CHEMICAL REVIEWS

Volume 100, Number 4 April 2000

Frontiers in Metal-Catalyzed Polymerization: Designer Metallocenes, Designs on New Monomers, Demystifying MAO, Metathesis Déshabillé

This thematic issue of *Chemical Reviews* does not come with the customary Guest Editor, normally a prominent researcher in the field. Rather, it is edited by an informed spectator, one of the regular Editorial staff. This might be viewed as a less auspicious strategy. However, the expertise of the authors is widely known, and their outstanding collection of articles speaks for itself. The subject is so topical and important, both in academic and industrial contexts, that little introduction is actually needed.

The modern era of metal-catalyzed polymerization begins of course with Ziegler and Natta. However, over the last 15 years—the approximate time frame of the advances reviewed herein—the field has evolved in ways that these founding fathers could never have dreamed of. These developments elegantly illustrate the synergies possible between pure and applied research. The latest improvements in analytical methods are applied to the detection of transient intermediates and a plethora of structural issues—such as the components in MAO or the nature of supported systems. Advances in computational chemistry or computing power are immediately brought to bear on complex mechanistic questions. These are further probed by sophisticated physical organic experiments that range from kinetic and equilibrium isotope effects to isokinetic relationships. Highly selective chiral recognition phenomena, and nonclassical binding modes previously regarded only as curiosities, have been unambiguously identified. These have been used as springboards and/or control elements for applications in related fields, such as catalytic enantioselective organic synthesis. Examples of "living" polymers, the growth of which can be directly observed, are increasingly available. Many of these advances are achieved by insightful planning and design and include ever-higher activity and functional group tolerance.

The issue begins with an article by Ittel, Johnson, and Brookhart on late metal catalysts for ethylene homo- and copolymerization. They detail the newest generation of catalysts to be commercially licensed. Alt and Köppl then introduce ethylene and propylene polymerization by metallocene catalysts. Structure—performance relationships for unbridged and bridged systems are delineated and contrasted. Coates subsequently analyzes the complex factors controlling stereochemistry in polymers derived from α-olefins, conjugated and nonconjugated dienes, cycloalkenes, and other monomers. This theme is further developed by Resconi, Cavello, Fait, and Piemontesi, who dissect the intricate nuances of mechanism and selectivity underlying propylene polymerization, from catalyst symmetry to kinetic models.

In a tour-de-force with respect to the arcane patent literature, Hlatky reviews heterogeneous single-site catalysts. This is complemented by an article by Fink, Steinmetz, Zechlin, Przybyla, and Tesche on the specific subject of propylene polymerization with silica-supported metallocene/MAO catalysts. The mechanistic role of MAO and other activators is then analyzed by Chen and Marks. They define structure—activity relationships that are certain to promote future research and advances.

Two contributions emphasize computational chemistry. Rappé, Skiff, and Casewit review the general modeling of metal-catalyzed alkene polymerization. Angermund, Fink, Jensen, and Kleinschmidt then treat the specific case of stereospecificity in α-olefin polymerization. A nontraditional mechanism that operates with some soluble Ziegler—Natta systems (as well as other metals), carbocationic alkene polymerization, is covered by Baird. The state-of-the-art with respect to functional monomers is then analyzed by Boffa and Novak, who discuss catalysts from the entire transition metal series.

Two articles follow which have very little in the way of polymerization data but point to exciting new possibilities for catalyst development. The first, by Siemeling, reviews chelate complexes of cyclopentadienyl ligands that bear pendant oxygen donors. The second, by Butenschön, treats analogous complexes with pendant phosphorus, arsenic, and sulfur donors. The "constrained geometry" catalysts that have been commercialized over the last 8 years feature similar chelates.

The last three contributions provide a distinct departure from metallocene and/or half-metallocene systems, focusing on metathesis-based polymerization in which metal—carbon multiple-bonded inter-

10.1021/cr000450+ CCC: $35.00 © 2000 American Chemical Society
Published on Web 04/12/2000

mediates carry the chain. The first, by Buchmeiser, covers homogeneous alkene metathesis polymerization by well-defined group VI and VIII metal alkylidene complexes. The second, by Bunz, reviews a novel class of polymers derived by alkyne metathesis, poly(aryleneethynylenes). This series is concluded by a review of poly(1,6-heptadiyne)-based materials, authored by Choi, Gal, Jin, and Kim.

The month in which this thematic issue appears marks the 65th birthday of one of the key leaders in the modern development of this field, Hans Brintzinger (University of Konstanz, born April 29, 1935). All of the authors have been inspired by his exemplary qualities as a scientist and an individual (including this writer, who attended his inorganic chemistry lectures while a University of Michigan undergraduate in 1970−71) and use this occasion to congratulate him and wish him the best in future scholarly and human undertakings.

In summary, this thematic issue covers a fast-moving field that encompasses principles from nearly all branches of chemistry. The articles beautifully illustrate both of the following: that research with a commercial driving force can lead to outstanding advances in fundamental chemistry and that fundamental research in chemistry can lead to outstanding technological and commercial advances.

J. A. Gladysz

Institut für Organische Chemie
Friedrich-Alexander Universität
Erlangen-Nürnberg

CR000450+