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CATALYTIC AND SELF-ASSEMBLY ROUTES TO INORGANIC POLYMERIC AND SUPRAMOLECULAR MATERIALS

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This paper provides an overview of our research program as described in a lecture at Baylor University in May 2010 in a Symposium to honor Professor F. G. A. Stone.

Keywords: block copolymers, inorganic polymers, organometallic polymers, self-assembly

INORGANIC SOFT MATERIALS

Inorganic elements represent the most abundant elements on earth and the ability of scientists to continue to explore, understand, and exploit their fundamental materials chemistry will have important implications for the future. Over the last 20 years our group has focused on the development of new synthetic reactions in inorganic chemistry and their applications in molecular synthesis, polymer and materials science, supramolecular chemistry, and nanoscience. Of particular interest to us is the development of inorganic soft materials. Inorganic materials have traditionally been hard solids with extended structures in 2, or more normally 3, dimensions. For linear 1D chains, materials properties are entirely different, permitting easy processing and a range of properties and functions that complement those available with synthetic organic polymers.

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Due to the outstanding and easy processing of polymers, the synthesis, properties, and applications of new classes of functional macromolecular materials constructed from main group or transition elements represent an attractive area. Projects in our group aim at developing routes to new main group and transition metal compounds, particularly strained rings, which may function as precursors to new inorganic polymer structures via ring-opening polymerization (ROP) techniques.^[1-4] At a fundamental level we are interested in the structures, bonding, and strain in such species and the mechanisms for ring-opening polymerization. The presence of inorganic elements in a polymer main chain also gives rise to intriguing properties of considerable scientific interest. Thus, the more applied side of our work involves the development of, for example, new charge transport materials, magnetic ceramic materials, elastomeric materials, nanomaterials, sensors, liquid crystal-line materials, and display technologies.^[5,6]

SELF-ASSEMBLY OF INORGANIC BLOCK COPOLYMERS

Our group has also developed controlled synthetic routes to well-defined polymers with main group or transition metals in the backbone.^[7-9] This allows the formation of block copolymers with inorganic blocks and studies of the self-assembly of such materials is of considerable interest. For example, we have developed living polymerization routes to polyferrocenylsilane and polyferrocenylphosphine block copolymers, which self-assemble in the solid state and in solution. We and our collaborators are investigating a range of potential applications of the resulting phase-separated thin films and micelles that possess nanoscopic metal-rich domains.^[10] Nanoscience applications currently under investigation include uses as nanowires, nanotubes, and as magnetic dot precursors. Living self-assembly allows the formation of controlled micelle architectures, including hierarchical structures.^[11]

CATALYTIC ROUTES TO SPECIES WITH CATENATED INORGANIC ELEMENTS

Another key area of research in our group involves applications of catalysis and other novel synthetic methodologies in inorganic chemistry.^[12,13] The development of transition metal-catalyzed reactions in the latter half of

the 20th century revolutionized synthetic organic chemistry both at the molecular and macromolecular level. In contrast, synthetic methodologies used to create frameworks based on inorganic elements are still generally rather haphazard and are of very limited scope; often the only predictable pathways rely on salt metathesis processes. We have been very interested in applying the concepts of metal catalysis to the development of rings, chains, cages, and polymers based on skeletons of alternating atoms of inorganic elements. The study of the chemistry and materials applications of reactive inorganic molecules is of fundamental interest and also because such species are potential polymerization monomers and reactive intermediates in polymerization reactions.

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