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Preface

Metallocene complexes as catalysts for olefin polymerization

They are more than 50 years old, they founded modern organometallic chemistry, they revolutionized the world of catalysis, they are still good for many surprises and they are as young as ever: metallocenes and metallocene complexes.

The discovery of the Ziegler catalysts, a combination of titanium(III) or (IV) chloride and aluminum alkyls, in the Max-Planck-Institut für Kohlenforschung, Mülheim, Germany, in the early 1950s, started a rally in titanium chemistry. Sure enough, titanocene complexes were the first candidates, in those days, to be tested for catalytic olefin polymerization reactions (Natta's and Breslow's groups, in 1957). Unfortunately, the activities of such catalysts were not satisfying due to the fact that the "right" cocatalyst was not available at that time (aluminumalkyl halides). The situation changed with the discovery and application of methylalumoxane (MAO) by Sinn and Kaminsky as an appropriate cocatalyst at the start of the 1980s. This was again initiated by an accident—Reichert had discovered, as early as 1973, that small amounts of water increased the activity of the trimethylaluminum cocatalyst. Often progress has its roots in accidents. Who in the world would add water to pyrophoric trimethylaluminum?

From this time on, metallocene complexes were the focus of research groups both in industry and academia because homogeneous catalysts have the important property that every single molecule can "do the job", not just a few active sites sitting on the surface of heterogeneous catalyst particles.

Brintzinger introduced bridged metallocene complexes, so-called ansa metallocenes (originally prepared with a different intention), and it became obvious that the symmetry of the catalyst precursor can determine the stereospecifity of the polymerization of prochiral olefins such as propene (pioneering work of Razavi!). These are highly active catalysts and their tremendous potential became apparent at end of the 1980s. In these days, metallocene catalysts for the stereospecific polymerization of propylene are of highest priority: not only to escape from the "Himont monopoly" (catalysts for the industrial production of isotactic polypropene) but also because it became obvious that tailored metallocene catalysts allowed the production of new polymers and copolymers ("Topas", a copolymer from ethene and norbornene, is just one example) and many such resins are superior to materials that are available on the market.

My group started to work with metallocene catalysts in 1988 and, at that time, I thought with a handful of catalysts every challenge in the field can be satisfied. This was not true! The original project became a never ending story. Since then, my group has synthesized, characterized and tested over 800 different metallocene catalysts (and some 700 other catalysts) and still this is not the end. Why? The most intriguing property of metallocene catalysts is the fact that tiny differences in catalyst structure can have a tremendous impact on the performance of the corresponding catalyst and the polymer produced (structure–property relationship). For instance, a "smart" metallocene catalyst can produce a polyethylene with evenly distributed alkyl branches and excellent mechanical and optical properties starting with ethylene as the only monomer. This is a result from my group in cooperation with Phillips Petroleum Company, USA, in the 1990s. The product is called mPact and is commercially produced by Chevron-Phillips Company, USA.

Barry Lever's timing was perfect to issue a volume dealing only with metallocene catalysts. Fourteen authors have contributed manuscripts, which will make this volume a classical source of metallocene know-how. This field is still growing so rapidly that one person alone has no chance to cover all aspects. I am glad that I gave up the idea to write a book about metallocene catalysts 6 years ago. It would have been obsolete as soon as it was published. I am sure, with this volume, readers will appreciate and enjoy the excellent pool of metallocene catalysts and will develop their own ideas about how to extend this promising research.

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