


ตัวเร่งปฏิกิริยาประเภทนอนเมทัลโลซีนที่มีเหล็กเป็นองค์ประกอบสำหรับโอลิโกเมอไรเซชันของ
เฮกซีน



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จุฬาลงกรณ์มหาวิทยาลัย

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**IRON-BASED NON-METALLOCENE CATALYSTS FOR
OLIGOMERIZATION OF HEXENE**



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จุฬาลงกรณ์มหาวิทยาลัย

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นางสาวอัญชลี สิริกุลขจร : ตัวเร่งปฏิกิริยาประเภทอนเมทัลโลซีนที่มีเหล็กเป็นองค์ประกอบสำหรับพอลิเมอไรเซชันของเฮกซีน (Iron-Based Non-metallocene Catalysts for Polymerization of Hexene) อ. ที่ปรึกษา : รศ. ดร. วิมลรัตน์ ตระการพุกภัย, จำนวนหน้า 142 หน้า, ISBN 974-17-2927-8

ได้สังเคราะห์ลิแกนด์คีเลตดิแกมมาไฮดรอกซี, ลิแกนด์ไดเอมีน $\text{RHN}(\text{CH}_2)_3\text{NHR}$ (a) และลิแกนด์ไดอิมีน $\text{RHN}(\text{CH}_3)\text{C}(\text{CH}_3)\text{CNR}$ (b) รวมทั้งลิแกนด์ซัลโฟเนต (salen) (c) และใช้เตรียมตัวสารเชิงซ้อนเหล็ก ตัวเร่งปฏิกิริยาประเภทอนเมทัลโลซีนที่มีเหล็กเป็นองค์ประกอบที่เตรียมขึ้น ได้แก่ $[\text{RHN}(\text{CH}_2)_3\text{NHR}]\text{FeCl}_3$ (**cpx 1a**) $[\text{RHN}(\text{CH}_3)\text{C}(\text{CH}_3)\text{CNR}]\text{FeCl}_3$ (**cpx 2b**) และ $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_2\text{FeCl}$ (**cpx 3c**) ($\text{R} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$) ทำการตรวจพิสูจน์เอกลักษณ์ลิแกนด์และสารประกอบเชิงซ้อนเหล็กด้วยเทคนิค $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, FT-IR, UV-VIS และการวิเคราะห์ธาตุ ศึกษาพอลิเมอไรเซชันของ 1-เฮกซีน โดยใช้ตัวเร่งปฏิกิริยาเหล็กที่มีเมทิลอะลูมิเนียมออกเซน (MAO) หรือสารประกอบโบรอน $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ และ $[\text{PhMe}_2\text{NH}][\text{B}(\text{C}_6\text{F}_5)_4]$ เป็นตัวเร่งปฏิกิริยาร่วม ศึกษาปัจจัยที่มีผลต่อความว่องไวของการเร่งปฏิกิริยา ได้แก่ ปริมาณตัวเร่งปฏิกิริยา ปริมาณตัวเร่งปฏิกิริยาร่วม อัตราส่วนโดยโมลของอะลูมิเนียมต่อเหล็ก อุณหภูมิในการพอลิเมอไรเซชัน ตัวทำละลาย และชนิดของอัลคิลเลตติ้ง เอเจนท์ พบว่าตัวเร่งปฏิกิริยาที่ว่องไวคือ **cpx 1a** และ **cpx 2b** ตรวจพิสูจน์เอกลักษณ์ผลิตภัณฑ์ที่ได้ซึ่งเป็นไดเมอร์ ไตรเมอร์ เพนตะเมอร์ และเฮกซะเมอร์ ด้วยเทคนิค FT-IR, $^{13}\text{C-NMR}$ และ GC-MS ทำการเปรียบเทียบกับตัวเร่งปฏิกิริยาเมทัลโลซีน $\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2$ ในการพอลิเมอไรเซชัน พบตัวเร่งปฏิกิริยาเมทัลโลซีนนี้ให้แอกติวิตี 510 กิโลกรัมพอลิเมอร์/โมลตัวเร่งปฏิกิริยา ตรวจพิสูจน์เอกลักษณ์พอลิเมอร์ที่ได้ด้วยเทคนิค FT-IR, $^{13}\text{C-NMR}$, $^1\text{H-NMR}$, DSC และ GPC พบว่าเป็นพอลิเฮกซีนชนิดไอโซแทคติกที่มีน้ำหนักโมเลกุล 48,600

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Chelating bidentate ligands: diamine ligand, $\text{RHN}(\text{CH}_2)_3\text{NHR}$ ligand (**a**) and diimine ligand, $\text{RHN}(\text{CH}_3)\text{C}(\text{CH}_3)\text{CNR}$ ligand (**b**) and the Schiff's base ligand, salen ligand (**c**) were synthesized and used for the preparation of iron complexes. Iron-based non-metallocene catalysts: $[\text{RHN}(\text{CH}_2)_3\text{NHR}]\text{FeCl}_3$ (**cpx 1a**) $[\text{RHN}(\text{CH}_3)\text{C}(\text{CH}_3)\text{CNR}]\text{FeCl}_3$ (**cpx 2b**) $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_2\text{FeCl}$ (**cpx 3c**) and $\text{C}_9\text{H}_7\text{NOFeCl}_3$ (**cpx 4**) ($\text{R} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$) were synthesized. These ligands and the complexes were characterized by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, FT-IR, UV-VIS and elemental analysis. 1-Hexene polymerization was performed with iron catalysts in the presence of methylaluminoxane (MAO) or boron compound, $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ and $[\text{PhMe}_2\text{NH}][\text{B}(\text{C}_6\text{F}_5)_4]$ as cocatalyst. Parameters influencing the catalytic activity, such as amount of catalyst, amount of cocatalyst, Al/Fe mole ratio, polymerization time (t_p), polymerization temperature (T_p), solvent and type of alkylating agent were investigated. Only **cpx 1a** and **cpx 2b** are found active. Dimer, trimer, pentamer and hexamer products from both complexes were characterized by FT-IR, $^{13}\text{C-NMR}$ and GC-MS. For comparison, polymerization using metallocene catalyst, $\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2$ was performed. The activity of 510 kg of polymer/mol catalyst was obtained. The polymer was characterized by FT-IR, $^{13}\text{C-NMR}$, $^1\text{H-NMR}$, DSC and GPC to be isotactic poly(1-hexene) with molecular weight of 48,600.

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LIST OF ABBREVIATIONS

Al/Zr	Aluminium per zirconium mole ratio
°C	Degree Celsius
CDCl ₃	Deuteriochloroform
C ₆ D ₆	Benzene-d ₆
cm ⁻¹	Unit of wave number
¹³ C-NMR	Carbon nuclear magnetic resonance
Cp	Cyclopentadienyl
Cp*	Pentamethylcyclopentadienyl
Cy	Cyclohexyl
Flu	Fluorenyl
¹ H-NMR	Proton nuclear magnetic resonance
MAO	Methylaluminoxane
MeCp	3-Methyl-cyclopentadienyl
Mes	2,4,6-Trimethylphenyl
M _n	Number average molecular weight
M _w	Weight average molecular weight
MWD or M _w /M _n	Molecular weight distribution
m/z	Mass per charge
<i>rac</i> -EBI	Racemic-ethylenebis(indenyl)
TIBA	Triisobutylaluminum
tmeda	Tetramethylethylenediamine
T _m	Melting temperature
T _p	Polymerization temperature
T _g	Glass transition temperature
t _p	Polymerization time
δ	Chemical shift