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Inorganic and Organometallic Polymers – An Overview

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SUMMARY: The need for new materials with lower density, higher strength, ability to withstand extremes of temperature and electrical conductivity ranging from semiconductors to superconductivity has stimulated research in polymer science.[1] The polymers chosen for these applications are often organometallic or metal-containing organic polymers. These materials combine the low density and great variety of functional groups and structural variation of organic materials with the ease of achieving multiple oxidation states and electrical conductivity and the high temperature stability characteristic of inorganic compounds.

In order to keep abreast of this rapidly expanding field, PMSE, sometimes jointly with the Polymer and Inorganic Divisions of the A.C.S., has sponsored symposia in 1971, 1977, 1979, 1985, 1989, and 1994. The authors of this paper have organized these symposia. A new journal, The Journal of Inorganic and Organometallic Polymers, is now completing its eighth year. Our goal in this review is to discuss developments in five areas – Silanes, Germanes and Stannanes, Poly(silsequioxanes), Polyphosphazenes, Metallocene Polymers, and Condensation Polymers and to discuss potential applications of these materials.

We are seeking several scientists in these fields from outside of the United States to help us to continue this series of symposia and to support the Journal of Inorganic and Organometallic Polymers.

Silanes, Germanes, and Stannanes

It was only in the 1980's that soluble, well characterized long silylene chains were produced.[4-6] The field has grown rapidly since then. The great interest in silane, germane, and stannane polymers arises because they show σ-delocalization[7] and σ-π delocalization when they are conjugated with arenes or acetylenes. The conductivity is greatly enhanced when holes are created by doping[8], by illumination[9], or by an electric field. The two most

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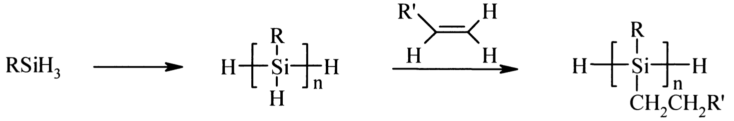
common methods of preparing polysilylenes are reductive coupling (1) and dehydrogenative coupling (2).

$$n\,R_2SiCl_2 + 2n\,Na\ \text{(or other metal)} \longrightarrow 2n\,NaCl + (R_2Si)_n \qquad (1)$$

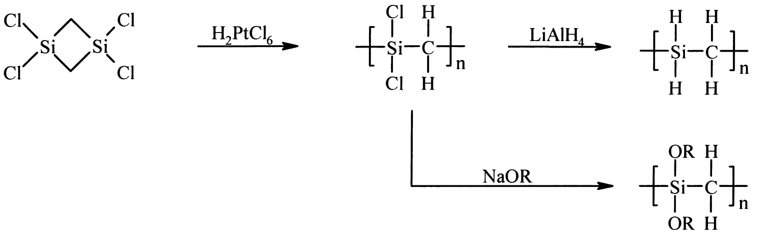
$$n\,R_2SiH_2 + \text{metal} \longrightarrow n\,H_2 + (R_2Si)_n \qquad (2)$$

Coupling of dichlorodisilanes with dilithium salts of 1, 2-diethynyldisilanes [10], $LiC \equiv C\text{-}SiR_2SiR_2\text{-}C \equiv CH$ or dilithio polythiophenes [11,12] $Li\ (C_4H_2S)_n\ Li$ (Method 1) produces alternating copolymers $[(SiR_2)_2\ C \equiv C\ (SiR'_2)_2\ C \equiv C\text{-})]_n$ and $[\text{-}(C_4H_2S)_n\ (SiR_2)_2\text{-}]_n$ which exhibit σ-π conjugation and also can undergo solid state transitions to form liquid crystalline mesophases.

Dehydrogenative coupling of dialkyl and monoalkyl silanes (Method 2) in the presence of a transition metal catalyst has provided an alternate route to polysilylenes.[13-19] If the side chains contain amine functions which may be quarternized or carboxyl functions which may be deprotonated, the polymers can be water soluble. [20]



Polygermanes and polystannanes have been prepared by routes similar to the polysilanes.[21-23] These materials show enhanced σ conductivity relative to the silanes and many have useful applications as light emitting diodes. [24] Poly(silaethylene) and several functional derivatives [25-26] have been prepared. (4)

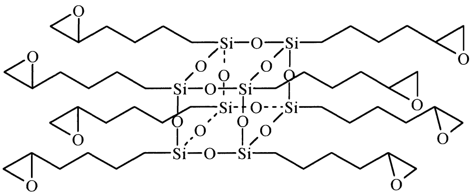


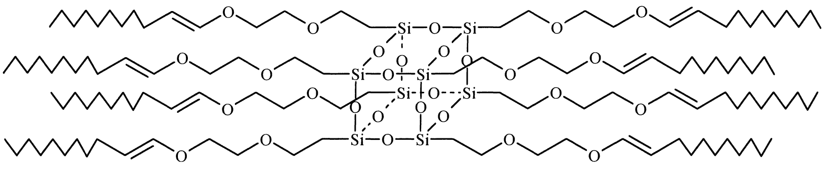
Polysilaethylene has an extremely low Tg (-135° to -140°C) and melts at room temperature $T_m = 25°$. The ease of substitution of the chloroderivative by alkoxide and possibly amines and other functionalities opens the door to a wide variety of materials and derivative chemistry similar to that known for the polyphosphazenes.

Fluorinated polysilaethylenes [27,28] have also been prepared. Poly (vinylidine fluoride), $(CF_2CH_2)_n$ is unique among existing commercial materials in its ability to form thin, tough, flexible films with very high piezo- and pyroelectric properties. Since Si-F bonds are more polar than C-F bonds, the Si analog will have a greater dipole moment and may possess enhanced piezo- and pyroelectric properties.

Poly(silsesquioxanes)

In recent years, the functionalization of silsesquioxanes and their polymerization to polyhedral oligomeric sesquisiloxanes (POSS)[29-30] has been studied. Eight armed "octopus" monomers with vinyl, allyl, hydrosilated, and epoxy groups are shown below. Sesquisiloxane polymers have been used in glassy, semicrystalline, liquid crystalline and elastomeric types of polymers. The USAF has demonstrated difunctional POSS reagents for use in thermoplastics, sol-gel, and conventional thermoset systems. Several general property trends have become apparent with POSS polymers[34] such as flammability reduction, lower thermal conductivity, increased gas permeability, increased Tg, and improved heat distorsion and melt strengths. The POSS cages themselves are not as susceptible to thermal motion as are polymer segments so POSS polymers should be more oxidatively stable and retain their mechanical properties better at high temperatures.

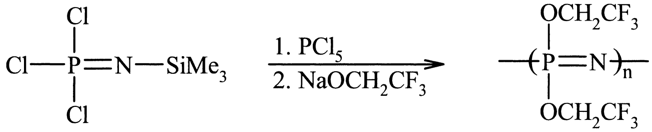




Living Polymerizations to Make Polyphosphazens

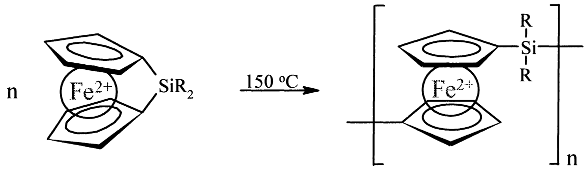
Polyphosphazines are a well developed versatile class of inorganic/organic hybrid macromolecules prepared by thermal ring-opening polymerization of the cyclic trimer $(N{=}PCl_2)_3$ followed by macromolecular substitution of nucleophiles for chlorine. Over 700 such polymers have been prepared in the past 30 years. [35]

Broader development of polyphosphazenes has suffered from the lack of synthetic methods to prepare well defined materials (eg. controlled molecular weights and polydispersities, dendritic materials, block copolymers, and specific end groups.) Now that void is being bridged. Recent studies have shown the room temperature cationic "living" polymerization of phosphoranimines can be catalyzed with PCl_5. [36-37] Block, star and graft polymers have been preapred.[38-39]

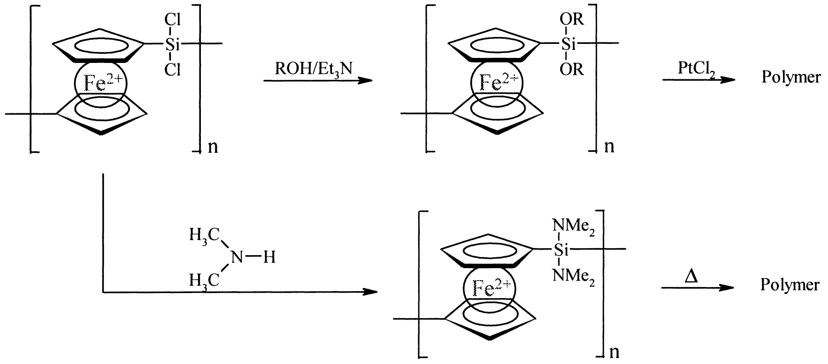


Metallocene Polymers

Synthesis of soluble, processable metallocene polymers which can be substituted with a broad variety of functional groups and which can be partially oxidized to conductive materials has long been a goal of polymer chemists. Research by Manners et al. [40] has shown that thermal or platinium catalyzed ring-opening polymerization, ROP, of sila [1]-ferrocenophanes can produce a wide variety of tractable high polymers.



The molecular weight of the polymers formed by $PtCl_2$ can be controlled by addition of trace amounts of Et_3SiH as a quencher. Graft, star, block, comb and stereoregular polymers have now been prepared.[40] An easy synthetic route to alkoxy and amino-substituted ferrocenoyl polymers has now permitted preparation of a rich array of derivatives by methods previously employed for substituted polyphosphazenes.



Condensation Polymers

Carraher et al [41-44] have investigated condensation polymers for the past 30 years, employing a vast array of metals which can act as Lewis acids and Lewis bases. These have been prepared by interfacial polymerization with the Lewis acid in the organic phase and the Lewis base in the aqueous phase.

$$ML_nX_2 + BRB \longrightarrow -\!\!\left(ML_n\text{—}B\text{—}R\text{—}B \right)\!\!-_m$$

n = 2, 3, 4

$B = NH_2, NR_2, O^-, S^-$

M = Ge, Sn, Pb, As, Sb, Bi, UO_2^{2+}

Most of these materials are insoluble, but their lack of solubility combined with ease of degradation can sometimes be an advantage, i.e. controlled release of drugs [42,43] or growth hormones.[44]

Conclusion

The authors of this paper are all approaching or have exceeded the age of 60. It has been exciting to follow the progress of this field for the last 30 years. We hope to find some younger scientists to help us continue coverage of new, exciting developments well into the new millennium.

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