# Inorganic and Organometallic Polymers

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# Inorganic and Organometallic Polymers

## Macromolecules Containing Silicon, Phosphorus, and Other Inorganic Elements

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# ACS Symposium Series

## M. Joan Comstock, *Series Editor*

# Foreword

The ACS SYMPOSIUM SERIES was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the Series parallels that of the continuing ADVANCES IN CHEMISTRY SERIES except that, in order to save time, the papers are not typeset but are reproduced as they are submitted by the authors in camera-ready form. Papers are reviewed under the supervision of the Editors with the assistance of the Series Advisory Board and are selected to maintain the integrity of the symposia; however, verbatim reproductions of previously published papers are not accepted. Both reviews and reports of research are acceptable, because symposia may embrace both types of presentation.

# Preface

THE FIELD OF INORGANIC-ORGANIC MACROMOLECULES is entering a phase of rapid development and change. For the past 20 years this area has grown steadily, mainly through fundamental studies by a small number of academic, government, and industrial scientists. Today, the burgeoning interest in this field is driven by the search for new high-performance materials and by the recognition that substances that combine the properties of organic polymers with those of inorganic solids can provide solutions to a wide range of hitherto intractable engineering problems. Thus, great interest is directed toward the electrical, photochemical, mechanical, and biomedical properties of the new polymers as well as their unusual behavior at low and high temperatures.

Polysiloxanes (silicones) began as a scientific curiosity in the 1930s, but their current widespread use in industrial and consumer applications is well-known. The recent emergence of polyphosphazenes, polysilanes, and organoelement-oxo polymers derived from the sol-gel process appears to be following a similar pattern—led first by long-range, fundamental, academic research, and then developed into an expanding technology by work in industrial and government laboratories. It is a stimulating experience to be a part of, or to follow, the current growth and expansion of this diverse field.

It is a direct consequence of the needs, opportunities, challenges, and broad interdisciplinary nature of the subject that prompted the symposium on which this book is based to survey the state of the art and current perspectives in inorganic and organometallic polymers. The contributions in this book fall into two categories: topical reviews and specialist reports by symposium participants and invited contributors. The topical reviews provide a thorough survey of a particular subject area and may also contain recent results from the authors' laboratories. The specialist contributions are shorter chapters that describe particularly exciting recent research progress. Together, the topical reviews and the specialist contributions provide an in-depth look into past accomplishments and currently stimulating new efforts.

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## Chapter 1

# An Introduction to Inorganic and Organometallic Polymers

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"Inorganic and organometallic" in the context of this Symposium is meant to describe macromolecules which usually contain inorganic elements in the chain and organic moieties as pendant groups. The subtitle delineates elements of primary focus: "Macromolecules Containing Silicon, Phosphorus and Other Inorganic Elements." The term "macromolecules" implies that the subject matter includes chain molecules that may be built up of repeat units, as well as more complex ring, branched, or crosslinked species (for example, see Organo-Oxo-Element Macromolecules Related to Sol-Gel Processes, and contributions by Murray (p. 408) or Seyferth (p. 143)).

Prior reviews concerning inorganic and organometallic macromolecules are contained in texts by Stone and Graham (1), Andrianov (2), Borisov (3), Allcock (4,5), and Voronkov (6), and volumes based on previous ACS symposia edited by Rheingold (7), and Carraher, Sheats and Pittman (8, 9). The present effort is topical in nature, and the order of presentation approximates that of the Symposium presentations.

The impetus for this symposium volume is the considerable progress which has been made in the last few years in inorganic and organometallic macromolecules. Totally new macromolecules have been brought into existence by the development of new synthetic methods or improvement of known synthetic routes. Thus, Neilson (p. 28 describes a new polymerization reaction that gives high molecular weight poly(diorganophosphazenes), $-(R_2PN)_n-$, in which organic pendant groups are bonded through P-C bonds. These polyphosphazene analogs of polysiloxanes were not previously accessible, and the development of structure-property relationships in this new subclass of macromolecules will no doubt yield important information and perhaps significant applications.

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Another example of interesting new inorganic polymers is found in the work of Lasocki (p. 166), who reports the synthesis of polysilazoxanes, $-[(R_2SiO)_x(R_2SiNR)_y]_n-$, and finds surprisingly better thermal stability compared with their polysiloxane analogs. The design of functionalized polymers with a specific utilization is seen in new polysiloxanes used by Zeldin (p. 199) as phase transfer catalysts. Novel functional polyphosphazenes have been reported as well by Allcock (p. 250). The introduction of transition metal cyclopentadienyl, metal carbonyl and carborane moieties into polyphosphazene macromolecules is representative of truly novel chemistry achieved after careful model studies with corresponding molecular systems.

West (p. 6), Miller (p. 43), Zeigler (10), and Sawan (p. 112) outline the synthesis of a wide variety of soluble, processable polydiorganosilanes, a class of polymers which not long ago was thought to be intractable. Matyjaszewski (p. 78) has found significant improvements in the synthetic method for polydiorganosilane synthesis as well as new synthetic routes to unusual substituted polydiorganosilanes. Seyferth (p. 21, 143) reports synthetic routes to a number of new polycarbosilanes and polysilazanes which may be used as precursors to ceramic materials.

New catalytic polymerization routes to polysilanes (Harrod, (p. 89)) and polysilazanes (Laine, (p. 124)) have been discovered. Singler (p. 268) describes the use of $BCl_3$ in the more efficient synthesis of $-(PNCl_2)_n-$, the starting high polymer for most polyphosphazene polymers currently under investigation. These results in the area of polymerization catalysts are important, as the systematic development of efficient catalytic routes for inorganic and organometallic macromolecules will make such materials more generally accessible and utilizable. This research is also closely related to understanding of mechanisms of chain growth.

Efforts aimed at the elucidation of polymerization mechanisms include those of Singler (p. 268) in polyphosphazenes , Lipowitz (p. 156) in polysilazanes, and Zeigler and Worsfold in polysilanes. In contrast with carbon chemistry, the mechanisms of polymerization reactions leading to inorganic and organometallic macromolecules are often not well understood. Such studies are critical in elucidating pathways of chain growth, termination, and branching so that these features may be controlled. Oftentimes mechanistic studies lead to more efficient synthetic methods, for example by improving yields or shortening reaction times.

In the section on boron-containing polymers, Paine (p. 378), Neilson (p. 385), and Paciorek (p. 392) present pioneering work aimed at the preparation of linear chain macromolecules with B-N backbones. This work is significant because condensation reactions of B-N compounds tend to produce compounds with ring structures rather than chains. One obvious potential utilization of such novel macromolecules is as preceramic materials, much in the same way as polyacrylonitrile is used as a precursor for carbon. Orientation of the B-N polymer may be transferred in part to the ceramic solid state again in manner similar to carbon chemistry. However, the properties of BN polymers and ceramic materials differ greatly from their carbon analogs due to localized electronic states in the BN bond. The consequences of this contrasting electronic structure on materials properties will be interesting to see as this new research area develops.

A plurality of papers in this volume concern linear chain macromolecules. Fundamental to understanding the physical and mechanical behavior and chemical and physical stability of these macromolecules is a familiarity with phase transition behavior, an area well known in organic polymer chemistry (11). As with organic polymers, amorphous and semicrystalline inorganic and organometallic macromolecules are known. Crystallinity arises from main chain order or side chain crystallization as discussed by Singler (p. 268) for polyphosphazenes and West (p. 6) and Miller (p. 43) for polysilanes. The latter work demonstrates that crystallization behavior plays a critical role in controlling main chain conformation and optical transitions in poly(diorganosilanes). Thus, important structure/property relationships are emerging that are relevant to electronic and optical materials applications for these materials. In a different vein, side chain crystallization has resulted in the first liquid crystalline inorganic and organometallic macromolecules, viz., unusual poly(dialkoxyphosphazenes) described by Allcock (p. 250) and Singler (p. 268). In this case, the flexible nature of the P-N chain places stringent structural requirements on the nature of the pendant group.

Unique combinations of properties continue to be discovered in inorganic and organometallic macromolecules and serve to continue a high level of interest with regard to potential applications. Thus, Allcock describes his collaborative work with Shriver (p. 250) that led to ionically conducting polyphosphazene/salt complexes with the highest ambient temperature ionic conductivities known for polymer/salt electrolytes. Electronic conductivity is found via the partial oxidation of unusual phthalocyanine siloxanes (Marks, p. 224) which contain six-coordinate rather than the usual four-coordinate Si.

Part of this symposium was directed to the synthesis, properties and applications of inorganic and organometallic macromolecules with network structures. The section on organo-oxo macromolecules relevant to sol-gel processing addresses the interesting synthesis and challenging characterization efforts in this area. Brinker (p. 314) outlines the complex chemical and physical factors which affect network formation and structure resulting from the hydrolysis of a tetraalkoxysilane. The interesting properties of hybrid organic/inorganic network structures are described in the work of Schmidt (p. 333) and Wilkes (p. 354).

In conclusion, some trends can be gleaned from an examination of the content of the symposium as a whole. The growth in research efforts addressing the synthesis and properties of poly(diorganosilanes) will likely continue. The unique photophysical properties of this newly developed class of inorganic macromolecules (12) together with ready synthetic routes will be contributing forces here, and no doubt new vectors will arise. Another area of increased attention will be organo-oxo macromolecules derived from sol-gel processing methods, either as copolymers or blends. Complex dependencies of organo-oxo macromolecular composition and structure on starting materials and processing conditions (including kinetic effects) will lead to challenging and interesting science. Important mechanical, optical and structural applications coupled again with emerging synthetic approaches will be among the drivers for continued high activity in this area.

Finally, one additional comment concerning the nature of progress from interdisciplinary research is evident from the results reported in this Symposium Volume. Once again it is seen that most rapid progress is made when synthetic chemists collaborate with their colleagues in materials science or physics to determine properties of new inorganic and organometallic polymers.

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# POLYSILANES AND POLYCARBOSILANES

# Chapter 2

# Polysilane High Polymers: An Overview

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The history and development of polysilane chemistry is described. The polysilanes (polysilylenes) are linear polymers based on chains of silicon atoms, which show unique properties resulting from easy delocalization of sigma electrons in the silicon-silicon bonds. Polysilanes may be useful as precursors to silicon carbide ceramics, as photoresists in microelectronics, as photoinitiators for radical reactions, and as photoconductors.

The polysilanes are compounds containing chains, rings, or three-dimensional structures of silicon atoms joined by covalent bonds. Recently, polysilane high polymers have become the subject of intense research in numerous laboratories. These polymers show many unusual properties, reflecting the easy delocalization of sigma electrons in the silicon-silicon bonds. In fact, the polysilanes exhibit behavior unlike that for any other known class of materials.

In this chapter, an introduction and overview of polysilane chemistry will be presented, concentrating on the linear high polymers (polysilanes) and their technological applications. Polysilane polymers were reviewed in 1986,(1) and a more general review of polysilane chemistry appeared in 1982.(2)

## Historical

Poly(diphenylsilylene) may have been prepared as early as the 1920's by F. S. Kipping, the grandfather of organosilicon chemistry; but the polymeric or oligomeric products were not characterized. The first certain preparation of a linear polysilane came in 1949, when Charles Burkhard of the General Electric Company Research Laboratories, published a classic paper describing the synthesis of poly(dimethylsilylene), $(Me_2Si)_n$.(3) The polymer was obtained by condensing dimethyldichlorosilane with sodium metal, in essence the same process used today for the synthesis of polysilanes. Burkhard described $(Me_2Si)_n$ quite clearly and accurately, as an insoluble, infusible, and generally quite intractable material. It is now clear that poly(dimethylsilylene) is atypical among polysilanes, but this

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was not realized at the time. The discouraging properties of poly(dimethylsilylene) perhaps contributed to the neglect of this field over the following 25 years.(4)

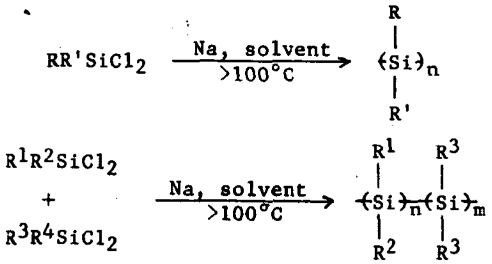
In any event, between 1951 and 1975, no papers appeared on polysilane high polymers. However, linear permethylpolysilanes of the type $Me(SiMe_2)_nMe$ were prepared and studied, especially by Kumada and his students,(5) and cyclic polysilanes were being investigated in several laboratories.(6,7) Studies of the permethylcyclosilanes, $(Me_2Si)_n$ where n = 4 to 7, showed that these compounds exhibit remarkable delocalization of the ring sigma electrons, and so have electronic properties somewhat like those of aromatic hydrocarbons.(6)

Interest in polysilane polymers was finally reawakened by the work of Yajima and Hayashi, who found that poly(dimethylsilylene) could be used as a precursor to silicon carbide.(9) The discovery, or rediscovery, of soluble polysilanes at Wisconsin was quite accidental.(10) In one attempt to prepare cyclosilanes containing both phenyl and methyl groups, $PhMeSiCl_2$ and $Me_2SiCl_2$ were co-condensed with alkali metal. A polymer was obtained instead of the desired ring compound, and to our surprise it proved to be somewhat soluble and meltable. The introduction of phenyl groups along the chain breaks up the crystallinity of $(Me_2Si)_n$ polymer. This adventitious finding led to synthesis of the "polysilastyrene" family of $Me_2Si$-PhMeSi copolymers.(11) At almost the same time, soluble polysilanes were reported by Trujillo(12) at Sandia Laboratories and by Wesson and Williams(13) at Union Carbide Co.

Research in polysilane polymers grew slowly at first after this reawakening. But within the past few years, both the unusual scientific interest and the technological possibilities of the polysilanes have been recognized, and activity in this field has increased sharply. Commercial manufacture of both poly(dimethylsilylene) and "polysilastyrene" is now being carried out in Japan, so that these two polymers are readily available in quantity.

## Synthesis of Polysilanes

Poly(silylene) polymers are usually made by the reaction of diorganodichlorosilanes with sodium metal, in an inert diluent at temperatures above 100°C.(11) Rapid stirring is ordinarily used so that the sodium is finely dispersed, speeding the rate of reaction. Either homopolymers or copolymers can be synthesized:



$$RR'SiCl_2 \xrightarrow[>100^\circ C]{Na,\ solvent} \left(\overset{\displaystyle R}{\underset{\displaystyle R'}{Si}}\right)_n$$

$$R^1R^2SiCl_2 + R^3R^4SiCl_2 \xrightarrow[>100^\circ C]{Na,\ solvent} \left(\overset{\displaystyle R^1}{\underset{\displaystyle R^2}{Si}}\right)_n\left(\overset{\displaystyle R^3}{\underset{\displaystyle R^3}{Si}}\right)_m$$

Considerable low molecular weight, oligomeric material is usually produced along with high polymer, so that the yield of true polymer is often less than 50%. In a typical workup, a small amount