Preparation of Metal Sols in Polymers by the Thermal Decomposition of Precursor Compounds	120
D. Synthesis of Polymer-Immobilized Nanoparticles by Reductive Methods	128
E. Electrochemical Methods for Preparing Polymer-Immobilized Nanoparticles	132
F. Preparation of Polymer-Immobilized Nanoparticles During Polymerization (Polycondensation) Stage	133
VI. Preparation of Hybrid Nanocomposites by the Sol-Gel Method	135
VII. Sol-Gel Preparation of Nanohybrid Multimetallic Materials	148
VIII. Intercalation of Polymers Into Porous and Layered Nanostructures	158
IX. Metal Chalcogenide-Polymer Inclusion Nanocomposites	166
X. Metallopolymeric Langmuir-Bidgett Films–Self-Organized Hybrid Nanocomposites	169
XI. Nanometer-Size Particles, Clusters, and Polynuclear Structures Immobilized in Biopolymers and Their Analogs	174
A. The Formation of Metallobiopolymeric Systems	175
B. Polynuclear Metalloenzymes as Components of Nanobiocomposites	181
C. Preparation of Template Synthetic Nanobiocomposites by the Sol-Gel Method	182
XII. Application of Polymer-Immobilized Metal Nanoparticle and Metal Cluster Nanocomposites	185
A. Modification of Polymer Matrices by Nanoparticles	186
B. Electrical and Magnetic Properties	188

C. Polymer-Immobilized Nanoparticles as Optical Materials and Semiconductors	190
D. Catalysis Using Polymer-Immobilized Nanoparticles and Clusters	192
XIII. Conclusion	195
XIV. Acknowledgments	197
XV. References	198
Index	221

Preface

Nanostructured materials have appeared in nature since the beginning of time. The driving force toward the use of nanomaterials is that they offer new properties or enhanced properties that are unobtainable with traditional bulk materials. Along with lightweight, high strength-to-weight features and small size, new properties are emerging because of the very high surface area-to-mass ratios present. These ratios determine where surface atomic and molecular interactions become critical. A definition of nanomaterials is when at least one phase dimension is on the order of 1 to 100 nm. Single linear polymer molecules are nanomaterials since the diameter of a single chain is within this range. Thus, efforts are underway to synthesize single-chain molecular conductors of electrons, light and self-assembled catalysts, and nanocomposites. Metal-containing polymers are at the heart of many of these efforts. The current volume reviews several important areas involved in the nanorevolution.

Series Preface

Most traditional macromolecules are composed of less than 10 elements (mainly C, H, N, O, S, P, Cl, 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.

Alaa S. Abd-El-Aziz
Charles E. Carraher Jr.
Charles U. Pittman Jr.
Martel Zeldin

CHAPTER 1

Nanocluster Assemblies and Molecular Orbital Interactions in Macromolecule-Metal Complexes

Laurence A. Belfiore and Sarah E. Fenton

*Colorado State University, Department of Chemical Engineering,
Polymer Physics and Engineering Laboratory, Ft. Collins, Colorado*

CONTENTS

I. INTRODUCTION	3
II. METHODOLOGY OF TRANSITION METAL COORDINATION IN POLYMERIC COMPLEXES	4
A. Polymeric Coordination Complexes with d-Block Salts that Exhibit an Increase in T_g	4
B. Chemical Bonding, Coordination, and Transition Metal Compatibilization	5
i. Ligand Field Stabilization Energy Description of the Enhancement in T_g for Polymeric Complexes with Transition Metals	6
ii. Energetic Ligand Field Models and the Methodology of Transition Metal Coordination	8
C. Well-Defined Low-Molecular-Weight Transition Metal Complexes that Increase T_g	9
D. Attractive Polymeric Ligands	10
E. Identifying Attractive Interactions via Hard and Soft Acids and Bases	10

*Macromolecules Containing Metal and Metal-Like Elements,
Volume 7: Nanoscale Interactions of Metal-Containing Polymers,*
edited by Alaa S. Abd-El-Aziz, Charles E. Carraher Jr., Charles U. Pittman Jr.,
and Martel Zeldin. Copyright © 2006 John Wiley & Sons, Inc.

F. Displacement of Weak Neutral Bases in the First-Shell Coordination Sphere by Stronger Bases	11
i. Anionic Ligands are the Last Ones that Should Be Displaced to the Second Shell	13
G. Complexes with the Same Local Symmetry Above and Below the Glass Transition	14
i. Complexes with Reduced Symmetry Above T_g	14
H. Consideration of Interelectronic Repulsion and Ligand Field Splitting When There Is Ambiguity in the d-Electron Configuration	15
III. JØRGENSEN'S PARAMETRIC REPRESENTATION OF LIGAND FIELD SPLITTING AND INTERELECTRONIC REPULSION	18
A. Polymeric Complexes with Enhanced Glass-Transition Temperatures	19
B. Polymeric Complexes with Reduced Glass-Transition Temperatures	20
C. Other Considerations	20
IV. PSEUDO-OCTAHEDRAL d^8 NICKEL COMPLEXES WITH POLY(4-VINYLPYRIDINE)	20
A. Ligand Field Stabilization Energies	20
B. Coordination Crosslinks vs. Coordination Pendant Groups	22
C. Ligand Field Model of the Glass Transition in Macromolecule–Metal Complexes	24
D. Linear Least Squares Analysis of $\Delta(\text{LFSE})$ via the Concentration Dependence of T_g in P4VP/ Ni^{2+} Complexes, Subject to the Constraint that $\beta \leq 1$	26
V. d^6 MOLYBDENUM CARBONYL COMPLEXES WITH POLY(VINYLAMINE) THAT EXHIBIT REDUCED SYMMETRY ABOVE THE GLASS-TRANSITION TEMPERATURE	27
A. Experimental Results	27
B. Ligand Field Splitting Parameters for Molybdenum Hexacarbonyl	28
C. Ligand Field Stabilization for Complexes of Molybdenum Hexacarbonyl and Poly(vinylamine) in the Glassy State	29
D. Quantum Mechanical Model Parameters and Trigonal Bipyramid 5-Coordinate d^6 Complexes of Molybdenum Hexacarbonyl and Poly(vinylamine) with D_{3h} Symmetry Above T_g	29
E. Square Pyramid 5-Coordinate d^6 Complexes of Molybdenum Hexacarbonyl and Poly(vinylamine) with C_{4v} Symmetry Above T_g	31
F. Pentagonal Planar 5-Coordinate d^6 Complexes of Molybdenum Hexacarbonyl and Poly(vinylamine) with D_{5h} Symmetry Above T_g	32
G. Ligand Field Stabilization of 5-Coordinate d^6 Complexes of Molybdenum Hexacarbonyl and Poly(vinylamine) Above T_g	33

VI. COBALT, NICKEL, AND RUTHENIUM COMPLEXES WITH POLY(4-VINYLPYRIDINE) AND POLY(L-HISTIDINE) THAT EXHIBIT REDUCED SYMMETRY IN THE MOLTEN STATE	34
A. Polymeric Coordination Complexes with d-Block Salts	34
B. Ruthenium d^6 Complexes	37
C. Cobalt d^7 Complexes	37
D. Nickel d^8 Complexes	38
E. d-Orbital Energies for Five-Coordinate Complexes above T_g	38
i. Trigonal Bipyramid d^n Complexes with D_{3h} Symmetry	38
ii. Square Pyramid d^n Complexes with C_{4v} Symmetry	39
iii. Pentagonal Planar d^n Complexes with D_{5h} Symmetry	39
F. Summary of LFSE Calculations for 5-Coordinate d^n Complexes	41
G. Stabilization of Metal d-Electrons in Mixed-Ligand Complexes	41
H. Consideration of Interelectronic Repulsion and Δ_0 When There Is Ambiguity in the d-Electron Configuration for Complexes with Pseudo-Octahedral Symmetry	43
I. Correlation between T_g Enhancement and the Difference Between Ligand Field Stabilization Energies in the Glassy and Molten States	44
J. Tetrahedral Co^{2+} Complexes Below T_g and 3-Coordinate Complexes in the Molten State	46
VII. TOTAL ENERGETIC REQUIREMENTS TO INDUCE THE GLASS TRANSITION VIA CONSIDERATION OF THE FIRST-SHELL COORDINATION SPHERE IN TRANSITION METAL AND LANTHANIDE COMPLEXES	48
A. Density Functional Estimates of Metal–Ligand Bond Dissociation Energies	48
B. The Energetics of Ligand Dissociation Reactions in Model Systems; Comparison with Experimental T_g Enhancements for d-Block and f-Block Complexes	49
VIII. SUMMARY	50
IX. ACKNOWLEDGMENTS	51
X. REFERENCES	51

I. INTRODUCTION

When transition metal cations from the d-block of the Periodic Table coordinate to ligands in the sidegroup of a polymer and modify the thermal response of a macromolecular complex, the enhancement in the glass-transition temperature (T_g) can be explained by focusing on ligand field stabilization¹ of the metal d-electrons. The methodology to identify attractive coordination complexes and predict relative

increases in T_g is described in terms of the local symmetry of the complex, molecular orbital energies, and the d-electron configuration.² Interelectronic repulsion is considered for pseudo-octahedral d^6 and d^7 complexes in the glassy state when there is ambiguity in the order in which the d-orbitals are populated. Ligand field stabilization energies are calculated for simple octahedral geometries and 5-coordinate complexes with reduced symmetry, such as square pyramidal, trigonal bipyramidal, and pentagonal planar, in molybdenum hexacarbonyl complexes with poly(vinylamine) above and below the glass-transition temperature. If pseudo-octahedral transition metal complexes bridge two different macromolecules in the glassy state via coordination crosslinks, then 5-coordinate complexes with one surviving metal-polymer bond above T_g represent reasonable geometries in the molten state. This model of thermochemical synergy in macromolecule-metal complexes with no adjustable parameters considers the glass transition as an endothermic process in which sufficient thermal energy must be supplied to dissociate intermolecular bridges or coordination crosslinks and produce coordinatively unsaturated molten state complexes. The enhancement in T_g correlates well with the difference between ligand field stabilization energies in the glassy and molten states for Ru^{2+} (d^6), Co^{2+} (d^7), and Ni^{2+} (d^8) complexes with either poly(4-vinylpyridine) or poly(L-histidine).² Larger relative increases in T_g are measured in complexes with the synthetic poly(α -amino acid) relative to those with poly(4-vinylpyridine). Poly(vinylamine) complexes with cobalt chloride hexahydrate³ and several lanthanide trichloride hydrates^{4,5} exhibit some of the largest increases in the glass-transition temperature that have been measured to date.

II. METHODOLOGY OF TRANSITION METAL COORDINATION IN POLYMERIC COMPLEXES

A. Polymeric Coordination Complexes with d-Block Salts that Exhibit an Increase in T_g

It is well known that organic plasticizers decrease a polymer's glass-transition temperature,⁶ as described by previous researchers via entropy continuity, volume continuity, free volume concepts,⁷ and the conformational entropy description⁸ of T_g when flexible diluents are employed. The glass-transition temperature is depressed more at higher diluent concentrations until phase separation occurs. Hence inexpensive brittle polymers can be used in applications that require more flexible and compliant materials if miscible plasticizers are available to lower the glass-transition temperature. When additives *increase* a polymer's T_g , explanations are based on the existence of specific interactions and the formation of molecular complexes or nanoclusters, because one does not typically employ diluents with glass-transition temperatures that are higher than that of the undiluted polymer. Complexation between amorphous polymers and transition metal salts are operative in organic-inorganic hybrids that exhibit enhanced glass-transition temperatures relative to T_g of the undiluted polymer.⁹ Chain mobility is hindered when transition metals coordinate to favorable ligands in the polymer's sidegroup via acid-base interactions. Coordination pendant

groups form when p-orbitals of the ligand with comparable energy and the same symmetry properties as d-orbitals of the metal form σ -bonds. If one functional sidegroup in the polymer occupies a vacant site in the first-shell coordination sphere of the metal center, then T_g increases by 10–30°C relative to the undiluted polymer.¹⁰ This occurs, for example, in poly(4-vinylpyridine) complexes with zinc acetate dihydrate.^{10,11} Coordination crosslinks occur when the transition metal forms σ -bonds with at least *two* functional sidegroups on different polymer chains.³ These interactions should produce mobility restricting nanoclusters in the polymeric matrix. Figure 1 illustrates two modes of complexation between macromolecules and metal cations, denoted by M ; intrachain coordination (upper left) vs. interchain coordination (lower left). Mixed-mode coordination is illustrated on the right side of the figure.

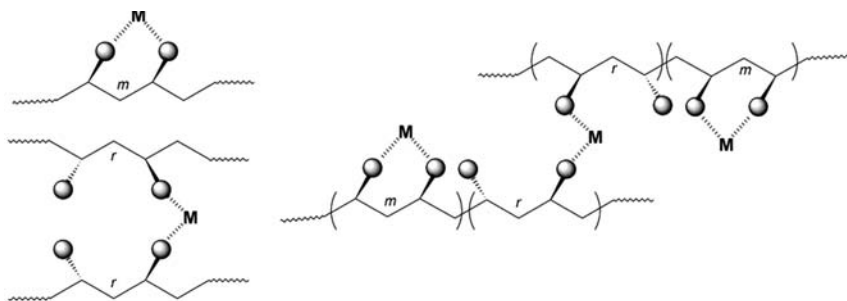


Figure 1 Intrachain vs. interchain coordination of metal centers to functional sidegroups in linear polymers.

It seems reasonable that the glass-transition temperature should experience larger enhancements when a single metal center coordinates to more functional sidegroups in several different polymer chains,³ analogous to multifunctional crosslinking agents. The overall objectives of this chapter are to estimate differences between electronic energies of d^n configurations for macromolecule–metal complexes in the glassy and molten states, and correlate these d-electron energy differences with enhancements in the glass-transition temperature.

B. Chemical Bonding, Coordination, and Transition Metal Compatibilization

Divalent late transition metals like cobalt (d^7), nickel (d^8), and copper (d^9) in the first row of the d-block can use five 3d orbitals, one 4s orbital, and three 4p orbitals to form 4-, 5-, or 6-coordinate complexes.¹² As a general rule, if there are N ligands in the first-shell coordination sphere of a transition metal complex, then there should be N bonding molecular orbitals, N anti-bonding molecular orbitals, and $9-N$ nonbonding molecular orbitals.¹² Exceptions to this rule occur in some square–planar complexes in which three orbitals with the same symmetry properties overlap and form chemical bonds.¹³ Usually, some coordination sites in the first-shell of the

metal center are occupied by neutral ligands such as waters of hydration, acetonitrile, benzonitrile, or carbon monoxide (i.e., $C\equiv O$). Anionic ligands in rather close proximity to the metal cation are required for charge neutrality. Pyridine ligands in poly(4-vinylpyridine), and copolymers that contain 4-vinylpyridine repeat units, coordinate to divalent zinc, copper, nickel, cobalt, and ruthenium.^{9,11} Alkene ligands in the mainchain or sidegroup of diene polymers, such as polybutadiene and polyisoprene, coordinate to palladium(II) and platinum(II), but not nickel(II).¹⁴⁻¹⁷ The imidazole ring in the histidine sidegroup of the synthetic poly(α -amino acid), poly(L-histidine), coordinates to divalent cobalt, nickel, copper, ruthenium, and palladium.^{18,19} One of the most attractive applications of this technology is transition metal compatibilization of polymers that are immiscible in the absence of the inorganic component. Complexation will induce miscibility if the transition metal center acts as a bridge between two dissimilar chains by coordinating to appropriate ligands in the sidegroup of both polymers. This has been demonstrated for copolymer blends^{9,11} of styrene/4-vinylpyridine and 4-vinylpyridine/butylmethacrylate. The proposed structure of this miscible ternary system is illustrated in Figure 2. Nickel acetate tetrahydrate and cobalt chloride hexahydrate function as transition metal compatibilizers and produce miscible 4-vinylpyridine copolymer blends. Dichlorobis(acetonitrile) palladium(II) compatibilizes diene polymer blends, such as atactic 1,2-polybutadiene with atactic 3,4-polyisoprene¹⁵ and 1,2-polybutadiene with cis-polybutadiene²⁰ via high-temperature palladium-catalyzed chemical crosslinking. Palladium(II) also compatibilizes 3,4-polyisoprene and (1) lightly sulfonated polystyrene, with or without Zn^{2+} neutralization of the sulfonic acid groups;²¹ and (2) random copolymers of ethylene and methacrylic acid.²¹ Tetrakis(triphenylphosphine)palladium(0) compatibilizes 1,2-polybutadiene with poly(4-bromostyrene)²² via a macromolecular analog of the Heck reaction (e.g., oxidative addition followed by olefin coordination, migratory insertion, and β -hydrogen elimination).²³

i. Ligand Field Stabilization Energy Description of the Enhancement in T_g for Polymeric Complexes with Transition Metals

When transition metals coordinate to ligands in the mainchain or sidegroup of amorphous polymers and modify the thermal response of a macromolecular complex, the enhancement in T_g is based on the well-known correlation of lattice enthalpies of hexa-aqua transition metal complexes from the first row of the d-block with octahedral ligand field stabilization energies if these complexes exhibit high-spin, weak-field electronic configurations.^{12,24} In complexes with octahedral or tetrahedral symmetry, if the energy difference between two nondegenerate metal-based d-orbitals is smaller than the repulsive energy that electrons experience when they are paired with opposite spin in the same orbital, then the electronic configuration is described as high-spin in a weak ligand field.¹² If one considers the increasingly exothermic enthalpy of formation^{12,24} of divalent hexa-aqua transition metal complexes (i.e., $M^{2+}(H_2O)_6$) as a function of the number of d-electrons from calcium (d^0) to zinc (d^{10}), then the additional exothermic effect relative to linear trends from Ca^{2+} to Mn^{2+} and Mn^{2+} to Zn^{2+} (Fig. 3) correlates with the stabilization of metal d-electrons for octahedral complexes in the first row of the d-block that exhibit weak-field

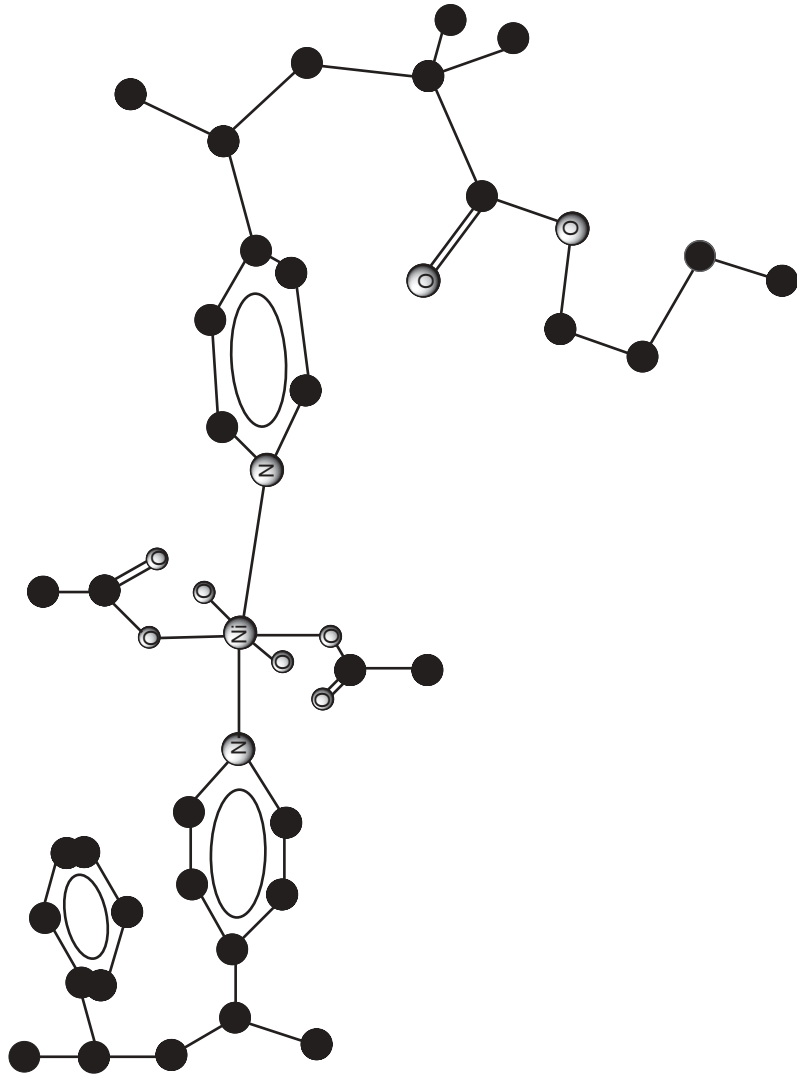


Figure 2 Molecular model showing the concept of transition metal compatibilization of two immiscible vinylpyridine copolymers. The octahedral bonding characteristics of nickel acetate tetrahydrate, together with its previously published crystal structure,^{37,38} are used to postulate the structure of the amorphous polymeric coordination complex. It is proposed that the divalent metal salt sheds two hard-base waters of hydration and coordinates to pyridine sidegroups in copolymers of styrene with 4-vinylpyridine (i.e., on the left) and butylmethacrylate with 4-vinylpyridine (i.e., on the right).