

การโคพอลิเมอไรเซชันของเอทิลีนกับหนึ่งออกทีนด้วยตัวเร่งปฏิกิริยาเซอร์โคโนซีน
บนตัวรองรับ MCM-41 ที่ถูกปรับปรุงด้วยโบรอน



นางสาว ศุภลักษณ์ เจียมวิจิตรกุล

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2549
ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

COPOLYMERIZATION OF ETHYLENE/1-OCTENE WITH BORON-MODIFIED
MCM-41-SUPPORTED ZIRCONOCENE CATALYST

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering

Department of Chemical Engineering

Faculty of Engineering

Chulalongkorn University

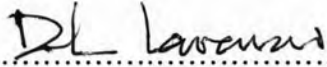
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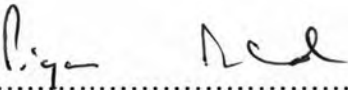
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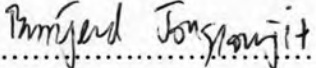
Thesis Title COPOLYMERIZATION OF ETHYLENE/1-OCTENE WITH
BORON-MODIFIED MCM-41-SUPPORTED
ZIRCONOCENE CATALYST
By Miss Supaluk Jiamwijitkul
Field of Study Chemical Engineering
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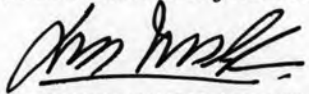
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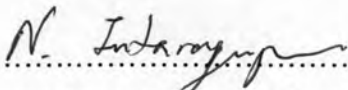
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นางสาวศุภลักษณ์ เขียมวิจิตรกุล: การโคพอลิเมอไรเซชันของเอทิลีนกับหนึ่งออกทีนด้วยตัวเร่งปฏิกิริยาเซอร์โคโนซีนบนตัวรองรับ MCM-41 ที่ถูกปรับปรุงด้วยโบรอน

(COPOLYMERIZATION OF ETHYLENE/1-OCTENE WITH BORON-MODIFIED MCM-41-SUPPORTED ZIRCONOCENE CATALYST)

อ. ที่ปรึกษา: ผศ. ดร.บรรเจิด จงสมจิตร, 131 หน้า

งานวิจัยนี้ได้ศึกษาผลของการปรับปรุงด้วยโบรอนต่อค่าความว่องไวของปฏิกิริยาโคพอลิเมอไรเซชันของเอทิลีนกับหนึ่งออกทีนด้วยตัวเร่งปฏิกิริยาเรซมิค-เอทิลีนบิสอินดีนิลเซอร์โคเนียมไดคลอไรด์ [$\text{rac-Et(Ind)}_2\text{ZrCl}_2$] โดยใช้ MCM-41 ที่มีขนาดรูพรุนต่างกันเป็นตัวรองรับ พร้อมกันนั้นได้มีการศึกษาคุณสมบัติของพอลิเมอร์ที่ผลิตได้อีกด้วย จากการทดลองพบว่า ระบบที่ใช้ MCM-41 ที่มีรูพรุนขนาดเล็กและถูกปรับปรุงด้วยโบรอนนั้นให้ค่าความว่องไวที่สูงกว่าระบบที่ใช้ MCM-41 ที่มีรูพรุนขนาดใหญ่และถูกปรับปรุงด้วยโบรอนที่สถานะเดียวกัน ซึ่งเป็นผลมาจากการกระจายตัวและการเกิดปฏิกิริยาระหว่างอะลูมิเนียมใน โมดิฟายด์เมทิลอะลูมิเนียมออกเซน (MMAO) และตัวรองรับ ซึ่งได้จากการวิเคราะห์ EDX และ TGA โดยพบว่าระบบที่ใช้ MCM-41 ที่มีรูพรุนขนาดเล็กมีปริมาณของอะลูมิเนียมใน โมดิฟายด์เมทิลอะลูมิเนียมออกเซน (MMAO) สูงกว่าระบบที่ใช้ MCM-41 ที่มีรูพรุนขนาดใหญ่ และค่าความว่องไวที่สูงที่สุดพบในระบบที่ใช้ MCM-41 ที่มีรูพรุนขนาดเล็กและถูกปรับปรุงด้วยโบรอนปริมาณ 1 เปอร์เซ็นต์โดยน้ำหนัก นอกจากนี้ยังพบว่าน้ำหนักโมเลกุลของพอลิเมอร์ได้จากระบบที่มีการใช้ตัวรองรับมีค่าสูงกว่าระบบที่ไม่ได้ใช้ตัวรองรับ สำหรับระบบที่มีรูพรุนขนาดเล็ก การเกิดปฏิกิริยาการถ่ายเทสายโซ่พอลิเมอร์ในระหว่างปฏิกิริยาพอลิเมอไรเซชันเกิดขึ้นกับในระบบที่มีการปรับปรุงด้วยโบรอนจึงทำให้น้ำหนักโมเลกุลของพอลิเมอร์มีค่าสูงกว่าซึ่งตรงกันข้ามกับระบบที่มีรูพรุนขนาดใหญ่ โดยพบว่า การปรับปรุงด้วยโบรอนนั้นทำให้ได้น้ำหนักโมเลกุลของพอลิเมอร์ที่ต่ำกว่า และพอลิเมอร์ที่ผลิตได้ทั้งในระบบที่ใช้ MCM-41 ที่มีรูพรุนขนาดเล็กและขนาดใหญ่ (โดยเฉพาะที่ปริมาณของโบรอนที่ต่ำ) นั้นพบว่า การปรับปรุงด้วยโบรอนทำให้ตำแหน่งที่ว่องไวต่อการเกิดปฏิกิริยามีความเป็นระเบียบมากขึ้นส่งผลทำให้ได้ค่าการกระจายตัวของน้ำหนักโมเลกุลของพอลิเมอร์ที่ผลิตได้นั้นแคบลงและไม่พบการเปลี่ยนแปลงของโครงสร้างทางโมเลกุลของพอลิเมอร์ซึ่งได้จากการวิเคราะห์ด้วย ^{13}C NMR และยังพบอีกว่า การเติมโบรอนลงไปในตัวรองรับ MCM-41 นั้นส่งผลต่อค่าการแทรกของ โมโนเมอร์หนึ่งออกทีน, อุณหภูมิหลอมเหลวและค่าความเป็นผลึกของพอลิเมอร์ที่ผลิตได้

ภาควิชา.....วิศวกรรมเคมี.....

สาขาวิชา.....วิศวกรรมเคมี.....

ปีการศึกษา.....2549.....

ลายมือชื่อนิสิต.....ศุภลักษณ์ เขียมวิจิตรกุล.....

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##4870495321 : MAJOR CHEMICAL ENGINEERING

KEY WORD : SUPPORTED METALLOCENE CATALYST / COPOLYMERIZATION OF ETHYLENE / ZIRCONOCENE

SUPALUK JIAMWIJITKUL : COPOLYMERIZATION OF ETHYLENE/1-OCTENE WITH BORON-MODIFIED MCM-41-SUPPORTED ZIRCONOCENE CATALYST. THESIS ADVISOR : ASST. PROF. BUNJERD JONGSOMJIT, Ph.D. 131 pp.

In this research, effect of boron modification on the catalytic activity of the ethylene/1-octene copolymerization with *rac*-ethylenebis(indenyl)zirconium dichloride [*rac*-Et(Ind)₂ZrCl₂] catalyst system using MCM-41 with different pore sizes as support was studied. The properties of polymer produced were also investigated. The MCM-41 having small pore system with boron (B) modification gave higher activity than that of the MCM-41 having large pore at the same condition. This was attributed to the dispersion and interaction between [Al]_{dMMAO} and supports as proven by EDX and TGA techniques. It was found that the small pore system exhibited higher amounts of [Al]_{dMMAO} than the large pore system. The highest activity was observed from MCM-41 with 1% wt of B modification. The molecular weight of polymer obtained from this supported system was higher than for the copolymer normally produced from the corresponding homogeneous system. For the small pore system, the inhibition of chain transfer reaction during polymerization apparently occurred upon the B modification indicating higher MW of polymer. On the contrary for the large pore system, it exhibited lower MW of polymer with B modification. For both the MCM-41 small pore and large pore (especially at low content of B) system, it was also suggested that B modification rendered more uniform catalytic sites leading to narrow MWD of polymer observed. There was no significant change in the polymer molecular structure by means of ¹³C NMR. It can be also stated that the addition of B into MCM-41 support affected the insertion of 1-octene, T_m and crystallinity of polymer produced.

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Academic year.....2006.....

ACKNOWLEDGEMENTS

I would like to express my gratitude to Assistant Professor Dr. Bunjerd Jongsomjit, my advisor. His advice is always worthwhile and without him this work could not be possible.

I cannot miss to thanks Assistant Professor Dr. Joongjai Panpranot for her kindness in a part of experiment.

I wish to thank Professor Dr. Piyasan Prasethdam, Associate Professor Dr. ML. Supakanok Thongyai, Assistant Professor Dr. Muenduen Phisalaphong and Dr. Nawaporn Intaragamjon as a chairman and members of this thesis committee for their valuable guidance and revision throughout my thesis, respectively.

Sincere thanks are given to Tosho Akzo, Japan, Exxon Chemical Co.,Ltd. for chemical supply. And many thanks to IRPC Co., Ltd., for GPC measurement, MEKTEC Manufacturing Corporation (Thailand) Ltd. for ^{13}C -NMR and DSC analysis, especially Mr. Sonti Khamsa-nga for the guidance of these analysis, Scientific and Technological Research Equipment Center (STREC) for SEM and EDX measurements.

I wish to extend my thanks to the graduate school at Chulalongkorn University for financial support for this work.

I cannot miss to thank the members of the Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University for friendship and their assistance especially the members of Z&M group. To the many others, not specifically named, who have provided me with support and encouragement, please be assured that I thinks of you.

Finally, I would like to express my highest gratitude to my family who are always beside me and support throughout this study.

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