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Advances in Polymer Science

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The series Advances in Polymer Science presents critical reviews of the present and future trends in polymer and biopolymer science. It covers all areas of research in polymer and biopolymer science including chemistry, physical chemistry, physics, material science.

The thematic volumes are addressed to scientists, whether at universities or in industry, who wish to keep abreast of the important advances in the covered topics.

Advances in Polymer Science enjoys a longstanding tradition and good reputation in its community. Each volume is dedicated to a current topic, and each review critically surveys one aspect of that topic, to place it within the context of the volume. The volumes typically summarize the significant developments of the last 5 to 10 years and discuss them critically, presenting selected examples, explaining and illustrating the important principles, and bringing together many important references of primary literature. On that basis, future research directions in the area can be discussed. Advances in Polymer Science volumes thus are important references for every polymer scientist, as well as for other scientists interested in polymer science - as an introduction to a neighboring field, or as a compilation of detailed information for the specialist.

Review articles for the individual volumes are invited by the volume editors. Single contributions can be specially commissioned.

Readership: Polymer scientists, or scientists in related fields interested in polymer and biopolymer science, at universities or in industry, graduate students.

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Walter Kaminsky
Editor

Polyolefins: 50 years after Ziegler and Natta II

Polyolefins by Metallocenes and Other Single-Site Catalysts

With contributions by

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Preface

Fifty years after the Nobel Prize was awarded to Karl Ziegler and Giulio Natta in 1963, the polymerization of olefins by metallorganic catalysts has grown to one of the most fascinating areas in academic and industrial polymer science and now has the largest use in polymer production. Ziegler had discovered 10 years earlier that a mixture of transition metal compounds, especially titanium chlorides and aluminum alkyls, was able to polymerize ethene by an insertion reaction. This spectacular milestone was expanded a year later when Natta prepared and characterized isotactic polypropylene and introduced stereospecific polymerization. In contrast to the high-pressure ethene polymerization invented in 1935 by ICI (Imperial Chemical Industries, Great Britain), the catalyzed olefin polymerization requires only low pressure and low temperature.

Today, more than 130 million tons of polyolefins are produced worldwide per year, the major part with the help of Ziegler–Natta catalysts. Polyolefins have changed the world! They are not only the polymers with the highest production volume, but they also show an unbroken production increase. Containing only carbon and hydrogen atoms, polyolefins are sustainable materials, light in weight, and offer a wide variety of properties. The production requires only easily available and nontoxic monomers and proceeds with almost no losses or side reactions. After their end of use, polyolefins can easily be recycled through mechanical procedures to simple articles, by pyrolysis to gas and oil, or by incineration to energy.

In recent decades, new generations of catalysts with higher activities and stereospecificities and modern production processes have been invented to produce a great variety of polyolefins ranging from high density polyethylene (HDPE) to linear low density polyethylene (LLDPE), high melting polypropylene, high modulus polyolefin fibers, ethene–propene rubber (EPR), ethene–propene–diene monomer rubber (EPDM). The chromium-based Phillips catalysts opened the field of gas phase polymerization for HDPE. New supported Ziegler–Natta catalysts make it possible to increase the activity, to control the morphology, and for polypropylene to increase the isotacticity by adding different kinds of donors.

A great development in this research field was the discovery of metallocene and other transition metal complexes activated by methylaluminoxane. These catalysts are up to 10 times more active than Ziegler–Natta catalysts, are soluble in hydrocarbons, show only one type of active site (single site catalysts), and can easily be modified in their chemical structure. These properties make it possible to predict the properties of the resulting polyolefins very accurately from the knowledge of the structure of the catalyst, and thus to control molecular weight and distribution, comonomer content, and tacticity by careful selection of the appropriate reactor conditions. The single site character of metallocene-based catalysts leads to a better understanding of the mechanism of olefin polymerization and to the introduction of other bulky cocatalysts.

The different chapters in this book deal with the development of olefin polymerization 50 years after the pioneering work of Ziegler and Natta. Academic and industrial developments of ethene and propene polymerizations are presented, including short biographies of Ziegler and Natta, research on Phillips catalysts, kinetic and active site measurements, and polyolefin characterization. Review chapters also describe the latest results of olefin homo-, living-, and copolymerizations by metallocene and other single site catalysts, such as the synthesis of ansa metallocenes, supported iron catalysts, syndiotactic polypropylene, long chain branched polyolefins, and cyclic and functional copolymers. Remarkable progress has been achieved in the synthesis of polyolefin nanocomposites by an in-situ polymerization process using clay, layered silicates, carbon fibers, and carbon nanotubes as fillers.

I thank all the authors very much for giving their time to write these exciting chapters.

Hamburg, Germany Walter Kaminsky

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