Metallorganic Catalysis for Synthesis and Polymerisation

Walter Kaminsky (Ed.)

Metalorganic Catalysts for Synthesis and Polymerisation

Recent Results by Ziegler–Natta and Metallocene Investigations

With 302 Figures and 177 Tables

Springer

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Bundesstraße 45
D-20146 Hamburg
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ISBN 3-540-65813-0 Springer-Verlag Berlin Heidelberg New York

Library of Congress Cataloging-in-Publication Data
Metalorganic catalysts for synthesis and polymerization: recent results
by Ziegler-Natta and metallocene investigations / W. Kaminsky (ed.).
p. cm.
Includes bibliographical references.
ISBN 3-540-65813-0 (hardcover)
1. Organometallic catalysts. I. Kaminsky, W. (Walter), 1941-.
QD411.M494 1999
547' .0504595--dc21 99-25652 CIP

Production: ProduServ GmbH Verlagsservice, Berlin
Typesetting: Camera-ready by author
Cover design: Erich Kirchner, Springer Heidelberg
SPIN:10692582 2/3020-5 4 3 2 1 0 - Printed on acid-free paper

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Springer
Berlin
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Preface

45 years after the discovery of transition metals and organometallics as catalysts for the polymerization of olefins and for organic synthesis, these compounds have not lost their fascination. The 100th birthday of Karl Ziegler, the great pioneer in this metalorganic catalysis, was in this year.

Since 1953 when Karl Ziegler has discovered the catalytic polymerization of ethylene leading to plastically formable polymers, synthetic polymers and rubbers becoming one of the most growing commercial markets. The stereoselective polymerization of propylene and other long-chain α-olefins, first detected by Giulio Natta, leads to an even broadened field of applications.

Today the importance of plastics is appreciated by many politicians. During the reception of the participants of this symposium in the Rathaus of Hamburg (townhall), the Mayor of the City of Hamburg emphasized: „Chemistry has changed the world. Even those only dealing a little bit with this topic see that particularly polymer chemistry has given important impulses for the growth of our economy and prosperity."

Polyolefins and polybutadienes produced by metallorganic catalysts are not only the most important plastics but they show an unbroken production increase. Containing only carbon and hydrogen atoms, polyolefins will substitute other plastics which cannot be produced or recycled under the same environmental conditions.

A great development in this field was given by the discovery of metallocene/methylaluminoxane catalysts in our Hamburg laboratory. Since the last ten years over 300 patents are announced every year from industrial and academic research groups all over the world dealing with metllocene and „single site" catalysts. Why is there so much interest in this field of research? Metallocene catalysts are soluble in hydrocarbons, show only one type of active site and their chemical structure can be easily changed. These properties allow one to predict accurately the properties of the resulting polyolefins by knowing the structure of the catalyst used during their manufacture and to control the resulting molecular weight and distribution, comonomer content and tacticity by careful selection of the appropriate reactor conditions. In addition, their catalytic activity is 10–100 times higher than that of the classic Ziegler–Natta systems.

This „International Symposium on Metalorganic Catalysts for Synthesis and Polymerization", held in Hamburg from September 13–17, 1998 gave an overview of today's point of research for olefine polymerizations with metalorganic compounds. The goals of the symposium were to show the ways for further development of catalysts, to find proper methods in molecular modeling, to investigate the kinetics and the overall mechanisms of the catalysis with heterogeneous and homogeneous catalysts, to povide with synthetic pathways for new polyolefins and copolymers with different properties and finally to develop tools and techniques for a comprehensive characterization of the polymers and processes.

In many aspects there remain a lot of yet (unsolved) problems and possibilities for the future.

On this symposium, 49 lectures and over 90 posters were presented. We are pleased to announce that 59 manuscripts of lectures and posters could be included in this proceedings book.

The organizers like to express their special thanks to the University of Hamburg, to the Gesellschaft Deutscher Chemiker, and to companies which have sponsored the symposium and this monograph, to all authors who prepared manuscripts, and to all participants for discussions.

Hamburg, May 1999 Walter Kaminsky

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1. Heterogeneous Ziegler–Natta Catalysis

Polyethylene: Polymer with Future

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Abstract

Polyethylenes play a very important role today, because these polymers have a lot of advantages in comparison to other materials. They are produced using easily accessible, reasonable raw materials, they are environmentally harmless, and they can be recycled or energetically exploited after loss of performance. However, the most important aspect is, that they can be tailored in an excellent way using well established modern, energy saving, and non-polluting technologies of large scale.

To make these products and to run these processes appropriate catalysts mostly together with cocatalysts are required. The catalyst or the catalyst/cocatalyst system plays the key role for catalytic polymerization of olefins. Now, a broad spectrum of high mileage catalyst systems is available and some new ones are under development. New catalyst systems open prospectives for future progress. The catalyst system and the polymerization process are forming the polymerization technology and both parts must be well-balanced to reach a high level of effectiveness.

Besides the polymerization technology, the correlations between polymer structure and polymer properties must be known to tailor products. Based on these three legs: catalyst or catalyst system, process, polymer properties/polymer structure relations, polyethylenes with new and so far unknown properties can be designed and brought to the market. With these polymers consumers needs can be better met saving material and energy for processing, transportation and finally, waste management.

Introduction

Polymers are today materials used in all fields of life. These materials have been discovered within this century and are now produced overall in the world [1]. Nowadays (1995) around 160 Mt of polymer–based materials (plastics, fibers, elastomers, duromers, dispersions) are consumed per annum. The largest part are plastics with around 100 Mt/a and among these the polyolefins have a share of about 60 Mt/a [2,3].
Within the next 10 years production and consumption of polyolefins will considerably increase to reach between 100 and 110 Mt/a. The key success factors for polyolefins are the following ones: the raw materials (monomers) are easily accessible and reasonable based on oil or natural gas. The production costs are low due to modern, energy saving and non-polluting large volume processes. The products are saving resources and they are environmentally harmless thus contributing to the principle of sustainable development [4,5]. After loss of