

**ETHYLENE POLYMERIZATION BY ZIEGLER-NATTA AND
METALLOCENE CATALYST SYSTEMS:
MORPHOLOGY STUDY AND CHARACTERIZATION**



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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science
The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with
The University of Michigan, The University of Oklahoma,
and Case Western Reserve University

1999

ISBN 974-331-937-6

I14337899 26 พ.ค. 2547

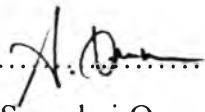
Thesis Title : Ethylene Polymerization by Ziegler-Natta and Metallocene Catalyst System: Morphology Study and Characterization

By : Mr. Punlop Horharin

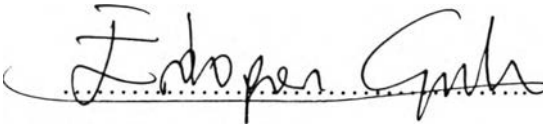
Program : Polymer Science


Thesis Advisors : Prof. Erdogan Gulari
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Accepted by the Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfillment of the requirements for the Degree of Master of Science.

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ABSTRACT

##94XXX : POLYMER SCIENCE PROGRAM

KEY WORDS : Polyethylene / Ziegler-Natta Catalyst / Metallocene
Catalyst

Mr. Punlop Horharin : Ethylene Polymerization by Ziegler-Natta and Metallocene Catalyst Systems: Morphology Study and Characterization. Thesis Advisors : Prof. Erdogan Gulari, Dr. Nantaya Yanumet, and Prof. Pramote Chaiyavech, 46 pp. ISBN 974-331-937-6

Since the discovery of $\text{TiCl}_4/\text{AlEt}_3$ catalyst for olefin polymerization in the early 1950s, many generations of such Ziegler-Natta catalysts have been developed. The most active generation is TiCl_4 supported on MgCl_2 . At the same time, other homogeneous-type catalysts have also been synthesized and used in ethylene polymerization. It was not until the mid 1980s that the first highly active uniform site catalyst for polyethylene was developed. It consisted of a Group IV transition metal complex, called metallocene, used together with excess methylaluminoxane (MAO). This catalyst system affords a wide range of polyolefins with controlled molecular weight and stereostructures. Because high amount of MAO over catalyst is required for acceptable activity, other kinds of cocatalyst have been developed to reduce the amount of MAO. In this work, bis(cyclopentadienyl) zirconium dichloride (Cp_2ZrCl_2) was used with trimethylaluminum (TMA) and tris(pentafluorophenyl)borane ($\text{B}(\text{C}_6\text{F}_5)_3$) to compare with $\text{TiCl}_4/\text{MgCl}_2$ Ziegler catalyst. The morphology of the polyethylene produced using these two catalyst systems was studied. MAO-free metallocene systems show less activity than the highly active Ziegler-Natta catalyst but still retain the advantages of a uniform site catalyst.

บทคัดย่อ

นายพัลลภ สอหรินทร์ : การสังเคราะห์พอลิเอททีลีนโดยใช้ระบบตัวเร่งปฏิกิริยา ซีคเกลอร์-นัตตา และเมทัลโลซีน : การศึกษาโครงสร้างและการตรวจสอบคุณสมบัติ (Ethylene Polymerization by Ziegler-Natta and Metallocene Catalyst Systems: Morphology Study and Characterization) อ. ที่ปรึกษา : ศ. เออร์โดแกน กุลาริ, ดร. นันทยา ยานูเมส และ ศ. ปราโมทย์ ไชยเวช 46 หน้า ISBN 974-331-937-6

ภายหลังการค้นพบตัวเร่งปฏิกิริยา ซีคเกลอร์-นัตตา เมื่อต้นทศวรรษ 1950 ได้มีการพัฒนาตัวเร่งปฏิกิริยาชนิดนี้กันอย่างกว้างขวาง ระบบที่มีประสิทธิภาพสูงสุดในปัจจุบันคือระบบที่มี $TiCl_4$ บนฐาน $MgCl_2$ ร่วมกับ ไตรเอททิลอลูมิเนียม (TEA) ในกลางทศวรรษ 1980 ระบบตัวเร่งปฏิกิริยาชนิดที่ละลายเป็นเนื้อเดียวกับตัวทำละลาย ได้รับการพัฒนาจนมีประสิทธิภาพดีเป็นครั้งแรก ระบบตัวเร่งปฏิกิริยานี้ ประกอบด้วยสารที่มีโครงสร้างซับซ้อนของโลหะทรานซิชันหมู่ 4 เรียกว่า เมทัลโลซีน ร่วมกับเมทัลลอลูมิเนียมออกเซน (MAO) ระบบตัวเร่งปฏิกิริยานี้ ต้องใช้ MAO เป็นจำนวนมากกว่าเมทัลโลซีนมาก จึงจะมีประสิทธิภาพเพียงพอสำหรับการผลิตในอุตสาหกรรม ทำให้ระบบนี้มีราคาแพง จึงได้มีความพยายามที่จะหาตัวเร่งปฏิกิริยาร่วมชนิดอื่นมาแทน MAO ในงานวิจัยนี้ใช้ ไตรเมททิลอลูมิเนียม (TMA) และ ทริส(เพนตะฟลูออโรฟีนิล)โบเรน ($B(C_6F_5)_3$) ร่วมกับ บิส(ไซโคลเพนตะไดอีนิล) เซอโคเนียม ไดคลอไรด์ (Cp_2ZrCl_2) เปรียบเทียบกับระบบตัวเร่งปฏิกิริยาซีคเกลอร์ - นัตตา พบว่าระบบตัวเร่งปฏิกิริยา เมทัลโลซีนซึ่งปราศจาก MAO นี้ มีประสิทธิภาพต่ำกว่า ระบบตัวเร่งปฏิกิริยา ซีคเกลอร์ - นัตตา มาก แต่พอลิเอททีลีนที่ได้ มีคุณสมบัติดีกว่า

ACKNOWLEDGEMENTS

The author would like to gratefully acknowledge all professors who have taught him at the Petroleum and Petrochemical College, Chulalongkorn University, especially those in the Polymer Science Program.

The author greatly appreciates the efforts of his research advisors, Professor Erdogan Gulari and Dr. Nantaya Yanumet for their constructive criticism, valuable suggestions and proof-reading of this manuscript. The author would like to give sincere thanks to his co-adviser, Professor Pramote Chaiyavech for his kind support. The author would also like to express appreciation to the National Petrochemical Public Company Limited (NPC) and Thai Polyethylene Company Ltd. (TPE) for supporting experimental materials in this work.

The author wishes to express his thanks to all of his friends who have given him many helps and encouragement, and also to all the college staff for their help in using research facilities.

Finally, the author is deeply indebted to his parents for their love, understanding encouragement, and for being a constant source of his inspiration.

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ABBREVIATIONS

Cp	=	Cyclopentadienyl
TEA	=	Triethylaluminum
TMA	=	Trimethylaluminum
MAO	=	Methylaluminoxane