CHAPTER 2

EXPERIMENTAL AND DATA ANALYSIS

2.1 Materials

Commercial *cis*-1,4-polyisoprene (97% of *cis* isomerization) having a molecular weight of approximately 800,000 was purchased from Aldrich Chemical Co.. Natural rubber (STR 5L) was provided from Chalong Latex Industry Co., Ltd., Thailand. Natural rubber latex (60% dry rubber content) was supplied from Thai Rubber Latex CO., Ltd., Thailand. The overall compositions of STR 5L and NRL are summarized in Appendix II, Table AII-A and Table AII-B, respectively. In all cases these starting polymers were used as received. Reagent grade chlorobenzene (MCB), toluene, xylene, triethylamine, hexane, and methylene chloride were purchased from Fisher Scientific Ltd.. All solvents were used without further purification. The hydrogen gas used, with purity of 99.99%, was supplied by Praxair Inc. Ru(CH=CH)(Ph)Cl(CO)(PCy$_3$)$_2$ (Martin, 1991), RuCl(CO)(OCOPh)(PPh$_3$)$_2$ (Guo et al., 1993), Ru(CH=CH)(Ph)Cl(CO)(PPr$^i_3$)$_2$ (Werner et al., 1986), RuCl$_2$(PPh$_3$)$_3$ (Muettertis et al., 1967) were prepared according to the procedures outlined in the literature. RuCl$_3$·3H$_2$O was obtained from Engelhard. RuCl$_2$(CHC$_6$H$_5$)(PCy$_3$)$_2$ and tricyclohexylphosphine was purchased from Strem Chemicals. 2-methoxyethanol, phenylacetylene, 3-chloropropionic acid, succinic acid, and *p*-toluenesulfonic acid (*p*-TsOH) were obtained from Aldrich Chemical Co.

2.2 Catalyst Preparation

The synthesis method described in Martin's thesis (1991) was employed to prepare RuHCl(CO)(PCy$_3$)$_2$ and RuCl(CO)(CH=CH(Ph))(PCy$_3$)$_2$.

2.2.1 RuHCl(CO)(PCy$_3$)$_2$

RuCl$_3$·3H$_2$O (2.54 g) was dissolved in deoxygenated 2-methoxyethanol (55 ml). The red-brown solution was stirred for 5 minutes. Crystallized tricyclohexylphosphine (8.32 g) was added. The deep red solutions was refluxed and stirred for 20 minutes under nitrogen atmosphere and subsequently deoxygenated triethylamine (6 ml) was added therein. The solution was refluxed for 6 hours under nitrogen. The stirring was

stopped and the solution was allowed to cool slowly for about 2 hours. Orange crystals precipitated out from the solution. The solution was filtered using Shlenck apparatus under nitrogen and the crystals were washed with deoxygenated toluene (15 ml) and subsequently dried at room temperature for 48 hours. Since the material is air sensitive, no yield calculation was attempted. However, previous yields of about 80% based on Ru have been attained by others using this procedure. The ^{31}P-NMR spectrum in C_6D_6/toluene showed a singlet at 46.9 ppm, with a small additional singlet at 36.1 ppm attributable to the dichloro species $RuCl_2(CO)(PCy_3)_2$ (Martin, 1991).

Samples of $RuHCl(CO)(PCy_3)_2$ were further recrystallized from toluene. In a typical procedure, the entire sample was dissolved in dry, deoxygenated refluxing toluene (75 ml) under nitrogen. The solution was then allowed to cool slowly to room temperature, then stored in the refrigerator overnight. Orange crystals were slowly formed. The crystals were washed twice with cold deoxygenated toluene (10 ml), then dried under vacuum at 60°C for 5 hours to remove strongly-bound solvent. The ^{31}P-NMR spectrum in C_6D_6/toluene showed only a singlet at 46.9 ppm with no other peaks. The ^{1}H-NMR spectrum showed a triplet, attributable to the metal-hydride, centered at –24.2 ppm, and the characteristic absorbances of the various cyclohexyl protons in the region from 2.5 to 1.2 ppm. Integration of the hydride and cyclohexyl protons gave a ratio of approximately 66 to 1 (Martin, 1991).

2.2.2 Ru(CH=CH(Ph))Cl(CO)(PCy₃)₂

A sample of hydride catalyst, $RuHCl(CO)(PCy_3)_2$ (approx. 7 g) was dissolved in refluxing, dry, deoxygenated toluene (75 ml). Phenylacetylene (1.6 ml) was added to the solution using a syringe. The orange color changed to red rapidly. The reaction was cooled and stirred at room temperature overnight. The fine pinkish solid precipitate was filtered in Shlenck apparatus, washed twice with dried, deoxygenated hexane (20 ml) and dried under vacuum. The sample was dissolved in refluxing dry distilled toluene and allowed to cool slowly. The solid was then refrigerated overnight. The supernatant was separated from the crystals, which were then dried under vacuum at 60°C for 48 hours. The solid gradually changed from deep red to pink as it dried.
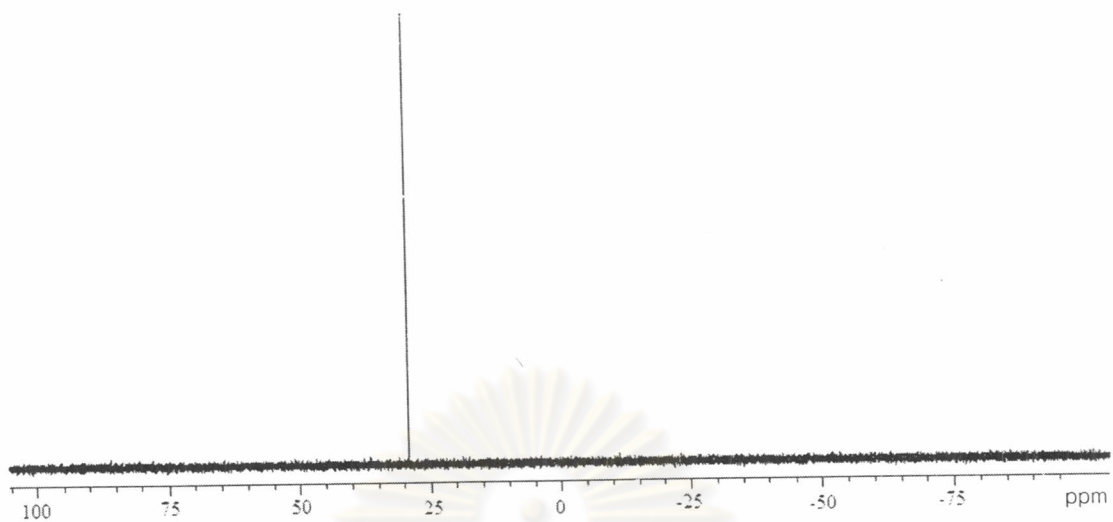
Figure 2.1: ^{31}P-NMR spectrum of Ru(CH=CHPh)Cl(CO)(PCy$_3$)$_2$
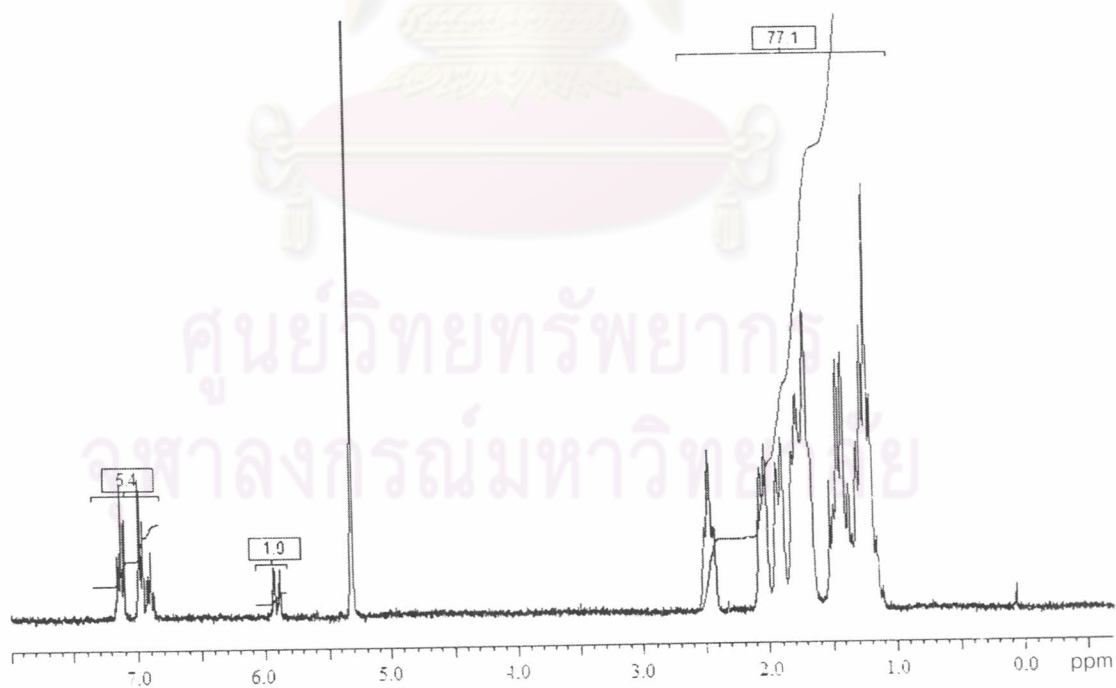
Figure 2.2: ^{1}H-NMR spectrum of Ru(CH=CHPh)Cl(CO)(PCy$_3$)$_2$

The solid sample was then dissolved in refluxing methylene chloride under nitrogen atmosphere. Hexane (15 ml) was added and the solution was slowly cooled to room temperature, then stored in the refrigerator. The precipitate was filtered in the Shlenck apparatus, washed with dry degassed hexane (20 ml), and dried in vacuum at room temperature for 48 hours. The filtrate solution volume was reduced to 30 ml by evaporation under vacuum and a further sample of solid was recovered, washed and dried in the same manner. ^{31}P-NMR showed only a singlet at 27.7 ppm, indicating that the material was pure (Figure 2.1). ^{1}H-NMR in $CDCl_3$ showed the aromatic, cyclohexyl and styryl protons in correct proportions as shown in Figure 2.2. No metal hydride was detected.

2.3   Gas Uptake Apparatus

The gas uptake apparatus utilized in this investigation is a computer controlled batch reactor system that was developed by Mohammadi and Rempel (1987b: 27-35). Reliable kinetic studies of the gas consuming catalytic reactions were carried out in the apparatus that was designed to maintain constant pressure and temperature while monitoring H_2 consumption as a function of real time. Figure 2.3 illustrates the operational schematic of the equipment. A drop in the autoclave pressure relative to the reference bomb RB-1 is detected by the differential pressure transducer (PT-1). This error signal functions as the input for the control algorithm residing within a personal computer. Via an i/p converter, the PC activates the pneumatic control value to permit H_2 from the supply cell to recharge the autoclave. This control system maintains the autoclave pressure no less than 0.3 psi below its set point.

PT-2 monitors pressure drop in the supply cell relative to RB-2 and the amount of H_2 lost during the reaction is an integrated measure of the hydrogenation rate. PT-2 converses the signal to millimoles of H_2 by calibrating its output voltage against the conversion of a known amount of substrate. This technique assumes that a change in pressure is linearly proportional to the H_2 loss from the supply cell. Such ideal gas behavior holds for H_2 at 1250 psi and 295 K, especially over small changes in pressure.
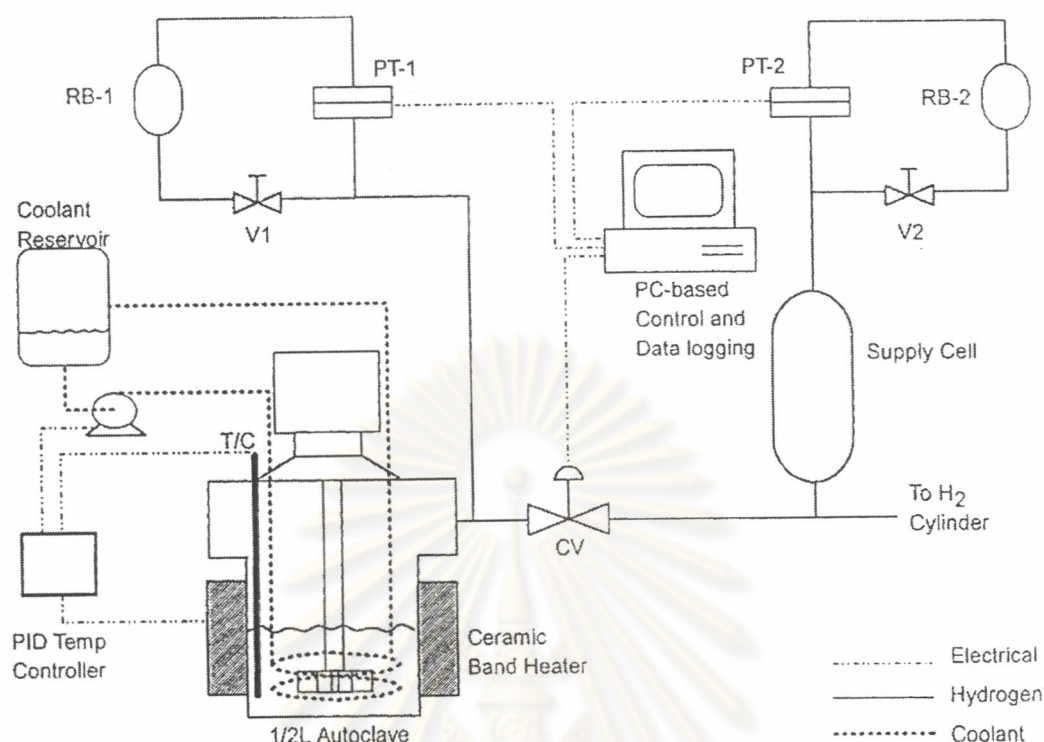
Figure 2.3: Schematic of gas uptake apparatus

2.4 Typical Hydrogenation in a Parr reactor

Hydrogenation reactions were carried out in a 300 ml Parr pressure reactor. In a typical experiment, a specific amount of the polymer was weighed and dissolved in 130 ml of solvent. The solution was transferred into the reactor. In a glovebox, the ruthenium complex catalyst was dissolved in the 20 ml of solvent and transferred into the catalyst addition device. Then, the reactor and the catalyst addition device were connected. The autoclave was purged with hydrogen gas. Subsequently, the reactor was pressurized to 32 bar before being heated up to the required reaction temperature. When thermal equilibrium was reached in the reactor (vapor/liquid), the catalyst solution was added by pressurized hydrogen gas and the hydrogen pressure was adjusted to the required reaction pressure. During hydrogenation, the mixture was stirred at a constant speed of 600 rpm. This reaction was maintained at the desired temperature and pressure for a given time. After hydrogenation, hydrogenated rubber

was precipitated in ethanol and finally dried under vacuum at room temperature for subsequent analysis.

2.5 Typical Kinetic Experiment Procedure

Kinetics of the hydrogenation of polyisoprene rubber catalyzed by the Ru (CH=CH(Ph))Cl(CO)(PCy$_3$)$_2$ complex were studied by measuring the amount of hydrogen consumed as a function of time using a gas uptake apparatus. The hydrogenation apparatus was maintained at constant temperature $\pm 1^{\circ}$C and pressure $\pm$ 0.02 bar throughout the reaction. Typically, 150 ml of polymer solution was prepared and charged into the reactor. Catalyst was weighed into a small glass bucket, which was placed in a port in the reactor head. The reactor was then assembled.

All kinetic experiments were performed with the rigorous exclusion of air. To purge the reactor headspace, three cycles of charging the reactor with the H$_2$ to 10 bar and venting were carried out without agitation. The autoclave was then immersed in an ice-water bath. A head pressure of 14 bar was charged and the agitator started at 200 rpm. The reactor was chilled to reduce the vapor pressure of solvent. Once cooled to below 10°C, the reactor pressure was once again vented and recharged to 14 bar. To degas the polymer solution, H$_2$ was purged continuously through the reactor headspace while agitating at 1200 rpm for 20 minutes. The reactor pressure was then vented and the ceramic band heater installed.

Achieving the desired reaction conditions required pressurizing the system to approximately 80% of the target value and initiating the temperature controller. The increase in the temperature of the sealed autoclave provided the remaining 20% of pressure set point. Once the chosen conditions had been attained, a minimum of 45 minutes was allowed for the system to equilibrate. The long equilibrium time was necessary to ensure that the autoclave vessel and all of its components, including the magnetic drive were isothermal.

The H$_2$ uptake-monitoring program employed two user- specified data logging intervals. The first was of short duration and was designed to monitor the reaction during its initial stages where the reaction rates are greatest. The second interval could be initiated by the operator to avoid the unnecessary collection of data periods of slow reaction. Once activated, the program waited one logging interval before starting the record time, reaction temperature and the amount of H$_2$ consumed. At this point, the

reference isolation valves V1 and V2 were closed and the catalyst bucket released into the solution.

Each experiment was allowed to proceed until gas consumption ceased. When the gas uptake was near completion or gas uptake corresponding to more than 90 percent conversion was observed, the program was terminated. The heater were shut down and removed, and the vessel was then brought to $50^{\circ}C$ using the cooling unit before venting off the pressure. The autoclave was disassembled and a sample of the hydrogenated product solution was cast onto a NaCl plate for infrared analysis. The remained product was isolated by precipitation with ethanol and drying under vacuum. The autoclave was reassembled containing about $150^{\circ}C$ of toluene and agitated to removed residue polymer solution. After the rinse, the reactor was blown dry with air before commencing the next trial.

2.6   Analysis Methods

2.6.1 Fourier Transform Infrared Spectroscopic Analysis

Infrared spectra were collected on a Bio-Rad FTS 3000X spectrometer. The rubber samples were run as cast films on a sodium chloride disk. The latex film was cast onto a Zn-Sn plate and dried at room temperature.

2.6.2 ^{1}H-NMR and ^{13}C-NMR Analysis

The final degree of olefin conversion was quantified NMR spectroscopic analysis. ^{1}H and ^{13}C-NMR spectra were recorded on 3% w/v solutions of the rubber in CDCl$_3$ using an Avance 300 MHz spectrometer, Bruker.

2.6.3 Gel Permeation Chromatography (GPC)

Gel permeation chromatography was performed using a Waters GPC system fitted with a Water Ultrastyragel 10^4 Angstrom column. It was operated at $30^{\circ}C$, with THF as the carrier solvent. Samples 0.2% solutions in THF were prepared. The system detectors were a multi-angle laser light scattering (MALLS) (Wyatt Dawn DSP-F) operating at 630 nm and a Waters DR 401 differential refractive index detector (DRI). Wyatt Astra software was used for data analysis. Due to unavailable Mark Houwink constants for the hydrogenated polyisoprene in the literature, no

precise molecular weight distribution information was obtained by GPC. Therefore, GPC was used to evaluate gross changes in the chain length after hydrogenation.

2.6.4 Viscosity Measurement

The relative viscosity of parent polymers and the hydrogenated products (0.12500 ± 0.00015 g of polymer / 25 ml of toluene) were also measured by means of Ubellohde capillary viscometer in toluene at $35^{\circ}C$. Samples were filtrated through a coarse, sintered-glass filter to remove insoluble gel before being introduced into the viscometer.

2.6.5 Thermogravimetric Analysis (TGA)

TGA of starting polymers and hydrogenated rubbers was performed on a NETZSCH STA 409C. The temperature was increased under nitrogen atmosphere from $50^{\circ}C$ to $800^{\circ}C$ at the constant heating rate of $10^{\circ}C/min$. The nitrogen gas flow rate was 50 ml/min. The onset of the degradation, the weight loss due to degradation and the residue remaining at $800^{\circ}C$ were evaluated. The initial decomposition temperature (T_{id}) and the maximum decomposition temperature (T_{max}) were determined.

2.6.6 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry analysis was carried out on a NETZSCH DSC 200. Typical analysis, about 20-mg sample was first cooled to $-100^{\circ}C$ with liquid nitrogen and then heated under nitrogen flow at the heating rate of $10^{\circ}C/min$ to $40^{\circ}C$. Al_2O_3 was used as the reference sample. The middle of incline was taken to be the glass-transition temperature (T_g).

2.7 Degree of Hydrogenation Determination

^{1}H-NMR spectra of hydrogenated polyisoprenes were used to determine the extent of hydrogenation. The lump peak area of saturated protons (-CH_2- and -CH_3) in the range of 0.8 - 2.3 ppm and the unsaturated protons peak area at 5.2 ppm were calculated as shown in Equation 2.1:

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

where A is lump peak area of saturated protons and B is peak area of unsaturated protons. The example of % hydrogenation calculation is described in Appendix I.

Gas uptake data files consisted of three columns: time in seconds, total gas uptake in millimoles, and temperature. Data files were exported to Microsoft Excel program for calculations. The total extent of hydrogenation measured by ^{1}H-NMR was used to correct the total gas uptake. The gas uptake data were converted to percent double bond conversion (X) using the known maximum extent of reaction.

A plot of ln(1-X) versus time was constructed and examined. The slope of the plot was determined by linear regression. R^2 from the regression was typically in excess of 0.95, indicating that the reaction was first order in the double bond concentration to relatively high conversion. The slope of the first order plot provided values of k'.

2.8 Kinetic Study Experimental Design

Several studies were necessary to determine the basic kinetic dependencies of the system. In each study, the dependence of the pseudo first order rate constant k' on a different parameter was determined. The rate of hydrogenation is known to be influenced by factors such as the concentration of catalyst, hydrogen, double bond concentrations, and temperature. The elucidation of the mechanism required the study of the kinetic effects of different solvents and the addition of catalyst ligand. A number of additional bulky phosphine catalysts were also studied.

Experiments within each of the basic kinetic dependencies were performed in random order to avoid the accumulation of systematic error. Replicate experiments at a base set of conditions were performed periodically to ensure that no systematic trend, such as catalyst degradation, was convoluting the measurement. Factor combinations of CPIP hydrogenation experiments have been assigned. This consists of a two level factorial design coupled with univariate experiments which inspect the influence of factors acting alone or in combination. Of principle interest were the influences of the concentrations of catalyst, polymer and H_2 on the rate of reaction. Of secondary interest were the effect of varying solvents, the reaction temperature, or adding PCy_3 to the system. A two-level factorial design was employed for principle factors to identify joint interactions. The influences of various solvents, temperature and added phosphine have been investigated by univariate experiments alone.

Selection of concentrations and temperatures considered weighing precision, polymer solution viscosities and limitations on the reaction rates that the apparatus could control and monitor effectively. The univariate factor combinations have been duplicated for hydrogenation of natural rubber and natural rubber latex to gain a fundamental understanding of the kinetic behavior of this system.