Polypropylene Handbook

Edward P. Moore, Jr.

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Polypropylene Handbook

Polymerization, Characterization, Properties, Processing, Applications

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Hanser Publishers, Munich Vienna New York

Hanser/Gardner Publications, Inc., Cincinnati

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Distributed in the USA and in Canada by
Hanser/Gardner Publications, Inc.
6600 Clough Pike, Cincinnati, Ohio 45244-4090, USA
Fax: (513) 527-8950
Phone: (513) 527-8977 or 1-800-950-8977

Distributed in all other countries by
Carl Hanser Verlag
Postfach 86 04 20, 81631 München, Germany
Fax: +49 (89) 98 12 64

Library of Congress Cataloging-in-Publication Data
Polypropylene handbook : polymerization, characterization, properties, applications/edited by Edward P. Moore, Jr.
p. cm.
Includes bibliographical references and index.
ISBN 1-56990-208-9
1. Polypropylene. I. Moore, Edward P.
TP1180.P68P65 1996
668.4'234–dc20 96-15822

Die Deutsche Bibliothek – CIP-Einheitsaufnahme
Polypropylene handbook : polymerization, characterization, properties, applications / ed. by Edward P. Moore. – Munich ; Vienna ; New York : Hanser ; Cincinnati : Hanser/Gardner, 1996
ISBN 3-446-18176-8
NE: Moore, Edward P. [Hrsg.]

Typeset in England by Techset Composition Ltd., Salisbury
Printed and bound in Germany by Druckhaus „Thomas Müntzer", Bad Langensalza

This book is dedicated to the spirit of creativity, discovery, and innovation that has made polypropylene technology and the consequent business growth so vigorous and exciting for four decades, and to the researchers who personify that spirit, represented by Prof. Giulio Natta, who gave birth to PP technology in 1954.

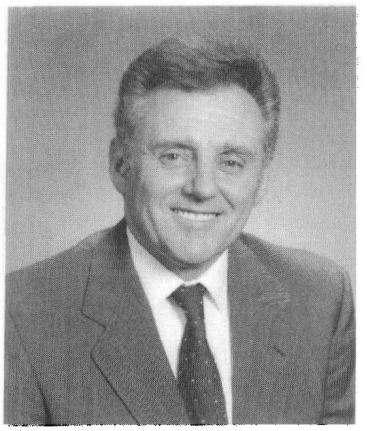
1903–1979

Fatto il polipropilene

Giulio Natta March 11, 1954

Prof. Giulio Natta was born on February 26, 1903. He received a degree in chemistry from Milan Polytechnic in 1924. In 1933, he became a professor of chemistry at Pavia, then in Rome in 1935. In 1938, Natta moved to Milan Polytechnic and became Director of the Institute of Industrial Chemistry. Following Ziegler's successful preparation of linear polyethylene in 1953, Natta prepared polypropylene on March 11, 1954. He promptly identified the crystal structure of PP and the stereospecific nature of the catalyst. Karl Ziegler and Giulio Natta shared the Nobel prize in chemistry in 1963.

Foreword



Professor Paolo Galli is President of the Montell Technology Company.

More than forty years have elapsed since the discovery of the stereospecific polymerization of polypropylene (PP). It is now widely recognized that the discovery not only represented the first and most significant step in the synthesis of crystalline PP at the scientific and industrial level, but, even more important, it meant the beginning of a new challenging adventure still in progress today. In the years following its discovery, PP went through such a dynamic industrial development that it is today one of the most widely used polymeric materials, and still has a very bright future.

The world market for PP has grown from around 1.5 mio tons in the 1970s, to about 13 mio tons in the 1990s, and is expected to be over 19 mio tons in 1995. In the year 2000 it could exceed 25 mio tons. Such explosive and unarrestable growth is due to the outstanding combination of cost performance, excellent physical properties, strong and continuous expansion of process versatility, and environmental friendly processes and materials, during manufacturing, use, and recycling stages. Nevertheless, this unique and enviable position was not expected nor foreseen, even up to the early '70s. Before this period, polypropylene was a marginal, low quality commodity, with little versatility. The process was complex, expensive and inflexible. It was also environmentally challenging, because of the complexity of its manufacturing and purifying cycles.

This unexpected surge, which started in the early '70s, and is still surprisingly vigorous, was made possible by focusing and investing in the thorough scientific understanding of the catalytic system, and its subsequent development.

After the discovery of polypropylene, obtained for the $TiCl_3$-based first generation catalyst, at the Polytechnic of Milan in 1954, nothing revolutionary happened until the discovery of the active $MgCl_2$-supported high yield Ziegler-Natta catalysts at the Ferrara Giulio Natta Research Center in 1968. That event was the beginning of the revolution that brought about the creation of the third and fourth generation catalysts. This represented a real "breakthrough" for PP technology. It was possible to design new, versatile, clean, and economical processes to create a new family of materials, including:

- PCMA* (polymeric composite material and alloys),
- Copolymers (random and heterophasic),
- Catalloy* (PP-based polyolefin alloys),
- Hivalloy* (PP-based engineering plastic alloys).

Figure 1 well illustrates how these new catalysts brought about the dramatic evolution of polypropylene technology, the processes, the product families, and consequently, the market.

* Montell Polyolefin Trade Marks.

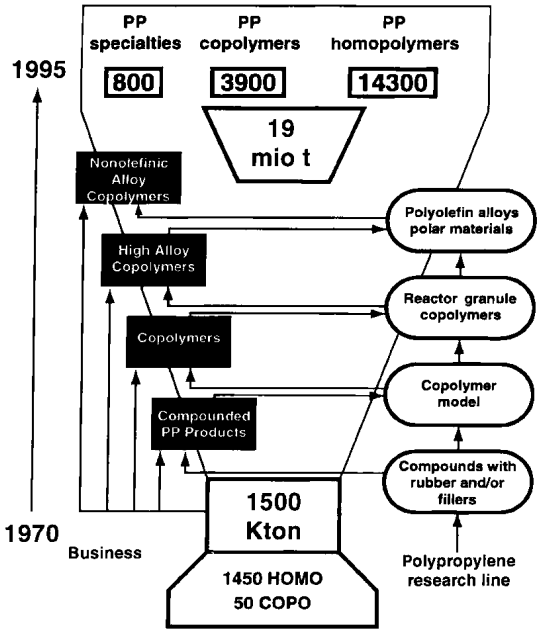


Figure 1 The polypropylene product cornucopia

The research line has continuously developed a systematic scientific understanding of the basic technology. The prompt and aggressive industrialization of all the technological results gave a rapid confirmation of its validity. The research was also driven by the market, which required particular needs, and demanded better and deeper scientific understanding. These needs gave impetus to the development of new basic research projects on catalysis and polymerization processes. The new scientific understanding showed the existence of new technological potentials, disclosing new opportunities in terms of new catalytic system performance, new product properties, and eventually new businesses.

The new understanding has been a continuous, autocatalytic process, whose dynamic development has been the real key to the outstanding polypropylene growth. This is a technological success that is based on the full exploitation of the close synergistic cooperation of catalyst and polymerization scientists, process engineers, and marketing experts in a real interdisciplinary action. In short, the research approach has generated and supported the revolution that brought about the dynamic development of the catalyst systems from the first to the fourth generations. This success gave rise to the creation of a rich cornucopia of the new product families shown in Fig. 2.

Where is PP going? The adventure is not over yet. As a matter of fact, the new catalyst generations, having always been the key to the process and product improvements, are impacting the technologies of two strong new families.

First, the superactive fourth generation catalysts are introducing an innovative and revolutionary new dimension to heterogeneous catalysis. Thanks to the specific, tailored "architecture" of the catalyst, it is now possible to give the catalyst the capability of determining the physical shape of the polymer generated and the external and internal

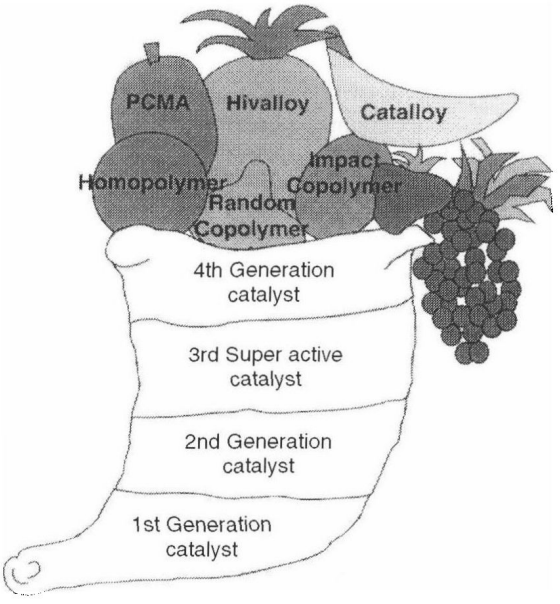


Figure 2 New product families Cornucopia

morphology, i.e., to control the type of specific distribution within the single granule. This capability is going to have a significant impact on our concepts of the process and the product.

Second, the metallocenes offer a new dimension in control, at the molecular level, of the molecular weight and monomer distributions with relevant impact on the final material properties. We forecast that over the next decade, the combination of the fourth generation catalyst linked to the metallocene catalysts will generate an explosive growth with a great impact on the processes and the products. It is becoming natural to expect a continuation of the dynamic evolution of polypropylene.

As a researcher in the company that more than any other trusted in PP, supported, drove the catalyst, process, product research, and commercialization, I am proud to participate in this precise and vivid presentation of polypropylene history and its continuing development. Montecatini SpA was the company that supported in the early fifties, the research of Prof. Natta who brought about the discovery of isotactic PP at the Polytechnic of Milan in 1954. In 1957 the first commercial production was achieved in the Ferrara plant only three years after the scientific discovery. The discovery of the revolutionary high yield catalyst in 1968 in Ferrara allowed Montecatini to once again provide a major advance in PP technology, which has driven the scientific and industrial evolution that followed in the 80s and 90s, and characterizes the PP history. This dynamic evolution, continuously surpassing itself, has been made possible by the continuous growth of scientific understanding of catalyst, process, and product developments, and the integration of these technologies into the market development process. This has been the approach that has driven the technology and the market evolution since the early 70s.

The most visible commercial consequence is that today over 80% of the global PP production capacity (over 19 M tons in 1995), is operated under Montedison patent or know-how licenses. Montecatini became Montedison in 1967, and then joined with Hercules to

form Himont in November 1983. Himont merged with Shell, becoming Montell in April 1995.

Montell supports the publication of this book on PP, which contains the contributions from many of its researchers and engineers, and is happy to have participated in this documentation of the vigorous PP industry. It is truly exciting to have been, and to continue being, a part of this adventure.

March 1996 *Paolo Galli*

Preface

The focus of interest in polypropylene has shifted over the last four decades from the first catalysts, to the nature of those early polymers, to the growing applications, then accelerating interest in the manufacturing process, leading to several new rounds of catalysts, processes, polymers, and applications, much of the latest round occurring in the last decade. The pace and magnitude of the recent changes, which became visible in the early '80s, have constituted a virtual revolution. While some recent books and articles have captured some of these activities, notably Van der Ven's excellent 1990 treatment of PP polymerization, none have been all-inclusive. This book is an attempt to present, in one comprehensive document, the new state of the PP industry, and to record and explain those fast-moving technological and business events that have resulted from that recent revolution, all in the light of the four-decade PP experience.

My own involvement with PP, while extensive, has been more broad than deep. From the secret project (polymerizing propylene) that an engineer friend was assigned at Hercules in 1955, through my operation of a continuous loop reactor in the late '50s, development, manufacture, and understanding of biaxially oriented films in the '60s, development of new polypropylene resins in the '70s, and finally, market development and assisting at managing the new technologies from the mid-'80s until retirement in 1993, I was, as a jack of all polypropylene trades, well qualified to ask penetrating questions of our authors. Perhaps more important, retirement gave me the time needed to attend to the editing chores for this book.

Although all of the authors are from Himont and Montell backgrounds, we have tried to present an industry-wide view of polypropylene, while including Montell developments that are, we believe, pertinent examples of the vigor that exists in the polypropylene industry today.

Thanks for helping make this book a reality go first to Hanser's Dr. Ed Immergut, who suggested that Himont take the lead in preparing this volume. Second, thanks to the Himont management for accepting that challenge, then persevering in that commitment when the difficulties of forming the Montell joint venture demanded so much attention. Third, to those who bore the true burden of creating this book, the authors who provided these chapters in a timely manner, and the many other contributors to those chapters, I and the future readers of this book are most grateful. Fourth, special thanks go to a few individuals whose contributions were above and beyond the call of duty: Luciano Noristi, for assembling and correcting, after our computer scrambled it, the extremely complex catalyst chapter; Roger Phillips, for his untiring pursuit of the scientifically correct explanation; Larry Thurrell and Chuck Oertel, for giving us the quick response when the need was critical; Dave Szasz, for converting so many of our rough scribbles into clear illustrations; and Enrico Zanoli, for providing rapid approvals at deadline time.

Finally, for her unswerving support of this project, and for cheerfully tolerating the many lonely hours it caused in the last few months, I thank my lovely and loving wife, Georgie.

Wilmington, DE
March 1996

Edward P. Moore, Jr.

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