

Stereospecific Olefin Polymerization with Chiral Metallocene Catalysts

Hans H. Brintzinger,* David Fischer, Rolf Mülhaupt, Bernhard Rieger,
and Robert M. Waymouth

Dedicated to all those excellent graduate students who are the true heroes of this story

Current studies on novel, metallocene-based catalysts for the polymerization of α -olefins have far-reaching implications for the development of new materials as well as for the understanding of basic reaction mechanisms responsible for the growth of a polymer chain at a catalyst center and the control of its stereoregularity. In contrast to heterogeneous Ziegler–Natta catalysts, polymerization by a homogeneous, metallocene-based catalyst occurs principally at a single

type of metal center with a defined coordination environment. This makes it possible to correlate metallocene structures with polymer properties such as molecular weight, stereochemical microstructure, crystallization behavior, and mechanical properties. Homogeneous catalyst systems now afford efficient control of regio- and stereoregularity, molecular weights and molecular weight distributions, and comonomer incorporation. By providing a means for

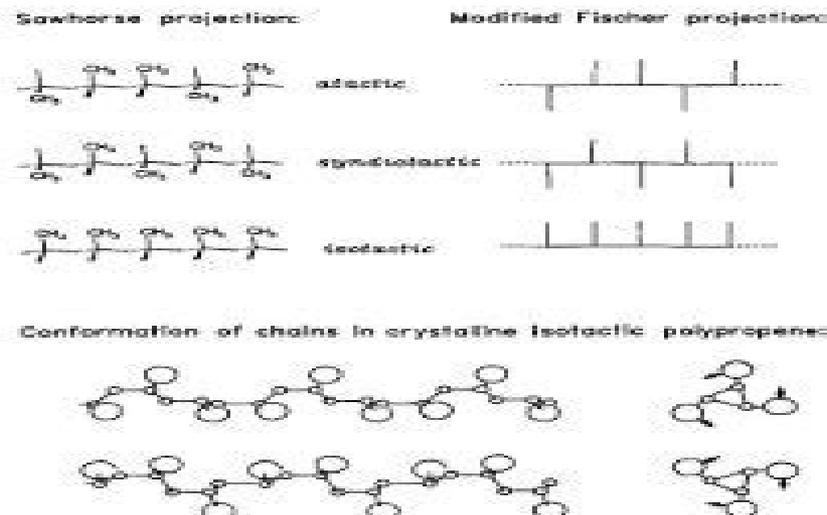
the homo- and copolymerization of cyclic olefins, the cyclopolymerization of dienes, and access even to functionalized polyolefins, these catalysts greatly expand the range and versatility of technically feasible types of polyolefin materials.

Keywords: alkenes · catalysis · metallocenes · polymerizations

1. Introduction

Forty years after Karl Ziegler's invention of transition metal catalyzed polymerization and Giulio Natta's discovery of the stereoselective polymerization of α -olefins,^{1,2} we are witnessing the evolution of new generations of catalysts and polyolefin materials, which originate from studies on homogeneous, metallocene-based polymerization catalysts. In the following, we will attempt to review some of these recent developments.^{3–7}

Research on metallocene-catalyzed olefin polymerization has derived much of its impetus from the desire to model the reaction mechanisms of heterogeneous polymerization catalysts. In the evolution of Ziegler–Natta catalysis, an empirical approach has proven highly successful. Modern $MgCl_2$ -supported catalysts have tremendous activities for the production of polypropene and other polyolefins; at the same time, they are



Scheme 1. Structural representations of isotactic, syndiotactic, and atactic polypropene in sawhorse and modified Fischer projections [100] (top), and conformation of the chain in crystalline isotactic polypropene, determined by Natta and Corradini [2] (bottom).

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