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

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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

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A. D. Pomogailo

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, 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.

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

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and Martel Zeldin.

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 stabilization[1] 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 hexahydrate[3] 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 description[8] 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.

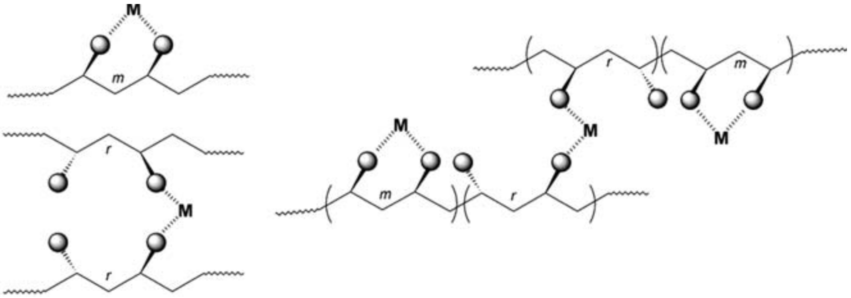

Figure 1 Intrachain vs. interchain coordination of metal centers to functional sidegroups in linear polymers.

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≡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-polyisoprene[15] and 1,2-polybutadiene with cis-polybutadiene[20] 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

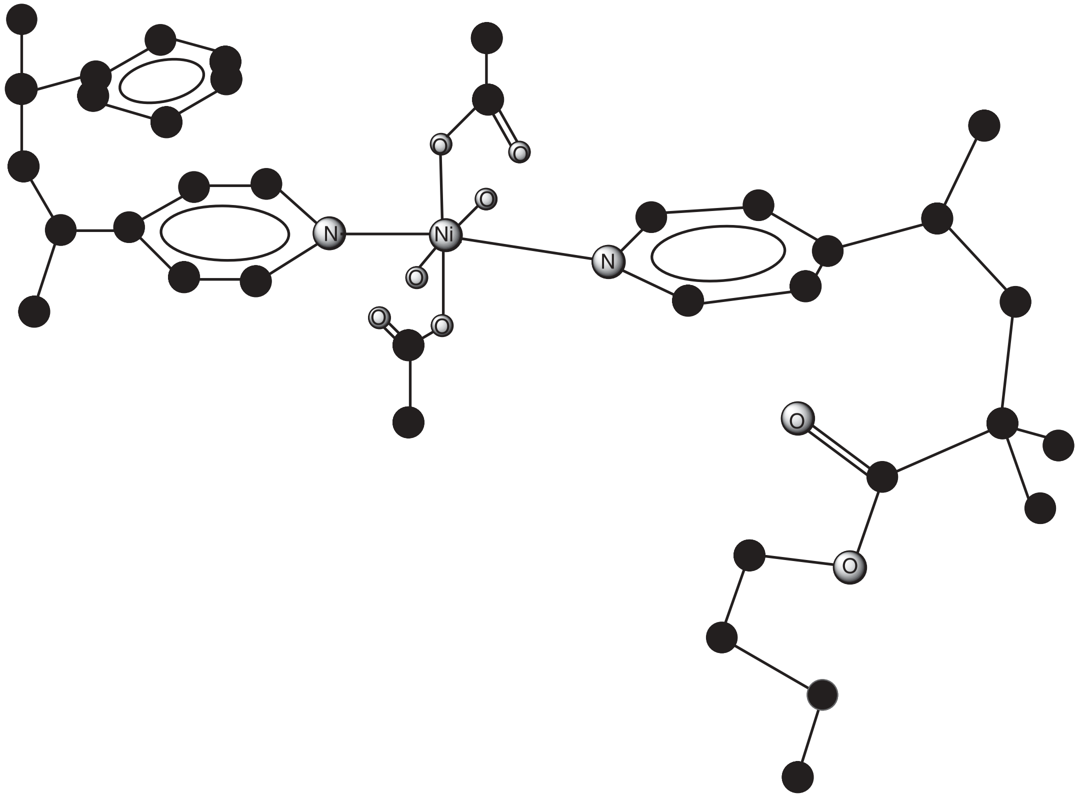

Figure 2 Molecular model showing the concept of transition metal compatibilization of two immiscible vinylpyridine copolymers. The octahedral bonding characteristics of nickel acetate tetrahydrate, together with its previously published crystal structure,[37,38] are used to postulate the structure of 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).