ไฮโดรจิเนชันของยางสังเคราะห์ซีส-1,4-พอลิไอโซพรีนและยางธรรมชาติเร่งปฏิกิริยาด้วยสารประกอบเชิงซ้อนรูทิเนียม (II)

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HYDROGENATION OF SYNTHETIC RUBBER CIS-1,4-POLYISOPRENE AND NATURAL RUBBER CATALYZED BY RUTHENIUM (II) COMPLEX

Miss Rungnapa Tangthongkul

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ไฮโดรจิเนชันเป็นวิธีการที่เป็นประโยชน์ซึ่งใช้ปรับปรุงความต้านทานออกซิเดชันและการสลายตัวของไดอีนพอลิเมอร์ การศึกษาโฮโมจีเนียสไฮโดรจิเนชันของยางสังเคราะห์ซีส-1,4-พอลิไอโซพรีน (CPIP), ยางธรรมชาติ (NR) และน้ำยางธรรมชาติ (NRL) ซึ่งใช้ Ru(CH=CH(Ph))Cl(CO)$(PCy_3)_2$ เป็นตัวเร่งปฏิกิริยาทำได้โดยการวัดปริมาณไฮโดรเจนที่ถูกใช้เมื่อปฏิกิริยาดำเนินไป ผลการศึกษาพบว่าอัตราการเกิดปฏิกิริยาไฮโดรจิเนชันของยางสังเคราะห์ซีส-1,4-พอลิไอโซพรีน, ยางธรรมชาติและน้ำยางธรรมชาติเป็นปฏิกิริยาอันดับหนึ่งกับความเข้มข้นพันธะคู่จนถึงค่าการเปลี่ยนสูงของพันธะคู่สำหรับทุกภาวะ, ผลจลนพลศาสตร์เสนอปฏิกิริยาเป็นอันดับหนึ่งกับความเข้มข้นตัวเร่งปฏิกิริยาและความดันไฮโดรเจน นอกจากนี้ปฏิกิริยาไฮโดรจิเนชันของยางสังเคราะห์ซีส-1,4-พอลิไอโซพรีนและยางธรรมชาติยังเป็นปฏิกิริยาผกผันอันดับหนึ่งกับปริมาณการเติมฟอสฟีน การเติมกรดพาราโทลูอีนซัลโฟนิกปริมาณเล็กน้อยเป็นการช่วยเร่งอัตราการเกิดปฏิกิริยาให้เร็วขึ้นอย่างมาก อย่างไรก็ตามสารปนเปื้อนในยางธรรมชาติลดแอกทิวิตีของสารประกอบเชิงซ้อนรูทิเนียม ข้อมูลทางจลพลศาสตร์นำไปสู่การเสนอกลไกของปฏิกิริยาไฮโดรจิเนชัน ในงานวิจัยนี้ได้เสนอแบบจำลองทางคณิตศาสตร์ของกระบวนการไฮโดรจิเนชันของยางสังเคราะห์ซีส-1,4-พอลิไอโซพรีนแบบต่อเนื่อง

การวัดด้วยอินฟราเรดและโปรตอนนิวเคลียร์แมกเนติกเรโซแนนซ์สเปกโทรสโคปีถูกนำมาใช้ในการหาระดับไฮโดรจิเนชัน องค์ประกอบทางเคมีของผลิตภัณฑ์ไฮโดรจิเนตที่ได้สามารถตรวจสอบด้วยเทคนิคคาร์บอนนิวเคลียร์แมกเนติกเรโซแนนซ์ ซึ่งพบว่าพอลิไอโซพรีนที่เกิดไฮโดรจิเนชันสมบูรณ์มีโครงสร้างเป็นเอทิลีน-พรอพิลีนโคพอลิเมอร์แบบสลับ จากการตรวจสอบสมบัติทางความร้อนของยางไฮโดรจิเนตพบว่ายางที่ผ่านกระบวนการไฮโดรจิเนชันมีสมบัติการต้านทานความร้อนเพิ่มขึ้นโดยไม่มีผลกระทบกับอุณหภูมิคล้ายแก้วของยางผลิตภัณฑ์

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RUNGNAPA TANGTHONGKUL : HYDROGENATION OF SYNTHETIC RUBBER CIS-1,4-POLYISOPRENE AND NATURAL RUBBER CATALYZED BY RUTHENIUM (II) COMPLEX. THESIS ADVISOR : PROF. PATTARAPAN PRASASSARAKICH, THESIS COADVISOR : PROF. GARRY L. REMPEL, 140 pp. ISBN 974-17-3951-6.

Hydrogenation is a useful method, which has been used to improve oxidative, and thermal degradation resistance of diene based polymers. A detailed study of the homogeneous hydrogenation of *cis*-1,4-polyisoprene (CPIP), natural rubber (NR) and natural rubber latex (NRL) using $Ru(CH{=}CH(Ph))Cl(CO)(PCy_3)_2$ as catalyst was carried out by monitoring the amount of hydrogen consumed during reaction. The hydrogenation rate of CPIP, NR and NRL followed pseudo first order kinetics in double bond concentration up to high conversions of double bond, under all sets of studied conditions . The kinetic results suggested a first-order behavior with respect to total catalyst concentration as well as with respect to hydrogen pressure. An inverse first order dependence on added PCy_3 was observed in hydrogenation of CPIP and NR. The addition of a small amount of *p*-toluenesulfonic acid to the reaction system led to a substantial increase in the reaction rate. However, the presence of impurities in natural polymer seems to decrease the catalyst activity of the Ru complexes. Mechanistic aspects of the catalytic process are discussed. A numerical analysis of a continuous process for CPIP hydrogenation is also presented.

Infrared and ^{1}H-NMR spectroscopic measurements confirmed the final degree of hydrogenation. The composition of hydrogenated product was characterized by ^{13}C-NMR spectroscopy. The quantitative hydrogenation of polyisoprene leads to an alternating ethylene-propylene copolymer. The thermal properties of the hydrogenated polymer were characterized. The results show that the hydrogenation can increase thermal stability of rubber without affecting its glass transition temperature.

Department	Chemical Technology	Student's signature ....
Field of study	Chemical Technology	Advisor's signature ....
Academic year 2003		Co-advisor's signature ....

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NOMENCLATURES

CPIP	:	Synthetic *Cis*-1,4-Polyisoprene
CSTR	:	Continuous Stirred Tank Reactor
DMTA	:	Dynamic Mechanical Thermal Analysis
DSC	:	Differential Scanning Calorimeter
EPDM	:	Ethylene Propylene Copolymer
FTIR	:	Fourier Transform Infrared Spectroscopy
HCPIP	:	Hydrogenated Synthetic *Cis*-1,4-Polyisoprene
HNR	:	Hydrogenated Natural Rubber
HNRL	:	Hydrogenated Natural Rubber Latex
Ir	:	Iridium
IRSG	:	International Rubber Study Group
K_H	:	Henry's Law Constant
k_{rds}	:	Limiting Reaction Rate Constant
MCB	:	Chlorobenzene
NBR	:	Nitrile Butadiene Rubber, Acrylonitrile-Butadiene Copolymer
NMR	:	Nuclear Magnetic Resonance Spectroscopy
NR	:	Natural Rubber
NRL	:	Natural Rubber Latex
Os	:	Osmium
PBD	:	Polybutadiene
PCy_3	:	Tricyclohexylphosphine
PDMB	:	Poly(2,3-Dimethylbutadiene)
PFR	:	Plug Flow Reactor
PHXD	:	Poly (2,4-Hexadiene)
Rh	:	Rhodium
Ru	:	Ruthenium
SBR	:	Styrene-Butadiene Rubber
T_g	:	Glass Transition Temperature
TGA	:	Thermogravimetric Analysis
THF	:	Tetrahydrofuran
T_{id}	:	Initial Decomposition Temperature

NOMENCLATURES (continued)

TMA	:	Thermomechanical Analysis
T_{max}	:	Maximum Decomposition Temperature
TSH	:	*p*-Toluenesulfonyl Hydrazine
p-TsOH	:	*p*-Toluenesulfonic Acid