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Polymer Science with Main Group Elements and Transition Metals

Ian Manners

Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, M5S 3H6, Canada
E-mail: imanners@chem.utoronto.ca

Summary: The efficient formation of soluble, processable polymers with main chains containing inorganic elements provides a synthetic challenge but represents potentially important approach to new macromolecular and supramolecular materials with interesting properties. This talk will survey some of the recent research performed in our group concerning the development of controlled routes to a variety of different inorganic polymer systems and the use of the resulting materials in self-assembly processes.

Keywords: nanolithography; nanostructures; photonic materials; polyferrocene; ring-opening polymerization

Introduction

Because of their processing advantages over ceramics and metals, organic polymeric materials are ubiquitous. The incorporation of inorganic elements such as transition metals into a polymer main chain offers unique potential for the preparation of processable materials with properties which differ significantly from those of conventional carbon-based polymers [1]. For example, the diverse range of coordination numbers and geometries which exist for transition elements offer the possibility of accessing polymers with unusual conformational, mechanical, and morphological characteristics. Metallocenters may also generate interesting electronic, optical, and magnetic properties. Transition metal-based polymers might also be expected to function as convenient and processible thermal or photochemical precursors to metal-containing ceramic films, fibers, and coatings with high stability and desirable and useful physical properties [1-3]. However, the development of the area of metal-containing polymers has been held up by considerable synthetic difficulties. Much of the early work in the field in the 1950's and 1960's targeted polymetallocenes. However, most of the attempted polymer syntheses utilized polycondensation reactions and the resulting products were generally of low molecular weight or insoluble and poorly-characterized [2,4].

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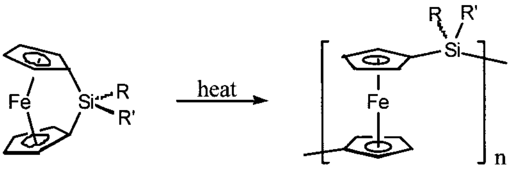
In the early 1990s we reported the discovery of a ring-opening polymerization (ROP) route to high molecular weight polyferrocenylsilanes from strained [1]silaferrocenophanes [5]. The latter species were first prepared in the mid 1970's via the reaction of the dilithioferrocene•tetramethylethylenediamine complex with organodichlorosilanes. ROP processes generally occur via a chain growth route which involve a highly reactive intermediate that reacts rapidly with monomer molecules. This allows the facile formation of long polymer chains making high molecular weight polymers easily accessible. This is vital as high molecular weights ($M_n >$ ca.10,000) are needed in order to realize the chain entanglement needed to access the advantageous properties of macromolecules such as ease of fabrication into films.

Polyferrocenylsilanes (PFSs)

A wide range of silicon-bridged [1]ferrocenophanes **1** have been prepared and similarly polymerized to high molecular weight ($M_W = 10^5 - 10^6$, $M_n > 10^5$) polyferrocenylsilanes (PFSs) **2**. Substituents such as hydrogen, chlorine, alkyl, aryl, trifluoropropyl, norbornenyl alkoxy, aryloxy, amino, and ferrocenyl groups have also been introduced [6].



1 **2**

Considerable effort has also been directed towards investigating and understanding the properties of the resulting PFS materials, the vast majority of which are soluble in organic solvents or water despite their very high molecular weights [6]. Cyclic voltammetric studies of the high polymers generally show the presence of two reversible oxidation waves in a 1: 1 ratio providing clear evidence for the existance of interactions between the iron atoms [7]. The presence of metal-metal interactions has led to studies of the charge transport properties of these materials. Oxidative doping of amorphous samples of poly(ferrocenyldimethylsilane) with I_2 have been shown to yield semiconducting materials. Recent collaborative work with the group of E. W. Sargent at Toronto has identified holes as the charge carriers [8]. Charge transport properties such as hole mobility, which are important for xerography and other device applications, have also been measured and are appreciable. Polyferrocenes also function as charge dissipation coatings which provide protection with respect to ionizing radiation such as electrons. The films of PFSs are believed to function in this regard via both radiation scattering and conduction mechanisms [9]. The magnetic properties of oxidized PFSs have also attracted some attention [10]. In addition, cationic and anionic water-soluble PFSs are useful in the preparation of organic-organometallic and all organometallic electrostatic superlattices by layer-by-layer assembly approaches [11].

PFS materials also exhibit interesting morphology and several of the symmetrically substituted derivatives will crystallize [6]. Alkoxy-substituted PFS materials such as **2** (R = R' = n-hexyloxy) possess T_g values down to - 51°C, a remarkable testament to the flexibility of polyferrocene chains which probably arises from the freely-rotating "molecular ball bearing" nature of the ferrocene unit. The first liquid crystalline PFS materials have also been prepared via hydrosilylation [12]. These show a nematic mesophase and the influence of redox state on the liquid crystalline properties is of significant interest.

Thermal ROP of metallocenophanes at elevated temperatures leads to virtually no control over molecular weight and the molecular weight distribution is broad. We have shown that silicon-bridged [1]ferrocenophanes undergo living anionic ROP [13]. This has permitted the synthesis of PFSs with controlled molecular weights and narrow polydispersities and has also allowed functionalization of polymer chain ends and the preparation of the first block copolymers containing skeletal transition metal atoms. Transition metal-catalyzed ROP of silicon-bridged [1]ferrocenophanes, which occurs in solution at room temperature, has also been reported using Pd, Pt, and Rh catalysts. Molecular weight control can also be achieved and materials with novel architectures such as star and graft polymers are accessible [14].

PFS Applications

PFSs function as preceramic polymers and have been shown to yield interesting magnetic Fe-containing ceramic composites at 500 - 1000°C [15-18]. The use of such involatile but processable polymeric precursors to ceramics is potentially attractive way of circumventing the difficulty of processing ceramic materials into desired shapes. In collaboration with the group of G.A. Ozin at

Toronto we have recently prepared PFS inverse opals and magnetic ceramic replicas using the preceramic polymer approach. The resulting materials possess periodic variations in refractive index at the micron scale [19]. The relatively high refractive indices possible with PFS materials ($n > 1.6$) make the structures of interest as redox-tunable photonic crystals. In addition, magnetic ceramic photonic crystals may allow photonic properties to modified with a magnetic field.

PFS block copolymers allow access to nanostructured materials via self-assembly processes in the solid state or solution [20]. In collaboration with the group of M. Winnik at Toronto we have shown that interesting architectures can be generated via the solution aggregation of PFS-based block copolymers [20]. Thus, block copolymers such as poly(ferrocenyldimethylsilane) - b - poly(dimethylsiloxane) ($n : m = 1 : 6$) with long polysiloxane blocks have been found to afford cylindrical, wormlike micelles in hexanes. These structures can be readily visualized by Atomic Force Microscopy or by TEM. These cylinders consist of a wire-like core of semiconducting PFS surrounded by a sheath or corona of insulating poly(dimethylsiloxane). Pyrolysis of such structures, particularly if crosslinked, offers the possibility of generating magnetic wire-like structures. The structures can also be used as nanoscopic etching resists to yield patterns of width 10 – 20 nm [19]. The analogous use of cylindrical micelles with PFS cores but an easily etchable organic corona (e.g. derived from polyisoprene) allows one to obtain structures of smaller width ca. 8 nm [21].

In summary, ring-opening polymerization has allowed facile access to a variety of high molecular weight PFSs. Much has been accomplished in terms of understanding the properties of these novel and interesting materials. Future work will be directed towards extending the polymerization approach to develop new polymers [22].

New Polymers Based on Main Group Elements: Polythionylphosphazenes and Polyphosphinoboranes

Our group has also been interested in the possibility of creating new macromolecular chains based on main group elements [23]. We have found, for example, that cyclic thionylphosphazene $[NSOCl(NPCl_2)_2]$ thermally polymerizes at 165°C to yield poly(pentachlorothionylphosphazene) $[NSOCl(NPCl_2)_2]_n$ which undergoes halide substitution in a manner similar to poly(dichlorophosphazene) (e.g. with amines) to form hydrolytically stable sulfur-nitrogen-phosphorus polymers [24]. Mechanistic studies of the ROP process suggested a cationic, chain growth ROP mechanism. Significantly, by using halide accepting, Lewis acids as catalysts we have found that the ROP can be performed at room temperature [25]. Interestingly, the polymerization shows a dramatic dependence on monomer concentration and no polymer is formed a below a concentration of 0.15 M. This is characteristic of a polymerization with a very small ΔH value which indicates that, unlike the case of [1]ferrocenophanes, monomer $[NSOCl(NPCl_2)_2]$ is virtually unstrained. The properties of polythionylphosphazenes are currently being studied. The backbone is stable to hydrolysis and indeed water soluble derivatives have been made. The high gas permeability of some of these materials has led to interest in their use as matrices for luminescent, oxygen sensors [26].

The preparation of polymers with backbones of alternating phosphorus and boron atoms attracted significant attention in the 1950's and early 1960's as a consequence of the envisaged high thermal stability and possible flame retardancy of these materials. The main synthetic route explored at that time involved thermally-induced dehydrocoupling of phosphine-borane adducts. However, these reactions only proceeded at 180-200°C and the main products were six-membered rings (which, promisingly, were resistant to hydrolysis by HCl at temperatures as high as 300°C in some cases) [27]. Only negligable yields of low molecular weight, partially characterized polymers were claimed, mainly in patents. Recently we have shown that the dehydrocoupling process is effectively catalyzed by late transition metal complexes (especially Rh species) which has permitted the formation of high molecular weight polyphosphinoboranes $[RPH\text{-}BH_2]_n$ ($M_w > 30{,}000$) [28].

The properties of these interesting, recently prepared polymers are now beginning to be explored. Polyphenylphosphinoborane, for example, is a white, air-stable powder and is formally an analog of polystyrene with a phosphorus-boron backbone [28]. Improved dehydropolymerization catalysts for P-B bond formation are highly desirable in order to further raise molecular weights and to hopefully allow more controlled polymerizations.

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