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จุฬาลงกรณ์มหาวิทยาลัย

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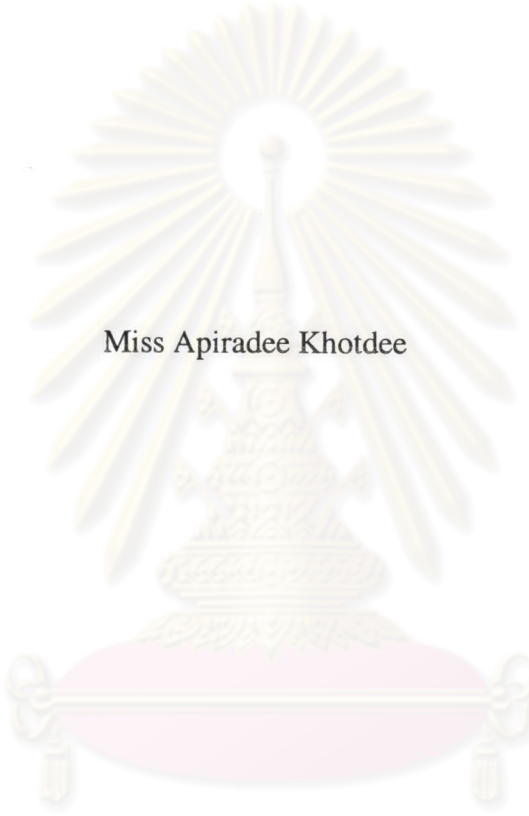
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COPOLYMERIZATION OF ETHYLENE AND NORBORNENE WITH
ZIRCONOCENE/ METHYLALUMINOXANE CATALYST



Miss Apiradee Khotdee

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย
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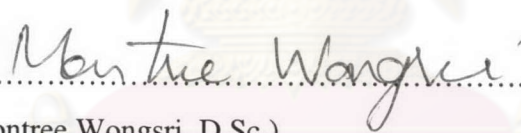
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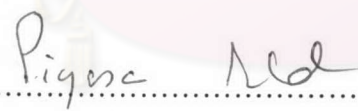
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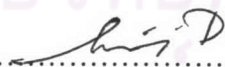
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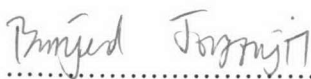

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อภิรดี คคดี : โคพอลิเมอร์ไรเซชันของเอทิลีนและนอร์บอร์นีนด้วยตัวเร่งปฏิกิริยาเซอร์โคโนซีน/เมทิลอะลูมิเนียมออกเซน (COPOLYMERIZATION OF ETHYLENE AND NORBORNENE WITH ZIRCONOCENE / METHYLALUMINOXANE CATALYST) อ.ที่ปรึกษา : ศาสตราจารย์ ดร. ปิยะสาร ประเสริฐธรรม, 95 หน้า ISBN 974-17-5173-7

งานวิจัยนี้ศึกษาการเกิดโคพอลิเมอร์ไรเซชันของเอทิลีนและนอร์บอร์นีนด้วยระบบตัวเร่งปฏิกิริยาเอทิลีนบิสอินดีนิลเซอร์โคเนียมไดคลอไรด์ โดยใช้เมทิลอะลูมิเนียมออกเซนเป็นตัวเร่งปฏิกิริยาร่วม ($\text{rac-Et}[\text{Ind}]_2\text{ZrCl}_2/\text{MAO}$, ตัวเร่งปฏิกิริยาที่ 1) ได้รวบรวมผลของภาวะโคพอลิเมอร์ไรเซชัน กล่าวคือ ปริมาณตัวเร่งปฏิกิริยาร่วม ความเข้มข้นของตัวเร่งปฏิกิริยา และอุณหภูมิในการทำปฏิกิริยา จากการศึกษาผลของตัวเร่งปฏิกิริยาเมทัลโลซีนชนิดต่าง ๆ ที่ใช้ในการทดลองนี้ ได้แก่ $\text{rac-Et}[\text{Ind}]_2\text{ZrCl}_2$, $(n\text{-BuCp})_2\text{ZrCl}_2$, Cp_2ZrCl_2 , Cp_2TiCl_2 , CpTiCl_3 , Cp^*TiCl_3 , และ Cp^*TiMe_3 , พบว่าระบบตัวเร่งปฏิกิริยาที่ 1 ให้ค่าความว่องไวสูงที่สุด ปริมาณการเข้าร่วมของนอร์บอร์นีนในสายโซ่โคพอลิเมอร์มากที่สุด และค่าความเป็นผลึกต่ำที่สุด นอกจากนี้ยังพบว่าระบบตัวเร่งปฏิกิริยา CpTiCl_3 , Cp^*TiCl_3 , และ Cp^*TiMe_3 ไม่สามารถทำให้เกิดโคพอลิเมอร์ไรเซชันของเอทิลีนและนอร์บอร์นีนได้ การเปรียบเทียบค่าความว่องไวระหว่างระบบตัวเร่งปฏิกิริยาที่ 1 และระบบตัวเร่งปฏิกิริยาบิสไซโคเพนตะไดอินดีนิลเซอร์โคเนียมไดคลอไรด์ ($\text{Cp}_2\text{ZrCl}_2/\text{MAO}$, ตัวเร่งปฏิกิริยาที่ 2) พบว่าระบบตัวเร่งปฏิกิริยาที่ 2 ให้ค่าความว่องไวสูงกว่าระบบตัวเร่งปฏิกิริยาที่ 1 ในการทำพอลิเมอร์ไรเซชันของเอทิลีน แต่ให้ค่าความว่องไวต่ำกว่าเมื่อทำโคพอลิเมอร์ไรเซชันของเอทิลีนและนอร์บอร์นีน เมื่อเพิ่มปริมาณนอร์บอร์นีนพบว่าทั้งสองระบบตัวเร่งปฏิกิริยาให้ค่าความว่องไวลดลง โดยระบบตัวเร่งปฏิกิริยาที่ 1 มีการลดลงสูงกว่าระบบตัวเร่งปฏิกิริยาที่ 2 ในการศึกษาเปรียบเทียบการทำโคพอลิเมอร์ไรเซชันในระบบที่ใช้โทลูอินและไซลีนเป็นตัวทำละลาย พบว่าทั้งสองระบบให้ค่าความว่องไวและปริมาณการเข้าร่วมของนอร์บอร์นีนในโคพอลิเมอร์ลดลงเมื่อเพิ่มเวลาในการทำโคพอลิเมอร์ไรเซชัน ดังนั้นชนิดของตัวทำละลายจึงไม่มีผลต่อการลดลงของปริมาณนอร์บอร์นีนในโคพอลิเมอร์เมื่อเวลาในการทำโคพอลิเมอร์ไรเซชันเพิ่มขึ้น และพบว่าไม่สามารถทำโคพอลิเมอร์ไรเซชันของเอทิลีนและนอร์บอร์นีนในระบบซึ่งใช้ตัวทำละลายที่มีโครงสร้างเป็นโซ่ตรง ได้แก่ 1-เฮกเซน 1-เฮปเทน และ 1-เดกเคน

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KEY WORD : COPOLYMERIZATION OF ETHYLENE AND NORBORNENE /
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APIRADEE KHOTDEE : COPOLYMERIZATION OF ETHYLENE AND
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In this research, ethylene and norbornene copolymerization was carried out with *rac*-ethylenebis(indenyl)zirconium dichloride catalyst system in the presence of methylaluminoxane as a cocatalyst (*rac*-Et(Ind)₂ZrCl₂/MAO, Catalyst 1). Effects of reaction conditions i.e. [Al]_{MAO}/[Metal] ratio, catalyst concentrations and reaction temperatures in copolymerization are summarized. The effect of different types metallocene catalyst such as *rac*-Et[Ind]₂ZrCl₂, (*n*-BuCp)₂ZrCl₂, Cp₂ZrCl₂, Cp₂TiCl₂, CpTiCl₃, Cp*TiCl₃ and Cp*TiMe₃ indicated that Catalyst 1 showed the highest catalytic activity and gave copolymers containing the highest amount of norbornene and the lowest crystallinity. However, the catalyst system of CpTiCl₃, Cp*TiCl₃ and Cp*TiMe₃ can not be conducted copolymerization of ethylene and norbornene. The comparison between Catalyst 1 and biscyclopentadienylzirconium dichloride (Cp₂ZrCl₂/MAO, Catalyst 2) catalyst systems, Catalyst 2 showed higher activity than Catalyst 1 in homopolymerization of ethylene however, an opposite trend in copolymerization of ethylene and norbornene was found for both systems. The catalytic activity decreased with increasing norbornene concentrations for both zirconocene catalyst systems. The decreased activity for Catalyst 1 is higher than that of Catalyst 2. Ethylene and norbornene copolymerization with *rac*-Et[Ind]₂ZrCl₂/MAO catalyst system was performed in toluene or xylene as a solvent. For the both systems, the catalytic activity and norbornene content in copolymer decreased with increasing the polymerization times therefore, the effect of different solvents was not observed. However, ethylene and norbornene copolymerization was not proceeded in the system which used aliphatic solvents, i.e. 1-hexane, 1-heptane and 1-decane.

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 ศูนย์วิจัยทรัพยากร
 จุฬาลงกรณ์มหาวิทยาลัย

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LIST OF ABBREVIATIONS

ABS	Acrylonitrile-Butadiene-Styrene
C-NMR	Carbon Nuclear Magnetic Resonance
COC	Cyclic Olefin Copolymer
DSC	Differential Scanning Calorimetry
ENB	Ethylene and norbornene copolymer
FT-IR	Fourier Transform Infrared Spectroscopy
GPC	Gel Permeation Chromatography
HDPE	High Density Polyethylene
IN	Indanyl norbornene
LDPE	Linear Density Polyethylene
LLDPE	Linear Low Density Polyethylene
MAO	Methylaluminoxane
MCOC	Cyclic Olefin Copolymer Produced with Metallocene Catalysts
MM	Molar Mass
MMD	Molar Mass Distribution
MWD	Molecular Weight Distribution
NB	Norbornene
PC	Polycarbonate
PN	Phenyl norbornene
ROMP	Ring Opening Metathesis Polymerization
SEM	Scanning Electron Microscopy
SSC	Single Site Catalyst
TEA	Triethylaluminum
TIBA	Triisobutylaluminum
TMA	Trimethylaluminum
TOPAS	Thermoplastic Olefin Polymer of Amorphous Structure
TREF	Temperature Rising Elution Fractionation
ULDPE	Ultra Low Density Polyethylene
VLDPE	Very Low Density Polyethylene