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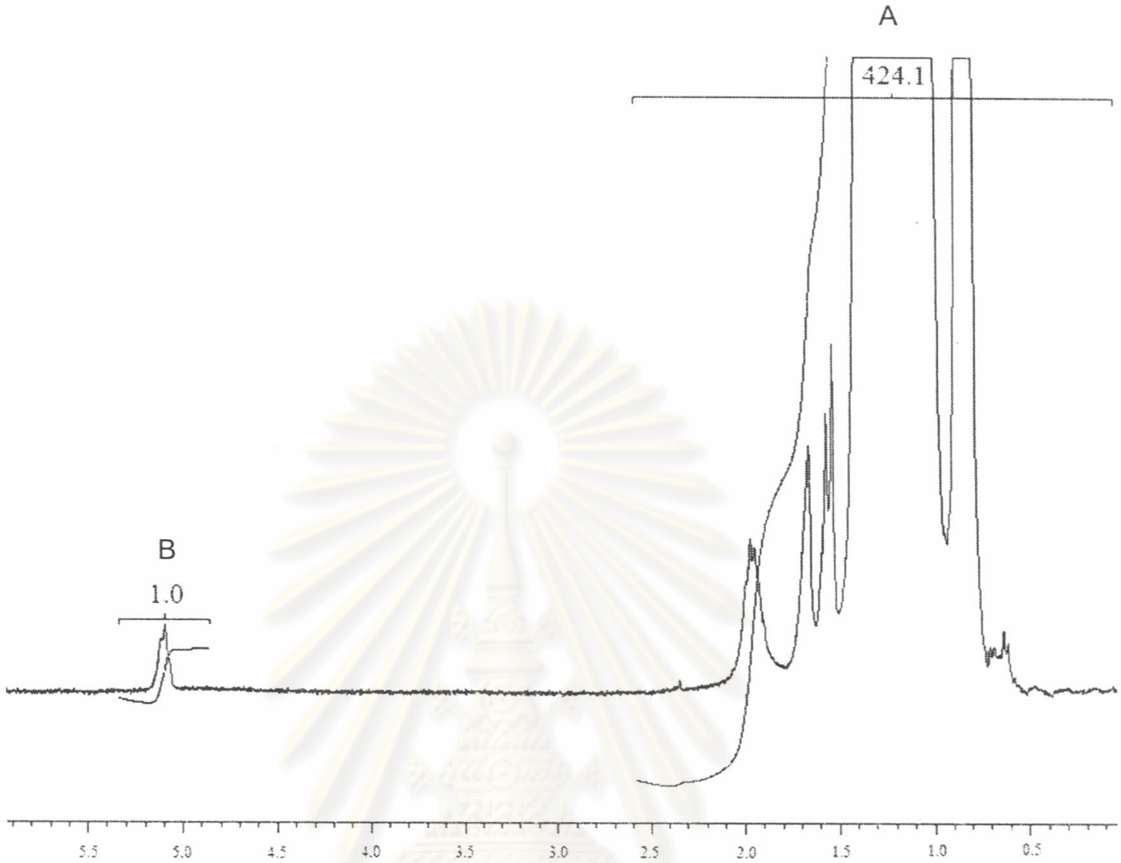
APPENDICES

Appendix I: Calculation of the Percentage of Hydrogenation



A = area of $–CH_2$ and CH_3

B = area of C=C

Figure AI-A: ^{1}H-NMR spectrum of 97.7% hydrogenated *cis*-1,4-polyisoprene (HCPIP)

From Equation 2.1

$$\%hydrogenation = \frac{A-7B}{A+3B} x100 \qquad (2.1)$$

From HCPIP spectrum

$$\%hydrogenation = \frac{424.1-(7x1)}{424.1+(3x1)} x100$$

Therefore,

$$\%hydrogenation = 97.7$$

Appendix II: The Overall Compositions of STR 5L and NRL

Table AII-A: The Properties of Standard Thai Rubber (PechSiam Technotrade; 2003)

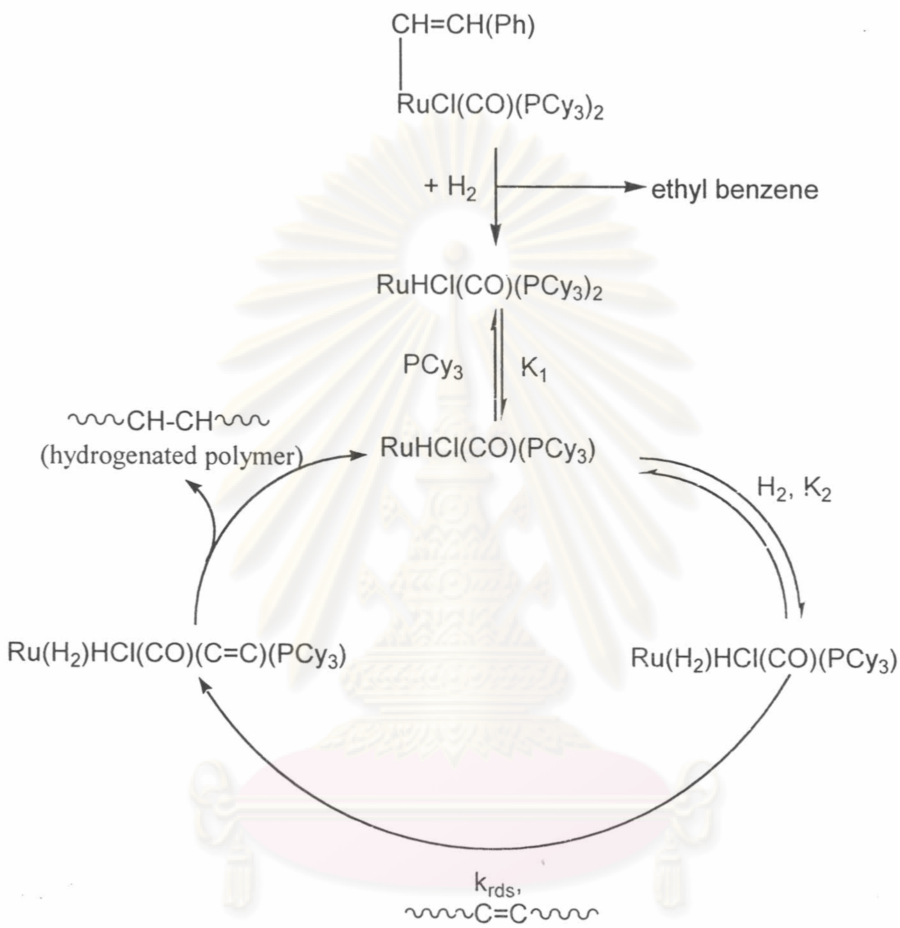
Parameter	STR 5L
Dirt (max) %wt	0.04
Ash (max) %wt	0.40
Nitrogen (max) %wt	0.60
Volatile Matter (max)	0.8
Initial Plasticity (min)	35
Plasticity Retention Index; PRI (min)	60
Color Lovibond (max)	6.0
Mooney Viscosity	NA

Table AII-B: The Properties of Natural Rubber Latex (PechSiam Technotrade; 2003)

Parameter	NRL
Dry rubber content (min)	60%
Total solid content (min)	61.5
Volatile Fatty Acid Number; V.F.A.	0.0250 – 0.20
Ammonia (High)	0.75% w/w
Mechanical Stability @ 55% T.S.C.-sec	650-1200
Color	white

Appendix III: Derivation of the Expression from the Proposed Kinetic Model

A) Derivation of the expression from the proposed mechanism for CPIP hydrogenation catalyzed by Ru(CH=CH(Ph))Cl(CO)(PCy_3)$_2$.



Using the steady state assumption for reaction intermediates, the following equilibria define the concentrations of each may be related to the rate determining step according to:

$$K_2 = \frac{[RuH(H_2)Cl(CO)(PCy_3)]}{[RuHCl(CO)(PCy_3)][H_2]} \longrightarrow$$

$$[RuHCl(CO)(PCy_3)] = \frac{[RuH(H_2)Cl(CO)(PCy_3)]}{K_2[H_2]} \qquad \text{(A1)}$$

$$K_1 = \frac{[RuHCl(CO)(PCy_3)][PCy_3]}{[RuHCl(CO)(PCy_3)_2]} \longrightarrow$$

$$[RuHCl(CO)(PCy_3)_2] = \frac{[RuH(H_2)Cl(CO)(PCy_3)][PCy_3]}{K_1K_2[H_2]} \qquad (A2)$$

A material balance on the ruthenium charged to the system yields;

$$[Ru]_T = [RuHCl(CO)(PCy_3)_2] + [RuHCl(CO)(PCy_3)] + [RuH(H_2)Cl(CO)(PCy_3)] \qquad (A3)$$

Which, using equations (A1) and (A2) is transformed to;

$$[Ru]_T = [RuH(H_2)Cl(CO)(PCy_3)]\left(1+\frac{1}{K_2[H_2]}+\frac{[PCy_3]}{K_1K_2[H_2]}\right) \qquad (A4)$$

Rearranging (A4) yields;

$$[RuH(H_2)Cl(CO)(PCy_3)] = \frac{K_1K_2[H_2][Ru]_T}{K_1+K_1K_2[H_2]+[PCy_3]} \qquad (A5)$$

$$[RuH(H_2)Cl(CO)(PCy_3)] = \frac{K_1K_2K_HP_{H_2}[Ru]_T}{K_1+K_1K_2K_HP_{H_2}+[PCy_3]} \qquad (A6)$$

where K_H is the Henry's Law constant for hydrogen on chlorobenzene.

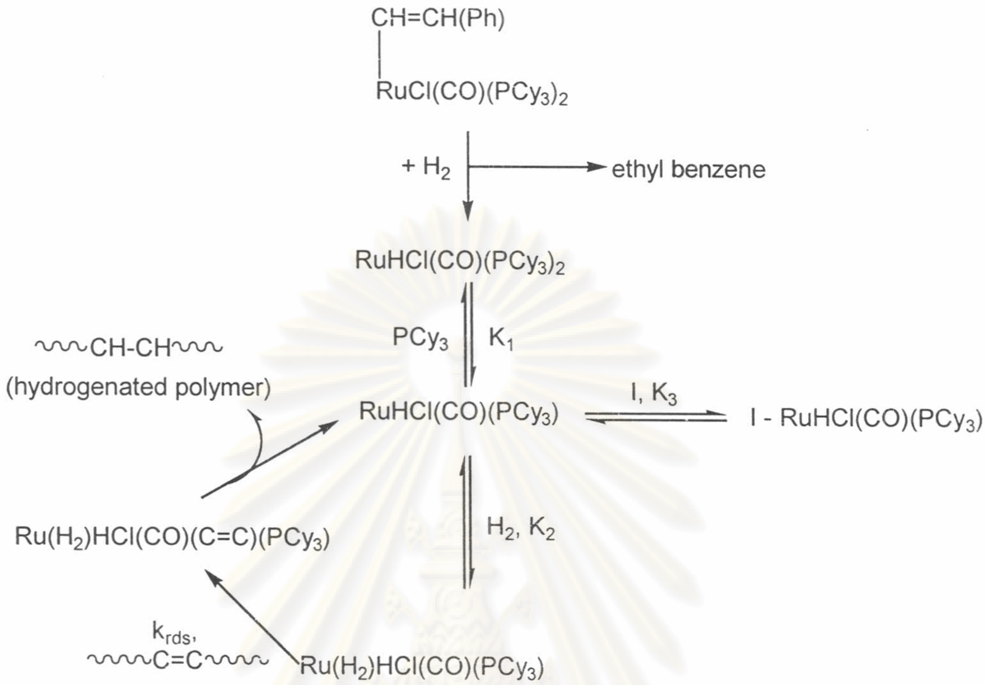
Given that the rate determining step of the process is;

$$-\frac{d[C{=}C]}{dt} = k_{rds}[RuH(H_2)Cl(CO)(PCy_3)][C{=}C] \qquad (A7)$$

The relationship of the hydrogenation rate to the operating conditions may be derived by the substitution of equation (A6) into (A7).

$$-\frac{d[C{=}C]}{dt} = \frac{k_{rds}K_1K_2K_HP_{H_2}[Ru]_T[C{=}C]}{K_1+K_1K_2P_{H_2}+[PCy_3]} \qquad (A8)$$

B) Derivation of the expression from the proposed mechanism for NR hydrogenation catalyzed by $Ru(CH{=}CH(Ph))Cl(CO)(PCy_3)_2$.



I : impurities in natural rubber

Using the steady state assumption for reaction intermediates, the following equilibria define the concentrations of each may be related to the rate determining step according to:

$$K_2 = \frac{[RuH(H_2)Cl(CO)(PCy_3)]}{[RuHCl(CO)(PCy_3)][H_2]} \longrightarrow$$

$$[RuHCl(CO)(PCy_3)] = \frac{[RuH(H_2)Cl(CO)(PCy_3)]}{K_2[H_2]} \qquad \text{(B1)}$$

$$K_1 = \frac{[RuHCl(CO)(PCy_3)][PCy_3]}{[RuHCl(CO)(PCy_3)_2]} \longrightarrow$$

$$[RuHCl(CO)(PCy_3)_2] = \frac{[RuH(H_2)Cl(CO)(PCy_3)][PCy_3]}{K_1K_2[H_2]} \qquad (B2)$$

$$K_3 = \frac{[I\text{-}RuHCl(CO)(PCy_3)]}{[RuHCl(CO)(PCy_3)][I]} \longrightarrow$$

$$[I\text{-}RuHCl(CO)(PCy_3)] = \frac{K_3[RuH(H_2)Cl(CO)(PCy_3)][I]}{K_2[H_2]} \qquad (B3)$$

A material balance on the ruthenium charged to the system yields;

$$[Ru]_T = [RuHCl(CO)(PCy_3)_2] + [RuHCl(CO)(PCy_3)] + [I - RuHCl(CO)(PCy_3)] + [Ru(H_2)HCl(CO)(PCy_3)] \qquad (B4)$$

Which, using equations (B1) - (B3) is transformed to;

$$[Ru]_T = [RuH(H_2)Cl(CO)(PCy_3)]\left(1 + \frac{1}{K_2[H_2]} + \frac{[PCy_3]}{K_1K_2[H_2]} + \frac{K_3[I]}{K_2[H_2]}\right) \qquad (B5)$$

Rearranging (B5) yields;

$$[RuH(H_2)Cl(CO)(PCy_3)] = \frac{K_1K_2[H_2][Ru]_T}{K_1 + K_1K_2[H_2] + [PCy_3] + K_1K_3[I]} \qquad (B6)$$

$$[RuH(H_2)Cl(CO)(PCy_3)] = \frac{K_1K_2K_HP_{H_2}[Ru]_T}{K_1 + K_1K_2K_HP_{H_2} + [PCy_3] + K_1K_3[I]} \qquad (B7)$$

where K_H is the Henry's Law constant for hydrogen on chlorobenzene.

Given that the rate determining step of the process is;

$$-\frac{d[C{=}C]}{dt} = k_{rds}[RuH(H_2)Cl(CO)(PCy_3)][C{=}C] \qquad (B8)$$

The relationship of the hydrogenation rate to the operating conditions may be derived by the substitution of equation (B7) into (B8).

$$-\frac{d[C{=}C]}{dt} = \frac{k_{rds}K_1K_2K_HP_{H_2}[Ru]_T}{K_1 + K_1K_2K_HP_{H_2} + [PCy_3] + K_1K_3[I]} \qquad (B9)$$

VITA

Miss Rungnapa Tangthongkul was born on May 4, 1977 in Bangkok, Thailand. She conferred her Bachelor's degree of Science in Department of Chemical Technology, Faculty of Science, Chulalongkorn University in 1999. She has continued her study in Ph.D. program at Department of Chemical Technology, Faculty of Science, Chulalongkorn University since 1999 and finished her study in 2003.