

**TRANSITION METAL CATALYZED PRECISE OLEFIN
POLYMERIZATION FOR HIGH PERFORMANCE MATERIALS**

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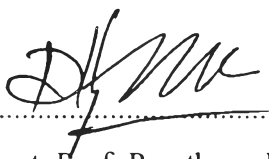
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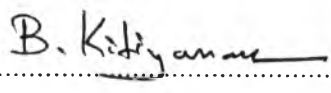
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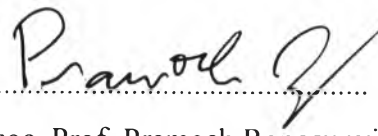

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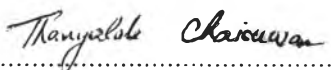
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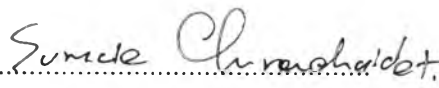

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ABSTRACT

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In this work, half-titanocenes of the type $\text{Cp}'\text{TiCl}_2(\text{L})$, where L is anionic ancillary donor ligand, was studied in ethylene copolymerization in the presence of cocatalyst to investigate the efficient catalyst for ethylene copolymerization and to synthesize the new polymers. Half-titanocenes containing imidazolin-2-iminato ligand, $\text{Cp}'\text{TiCl}_2[1,3\text{-R}_2(\text{CH}_2\text{N})_2\text{C}=\text{N}]$, were used in the presence of MAO for ethylene/ α -olefin copolymerization. The results suggested that $\text{CpTiCl}_2[1,3\text{-}^t\text{Bu}_2(\text{CHN})_2\text{C}=\text{N}]$ exhibited remarkable catalytic activity, affording ultrahigh molecular weight copolymers with uniform molecular weight distributions. This complex also showed remarkable catalytic activity with efficient norbornene incorporation in ethylene/norbornene copolymerization. The resultant copolymer possessed high molecular weight with uniform molecular weight distribution. In the study of terpolymerization of ethylene, 1-hexene and styrene, aryloxo-modified half-titanocenes, $\text{Cp}'\text{TiCl}_2(\text{O-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)$, were used in the presence of cocatalyst. The results showed that $\text{Cp}^*\text{TiCl}_2(\text{O-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ and $^t\text{Bu}(\text{C}_5\text{H}_4)\text{TiCl}_2(\text{O-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ provided high molecular weight polymers with unimodal distributions and efficient comonomer incorporation. To introduce vinyl group into polymer chain, terpolymerization of ethylene and styrene or 1-hexene with 3,3-divinylbiphenyl was conducted by using aryloxo-modified half-titanocenes. Efficient comonomer incorporations were achieved by this type of catalyst and the content of each comonomers could be varied by their concentration charged. Post-polymerization of styrene could also be obtained by initiating the vinyl group remained in the side chain by treatment with *n*-BuLi.

บทคัดย่อ

วรรณิตา อภิสุข : โอลิฟินพอลิเมอร์ไรเซชันโดยตัวเร่งปฏิกิริยาโลหะทรานซิชัน (Transition Metal Catalyzed Precise Olefin Polymerization for High Performance Materials) อ. ที่ปรึกษา : ผศ. ดร. บุญยรัชต์ กิตยานันท์ และ ศ. ดร. โคโตฮิโร โนมูระ 80 หน้า

ในการศึกษานี้ ตัวเร่งปฏิกิริยาโลหะทรานซิชันชนิดฮาล์ฟไททาโนซีนที่มีแอนไอออน ลิแกนด์ถูกนำมาใช้ในปฏิกิริยาโคพอลิเมอร์ไรเซชันของเอทิลีนโดยมีตัวเร่งปฏิกิริยาร่วม เพื่อค้นคว้าตัวเร่งปฏิกิริยาที่มีประสิทธิภาพสำหรับการสังเคราะห์วัสดุพอลิเมอร์ผสม จากการ ศึกษาพบว่าฮาล์ฟไททาโนซีนที่มีลิแกนด์อิมิดาโซลีน-2-อิมิโนโด เป็นตัวเร่งปฏิกิริยาที่ดี สำหรับพอลิเมอร์ไรเซชันของเอทิลีน โคพอลิเมอร์ไรเซชันของเอทิลีนกับ 1-เฮกซีน และโคพอลิเมอร์ไรเซชันของเอทิลีนกับนอร์บอร์นีน พอลิเมอร์ที่สังเคราะห์ได้มีน้ำหนัก โมเลกุลสูง และมีการกระจายตัวของน้ำหนักโมเลกุลที่สม่ำเสมอ ฮาล์ฟไททาโนซีนที่มี ลิแกนด์แอริลลอกไซด์ ถูกนำมาใช้ในการศึกษาปฏิกิริยาเทอร์พอลิเมอร์ไรเซชันของเอทิลีนกับ 1-เฮกซีน และสไตรีน พบว่าสามารถสังเคราะห์พอลิเมอร์ผสมที่มีน้ำหนักโมเลกุลสูง และมีการกระจายตัวของน้ำหนักโมเลกุลที่สม่ำเสมอเช่นกัน นอกจากนี้ตัวเร่งปฏิกิริยาชนิดนี้ ยังสามารถใช้ในการสังเคราะห์พอลิเมอร์ที่มีหมู่ไวนิลในสายโซ่ โดยการพอลิเมอร์ไรเซชันเอทิลีน กับสไตรีนและ 3,3-ไดไวนิลไบฟีนิล ซึ่งพอลิเมอร์ผสมที่สังเคราะห์ได้สามารถนำไปทำปฏิกิริยากับ นอร์มอลบิวทิลลิเทียมและสไตรีน เพื่อให้ได้พอลิเมอร์ผสมที่มีกิ่งสาขาของสไตรีนแทนที่หมู่ไวนิล

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