Macromolecules Containing Metal and Metal-Like Elements

Volume 4

Group IVA Polymers

Edited by

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Preface

The Group IVA elements represent the most dramatic transition from non-metallic (carbon), to metal-like (silicon and germanium), to metallic (tin and lead) of any family. Organosilicon polymers are the most widely used metal-like materials and organotin compounds are the most frequently employed organometallic materials. Polysiloxanes are widely utilized as biomaterials while organotin compounds are widely employed because of their bioactivity. Polysilanes, polygermanes, and polystannanes are being increasingly investigated because of their unique conducting properties. This volume contains comprehensive review chapters covering germanium, tin, and lead polymers as well as reviews that illustrate the breadth of materials offered by polymers containing Group IVA metals and metal-like elements. Material referring to Group IVA containing polymers, including silicon, was previously covered in Volume 1 of this series. A future volume will focus on silicon-containing macromolecules.

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Charles U. Pittman, Jr.
Martel Zeldin

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 larger 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

Overview-Group IVA Polymers

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I. INTRODUCTION

The chemistry of Group IVA (Group 14) organometallic monomeric[1–17] and polymeric[18–24] species has been described in great detail. Reaction mechanisms for these elements have also been described.[1,2]

The trend in chemical Group IVA behavior from nonmetallic to metallic elements is clearly evident in Group IV.[3] Carbon is non-metallic. Silicon and germanium are metalloids, and their monomers and polymers represent bridges in behavior between those of metallic tin and lead and those of non-metallic carbon. While this trend from non-metallic to metallic behavior is significant from the lighter to the heavier elements in this family, there is probably no more dramatic change than that between carbon and silicon. Generally, carbon is unable to expand its valence shell beyond the octet; however, the other elements in the family are know to experience hypervalency, presumably owing to the availability of valence shell *d* orbitals in Si and Ge and *d* and *f* orbitals for Sn and Pb, which are able to accept electrons from nucleophiles.

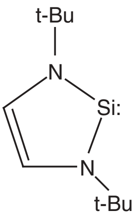
Significantly, the tendency toward catenation decreases precipitously from carbon to lead, which is evidenced by the existence of an enormous number of linear and branched polyalkanes, numerous polysilanes, some polygermanes, a few polystannanes, and no polyplumbanes. This behavior has been explained partially in terms of the decreasing strength of the catenated bond: i.e., C–C = 347 kJ/mol, Si–Si = 220 kJ/mol, Ge–Ge = 170 kJ/mol, and Sn–Sn = 150 kJ/mol, and other thermodynamic and kinetic considerations. Furthermore, the strength of single bonds between the Group IV and the other elements also decreases from the lighter to the heavier elements (Table 1), which to some extent parallels the covalent character of these bonds.

While most of the compounds of the Group IV elements are tetravalent, the trend toward divalency increases with atomic number. For example, stable C(II) compounds are unknown; however, Moser et al.[26] have recently prepared and identified a stable divalent silicon species, **1**. This subject has been reviewed.[27]

Table 1 Electronegativities, Covalent Radii, and Some Mean Bond Energies[a] (kJ/mol) for Group IV Elements

Element	C	Si	Ge	Sn	Pb
Electronegativity (Pauling)	2.54	1.90	2.01	1.96	2.33
Covalent Radius, nm	0.077	0.117	0.122	0.141	0.154
M–H	412	318	310	300	—
M–C	347	301	242	—	—
M–Cl	338	401	339	314	—
M–Br	276	310	280	270	—
M–I	238	230	210	190	—
M–O	360	466	—	540	—

[a] Mean bond energies are taken from several sources.[25]



1

There is a difference between coordination number and oxidation number. For example, the general tendency is for tin in organotin compounds to have a formal oxidation number of 4. Nevertheless, it is common for inorganic and organotin compounds to have coordination numbers of 4, 5, and 6, with 4 and 6 prevailing. Furthermore, Sn(IV) compounds are more apt to form cations through ionization. Another trend for Sn(IV) compounds is their tendency in the solid state to form supramolecules in which the connective lengths between various units approximate internal covalent bonds, which qualify them as covalently bonded species that form linear, two-, and three-dimensional arrays. A similar tendency has been observed for the other non-carbon Group IV elements with an order $Pb > Sn > Ge > Si$ that is related, at least in part, to the larger atoms being more capable of attracting neighboring atoms over a longer distance.[1–4]

While carbon readily forms (p-p) π multiple bonds with itself and other elements, this phenomenon is not achieved with the other Group IV elements beyond silicon. However, (d-p) π bonding does appear to occur for Si, Ge, and Sn. Thus for polymers such as polysiloxanes and polysilazanes unshared electrons on oxygen or nitrogen appear to "backbond" to the *3d* orbitals of silicon. This multiple bond character in Si–O and Si–N may play a significant role in the thermodynamic stability of these species. The use of vacant *d* orbitals is also indicated by some substitution reactions involving nucleophilic attack on tetrahedral metal atoms sites. For Si and Ge, reaction mechanisms analogous to the dissociative (e.g., S_N1) mechanisms in carbon compounds do not seem to occur readily. Rather, many Group IV organometals and organometalloids undergo substitution reactions via the associative pathway, which involves the formation of, for example, a five-coordinate transition state.[1,2] This subject has been recently reviewed by Eaborn.[2b] In general, most experimental and theoretical data are consistent with an order of availability of outer *d* orbitals of $Pb > Sn > Ge > Si$ so that the larger metals are more apt to form 5- or 6-membered complexes (or transition states) as a prelude to associative interchanges.[1–4]

Hydrolysis of various silicon and germanium halides forms the synthetic basis for the formation of well-defined polysiloxanes and polygermoxanes. Most organolead halides are insoluble in water and are not as susceptible to hydrolysis. Organotin halides are often resistant to hydrolysis because of their general hydrophobic nature. Thus dibutyltin dichloride can be set in boiling water for hours with little indication that hydrolysis; however, hydrolysis does occur on addition of a wetting solvent such as dimethyl sulfoxide (DMSO) or acetone. In such reactions, compounds with amazing structural diversity have been identified and characterized.[28]

II. GROUP IV POLYMERS

The order of commercial importance of Group IV metal-containing polymers is $Si \gg Sn \gg Ge > Pb$.[18–24] Although by number there are more organotin compounds used industrially, polysiloxanes represent the largest bulk use and net worldwide sales for organometallic polymers. Lead-containing polymers rank last in the Group IV series, owing to the lack of solubility of suitable monomers and, of course, their toxicity.

A general introduction of silicon-, germanium-, tin- and lead-containing polymers is presented in Chapter 6 of Volume 1 in this series.[19] A more extensive treatment of organogermanium, organotin, and organolead polymers is presented in this volume in Chapter 9, Chapter 10, and Chapter 11, respectively. The remainder of this volume (Chapters 2–8) focuses attention of special aspects and new developments in silicon-containing polymers.

Specifically, Chapter 2, by Zheng et al., is a discussion of the design and synthesis of a variety of soluble and thermally stable hyperbranched poly(silylenearylene)s via catalytic alkyne polycyclotrimerization reaction. Organosilicon hyperbranched polymers are promising candidates as functional ceramics, degradable templates, and high-temperature elastomers. The particular poly(silylenearylene)s prepared and discussed by the authors not only exhibit efficient photoluminescence with high quantum yields ($\sim$98%) but also display significant non-linear optical properties. In Chapter 3, Lam et al. discuss the synthesis, photoluminescence (aggregation-induced emission in poor solvents), and fabrication of light-emitting diodes of silole-containing conjugated polymers. In Chapter 4, Rosenberg provides a review of the synthesis, characterization, and study of the metal sequestering-ability of silica-polyamine composites. These materials can be used for metal ion recovery and remediation. Rosenberg evaluates these new composite materials in metal recovery from acid mine drainage, solvent extraction raffinates, and acid ore leaches.

Chapter 5 is a review of polyhedral oligomeric silsesquioxanes (POSS), hybrid POSS-organic copolymers, and POSS resin nanocomposites. Although silsesquioxanes have been known since the 1960s, only recently, through controlled synthesis and purification, have their structure and unique properties been determined and their useful applications been explored. This chapter is complemented by a discussion of the synthesis and properties of silica- and silsesquioxanes-containing polymer nanohybrids in Chapter 6. Chapter 7 involves a review of the preparation and characterization of siloxane-based polyviologens, polyurethanes, and divinylbenzene elastomers.

In Chapter 8, Patwardhan and Carlson delve into the use of proteins extracted from plants, such diatoms, grasses, and sponges, for the in vitro precipitation of silica from silica precursors (e.g., tetraalkoxysilanes). Thus the extracted proteins serve as catalysts, templates, and/or scaffolds for the bioinspired synthesis of silica networks. The resulting spherical and non-spherical micro- and nano-size bioinspired silicas are compared using, for example, SEM techniques.

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