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สาขาวิชาเคมีเทคนิค ภาควิชาเคมีเทคนิค

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

Miss Rungnapa Tangthongkul

ศูนย์วิทยบรังษยการ
จุฬาลงกรณมหาวิทยาลัย

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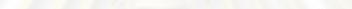
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By	Miss Rungnapa Tangthongkul
Field of Study	Chemical Technology
Thesis Advisor	Professor Pattarapan Prasassarakich, Ph. D.
Thesis Co-advisor	Professor Garry L. Rempel, Ph. D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial
Fulfillment of the Requirements for the Doctor's Degree

 Dean of Faculty of Science
(Professor Piamsak Menasveta, Ph. D.)

THESIS COMMITTEE

T. V. tidsart

Chairman

(Associate Professor Tharapong Vitidsant, Ph. D.)

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(Professor Pattarapan Prasassarakich, Ph. D.)

Larry L. Rempel Thesis Co-advisor

(Professor Garry L. Rempel, Ph. D.)

Bramote Chaiyavech Member

(Professor Pramote Chaiyavech, Ph. D.)

 Member

(Associate Professor Pornpote Piumsomboon, Ph.D.)

W. Mahanprak Member

(Associate Professor Wimonrat Trakarnpruk, Ph. D.)

รุ่งนภา ตั้งทองกุรา : ไฮโดรเจนเข็นของยางสังเคราะห์ cis-1,4-พอลิไอโซพรีนและยางธรรมชาติเร่งปฏิกิริยาด้วยสารประกอบเชิงซ้อน Ruthenium (II) (HYDROGENATION OF SYNTHETIC RUBBER CIS-1,4-POLYISOPRENE AND NATURAL RUBBER CATALYZED BY RUTHENIUM (II) COMPLEX) อ. ที่ปรึกษา : ศ. ดร. ภัทรพรวณ ประศาสน์สารกิจ, อ.ที่ปรึกษาร่วม : Prof. Garry L. Rempel 140 หน้า ISBN 974-17-3951-6

ไฮโดรเจนเข็นเป็นวิธีการที่เป็นประโยชน์ซึ่งใช้ปรับปรุงความต้านทานออกซิเดชันและการสลายตัวของไดอีนพอลิเมอร์ การศึกษาไฮโมจีเนียลไฮโดรเจนเข็นของยางสังเคราะห์ cis-1,4-พอลิไอโซพรีน (CPIP), ยางธรรมชาติ (NR) และน้ำยางธรรมชาติ (NRL) ซึ่งใช้ $Ru(CH=CH(Ph))Cl(CO)(PCy_3)_2$ เป็นตัวเร่งปฏิกิริยาทำได้โดยการวัดปริมาณไฮโดรเจนที่ถูกใช้เมื่อปฏิกิริยาดำเนินไป ผลการศึกษาพบว่าอัตราการเกิดปฏิกิริยาไฮโดรเจนเข็นของยางสังเคราะห์ cis-1,4-พอลิไอโซพรีน, ยางธรรมชาติและน้ำยางธรรมชาติเป็นปฏิกิริยาอันดับหนึ่งกับความเข้มข้นพันละคุ่จนถึงค่าการเปลี่ยนสูงของพันละคุ่สำหรับทุกภาวะ, ผลลัพธ์แสดงว่าเป็นปฏิกิริยาอันดับหนึ่งกับความเข้มข้นตัวเร่งปฏิกิริยาและความดันไฮโดรเจน นอกจากนี้ปฏิกิริยาไฮโดรเจนเข็นของยางสังเคราะห์ cis-1,4-พอลิไอโซพรีนและยางธรรมชาติยังเป็นปฏิกิริยาผกผันอันดับหนึ่งกับปริมาณการเติมฟอสฟีน การเติมกรดพาราโทลูอีนชัลฟอนิกปริมาณเล็กน้อยเป็นการช่วยเร่งอัตราการเกิดปฏิกิริยาให้เร็วขึ้นอย่างมาก อย่างไรก็ตามสารปนเปื้อนในยางธรรมชาติติดแยกทิวิติของสารประกอบเชิงซ้อน Ruthenium ข้อ มูลทางจลพลศาสตร์นำไปสู่การเสนอกลไกของปฏิกิริยาไฮโดรเจนเข็น ในงานวิจัยนี้ได้เสนอแบบจำลองทางคณิตศาสตร์ของกระบวนการไฮโดรเจนเข็นของยางสังเคราะห์ cis-1,4-พอลิไอโซพรีนแบบต่อเนื่อง

การวัดด้วยอินฟราเรดและโปรตอนนิวเคลียร์แมกโนติกเรโซแนนซ์สเปกโตรสโคปีถูกนำมาใช้ในการหาระดับไฮโดรเจนเข็น องค์ประกอบทางเคมีของผลิตภัณฑ์ไฮโดรเจนต์ที่ได้สามารถตรวจสอบด้วยเทคนิคคาร์บอนนิวเคลียร์แมกโนติกเรโซแนนซ์ ซึ่งพบว่าพอลิไอโซพรีนที่เกิดไฮโดรเจนเข็นสมบูรณ์มีโครงสร้างเป็นเอทิลีน-พรอพิลีนโคพอลิเมอร์แบบสลับ จากการตรวจสอบสมบัติทางความร้อนของยางไฮโดรเจนเข็นพบว่ายางที่ผ่านกระบวนการไฮโดรเจนเข็นมีสมบัติการต้านทานความร้อนเพิ่มขึ้นโดยไม่มีผลกระทบกับอุณหภูมิคล้ายแก้วของยางผลิตภัณฑ์

ภาควิชา เคมีเทคนิค
สาขาวิชา เคมีเทคนิค¹
ปีการศึกษา 2546

ลายมือชื่อนิสิต.....รังสรรค์ กุ๊กกะน้ำ.....
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ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.....Prof. Garry L. Rempel

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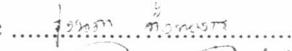
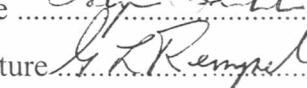
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RUNGNAPA TANGTHONGKUL : HYDROGENATION OF SYNTHETIC
RUBBER CIS-1,4-POLYISOPRENE AND NATURAL RUBBER
CATALYZED BY RUTHENIUM (II) COMPLEX. THESIS ADVISOR :
PROF. PATTARAPAN PRASASSARAKICH, THESIS COADVISOR :
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Hydrogenation 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)(PCy₃)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 PCy₃ 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 ¹H-NMR spectroscopic measurements confirmed the final degree of hydrogenation. The composition of hydrogenated product was characterized by ¹³C-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.

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Student's signature
Advisor's signature
Co-advisor's signature 

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จุฬาลงกรณ์มหาวิทยาลัย

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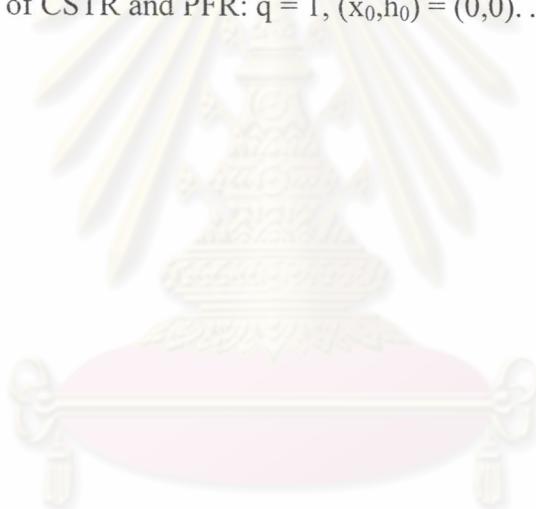
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 ศูนย์วิทยทรัพยากร
 จุฬาลงกรณ์มหาวิทยาลัย

NOMENCLATURES

CPIP	:	Synthetic <i>Cis</i> -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 <i>Cis</i> -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

