

Preface

Millions of tons of polyolefin-based materials are produced yearly, in most cases under relatively mild conditions mediated by transition-metal catalysts. Through a simple insertion reaction, inexpensive and abundant olefins (such as ethylene and propene) are transformed into polymeric materials for a wide range of applications, including plastics, fibers, and elastomers. The discovery of the Ziegler–Natta catalysts and the seminal works at Phillips Petroleum in the 1950s not only revolutionized polyolefin production, but also paved the way to the development of modern organometallic chemistry. Despite its long history, the polyolefin industry keeps growing steadily and remains technologically driven by the continuous discovery of new catalysts, processes, and applications.

Since Ziegler–Natta’s time, important milestones in the field of homogeneous oligomerization/polymerization catalysis were set-up one after the other; from nickel complexes with phosphine donors (SHOP-type catalysts) for the highly selective and efficient production of α -olefins to Group IV metallocene polymerization catalysts and their subsequent industrial exploitation (in the early 1980s) due to the discovery of partially hydrolyzed organoaluminum compounds (MAOs) as co-catalysts/activators. All these scientific successes have shown how discrete “single-site” molecular catalysts could offer unmatched opportunities, compared with heterogeneous systems, towards the tailored synthesis of new polymeric architectures as well as the in-depth understanding of complex reaction mechanisms.

Until a few years ago there have been relatively few reports on late transition metal complexes capable of catalyzing the polymerization of ethylene and α -olefins efficiently. A distinct feature of the latter systems is a high rate of chain transfer which favors their application as oligomerization catalysts. The discovery of new ligands and activators has been fundamental to fill the gap and make late transition metal catalysts as efficient (and in some cases even more versatile) as metallocene-based systems for the oligomerization and polymerization catalysis.

In 1995, Brookhart and co-workers synthesized a new class of Ni^{II} and Pd^{II} complexes stabilized by bulky α -diimine ligands (Schiff bases) which represented

a real breakthrough into the development of late transition metal catalysts for the efficient olefin polymerization/oligomerization.

Since then, an almost infinite variety of imine-based ligands or, more generally, nitrogen-containing ligands in combination with either *d*- and *f*- block metals have been explored as efficient and selective oligomerization and polymerization catalysts. The major advantages of this ligand class are represented by the facile control of their stereoelectronic properties, their simple preparation from available and cheap building blocks and their easy handling and storage. All these considerations, together with the capability of most of their metal derivatives to impart high activity and selectivity in olefin upgrading processes, have contributed to make nitrogen-containing catalysts highly desirable for industry and academy.

The aim of these books is to provide an overview on the state-of-the-art and the perspectives in the field of oligomerization/polymerization catalysis mediated by metal complexes (spanning from early to late and lanthanide series) stabilized by ligands containing nitrogen donor groups. Rather than a systematic revision of the major break throughs achieved over the last decades, these two volumes offer to the readership the critical point of view of researchers active in specific fields of polymerization catalysis. The amplitude and rigor of each contribution also provide an exhaustive account on the topic: from the synthesis of ligands and related complexes to mechanistic details, the investigation of the catalyst performance and future perspectives. Although the chapters' extension has made the book division into two separate volumes necessary, this partition is merely due to editorial reasons.

Finally, the editors are extremely grateful to all book co-authors for their enthusiasm in participating to this editorial project and for writing up their contribution at their best. A special thank is also due to Sonia Ojo, Claudia Culierat and Ilaria Tassistro from the London Springer office, whose precious assistance in facing technical and logistic details has been essential for the success of the Editors' efforts.

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Complexes I

State-of-the-art and Perspectives

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