Macromolecules Containing Metal and Metal-Like Elements

Volume 8

Boron-Containing Polymers

Edited by

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Preface

Boron has been known as an element since its discovery in 1808 by Davy, Gay-Lussac, and Thenard, but it was not purified until 1909. The first polymers containing boron were synthesized by Stock about 80 years ago. Since then there has been a growing number and variety of boron-containing polymers produced. The emphasis for much of the development of boron polymers involves boron's ability for delocalizing electrons because of the presence of an empty p orbital. Furthermore, boron's ability to capture neutrons and its ability to form protective coatings have been driving forces to produce polymers. Finally, boron polymers with high percentages of nitrogen and boron have been sought as precursors to the ceramic boron nitride and boron nitride fibers. This volume presents the state-of-the-art developments with respect to boron-containing polymers. It captures the explosive development of these important materials in the areas of ceramics, coatings, nanomaterials, catalysts, therapeutic agents, and especially electronic applications such as nonlinear optical and fluorescent light-emitting materials. The chapters give supportive and historical developments that allow a person unfamiliar with boron polymers to appreciate and understand the topics presented. Practical application of boron-containing materials is also emphasized. Thanks to the efforts of the leading scientists in the fields represented, the full range of activity is included in this volume.

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 lenses, 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 are 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 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.
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CHAPTER 1

The State of the Art in Boron Polymer Chemistry

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Volume 8: Boron-Containing Polymers, edited by Alaa S. Abd-El-Aziz,
Charles E. Carraher Jr., Charles U. Pittman Jr., and Martel Zeldin.

I. INTRODUCTION

A. A Brief Historical Perspective on Boron and Its Polymers

Boron (*Buraq* in Arabic/*Burah* in Persian, which is the word for "white," the color being attributed to borax (sodium tetraborate, $Na_2B_4O_7.10H_2O$)) was discovered in 1808 independently by the British Chemist, Sir Humphry Davy, and two French chemists, Joseph Louis Gay-Lussac and Loius Jacques Thenard.[1] They isolated boron in 50% purity by the reduction of boric acid with sodium or magnesium. The Swedish chemist Jons Jakob Berzilius identified boron as an *element* in 1824. The first pure sample of boron was produced by the American chemist William Weintraub in 1909. Boron does not appear in nature in elemental form, but is found in its compounded forms of borax, boric acid, colemanite, kernite, ulexite, and borates. In ancient times, compounds of borax ores known as tincal were exported from Tibet. Historically, boron is known to have been used for refining gold and silver in Arabia, for ceramic glazes in China, and for embalming in Egypt. Egyptians are known to have used the salt natron, which contains borates along with other common salts such as sodium bicarbonate, and sodium chloride in the mummification process. Marco Polo is believed to have brought natron to Italy where it was used by the artisans of the time.[2]

The United States and Turkey are the world's largest producers of boron.[1] Economically important sources are from the ores rasorite (kernite) and tincal, which are both found in the Mojave Desert of California, with borax being the most important source there. The famous "20-Mule-Team Borax," now a part of chemistry folklore, originates from the time when teams of 20 mules used to haul colemanite from Furnace Creek in Death Valley 166 miles south to Mojave. Elemental boron in its impure form can be obtained by the reduction of the oxide B_2O_3 by magnesium, and in the pure form by the reduction of BCl_3 by hydrogen on hot filaments.[1]

Boron with an atomic number of 5 is electron deficient, possessing a vacant p orbital (one of the 2p orbitals) making it a good electrophile. In terms of hybridization of atomic orbitals, boron has three sp^2 hybridized orbitals pointing to the vertices of an equilateral triangle with its vacant p orbital positioned perpendicular to the plane of the equilateral triangle containing the sp^2 orbitals. Thus, compounds of boron often behave as Lewis acids, readily bonding with electron-rich substances to compensate for its electron deficiency. Boron, on reaction with hydrogen, is known to form clusters of borohydrides called boranes.[3] Borane clusters, wherein a few of the boron atoms have been substituted by carbon atoms, yield a class of compounds known as carboranes. Boron also exists in "inorganic benzene-like" ring systems such as borazine, boroxine, and triphosphatriborin with nitrogen, oxygen, and phosphorus, respectively. The element boron exists in nature in high abundance both as boron 10 and boron 11 isotopes, with the nucleus of the latter possessing one additional neutron.[2] Boron 10 nucleus is the only *light* element that is capable of binding a slow neutron (or thermal neutron) to yield an excited boron-11 nucleus.[2]

The first reports on the formation of boron polymers were from Alfred Stock in the 1920s on the generation of a boron hydride polymer during his pioneering studies on boron hydride (borane) chemistry.[4] He discovered that fairly complicated compounds analogous to hydrocarbons could be built up from boron and its hydrides. Following Stock's work, Herbert Schlesinger and Anton Burg raised the chemistry of boron hydrides to new heights.[5] Based on the aminoborane adducts ($R_3N{\cdot}B_2H_5$), with electron deficient bonds (or B—H—B three-centered bonds), obtained from amines such as NH_3 or $NHMe_2$ and diborane, Burg and co-workers explored the chemistry of similar diborane adducts with phosphine. Phosphine and diborane were found to yield the trimer $[(CH_3)_2PBH_2]_3$ (**1**) (Fig. 1), which was discovered to be stable when heated to 400°C, with little decomposition, and to reduction by sodium in liquid ammonia.[6] This result, originating from a project sponsored by the Office of Naval Research (ONR), was a serendipitous one, as the initial intent was to make highly water-reactive boron hydride derivatives that might be used to propel underwater torpedos much faster. From then on, ONR extensively supported the development of stable rubbers containing B—H bonds. Out of such efforts, the carboranosiloxane rubbers, renowned under the tradename DEXSIL, was engineered into existence by Heying and Schroeder at the Olin Laboratories in New Haven, Connecticut.[7] Burg and co-workers discovered that when the $(CH_3)_2PBH_2$ unit was made in the presence of a slight excess of base, a long open-chain compound with as many as 300 repeating units was formed. In anticipation of their high-temperature stability and flame retardancy, the exploration of polyphosphinoboranes, materials based on skeletons of alternating phosphorus and boron atoms, was undertaken in the 1950s and 1960s.[8] However, these pioneering forays could only produce products with low yields and low molecular weights.[9]

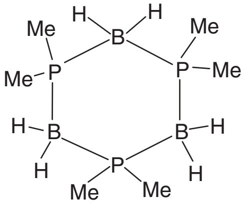

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Figure 1 The triphosphatriborin cyclic product $[(CH_3)_2PBH_2]_3$ **(1)** obtained from PMe_3 and B_2H_6. (Adapted from ref. 6.)

In their search for thermally stable polymers, the team of Schroeder and Heying at Olin Laboratories synthesized the first polymer (**2**) (Fig. 2) with P—O—P linkages containing the open boron cluster decaborane within the chain architecture (with a molecular weight of ca. 27,000) by the triethylamine-catalyzed condensation reaction between bis(chlorodiphenylphosphine)decaborane and bis(hydroxydiphenylphosphine)-decaborane.[10] The selection of boron as the primary element was based both on bond-strength considerations (after Burg's results) and its ability to form appropriate cluster compounds. Simultaneously, they synthesized a P—N═P (phosphonitrile) bonded decaborane polymer by the reaction of two difunctional monomers, a diphosphine and a diazide compound derived from diborane. Both of these thermally stable polymers were observed to flow during cross-linking through their dicarborane units. However, these materials were found to be unsuitable for use as molding compounds. Subsequently, in the interest of making elastomeric high-temperature rubbers, the Olin team focused its efforts on the synthesis of silylcarborane systems involving the icosahedral carboranes, *o*-, *m*-, and *p*-carborane.

In Olin's attempts to derivatize dilithiated products of *o*-carborane with chlorosilanes for further reaction with ammonia, it was observed that cyclic compounds, instead of polymers, were produced by the interaction of the substituents on the adjacent carbon atoms in the *o*-carborane units.[11] However, when a linear dimethoxy intermediate of *m*-carborane was reacted as an equimolar mixture with dichlorosilane in the presence of the catalyst $FeCl_3$, the quantitative evolution of CH_3Cl was observed producing a crystalline polymer, which Olin named as DEXSIL 200 (SiB-2) (**3**) (Fig. 2); (M.P. = 151°C).[12] Since the number of repeating units in these polymers was low (5–10 units), some siloxyl moieties with pendant 1-vinyl-*o*-carboranyl groups were introduced in these polymers to improve their curing characteristics, resulting in DEXSIL 201 (**4**) (Fig. 2).[13] DEXSIL 201, upon curing, was found to have a tensile strength of 100 to 150 psi and an elongation of 120 to 250%, both of which were improvable upon addition of selected fillers.[14] Subsequently, it was discovered that carborane polymers (**5**) (Fig. 2) containing tin bridges were amenable to synthesis with higher molecular weights than **3** or **4**. These polymers (with a M.P. of 250–255°C) were produced by the reaction of $(C_6H_5)_2SnCl_2$ with *m*-$B_{10}H_{10}C_2Li_2$ and contained up to 30 repeating units when formed in Decalin.[15] Continuing its quest for high-temperature polymers, the Olin team attempted the inclusion of *p*-carborane units in these polymers. When the dilithio salt of *p*-carborane was treated with diphenyltin chloride, the polymers were observed to form with an average chain length of only 11 repeating units melting in the 300–400°C range.[16]

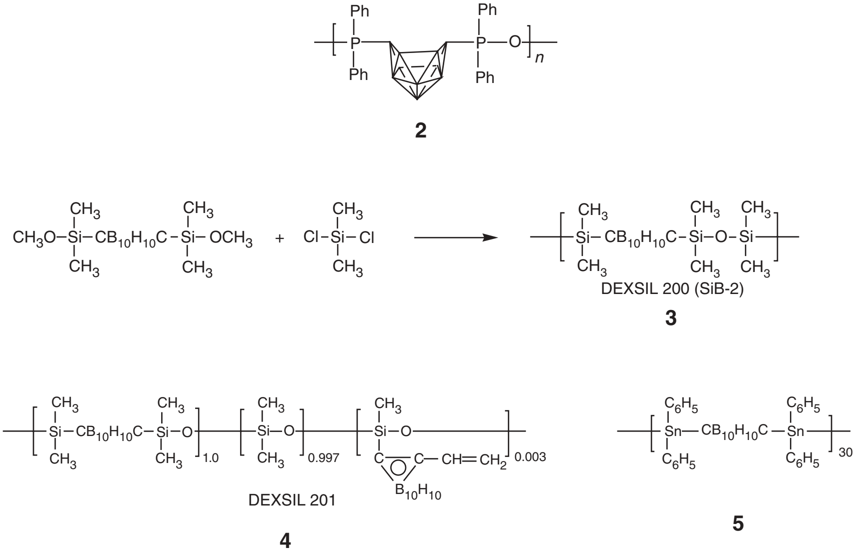

Figure 2 Schematic representations of the Olin polymers: **2** (with —P—O—P— linkages), **3** and **4** (DEXSIL carborane polymers), and **5** (carborane polymers with tin bridges). (Adapted from ref. 7.)

While the Olin efforts on the production of high-temperature polymers were centered mainly on $FeCl_3$-catalyzed condensation reactions, subsequent efforts from Union Carbide, Inc. utilized an aminosilane route and a ureidosilane route (Fig. 3) to synthesize carboranylenesiloxane polymers of high molecular weights. Using the former route, the polymer was produced by a condensation reaction between a carborane-disilanol and bis(dimethylamino)dimethylsilane, during which an expulsion of a dimethylamine by-product occurred.[17] In the latter route, the bis(dimethylamino) dimethylsilane reagent was replaced with a bisureidosilane monomer to yield phenyl urea as the by-product during the polymerization.[18] The aminosilane reaction had the advantage that it did not require a catalyst and was performable between −10 and 25°C. However, the molecular weights of the polymers synthesized by this route seldom exceeded 20,000. The low molecular weights were attributed to the scission of the backbone of the polymer by the dimethylamine by-product. The aminosilane route was abandoned and the ureidosilane route was seriously pursued. In the initial trials of the reaction, where the bisureidosilane monomers were prepared and utilized *in situ*, the molecular weights of the resulting polymers were found to be quite low. At the high polymerization temperature of 160–170°C, the carboranedisilanol underwent self-condensation, thereby causing the molecular weights of the polymers to drop. This self-condensation problem was circumvented by the development of a low-temperature, solution polycondensation reaction, that included the slow addition of the solid carboranedisilanol monomer into a solution of the bisureidosilane.[19] The molecular weights of the polymers obtained by this modified route were as high as 200,000. Subsequently, the synthesis of ultra-high molecular weight (molecular weight of several millions) carboranylenesiloxane polymers was achieved by the Union Carbide team by a modification of the low temperature ureidosilane procedure.[20]

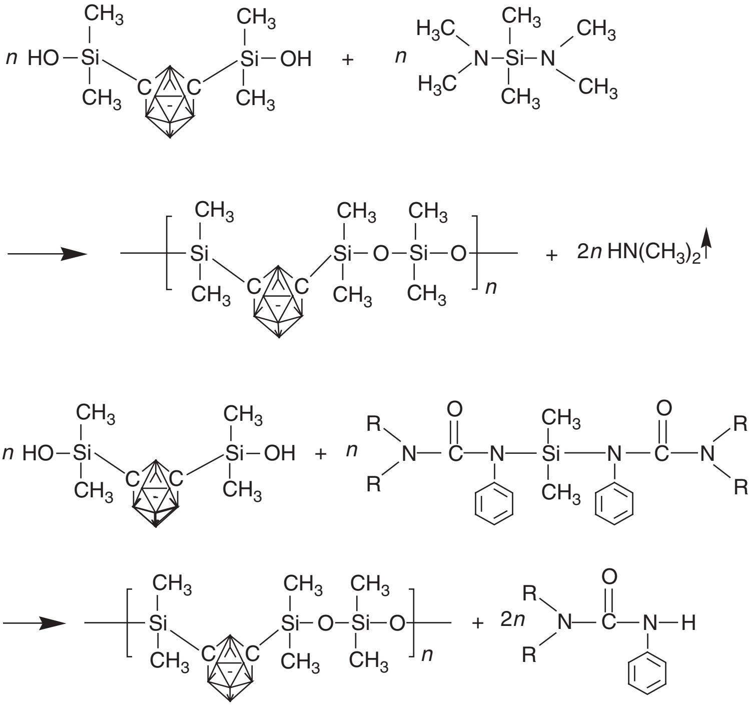

Figure 3 Reaction schemes for the aminosilane (top) and the ureidosilane (bottom) routes for the synthesis of carboranylenesiloxane polymers. (Adapted from ref. 23.)