HANDBOOK OF TRANSITION METAL POLYMERIZATION CATALYSTS

Edited by

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Chemplex Company (Retired)
Adjunct Faculty, Roosevelt University
Schaumburg, IL

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CONTENTS

GENERAL INTRODUCTION

Polymer synthesis employs two main reaction types: step growth and chain growth. Chain growth polymerizations account for a large portion of commodity plastics and synthetic elastomers. The polymerization mechanisms involve all of the highly reactive intermediates of organic chemistry: free radicals, carbonium ions, carbanions, and coordinatively unsaturated metal species.[1] The action of these reactive intermediates on appropriate monomers fits the classical definition of catalysts. They repeatedly promote the same reaction of monomer addition, taking part in each step of monomer molecule addition, and they do this by lowering the activation energy of the incorporation step.

This book was started with the intention that it be a comprehensive handbook for a particular group of polymerization catalysts. The criterion for a catalyst to be in the group was that, in each case, the catalyst exerts some distinctive control on the nature of the polymers formed. Traditional free-radical initiators were excluded because with these the polymer properties depend more strongly on the monomer-derived radicals at chain ends than on the chemical structure of the initiating compounds, whether they are peroxides or hydroperoxides, azo compounds, or redox initiators.[1]

This book includes recent advances and historically important catalysts. Additionally, selective chapters will serve as an informative guide to methods and reagents that are widely used in the field.

Transition metal catalysts for olefin polymerization, often called coordination catalysts, fit the criterion for inclusion in this book. They involve coordinatively unsaturated reactive intermediates. The site of growth for the polymer chains is a metal–carbon bond into which new monomer molecules are successively inserted. Because the metal atom is exactly at the monomer insertion point, the identity of the metal and its ligands greatly influence polymer properties compared to normal free-radical initiators. In 1973, W. L. Carrick[2] described how different metal atoms, such as vanadium, titanium, zirconium, and hafnium, influenced reactivity ratios for olefin copolymerizations. In contrast, the composition of copolymers in traditional free-radical polymerization depends on the *Q*–*e* electronic numbers[1] of the monomers.

It is certain that many other catalysts as defined above should also be in this book. Certain compounds involved in metal-mediated free-radical polymerization and ring-opening polymerization agents may meet the criterion. For example, in the first case there are the compounds involved in catalytic chain transfer polymerization which feature a weak cobalt–carbon bond. For the second case, ring–opening polymerizations of cyclic esters with appropriate metal alkoxides are proposed to proceed by monomer coordination and addition at a metal-to-oxygen bond with distinctive results dependent on not only the metal identity but also the structure of the metal compound as well.[3] Unfortunately these subjects are also excluded.

Some readers may be familiar with the myriad of catalysts for petroleum refining and the technology of their use in industry. They are a vast part of the world's catalysis enterprise. But there is an important difference in the use of petroleum-refining catalysts and the modern polymerization catalysts of industry that may be relevant to newer polymerization catalysts. In the petroleum industry hydrotreating, hydrocracking, reforming, and isomerization catalysts are all retained in some type of bed while reactant streams pass through and reaction mixtures exit. When these catalysts become inefficient with age, they are for the most part regenerated. Regeneration may even be carried out continuously. On the other hand, as of the year 2008, no well-known polymerization catalyst is regenerated. In many polymerization processes the solid polymer products are isolated with intermingled catalyst residues. This is true for various polyolefin processes, solution, slurry, and gas-phase polymerization. Extraction of the residues is a costly step on a commercial scale.

Ziegler–Natta catalysts for polyethylene and polypropylene are one of the main varieties of coordination catalysts. In their early years, some treatment to remove catalyst residues was necessary for acceptable commercial products. However, with the highly reactive catalysts now used for the manufacture of polyolefins, the products are suitable for most end uses without removal of the residues, and in each case the cost of the catalyst is only a small fraction of the total cost of manufacturing. This book deals with polymerization catalysts that afford commercially acceptable high yields of polymer with respect to catalyst mass (catalyst productivity).

This book also deals with catalysts that currently have modest or low productivity under the best known conditions. There is interest in these catalysts because they have a real potential for the synthesis of polymer products of much greater value. A hypothetical example is a polymer made with a palladium catalyst that is far superior to anything known for fabricating an artificial heart valve. The value of such an application could bear the cost of palladium recovery and modest productivity. Probably with such a catalyst, the best strategy for recovering palladium might be to retain it on a monolithic support as in automobile catalytic converters or on pellets in a manner similar to petroleum-refining catalysts. This necessitates that the polymer be kept in solution following chain transfer while the catalyst remains bonded to the support.

It is notable that the chromium catalysts discovered by Hogan and Banks[4] have been improved by diligent research, and, in fact, the Phillips chromium catalysts are now superactive with commercial productivites of a million pounds of polyethylene per pound of chromium common. However, they had low productivity in the beginning, and in the 1958 patent[4] Hogan and

Banks reported using the catalysts in captive beds and proposed regeneration. If it turns out that ruthenium or palladium polymerization catalysts are commercialized by means of retaining the catalyst on a fixed or semifixed bed, credit should be given to chemists of the last century who already had the idea.

Most polymerization catalyst chemists are familiar with the propagation step in olefin polymerization by coordination catalysts. The series of proposed propagation mechanisms started with the Cossee hypothesis in 1964. Then, the Green–Rooney mechanism in 1978 was followed in 1983 by a modification involving agostic interaction proposed by Maurice Brookhart and Malcolm L. H. Green.[5] The latter modification has been of great use in explaining the highly branched ethylene polymers formed by nickel and palladium catalysts.[6]

These mechanisms presume the existence of a metal-to-alkyl group bond into which the monomers are successively inserted. They do not explain how this first metal–alkyl bond, if needed, is formed. The main concern of Cossee was the original Ziegler–Natta catalysts which comprise the reaction mixtures formed by transition metal compounds and certain reactive metal alkyl and hydride compounds. In one of Karl Ziegler's early patents filed in 1958 the transition metals of the compounds in claim 1 are those of "Groups IVB, VB, VIB, including thorium and uranium, metals of group VIII of the periodic system and manganese."[7] It was hypothesized that among the products in the reaction mixtures there were compounds with a transition metal–alkyl or transition metal–hydride bond with the alkyl or hydride coming from the second reagent.[2] In modern terms the transition metal compound is called the catalyst, and the second reagent is the cocatalyst. There are three related facts: (1) With the thermally activated chromium-on-silica catalysts invented by Paul Hogan and Robert L. Banks of Phillips Petroleum Company no cocatalyst of any kind is needed to obtain great reactivity. (2) Although many metallocene compounds used as polymerization catalysts have metal–alkyl bonds by prior synthesis, cocatalysts such as MAO (methylaluminoxane) or discrete Lewis acidic activators that both give rise to a positively charged metal alkyl partnered with a weakly coordinating anion are nonetheless needed for high polymerization activity under convenient conditions.[8] (3) In ROMP (ring-opening metathesis polymerization) suitable metal compounds sometimes require cocatalysts for activity[9] but also there metal carbene complexes that do not.[10] For more about these three facts please refer to appropriate chapters in this book (A Review of the Phillips Chromium Catalyst for Ethylene Polymerization, Product Morphology in Olefin Polymerization with Polymer-Supported Metallocene Morphology, and Ring-Opening Metathesis Polymerizations (ROMP) and Acyclic Diene Metathesis (ADMET) with Homogeneous Ruthenium and Molybdenum Catalysts).

The first chapter deals with metal alkyls and other compounds that function as cocatalysts with a large number of catalysts. The second chapter examines the varieties of porous silica that are either necessary or valuable in certain catalyst formulations. The following chapter on computer modeling explains a useful tool for catalyst chemists. Not all of the catalysts in this book have been, or ever will be, manufactured on the scale needed for the production of commodity polyolefin plastics. However, there are chapters on catalyst scale-up and commercialization which are introductions to these necessary activities. These two chapters contain information that will probably be helpful to all polymerization catalyst chemists.

In the Ziegler patent cited above, copper was not claimed as a catalyst component although all of the other 3*d* transition metals were. This book has a chapter Copper Catalysts for Olefin Polymerization. Since Ziegler's time the preferred numbering of the groups in the periodic table has changed. Dr. Galletti has copper in group 11 but Karl Ziegler would have written group IB.

As stated above, one of the most important attributes of catalysts used in the manufacture of major synthetic plastics and elastomers is high productivity. The catalyst systems, however, in concert with monomer concentrations and reaction temperatures, also control polymer properties. Catalyst systems are key to tailoring (1) molecular weight (MW) and molecular weight distribution (MWD), (2) comonomer incorporation and molecular shape, (3) stereoregularity (including at least isotacticity, syndiotacticity, and cis, trans, and 1,2-additions for dienes), and for polymers made in slurry- and gas-phase processes (4) polymer particle morphology. The first three of these are consequences of the chemical nature of the active sites within the catalyst system, but the fourth depends as well on the geometric arrangement of the active sites within catalyst particles or a support.

Well-regulated particle morphology permits higher space–time yields in polymerization plants, increases the bulk density, eliminates fines and minimizes dust explosions, and, perhaps most important, helps prevent reactor fouling. In an extreme ideal case excellent particle shape may allow elimination of the common pelletizing step. Information on morphology control may be found in these chapters: Porous Silicas for Transition Metal Polymerization Catalysts, Supported Magnesium/Titanium–Based Ziegler Catalysts for the Production of Polyethylene, Stereospecific Polymerization with "Traditional" Ziegler–Natta Catalysts, $MgCl_2$-Supported Ti Catalysts for the Production of Morphology-Controlled Polyethylene, and Product Morphology in Olefin Polymerization with Polymer-Supported Metallocene Catalysts.

With solution polymerization processes particle morphology does not apply, but the catalyst system remains the major tool to tune polymer properties. Finding a catalyst for a new polymer type and then designing and modifying it to secure the optimum properties and synthesis condition is demanding. We hope this book and what others may do with it will help.

The authors who have contributed to this book have great knowledge and impressive credentials. Brief biographies for each of them follow immediately after the references for this introduction.

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ABOUT THE AUTHORS

Dennis B. Malpass Dennis Malpass was born and raised in Biloxi, Mississippi. He studied chemistry at Tulane University in New Orleans, Louisiana, and received a B.S. in 1966. He then attended graduate school at the University of Tennessee in Knoxville, Tennessee, and studied main-group organometallic chemistry under Professor Jerome F. Eastham. He received his Ph.D. in 1970 and began his career with Texas Alkyls (now Akzo Nobel). His industrial career spanned 33 years working on synthesis, characterization, and application of metal alkyls, especially aluminum alkyls in Ziegler–Natta polymerization of olefins.

His work included development of viable commercial processes for trimethylaluminum, a crucial raw material for many single-site catalyst systems. He was also codiscoverer of *n*-butylethylmagnesium (BEM) in 1978, still employed today to produce catalysts in the manufacture of many millions of tons of polyethylene worldwide.

He has more than 70 patents and publications. He retired in 2003 and now lives in Magnolia, Texas.

Robert E. Patterson Dr. Robert E. Patterson is director of R&D operations for PQ Corporation of Valley Forge, Pennsylvania, a leading producer of silicates, zeolites, glass beads, and silica gels. He joined PQ in 1978 after receiving his B.S. and Ph.D. degrees in chemistry from Rensselaer Polytechnic Institute, where his doctoral thesis was on foams and antifoams. This experience later proved useful at PQ, where Dr. Patterson led the company's research program on precipitated silica defoamers.

After a-3½ year hiatus as corporate planning manager, Patterson returned full time to R&D in 1991 and in 1999 assumed technical responsibility for all silica products, incl uding adsorbents for beer stabilization and edible oil purification, as well as supports for chromium catalysts in the production of high-density polyethylene. His responsibilities were later expanded to focus on market development of higher value new end uses for silica products. More recently he was made site manager for PQ's corporate research laboratory and pilot plant as well as manager of the facility's analytical and information services departments.

Dr. Patterson is the author of over 35 technical publications, including papers, posters, and patents. He has contributed chapters to four books and is the author of the article on silica in the *Kirk Othmer Encyclopedia of Chemical Technology*. He was previously chairman at the Specialty Silica Summit 2007 and a co-chairman at the Ralph K. Iler Memorial Symposium on the Colloid Chemistry of Silica.

Thomas J. Pullukat After receiving his Ph.D. from Purdue University, West Lafayette, Indiana, Thomas J. Pullukat joined Chemplex Company (Rolling Meadows, Illinois) in 1967. His initial assignment was in catalyst research. At Chemplex, he developed new silica-supported chromium catalysts (Phillips type) for the economical particle form (PF) process. The first direct synthesis of polyethylene milk bottle grade in the PF process was commercialized in 1971. Several other silica–chromium catalysts for the production of polyethylene for use in cereal package liners, 55-gallon drums, geomembrane, and construction barricades were commercialized. A silica-based Ziegler–Natta catalyst for the gas-phase fluidized-bed polyethylene process also was developed. Another silica-based polypropylene catalyst resulted from research on catalysts for the BASF gas-phase process. Over the years, Chemplex merged with Northern Petro and then with USI. The new company was named Quantum. During the mergers, he held several positions: manager, catalysis/polymer physics/analytical and senior research manager, catalyst research/scale-up.

In 1991, Dr. Pullukat left Quantum (now Equistar) to join PQ Corporation (Valley Forge, Pennsylvania). At PQ, he directed the development of technology for the production of silica-based catalysts. Several high-pore-volume chromium catalysts have been commercialized. A silica-based Ziegler–Natta catalyst and silica supports for single-site catalysts have been developed. In 2000 he became responsible for global marketing and technical service of silica catalyst products.

At present he is the president of SILCAT Consultants, a technology and marketing company involved in developing solutions to improve the economics of polyethylene production. He is the author of 45 U.S. patents and over 15 scientific publications. He also has chaired several scientific conferences and is an invited speaker in catalysis symposiums.

Artur Michalak Dr. Artur Michalak (born in 1968) graduated from Jagiellonian University (Kraków, Poland). He received his Ph.D. in theoretical chemistry in the Department of Theoretical Chemistry, Faculty of Chemistry, Jagiellonian University, and then held a postdoctoral fellowship at the University of Calgary, joining the research group of Professor Tom Ziegler. In 2004 he received his D.Sc. degree (habilitation). He is employed as associate professor in the Faculty of Chemistry, Jagiellonian University. He is currently a vice-dean of the Faculty of Chemistry. His main research subjects include chemical bond theory, theoretical description of organometallic systems, and modeling of catalytic processes, in particular polymerization and copolymerization of α-olefins catalyzed by transition metal complexes. He authored over 50 articles in international scientific journals.

Monika Srebro Monika Srebro was born in Tarnow, Poland, in 1982. In 2006, she received her M.Sc. in Chemistry and has started her Ph.D. studies under the supervision of Dr. Artur Michalak in the Department of Theoretical Chemistry at the Jagiellonian University in Cracow. In 2007, she obtained her B.Eng. in Materials Engineering from the University of Science and Technology in Cracow. Her main research topic is molecular modeling of polymerization of α-olefins and their copolymerization with polar monomers catalyzed by transition-metal-based complexes.

C. P. Cheng Dr. Chung Ping (C. P.) Cheng received his B.S. in Chemical Engineering at the University of Wisconsin-Madison and his M.Ch.E. and Ph.D. from the University of Delaware. After graduation, he joined Akzo-Nobel (then Stauffer Chemical) and began his long career in Ziegler–Natta catalysts. While at Akzo-Nobel, he worked on development of the manufacturing processes for first- and third-generation Ziegler–Natta catalysts. In 1988, Dr. Cheng joined Quantum Chemical (now part of Lyondell-Basell) as section leader in catalyst scale-up working on the development of various polypropylene and polyethylene catalysts. In 1991, he moved to Catalyst Resources Inc. (CRI, then part of Phillips Petroleum, and after several changes of ownership, now part of BASF) and worked for 16 years on the development of polyolefin catalysts and the application of these catalysts in polymerization processes. He is part of the team that successfully commercialized the Lynx polypropylene catalyst to all polymerization process platforms. Since 2007, he has been with Süd-Chemie as the chief technology officer of the Polyolefin Catalyst Division, working out of Shanghai, China. Dr. Cheng has several patents and many publications in the polyolefin area and is a frequent speaker at international polyolefin conferences.

C. E. Capshew Dr. Charles Capshew majored in chemistry and mathematics at today's SWOSU (Weatherford, Okhahoma). For the next five years he was a U.S. Air Force pilot and was deployed three times to Vietnam and Southeast Asia flying reconnaissance and bombing missions. After earning a Ph.D. in Organic Chemistry at the University of Texas at Austin under Dr. Rowland Pettit, he joined the Phillips Petroleum Company (and Chevron Phillips Chemical Company in 2000) and spent 27 years in polyolefins, retiring in 2004. His career span R&D, product development, marketing, manufacturing, and quality management. His career required frequent worldwide travel. He is credited with 13 U.S. patents and seven other publications. In 1994 his industrial accomplishments were recognized by his alma mater where he was honored as a distinguished graduate. Since his formal retirement from Phillips and Chevron Phillips, Dr. Capshew has been serving as an independent contracting consultant in polyolefins to Chevron Phillips. His volunteer efforts have included work with the Society of Plastics Engineers, the American Chemical Society, and civic organizations, and he has spent many hours supporting various school athletic teams and "retired" after being a quarterback club president. He and his wife, Loni, have been married 38 years and have three children and three grandchildren.

Thomas E. Nowlin Thomas Nowlin received a B.S. in Chemistry from the University of Iowa in 1967, Ph.D. in Chemistry from Michigan State University 1971, and M.B.A. degree from Rutgers University in 1982. He was commisioned a second lieutenant in the USAR Chemical Corps in February 1971 and served two years active duty at Edgewood Arsenal from 1971 to 1973. He retired as a LTC from the USAR Chemical Corps in 1989 with 20 years of service. Dr. Nowlin was a research Chemist for Union Carbide Corporation from 1973 to 1979 in Bound Brook, New Jersey, and worked for Mobil Chemical Company, Edison, New Jersey, as a research chemist from 1980 to 2000. He investigated olefin polymerization catalysts from 1977 to 2000 and received over 50 U.S. patents for Mobil Oil Corporation, mostly in the area of Ziegler and metallocene catalysts for ethylene polymerization. He has published 20 papers in chemical journals from 1971 to 2000.

Robert I. Mink Robert I. Mink received his Ph.D. from the University of Illinois at Urbana and then held a postdoctoral fellowship at Cornell University. He has worked for Akzo Nobel and Mobil Chemical Company. His area of research has focused on the synthesis of ethylene and propylene polymerization catalysts. He holds over 40 U.S. patents in the area of polymerization catalysts and has co-authored publications related to polymerization catalysts and the chemical mechanisms in olefin polymerization reactions.

Yury V. Kissin Yury Kissin (born in 1937) received his degree in polymer chemistry in 1965 at the Institute of Chemical Physics in Moscow investigating α-olefin polymerization reactions with heterogeneous Ziegler–Natta catalysts. Since 1960 until 1977 he worked at the Institute of Chemical Physics studying kinetics of polymerization reactions of ethylene, propylene, and higher α-olefins and the structure of polyolefins and catalysts by infrared. He immigrated to the United States in 1979 and worked as a research associate first at Gulf Research and Development Company in Pittsburgh, Pennsylvanie (1980–1985), and then at Edison Research Center of Mobil Chemical Company, New Jersey (1985–2000). His main research subjects were synthesis of Ziegler–Natta catalysts, kinetics of polymerization and oligomerization reactions, and spectroscopic studies of polymerization catalysts. Since 2000 he is a visiting scientist at the Department of Chemistry of Rutgers University, New Jersey, where he studies kinetics of olefin polymerization reactions with Ziegler–Natta and late-period transition metal catalysts. He authored 3 books (*Isospecific Polymerization of Olefins*, Springer, 1985; *Polymers and Copolymers of Higher α-Olefins, Hanser*, 1997; *Alkene Polymerization Reactions with Transition Metal Catalysts*, Elsevier, 2008), 20 articles in chemical/polymer encyclopedias, approximately 200 scientific articles, and over 40 patents in the fields of synthesis of Ziegler–Natta and metallocene catalysts.

John Severn John Severn completed his Ph.D. in Organometallic Chemistry at the University of Sussex under the supervision of Professor M. F. Lappert in 1998. In 1999 he joined the group of Professor R. van Santen at Eindhoven University of Technology as a postdoc, working on the immobilization of α-olefin polymerization catalysts and the use of silsesquioxanes as homogeneous models. Then he joined the Dutch Polymer Institute in 2001, working with Dr. John Chadwick on the immobilization of single-site α-olefin polymerization catalyst, before joining Avantium Technologies B.V. in 2004, developing high-throughput experimentation (HTE) techniques for polyolefin catalysis. Since 2005 he has been with Borealis Polymer Oy, Finland, initially as a researcher and is currently task leader for single-site catalysis and HTE implementation within Borealis.

Robert L. Jones, Jr. Robert L. Jones started his studies at the University of Houston, completing graduate programs in both biology (M.Sc. 1979) and chemistry (M.Sc. 1990). In 1985 he joined the research team of Dr. John A. Ewen at Fina (LaPorte, Texas), where he synthesized ligand and metallocene complexes and performed polymerizations with commercial and experimental polyolefin catalysts. In 1990 he joined Himont (Lake Charles, Louisiana) as the plant polymer chemist specializing in ultrahigh molecular weight polyethylene (UHMWPE). In 1992 he moved into Himont R&D, working in the field of long-range catalyst research in Ferrara, Italy, at the Giulio Natta R&D Center, then Montell Polyolefins North American R&D Center in Elkton Maryland, and with Basell Polyolefines in Germany (Ludwigshafen and Frankfurt/Höchst). In 2005 he completed his doctorate at the Technical Universität Kaiserslautern under the direction of Professor H. Sitzmann. In 2007 he joined The Polymer Technology Group in Berkeley, California, where he is currently a staff scientist, designing and synthesizing polymers for biomedical application.

Sieghard E. Wanke Sieghard Wanke obtained his B.Sc. and M.Sc. in Chemical Engineering from the University of Alberta and a Ph.D. in Chemical Engineering from the University of California, Davis. He worked for Celanese, Canada and Celanese Research in New Jersey for two years in the area of heterogeneous catalysis. In 1970, he joined the Department of Chemical Engineering, now the Department of Chemical and Materials Engineering, at the University of Alberta as an assistant professor and he has been a professor since 1978; he served as the department chair for 14 years. His research areas are heterogeneous catalysis and reaction engineering with emphasis on supported metal catalysts and catalytic olefin polymerization.

Long Wu Long Wu graduated from Tianjin University with a B.Eng. in Polymer Science and Engineering in 1986. From 1986 to 1993, he conducted research on Ziegler–Natta catalysts and olefin polymerization at the Shanghai Research Institute of Chemical Industry. In 1999, he received a Ph.D. in Chemical Engineering from the University of Alberta, under the supervision of Drs.

David T. Lynch and Sieghard E. Wanke. He then remained in Dr. Wanke's group as a research associate. The main focus of his research at the University of Alberta has been on catalysis and reactor engineering, with a particular emphasis on morphology-controlled olefin polymerization.

Max P. McDaniel Dr. Max P. McDaniel received a Ph.D. in Physical Chemistry in 1973 from Northwestern University where he studied the porosity and redox capacity of chromia, followed by a year in Lyon, France, as a CNRS Chercheur Associé de Catalyse. McDaniel joined Phillips Petroleum Company in 1975 to work on Cr/silica catalysts under J. Paul Hogan, discoverer in 1951 of the Phillips polymerization catalyst and founder of the high-density polyethylene (HDPE) industry. McDaniel held various technical and leadership positions at Phillips (now Chevron-Phillips), always involved in its polyethylene catalyst, resin development, and licensing programs. An inventor of much of the Phillips catalyst technology, McDaniel has authored some 100 scientific publications and lectures and holds over 250 U.S. patents.

Kevin Cann Kevin Cann received his Ph.D. from the University of Texas at Austin. He joined Union Carbide Corporation in 1979 working in the polyolefin catalyst area. Since the merger with The Dow Chemical Company (2001), he has worked for Univation Technologies, which continues to license Unipol™ gas-phase polyethylene technology worldwide. His research areas have included development of Ziegler–Natta, chromium, and single-site catalysts for production of linear low-density polyethylene, high-density polyethylene, ethylene propylene diene monomer rubber (EPDM), and polybutadiene polymers in the fluid bed gas-phase process. He has over 35 U.S. patents and more than 30 publications and papers.

Scott Collins Professor Scott Collins was born and educated in Calgary, Alberta, Canada. He received his B.Sc. degree in 1979 and his Ph.D. in 1983, both from the University of Calgary, working with Thomas G. Back in the area of synthetic, organoselenium chemistry. He had a postdoctoral stay with Satoru Masamune at M.I.T., working on the synthesis of doubly bonded group 14 (Si, Ge, and Sn) compounds and bicyclic, tetrasilanes for a period of about 1½ years. He joined the Chemistry Department at the University of Waterloo in 1985, where he initiated a research program in asymmetric and polymerization catalysis using chiral, ansa-metallocene complexes. He was the first scientist in Canada to study metallocene-catalyzed olefin polymerization and cyclic olefin polymerization using metallocene catalysts, and his group also discovered group transfer polymerization of acrylates and methacrylates using zirconocene initiators. He held the Nova/Natural Sciences and Engineering Research Council Industrial Research Chair for a period of five years while at the University of Waterloo and was involved in the development of new, single-site group 4 catalysts for ethylene polymerization, novel anchoring technology for single-site catalysts, and the study of new cocatalysts and scavengers for single-site catalyst activation. He joined the faculty in the Department of

Polymer Science at The University of Akron in 2000 where he initiated work in Ni-catalyzed ethylene polymerization and cationic polymerization of isobutene using chelating diboranes, including the first aqueous suspension polymerization of isobutene. He will be leaving Akron to join the Instituto Universitario de Investigación de Catálisis Homogénea (IUCH) affiliated with the Universidäd de Zaragoza, España, in 2009.

Bernhard Rieger Bernhard Rieger obtained his Ph.D. in Chemistry at the Ludwig-Maximilians-Universität, Munich, in 1988. After a postdoctoral research at the University of Massachusetts at Amherst, Department of Polymer Science and Engineering, from 1988 till 1989, he joined the BASF Company from 1989 until 1991 for research about metallocene polymerizations. After his habilitation from 1991 until 1995 at the Eberhard-Karls-University in Tübingen, he was a professor at the University of Ulm from 1995 on as well as head of the Department of Materials and Catalysis until 2006. Since then he has been head of the WACKER Chair of Macromolecular Science at the Technische Universität, München. His main research interests are homogeneous polymerization catalysis, where numerous publications concern the alkene/CO copolymerization as well as silicon-containing polymers and self-assembled functional surface structures.

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Maria Leute Maria Leute graduated from the University of Ulm in 2003 with a chemistry major and "Mit Auszeichnung" (excellent) grade. Her Ph.D.

is also from the University of Ulm where she worked under Dr. Bernhard Rieger. (Thesis title: "Macromolecules with Phosphorus Functionalities"). She now has the position of R&D Manager with Wacker Chemie AG in Munich, Germany.

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Ray Hoff Ray Hoff graduated from Beloit College in Wisconsin with a B.S. in Chemistry in 1956, and immediately began research work on phenol-formaldehyde resins at the Westinghouse Research Center in Churchill Borough, Pennsylvania. In 1964 he obtained a Ph.D. in Organic Chemistry from the University of Utah and began work at the B.F. Goodrich Research Center in Brecksville, Ohio. He was primarily involved with synthetic rubber projects using cobalt Ziegler–Natta catalysts and aklylithium anionic initiators. From 1967 to 1993 he was engaged in ethylene polymerization catalyst work with Chemplex Company and its successors. The main catalyst types were Phillips thermally-activated chromium catalysts and magnesium-modified Ziegler catalysts. Since 1993 he has worked as a consultant and chemistry teacher, most recently as adjunct faculty with Roosevelt University, Schaumburg, Illinois.

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1 Commercially Available Metal Alkyls and Their Use in Polyolefin Catalysts

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1.1 INTRODUCTION

Organometallics are defined as compounds that contain a *direct* carbon–metal bond. Such compounds may be regarded as the interface between organic and inorganic chemistry. There are two basic types of organometallics: metallocenes and metal alkyls. Metallocenes contain a carbon–metal *pi* (π) bond and most often involve transition metals from groups 3–11 of the periodic table and aromatic ligands such as cyclopentadienyl ("Cp") or indenyl.[1,2] Metal alkyls are defined as organometallic compounds containing a carbon-to-metal *sigma* (σ) bond.

Metal alkyls are essential to the performance of industrial Ziegler–Natta (ZN) catalysts and most single-site catalysts (SSCs that do not require cocatalysts were recently reported[3] but are not yet in industrial use). This chapter will stress practical aspects of metal alkyls, particularly those used with transition metal polyolefin catalysts. We will answer questions such as:

- What are the distinguishing properties of metal alkyls?
- Which are the commercially important metal alkyls?
- How do metal alkyls function in polyolefin catalyst systems?
- What are the impurities in commercial metal alkyls and how do these impurities influence catalyst performance?
- What selection criteria are used for metal alkyls in polyolefin catalyst systems?

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Key synthetic chemistries will be mentioned but are not discussed in depth. Detailed reviews of production, properties, and applications of metal alkyls are available elsewhere.[4–12]

In manufacture of polyolefins, the most important metal alkyls are those of aluminum and magnesium. Other organometallics are employed in production of polyolefins but in much smaller quantities. These include organometallic compounds containing boron and zinc and a range of metallocenes. First-generation supported chromium catalysts ("Phillips catalysts") do not require metal alkyls.[13] However, performance of some chromium catalysts developed in the 1970s–1980s is improved by metal alkyls.[13,14] Metallocenes will not be discussed in detail in this chapter but will be addressed in the context of SSCs in subsequent chapters.

Note that the definition of organometallics excludes compositions such as metal alkoxides, metal carboxylates, and chelated metal complexes involving nitrogen and phosphorus, since there is an intervening heteroatom between the carbon and the metal. Hence, many nonmetallocene SSCs based on late transition metals[15,16] are not technically organometallic compounds, though active centers are believed to contain direct metal–carbon σ bonds.

1.2 METAL ALKYLS IN ZIEGLER–NATTA CATALYSTS

Aluminum alkyls and magnesium alkyls fulfill several roles in ZN polymerization catalyst systems. The two most important are as raw materials for catalyst synthesis and as cocatalysts (sometimes called "activators") for the transition metal catalyst. These key functions are illustrated in simplified equations below.

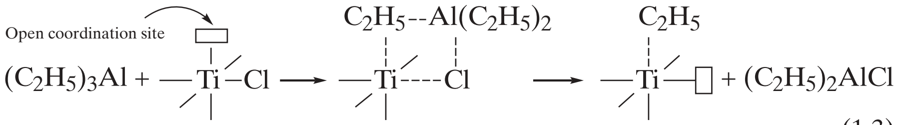
- *Metal alkyls in catalyst synthesis:* Reduction of the transition metal "precatalyst," exemplified below with titanium tetrachloride and ethylaluminum sesquichloride (EASC):

$$2TiCl_4 + 2(C_2H_5)_3Al_2Cl_3 \rightarrow 2TiCl_3\downarrow + 4C_2H_5AlCl_2 + C_2H_4 + C_2H_6 \quad (1.1)$$

  Production of a support, as shown in Eq. 1.2 with a dialkylmagnesium compound and anhydrous HCl:

$$R_2Mg + 2HCl \rightarrow MgCl_2\downarrow + 2RH\uparrow \quad (1.2)$$

- *Metal alkyls as cocatalysts:* Alkylation of the reduced transition metal compound to produce active centers for polymerization, illustrated below with triethylaluminum (TEAL) and $TiCl_3$:



(1.3)

Aluminum alkyls also serve the purpose of scavenging catalyst poisons (water, O_2, etc.). Poisons enter as parts-per-million (ppm) contaminants in materials commonly used in polyolefin processes such as monomer, comonomer, solvents, and chain transfer agents. Reaction of the aluminum alkyl with contaminants generates alkylaluminum derivatives that are not as damaging to catalyst performance. For example, water reacts with TEAL to produce small amounts of ethylaluminoxane:

$$2(C_2H_5)_3Al + H_2O \rightarrow (C_2H_5)_2Al{-}O{-}Al(C_2H_5)_2 + 2C_2H_6\uparrow \qquad (1.4)$$

Typically, aluminum alkyls are used in large excess in ZN catalyst systems. Aluminum–titanium ratios of 20–40 are common in industrial polyethylene processes. Hence, there is ample TEAL to fulfill the roles discussed above. Aluminum alkyls also are involved in chain transfer, but this is a minor function. (Hydrogen is used most often for chain transfer/termination reactions with modern ZN catalysts.)

Aluminum alkyls are preferred as cocatalysts because other metal alkyls are either too expensive or perform poorly. When tried as cocatalysts, magnesium alkyls may completely deactivate ZN catalysts. The reason for this is unknown, but it may stem from overreduction of the transition metal or blockage of active centers caused by strong coordination of magnesium alkyl. Use of zinc alkyls often lowers catalyst activity and reduces polymer molecular weight by acting as a chain transfer agent.

The vast majority of modern ZN catalysts employ aluminum alkyls as cocatalysts, while magnesium alkyls are used solely as raw materials for the production of catalysts.

1.3 ALUMINUM ALKYLS

The term “aluminum alkyl” is meant to include any compound that contains an alkylaluminum grouping and encompasses R_3Al, R_2AlCl, $R_3Al_2Cl_3$ (the so-called sesquichlorides), $RAlCl_2$, R_2AlOR', and R_2AlH. Among commercially available aluminum alkyls, R is typically a C_1–C_4 alkyl. Methylaluminoxanes are also aluminum alkyls and have become important in recent years as cocatalysts for SSCs. However, methylaluminoxanes exhibit significantly different properties than conventional aluminum alkyls and will be discussed separately (see Section 1.5).

Aluminum alkyls have been produced commercially since 1959 using technology originally licensed by Nobel laureate Karl Ziegler.[9] Aluminum alkyls are pyrophoric and violently reactive with water.[4,6,12] Considering these properties, it is remarkable that millions of pounds of aluminum alkyls are produced each year and have been supplied to the polyolefin industry worldwide for half a century with relatively few safety incidents.

Principal aluminum alkyls available in the merchant market (and their common acronyms) are provided in Table 1.1. Typical properties of commercially available aluminum alkyls are summarized below:

- Most ignite spontaneously when exposed to air and are explosively reactive with water. (Please see the appendix for a discussion of pyrophoricity of metal alkyls.)
- Aluminum alkyls are typically clear, colorless liquids at ambient temperature and are miscible in all proportions with aliphatic hydrocarbons (HCs). Large quantities of aluminum alkyls are supplied as solutions in HCs, because solutions are *perceived* to be safer.
- R_3Al compounds (R = ethyl or higher) contain small amounts of R_2AlH. Hydride content is expressed as AlH_3 by tacit convention among major suppliers and typically ranges from about 0.02% (wt) in TEAL to about 0.5% in triisobutylaluminum (TIBAL).

R_3Al compounds also commonly contain small amounts of other trialkylaluminum compounds (R'_3Al). This is usually a consequence of the purity of starting materials or of side reactions during manufacture, such as addition of an ethylaluminum moiety in TEAL across ethylene to produce an *n*-butylaluminum group (Figure 1.1).

R'_3Al contents are low, often <0.5% (by wt). An exception is TEAL where *n*-butylaluminum content (from the reaction above, expressed as tri-*n*-butylaluminum) is typically ~5%.

In the vast majority of ZN catalyst systems, hydride content and the presence of small amounts of other trialkylaluminum compounds (R'_3Al) are not damaging to performance. However, for certain polypropylene (PP) catalysts that employ alkoxysilanes as external donors, hydride can cause a reduction in isotactic content and lowered catalyst activity.[51] Additional tests with TEAL containing up to 16% R'_3Al with a modern supported PP catalyst showed no loss of isotacticity and no loss of activity.[51]

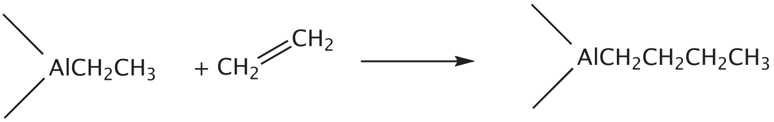


Figure 1.1 Insertion of ethylene into an ethyl group–aluminum bond to form butylaluminum.

TABLE 1.1 Principal Commercially Available Aluminum Alkyls

Product	Acronym	Formula	CAS Number	Theoretical wt % Al
Trimethylaluminum	TMAL	$(CH_3)_3Al$	75-24-1	37.4
Dimethylaluminum chloride	DMAC	$(CH_3)_2AlCl$	118-58-3	29.2
Methylaluminum sesquichloride	MASC	$(CH_3)_3Al_2Cl_3$	12542-85-7	26.3
Triethylaluminum	TEAL	$(C_2H_5)_3Al$	97-93-8	23.6
Diethylaluminum chloride	DEAC	$(C_2H_5)_2AlCl$	96-10-6	22.4
Diethylaluminum iodide	DEAI	$(C_2H_5)_2AlI$	2040-00-8	12.7
Ethylaluminum sesquichloride	EASC	$(C_2H_5)_3Al_2Cl_3$	12075-68-2	21.8
Ethylaluminum dichloride	EADC	$C_2H_5AlCl_2$	563-43-9	21.3
Isobutylaluminum dichloride	MONIBAC[a]	$i\text{-}C_4H_9AlCl_2$	1888-87-5	17.4
Tri-*n*-butylaluminum	TNBAL	$(C_4H_9)_3Al$	1116-70-7	13.6
Triisobutylaluminum	TIBAL	$(i\text{-}C_4H_9)_3Al$	100-99-2	13.6
Diisobutylaluminum hydride	DIBAL-H	$(i\text{-}C_4H_9)_2AlH$	1191-15-7	19.0
Tri-*n*-hexylaluminum	TNHAL	$(C_6H_{13})_3Al$	1116-73-0	9.6
Tri-*n*-octylaluminum	TNOAL	$(C_8H_{17})_3Al$	1070-00-4	7.4
Di-*n*-octylaluminum iodide	DNOAI	$(C_8H_{17})_2AlI$	7585-14-0	7.1
"isoprenylaluminum"	IPRA	Not available	70024-64-5	Not available
Diethylaluminum ethoxide	DEAL-E	$(C_2H_5)_2AlOC_2H_5$	1586-92-1	20.7
Ethylpropoxyaluminum chloride	EPAC	$(C_2H_5)(C_3H_7O)AlCl$		17.9
Diisobutylaluminum butylated oxytoluene	DIBAL-BOT	$(i\text{-}C_4H_9)_2AlO[C_6H_2(CH_3)(t\text{-}C_4H_9)_2]$	56252-56-3	7.5

Note: IPRA: Also called ISOPRENYL. Complex composition produced by reaction of isoprene (2-methyl-1,3-butadiene) with TIBAL or DIBAL-H.
DIBAL-BOT: Also called diisobutylaluminum 2,6-di-*t*-butyl-4-methylphenoxide; produced by equimolar reaction of TIBAL with BHT.
MONIBAC: Acronym from "monoisobutylaluminum dichloride."

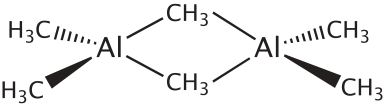


Figure 1.2 Trimethylaluminum dimer.

Aluminum alkyls also contain ppm amounts of aluminoxanes and alkoxides resulting from reaction with water (see Eq. 1.4 and oxygen, respectively. Water and oxygen enter as contaminants (typically <5 ppm) in process materials, for example, nitrogen, ethylene, and hydrogen. Aluminoxanes and alkoxides are usually undetectable (below 500 ppm) and, at these levels, cause no problems in polyolefin catalyst systems.

Total assays are not routinely conducted on commercially available aluminum alkyls. Since impurities mentioned above are also organometallics, total organometallic content of commercially available metal alkyls will typically exceed 99%. The balance is mostly process oils (a purified white mineral oil is used as lubricant and in agitator seals) and small amounts of solvents (mostly C_6–C_8 aliphatic HC) used to wash reactors and process lines.

- Aluminum alkyls are highly reactive with many of the common organic solvents. Indeed, reaction with halogenated hydrocarbons (CCl_4, $CHCl_3$, etc.) may be explosive after a quiescent period.[17] Organic compounds with acidic protons, such as alcohols and carboxylic acids, may be violently reactive with aluminum alkyls. Carbonyl compounds, such as ketones, aldehydes, and esters, react with aluminum alkyls. Ethers and tertiary amines form exothermic coordination complexes.
- R_3Al are reactive with CO_2.[18] In fact, reaction of trimethylaluminum (TMAL) with CO_2 has been used to produce methylaluminoxane cocatalysts for SSCs[19–21] (see Section 1.5.3). The R_3Al/CO_2 reaction is easily controlled and has been used to passivate aluminum alkyl waste streams.[22] However, R_3Al are unreactive with CO. Aluminum alkyls containing halogen or oxygen (DEAC, DEAL-E, etc.) are not reactive with CO_2.
- Lower molecular weight aluminum alkyls (C_1, C_2, and isoC_4) are distillable under vacuum. However, higher homologs (n-C_4 to n-C_8) are not distillable in industrial process equipment and are purified by filtration.
- Most trialkylaluminum compounds are associated as dimers, except when steric bulk of alkyl groups (*t*-butyl, isobutyl, etc.) prevents association. For example, TMAL associates via three center–two electron bonding[24] (also called "electron-deficient" bonding[25]) as depicted in Figure 1.2.
- At low temperature, proton nuclear magnetic resonance (NMR) spectra of TMAL show separate signals for terminal and bridging methyls. However, at room temperature, rapid alkyl exchange occurs and methyls are indistinguishable by NMR.