CHAPTER II

HYDROGENATION OF CIS-1,4-POLY(ISOPRENE) CATALYZED BY OsHCl(CO)(O$_2$)(PCy$_3$)$_2$

2.1 Introduction

Polydiene-based polymers are widely used as rubbers, binders and adhesives due to their high strength and good elastic properties. However, a disadvantage of these materials is their aging behavior, which is caused by the oxidation of residual double bonds in the polydienes, which could deteriorate the properties of the polymers. Chemical modification of polydiene-based polymers by hydrogenation is one of the important methods for improving and changing the properties of unsaturated elastomer toward greater stability against thermal, oxidative, and radiation-induced degradation.

There are many reports of hydrogenation of polybutadiene, acrylonitrile-butadiene copolymer, and styrene-butadiene copolymer using transition metal compound catalysts [41, 43, 44]. Ru and Rh, for example, RuCl$_2$(PPh$_3$)$_3$ and RhCl(PPh$_3$)$_3$ complexes were found to be a suitable catalyst system for the hydrogenation of polybutadiene [36] and acrylonitrile-butadiene copolymer [27], respectively. In addition, a metallocene catalyst system, primarily the bis(η^5-cyclopentadienyl)cobalt (Cp$_2$Co) combined with n-butylithium (n-BuLi), was found to be active for hydrogenation of polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS) block copolymer [40]. A Ziegler-Natta type catalyst prepared with nickel acetylacetonate and n-butyllithium was used to hydrogenate styrene-butadiene copolymer in cyclohexane [39].

Of many metal complexes capable of catalyzing olefin hydrogenation, those based on Rh, Ru and Pd have been successful. Recently, study of the hydrogenation of acrylonitrile-butadiene copolymers catalyzed by Os complex catalyst has shown that it is amongst the most active and mechanism for the reaction was elucidated [8]. The mechanism was most unusual in that under certain conditions, a second order dependence on hydrogen concentration was observed.

Poly(isoprene) has been used in the automobile and adhesive industries. It is preferably used in blends with other rubbers, such as poly(butadiene) or poly(styrene-co-

butadiene), to improve their processability. Thus, hydrogenation of poly(isoprene) improves the heat and oxygen resistance of the rubber producing essentially an alternating copolymer of ethylene-propylene, which is difficult to be prepared by conventional polymerization [45].

Poly(isoprene) has been hydrogenated by a number of methods including using noncatalytic reagents, such as *p*-toluenesulfonyl hydrazide (TSH) [46]. Shahab and Basheer [47] studied different catalytic methods for poly(isoprene) in the form of natural rubber. One method used a homogeneous catalyst, $RhCl(PPh_3)_3$, and a heterogeneous catalyst, Pd supported on $CaCO_3$. These methods suffer a drawback in that long reaction times with high catalyst loading [7].

The purpose of this work is to study the hydrogenation of cis,1,4-poly(isoprene) in the presence of $OsHCl(CO)(O_2)(PCy_3)_2$ as catalyst. Kinetic data was collected within a statistical framework, which defined the effect of concentration of catalyst and polymer, hydrogen pressure, and temperature on catalytic activity. The kinetics of the reaction and the purposed mechanism for cis-1,4-poly(isoprene) hydrogenation by $OsHCl(CO)(O_2)$ $(PCy_3)_2$ are reported.

2.2 Experimental

2.2.1 Materials

$RhCl(PPh_3)_3$ [21], $RuCl(CO)(styryl)(PCy_3)_2$ [48] were prepared by literature methods. $[Ir(COD)py(PCy_3)]PF_6$ was obtained from Strem Chemicals. $OsHCl(CO)(O_2)$ $(PCy_3)_2$ was prepared by refluxing $OsCl_3.3H_2O$ with PCy_3 (both from Strem Chemicals) in methoxyethanol according to the procedures of Esteruelas and Werner.[18] The corresponding dioxygen adduct, $OsHCl(CO)(O_2)(PCy_3)_2$, was prepared by exposing a suspension of $OsHCl(CO)(PCy_3)_2$ in hexane to pure O_2 as detailed by Esteruelas et. al [16]. The reaction gas used in the hydrogenation was oxygen-free hydrogen with a purity of 99.99% obtained from Praxair Inc. Reagent grade toluene was obtained from BDH. Chlorobenzene, xylene, ethanol, methoxyethanol, hexane, and tetrahydrofuran were purchased from Fisher Scientific Ltd. All solvents were used as received. The high molecular weight cis-1,4-poly(isoprene) with 97% of cis isomer used in this study was provided by Bayer Inc. and Scientific Polymer Products Inc.

2.2.2 Hydrogenation by Batch Reactor

Hydrogenation reactions were carried out in a 300 mL Parr reactor. 2.65 g of cis-1,4-poly(isoprene) was mixed with 130 mL of organic solvent. The catalysts were weighed and dissolved with 20 mL of organic solvent and filled into a catalyst addition device. The mixture in the autoclave was degassed by bubbling hydrogen gas through for 20 min at 13.8 bar H_2 pressure at room temperature. The autoclave was then heated to the desired reaction temperature with agitation at 600 rpm. When the temperature of the autoclave stabilized, the catalyst addition device was pressurized to the reaction pressure with hydrogen gas in order to charge the catalyst solution into the mixture. The autoclave was then pressurized to the reaction pressure. Hydrogen gas was pressurized into the autoclave as required in order to maintain a constant reaction pressure throughout the reaction period. After reaction, the hydrogenated product was isolated by precipitation with ethanol, filtered, and dried under vacuum.

2.2.3 Hydrogenation by Gas Uptake Apparatus

a) Apparatus

The hydrogenation of cis-1,4-poly(isoprene) by batch reactor was carried out in a 300 mL, fixed head o-ring seal with 4842 controller Parr reactor. Kinetics of cis-1,4-poly (isoprene) by $OsHCl(CO)(O_2(PCy_3)_2$ were obtained using an automated gas uptake apparatus. Raw kinetic data consisted of time-resolved measurements of both the amount of hydrogen consumed by the reaction and the temperature of the rubber solution. The hydrogenation apparatus, a high-pressure variation of that developed by Mohammadi and Rempel [49], has proven to be capable of monitoring the reaction process in real time. An operational schematic of the equipment is provided in Figure 2.1. Detailed drawings and descriptions of specific components have been reported by Matin [9].

The apparatus is designed to maintain isothermal and isobaric conditions while monitoring H_2 consumption. 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 serves as the input for the control algorithm residing within a personal computer. Via an i/p converter, the PC actuates the pneumatic control valve to permit H_2 from the supply

cell to recharge the autoclave. This control system maintains the autoclave pressure to no less than 0.3 psi below its set point.

The amount of H_2 lost from the supply cell during the reaction is integrated measure of the hydrogenation rate. This is monitored by PT-2, which detects the drop in the supply cell pressure relative to RB-2 created by the transfer to H_2 to the autoclave. Conversion of the signal generated by PT-2 to millimoles of H_2 is accomplished 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 H_2 lost from the supply cell. Such ideal gas behavior holds for H_2 at 1250 psi and 295 K, especially over small changes in pressure.
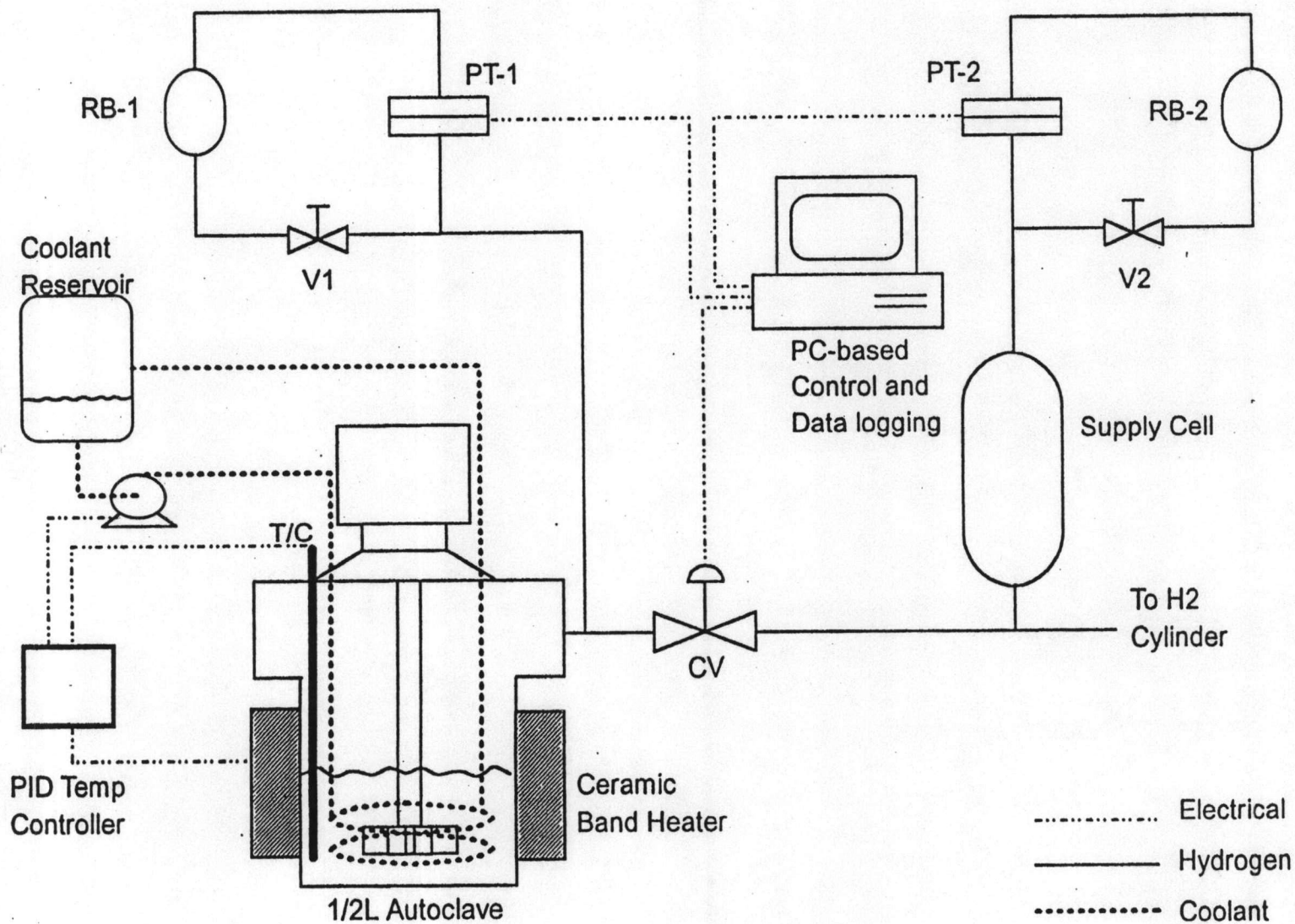
Although the pressure control algorithm operates with excellent precision, the degree to which the measured gas uptake profile corresponds to the progress of the hydrogenation is dictated by the accuracy of the temperature control. Autoclave temperature fluctuations of $\pm 1°C$ create pressure swings to which the pressure controller responds. The resulting reaction profile may therefore become the sum of the intrinsic reaction rate and artifacts of the temperature control. This is especially problematic at operating pressures above 40 bar where pressure is increasingly sensitive to autoclave temperature variations.

The original apparatus did not include a cooling system and was susceptible to severe reaction exotherms. To improve the quality of the kinetic data and facilitate the study of more rapid reactions, a dual output PID controller (Parr model 4842) was installed. Acting upon the ceramic insulated heating mantle and oil circulating pump (Masterflex model 2020C), the new system controlled the solution temperature to within $\pm 1°C$ of the set point. As a further precaution, the vessel temperature was logged with the H_2 consumption data to provide a means of assessing the controller performance.

b) Standard Reaction Procedure

Polymer solutions were prepared by dissolving the desired mass of rubber in toluene within a 100 cm^3 volumetric flask. This took approximately 24 hours, during which the flask was placed in the dark. This solution was transferred to autoclave and the volumetric rinsed with 50 cm^3 of toluene to make the total solution volume in the 150 cm^3.

Figure 2.1 Gas Uptake Apparatus.

RB-1

PT-1

PT-2

RB-2

V1

V2

Coolant
Reservoir

PC-based
Control and
Data logging

Supply Cell

T/C

To H2
Cylinder

CV

PID Temp
Controller

Ceramic
Band Heater

1/2L Autoclave

.... Electrical

———— Hydrogen

•••••••••• Coolant

27

The required mass of catalyst precursor was weighed by difference into a dry, glass bucket to an accuracy of $\pm$ 0.0001g. This bucket was then loaded into a catalyst chamber that was designed to suspend it above the polymer solution during the degassing and heating processes. The autoclave, having been charged with the catalyst bucket, was assembled according to the manufacturer's instructions.

Beyond the time of weighing the catalyst, all kinetic experiments were performed with the rigorous exclusion of air. To purge the autoclave headspace, three cycles of charging the reactor with H_2 to 10 bar and venting were carried out with no agitation. The autoclave was then immersed in an ice-water bath. A head pressure of 14 bar of H_2 was charged and the agitator started at 200 rpm. Chilling the vessel to reduce the vapour pressure of toluene was a precautionary measure. Once cooled to 5°C, the reactor pressure was once again vented and recharged with 14 bar H_2. The polymer solution was degased as, 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 with H_2 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 the pressure set point. Once the chosen conditions had been attained, the system was allowed a minimum of 45 minutes to equilibrate. During this period all of the reactor components would warm up, causing a slight rise in the overall system pressure. A failure to observe this equilibration time resulted in an uptake plot that was adversely influenced by this pressure increase. Experiments performed above 30 bar or those suspected of a duration greater than 40 minutes were allowed an additional 30 minutes to stabilize before initiation of the reaction.

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 during periods of slow hydrogenation. Once activated, the program waited one logging interval before starting to record the time, reaction temperature and amount of H_2 consumed. At this point, the reference isolation valves V1 and V2 were closed and the catalyst bucket dropped, dispersing the catalyst powder in the polymer solution using an agitation rate of 1200 rpm. For extremely fast reactions the cooling unit was manually started as the

catalyst was dispersed. This technique could limit the influence of the initial exotherm to less than a 1°C temperature rise.

Each experiment was allowed to proceed until gas consumption ceased. The reactor was then brought to 50°C using the cooling unit before venting off the pressure. The autoclave was disassembled and a sample of the hydrogenated cis-1,4-poly(isoprene) solution cast onto a NaCl plate for infrared analysis. The autoclave was then reassembled containing about 150 cm^3 of toluene and agitated to remove residual polymer solution. After this rinse, the reactor was blown dry with air before commencing the next trial.

2.2.4 Characterization

The final degree of olefin conversion measured by gas uptake was confirmed by infrared spectroscopy and ^{1}H-NMR spectroscopic analysis. ^{1}H-NMR and ^{13}C-NMR spectra of polymer samples were recorded on a Bruker 200 MHz spectrometer, using CDCl$_3$ as the solvent. FT-IR spectra were obtained with a Bio-Rad FTS 3000X spectrometer. The infrared samples were prepared by casting polymer films from solution onto sodium chloride disks.

2.2.5 Viscosity Measurement

The viscosity of dilute polymer solutions (0.12500 $\pm$0.00015 g of hydrogenated cis-1,4-poly(isoprene) / 25 mL of toluene) was measured at 35°C by using an Ubellohde capillary viscometer. Sample filtration through a coarse, sintered-glass filter provided a means of detecting insoluble gel. The relative viscosity data (η_{rel}) are reported as the polymer solution viscosity relative to that of toluene solvent at 35°C.

2.2.6 Experimental Design

Specific combinations of factor levels were selected according to a structure design [50]. The principal factors of interest were the influences of the concentration of catalyst ([Os]) and cis-1,4-poly(isoprene) ([C=C]), and hydrogen concentration ([H$_2$]) on the rate of hydrogenation. The secondary factors of interest were the effect of varying the

reaction temperature and solvent type on hydrogenation. Principal factor combinations conformed to a central composite structure, consisting of a univariate or " one-at-a-time " series to study the influence of each factor while holding all others constant, and a two-level factorial series of experiments to identify joint interactions. The influences of temperature, and solvent have been investigated by univariate experiments alone. Selection of the factor level ([Os], [C=C], [H_2]) considered catalyst weighing precision, the viscosity of polymer solution and the hydrogenation rate which the apparatus could effectively control and monitor.

2.3 Results and Discussion

2.3.1 Initial Studies in the Batch Reactor

The hydrogenation of cis-1,4-poly(isoprene) in presence of $OsHCl(CO)(O_2)$ $(PCy_3)_2$ can be represented by Figure 2.2. The final degree of hydrogenation of cis-1,4-poly(isoprene) was confirmed by IR spectroscopy and ^{1}H-NMR spectroscopic analysis. Figure 2.3 a and b shows the FT-IR spectra of cis-1,4-poly(isoprene) and hydrogenated cis-1,4-poly(isoprene). The most apparent change in the FT-IR spectra are the reduction in the bands at 1,663 and 836 cm^{-1} due to C=C stretching and olefinic C-H bending, as the extent of hydrogenation of C=C increased.
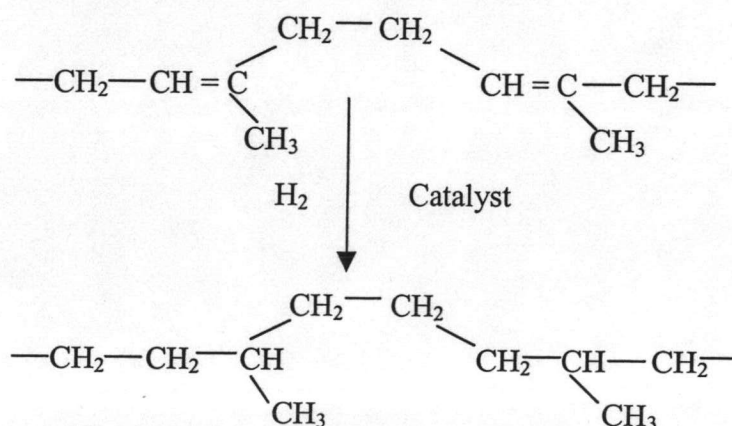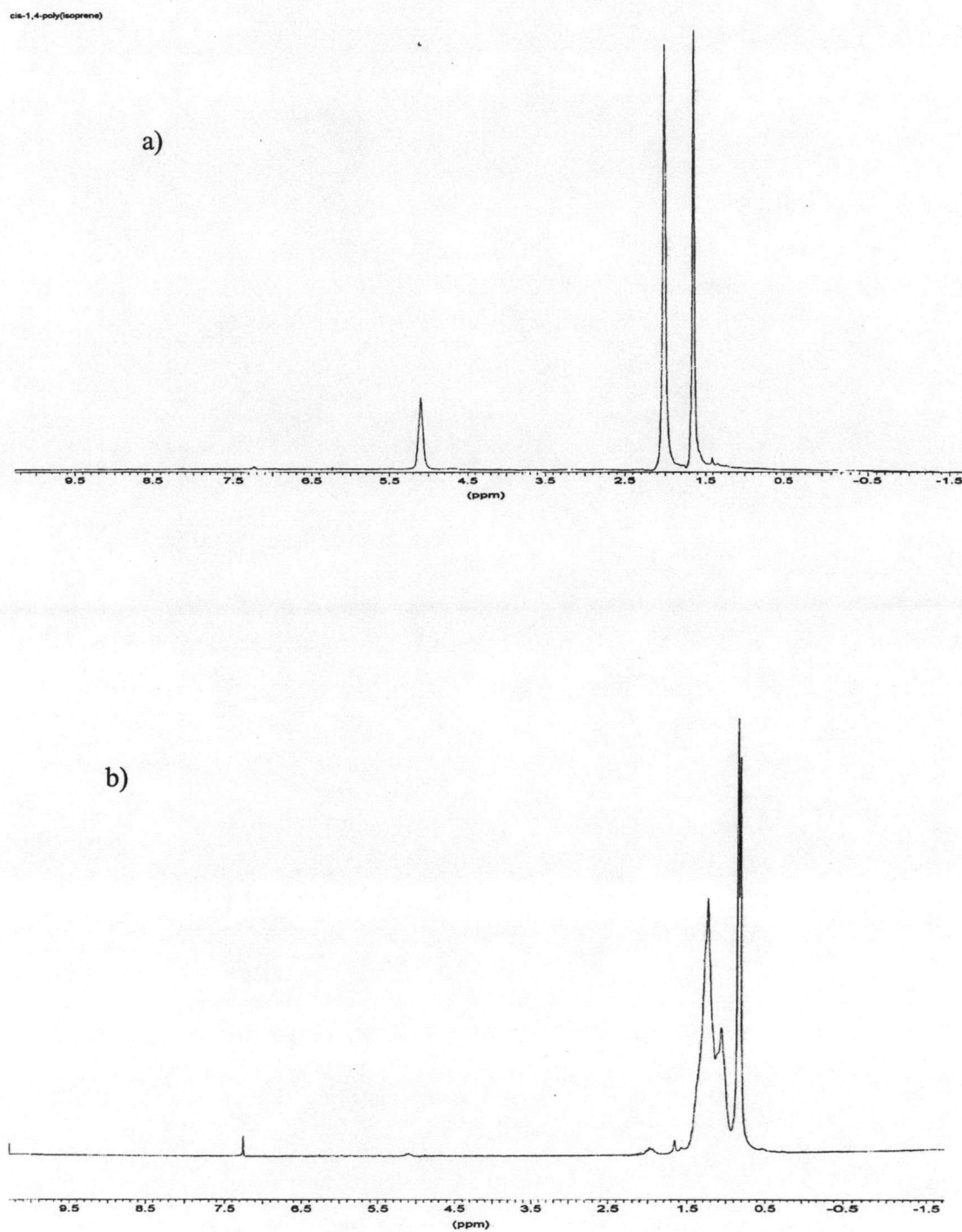

Figure 2.2 The hydrogenation reaction of cis-1,4-poly(isoprene).
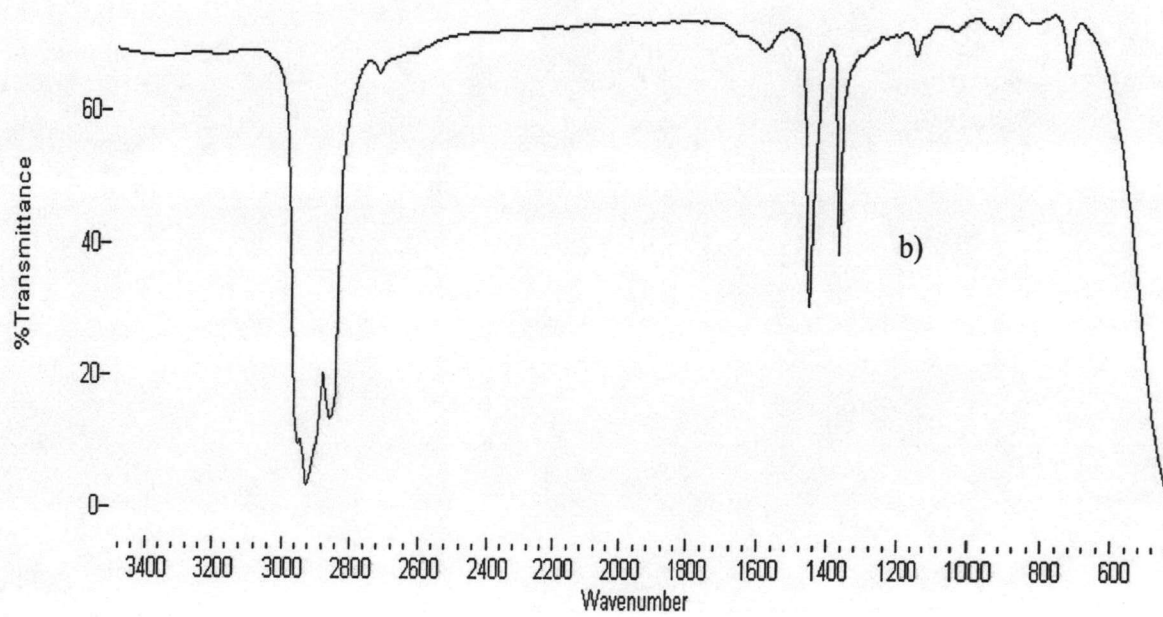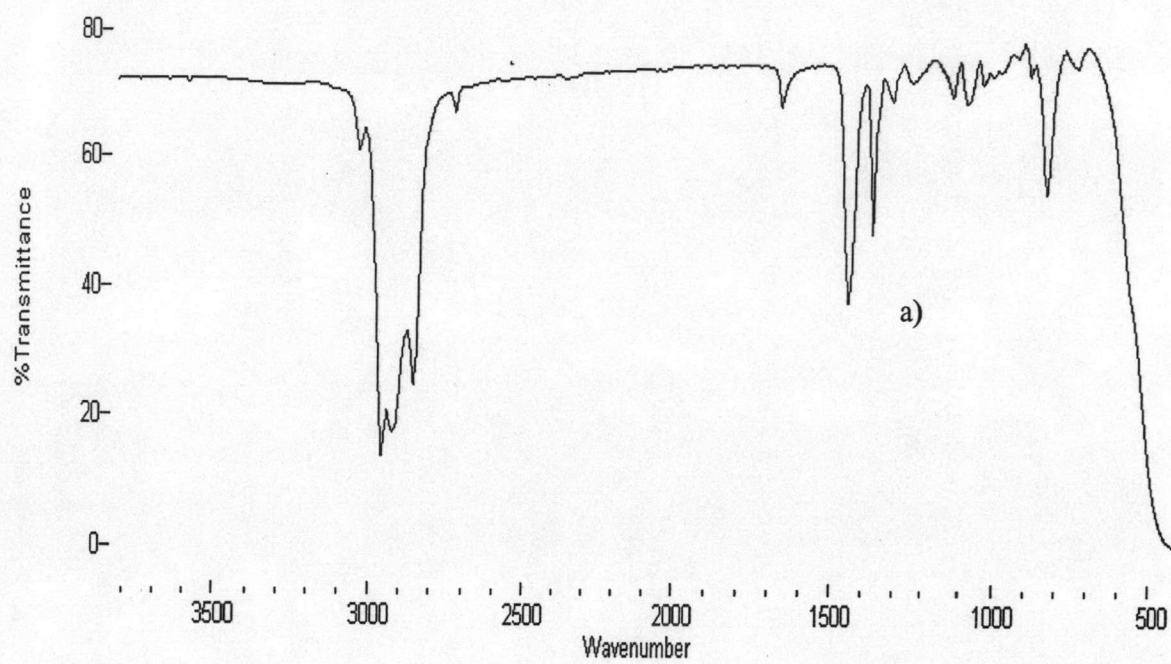
Figure 2.3. FT-IR spectra of: a) cis-1,4-poly(isoprene) and b) hydrogenated cis-1,4-poly (isoprene).

cis-1,4-poly(isoprene)

a)

b)

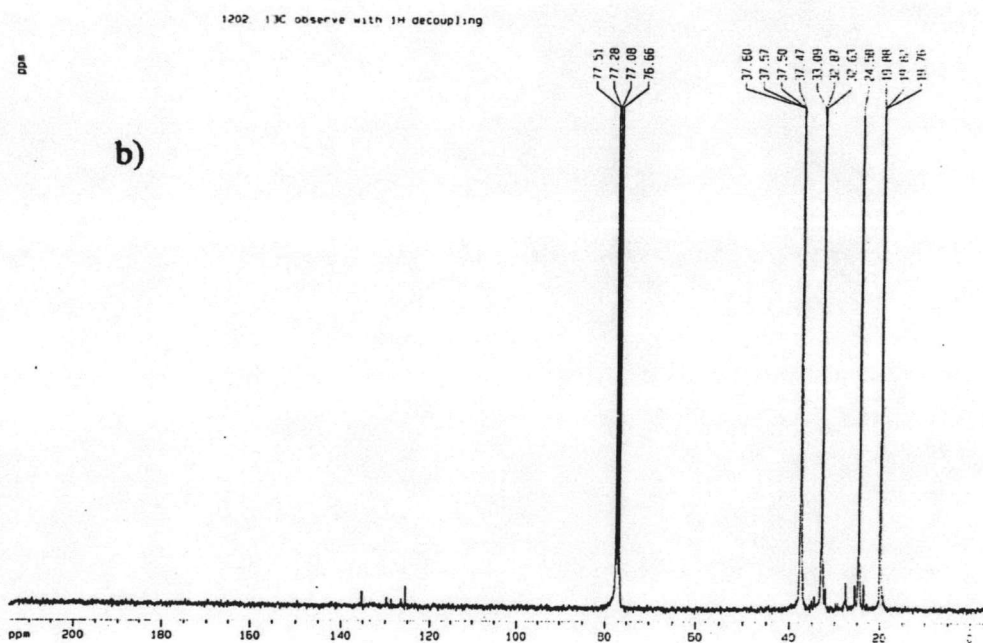**Figure 2.4** ^{1}H-NMR spectra of: a) cis-1,4-poly(isoprene) and b) hydrogenated cis-1,4-poly(isoprene).

Polyisoprene high MW., 13C observe with 1H decoupling

147.5 135.8 135.6 135.4 135.3 135.2 135.1 125.1 125.1 125.0 124.7 124.3 123.8 111.5 78.1 77.6 77.5 77.3 77.1 76.8 76.7 48.0 40.1 32.4 32.3 32.1 32.1 31.3 29.9 29.8 28.4 26.7 26.6 26.5 26.4 23.6 23.5 18.7 16.0

a)

1202 13C observe with 1H decoupling

77.51 77.28 77.08 76.66 37.60 37.57 37.50 37.47 33.09 32.87 32.63 24.58 19.88 19.83 19.76

b)

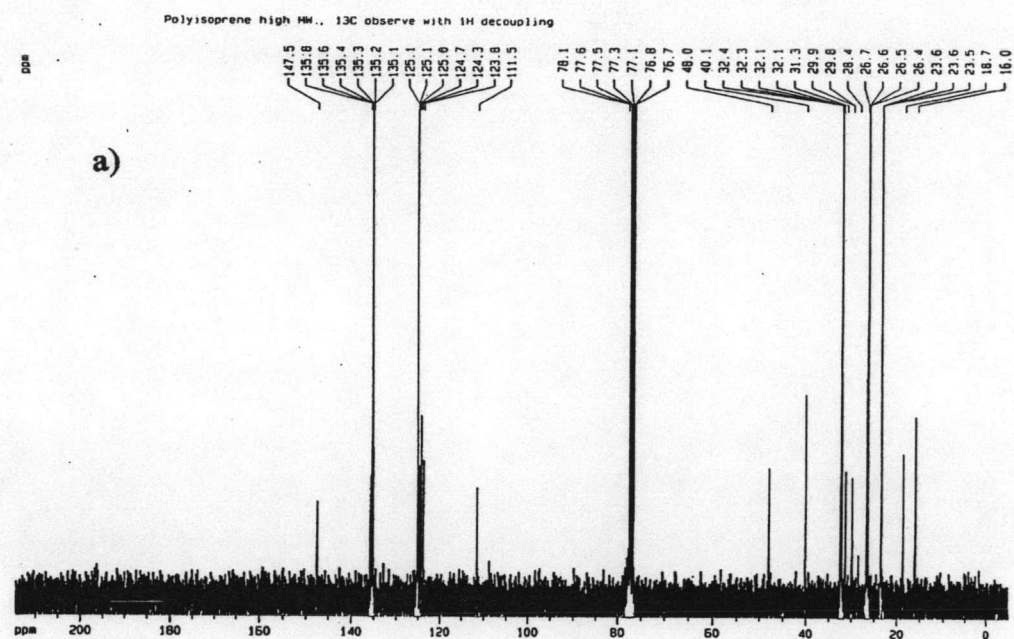**Figure 2.5** ^{13}C-NMR spectra of: a) cis-1,4-poly(isoprene) and b) hydrogenated cis-1,4-poly(isoprene).

Table 2.1 Results of Cis-1,4-Poly(isoprene) Hydrogenation Using Different Catalysts

Catalyst	[Catalyst] (mM)	Temp ($^\circ$C)	P_{H_2} (bar)	[C=C][c] (mM)	Solvent	Results
RhCl(PPh$_3$)$_3$	0.3943	100	27.6	260.10	Toluene	A little hydrogenation, after 20 h
	0.0721	130	27.6	260.10	Toluene	No hydrogenation
	0.0721	120	55.2	260.15	MCB	A little hydrogenation, after 20 h
RuCl(CO)(styryl)(PCy$_3$)$_2$	0.0804	100	27.6	260.20	Toluene	Very little hydrogenation, after 20 h
	0.0804	160	27.6	260.10	Toluene	>90% hydrogenation, after 20 h
[Ir(COD)py(PCy$_3$)]PF$_6$	0.0828	100	27.6	260.20	Toluene	A little hydrogenation, after 20 h[a]
	0.0828	100	27.6	260.20	CHCl$_3$	>90% hydrogenation, after 7 h
	0.0828	100	27.6	260.10	MCB	>90% hydrogenation, after 6 h
OsHCl(CO)(O$_2$) (PCy$_3$)$_2$	0.0787	100	27.6	260.20	Toluene	>90% hydrogenation, after 16 h
	0.0787	130	27.6	260.20	Toluene	>90% hydrogenation, after 30 min
	0.0787	130	27.6	260.10[b]	Toluene	>90% hydrogenation, after 30 min
	0.0787	130	27.6	260.10[b]	MCB	>90% hydrogenation, after 30 min
	0.0787	130	27.6	260.10[b]	Benzene	>90% hydrogenation, after 30 min

[a] The catalyst was poorly soluble in the solvent.

[b] cis-1,4-poly(isoprene) was obtained from Bayer Inc.

[c] [C=C] is defined as the weight of cis-1,4-poly(isoprene) divided by molecular weight of repeating unit.

The ^{1}H-NMR spectra of cis-1,4-poly(isoprene) and hydrogenated cis-1,4-poly(isoprene) are shown in Figure 2.4 a and b. The ^{1}H-NMR spectrum of cis-1,4-poly(isoprene) shows signals at 1.75, 2.12, and 5.25 ppm which are attributed to –CH$_3$, –CH$_2$–, and olefinic protons, respectively. In comparison, the signal in the ^{1}H-NMR spectrum of hydrogenated cis-1,4-poly(isoprene) at 5.12 ppm is very small and new signals appear at 0.8 and 1.2 ppm, attributed to –CH$_3$ attached to saturated carbon.

A typical ^{13}C-NMR spectrum of cis-1,4-poly(isoprene) (a) together with a spectrum for a hydrogenated cis-1,4-poly(isoprene) sample (b) is shown in Figure 2.5. The peaks at 135.36 and 125.20 for olefinic carbons vanished; and four new peaks emerged at 37.79, 33.09, 24.78, and 20.00, which are assigned for C$_{\alpha\gamma}$, -CH-, C$_{\beta\beta}$, and –CH$_3$ carbons, respectively. It can be confirmed that the hydrogenated cis-1,4-poly(isoprene) is an alternating ethylene-propylene copolymer.

Table 2.1 shows the results for the hydrogenation of cis-1,4-poly(isoprene) in a batch reactor using different catalysts, organic solvents, and reaction temperatures. All catalysts investigated are active for diene polymer hydrogenation. However, RhCl(PPh$_3$)$_3$ was not an active catalyst for hydrogenation of cis-1,4-poly(isoprene) an little or no hydrogenation was seen under the investigated conditions. However, Singha et al. [7] reported that 80% hydrogenation of natural rubber was obtained using 1.3 mol% of RhCl (PPh$_3$)$_3$ as a catalyst in toluene at a hydrogen pressure of 40 kg/cm^2, and reaction temperature of 100°C for 22 h. It is proposed that the difference of results observed was due to the higher amount of catalyst and hydrogen pressure used by Singha et al. The rate of hydrogenation of natural rubber is slower than that of poly(isoprene), therefore, a relatively high catalyst concentration and high hydrogen pressure were required.

RuCl(CO)(styryl)(PCy$_3$)$_2$, OsHCl(CO)(O$_2$)(PCy$_3$)$_2$, and [Ir(COD)py(PCy$_3$)]--PF$_6$ were found to be active for hydrogenation of cis-1,4-poly(isoprene). At 160 °C using RuCl(CO)(styryl)(PCy$_3$)$_2$ as catalyst in toluene solvent, >90% hydrogenation can be achieved after 20 h. Martin [9] reported that RuCl(CO)(styryl)(PCy$_3$)$_2$ could be used successfully as a catalyst for hydrogenation of poly(isoprene) providing 80% hydrogenation in chlorobenzene using 77.76 µM catalyst at a reaction temperature of 160°C and hydrogen pressure of 40.3 bar. However, the hydrogenation rate was extremely slow, with a pseudo first order rate constant (k') of 0.00009 s^{-1} and roughly 80% conversion was attained before the gas uptake monitoring program was stopped [9].

[Ir(COD)py(PCy$_3$)]PF$_6$ was dissolved in polar solvents, which could also dissolve cis-1,4-poly(isoprene). Solvents such as chloroform and monochlorobenzene were the best solvents for this study. We found that the optimal reaction temperature for this catalyst system appeared to be 100°C; with 90% hydrogenation in chlorobenzene and chloroform could be obtained after 6 and 7 h, respectively.

OsHCl(CO)(O$_2$)(PCy$_3$)$_2$ was observed to be a very efficient catalyst for hydrogenation of cis-1,4-poly(isoprene). The rate of hydrogenation was faster than obtained with either the RuCl(CO)(styryl)(PCy$_3$)$_2$ or the [Ir(COD)py(PCy$_3$)]PF$_6$ catalysts. The extent of hydrogenation increased with increasing reaction temperature. At 130°C, the OsHCl(CO)(O$_2$)(PCy$_3$)$_2$ was capable of hydrogenating >90% of the C=C bonds of the synthetic natural rubber within 30 minutes. From the results of these preliminary experiments, OsHCl(CO)(O$_2$)(PCy$_3$)$_2$ was chosen for examination in a detailed mechanistic study of cis-1,4-poly(isoprene) hydrogenation.
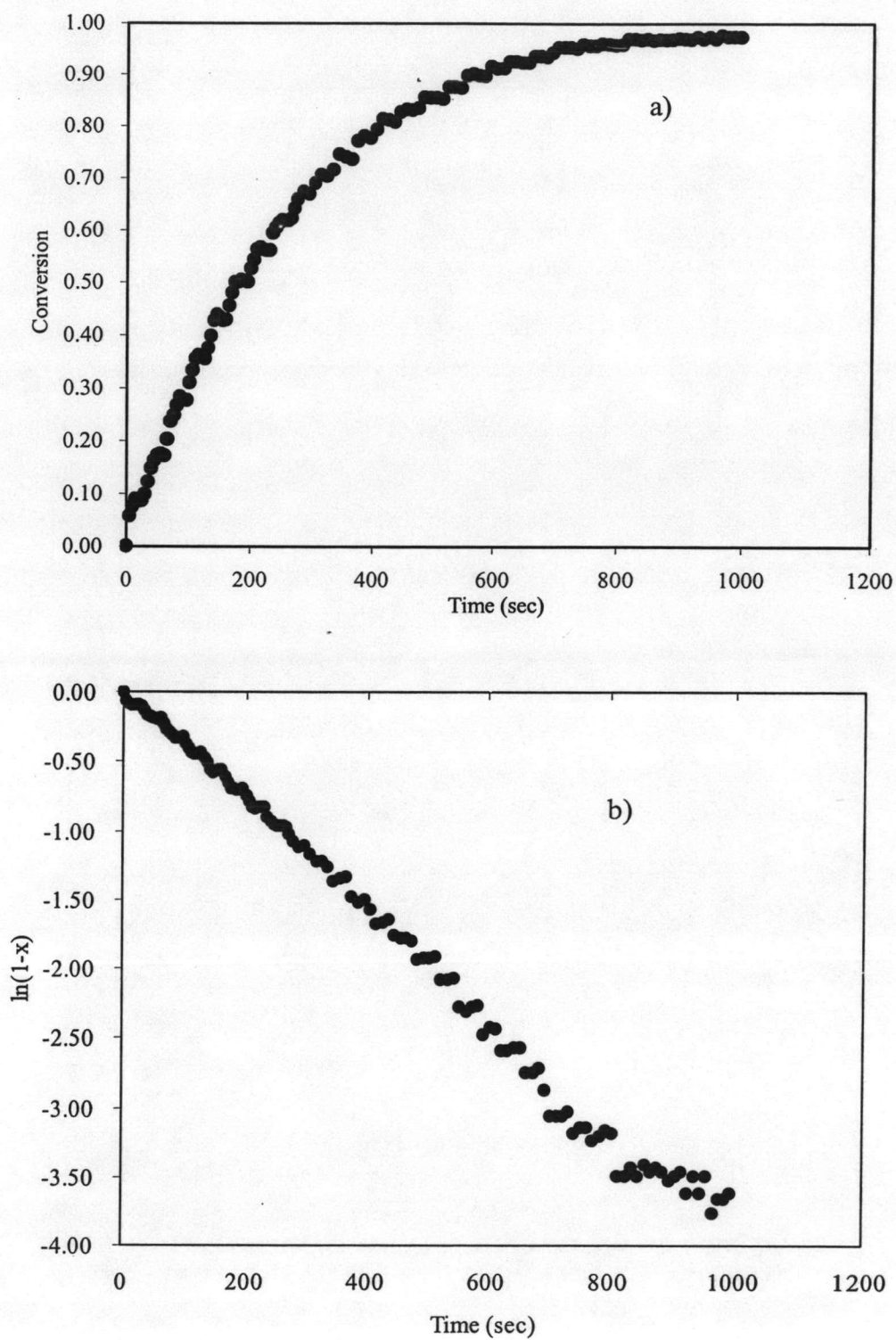
2.3.2 Hydrogenation of Cis-1,4-Poly(isoprene) using OsHCl(CO)(O$_2$)(PCy$_3$)$_2$

Over the range of process conditions studied, OsHCl(CO)(O$_2$)(PCy$_3$)$_2$ functioned as an efficient catalyst system for the quantitative hydrogenation of cis-1,4-poly(isoprene) in toluene. A representative hydrogen uptake profile corresponding to the hydrogenation of olefin is presented in Figure 2.6a. A hydrogen consumption plot shows an apparent first-order rate dependence for hydrogenation of the carbon-carbon double bond concentration. The first order rate constant was derived from the slope of the linear ln(1-x) versus time plot (Figure 2.6b) in accordance with eq. (2.1) (where x is conversion and k' is the pseudo first order rate constant).

$$\frac{-d[C=C]}{dt} = k'[C=C] \qquad (2.1)$$

2.3.3 Factorial Design Experiments

A thorough kinetic study improves our knowledge not only of how each factor affects k' alone (as probed by the univariate experiments) but also whether factors act in combination. In this section of work, the three variables, which are expected to have an

Figure 2.6 Hydrogenation of cis-1,4-poly(isoprene): a) olefin conversion profile and b) first-order log plot. [Os] = 70 μM; P_{H_2} = 20.7 bar; [C=C] = 260 mM; T = 130 °C.

effect on k' are the concentration of catalyst, carbon-carbon double bond concentration, and hydrogen pressure. When using two level fractional factorial design, the number of experiments can be optimized. For each variable, a lower "- level" and higher "+ level" was chosen in the range to be studied. The catalyst concentration, carbon-carbon double bond concentration, and hydrogen pressure range from 40 to 80 µM, 260 to 530 mM, and 13.8 to 27.6 bar, respectively. The results of the factorial experiments are summarized in Table 2.2. A Yates calculation [50] for the hydrogenation of cis-1,4-poly(isoprene) and the results of the factorial analysis are shown in Table 2.3 and 2.4, respectively. Comparison of the estimation with their standard errors suggests that the main effect of catalyst concentration, [Os], and hydrogen pressure, [H_2] require interpretation, while the existence of other two- and three-factor interactions are not highly significant.

The main effect of a variable should be individually interpreted only if there is no evidence that the variable interacts with other variables. When there is evidence of one or more such interaction effects, the interesting variables should be considered jointly. Table 2.4 shows that the catalyst concentration and hydrogen pressure have the positive effect and the carbon-carbon double bond concentration has a very small negative effect on the rate constant. The strongest effect was the catalyst concentration (0.00174 $\pm$ 8.03E-05).

2.2.4 Univariate Kinetic Experiments

The result of the factorial analysis established the significance of joint factor interactions without determining their functional form. The univariate components of the central composite design augment the factorial study by exploring how each factor influences the hydrogenation rate in isolation.

a) Effect of Catalyst Concentration

In order to investigate the effect of catalyst concentration on the initial rate of polymer hydrogenation, a series of hydrogenation experiments in which the catalyst concentration was varied over the range of 20 to 150 µM was carried out. The concentration of carbon-carbon double bond was 260 mM, at 130°C in toluene. The hydrogen pressure was varied from 13.8 to 34.5 bar. The results of these experiments are

Table 2.2 Result from 2^3 Factorial Design for Cis-1,4-Poly(isoprene)

Hydrogenation

Expt.	[Os] (mM)	[C=C] (mM)	P_{H_2} (bar)	Temp ($^{\circ}$C)	k' x 10^3 (s^{-1})
1	0.0404	259.80	13.8	130	2.59
2	0.0403	260.20	13.8	130	2.55
3	0.0801	260.20	13.8	130	4.20
4	0.0798	259.90	13.8	130	4.05
5	0.0401	259.80	27.6	130	3.27
6	0.0403	259.80	27.6	130	3.40
7	0.0798	260.10	27.6	130	5.25
8	0.0802	260.00	27.6	130	4.90
9	0.0402	520.49	13.8	130	2.44
10	0.0398	520.49	13.8	130	2.10
11	0.0798	520.49	13.8	130	4.20
12	0.0802	520.29	13.8	130	4.16
13	0.0402	519.90	27.6	130	3.03
14	0.0398	520.49	27.6	130	3.25
15	0.0798	520.00	27.6	130	4.46
16	0.0798	520.29	27.6	130	4.75

Table 2.3 Yates's Algorithm Calculation of the 2^3 Factorial Experiments

Test	Design Matrix Variables			Algorithm						
	[Os]	[H$_2$]	[C=C]	k' averg	1	2	3	Divisor	Estimate	Identification
1	-	-	-	0.00257	0.00670	0.01511	0.02888	8	0.00361	Average
2	+	-	-	0.00413	0.00841	0.01377	0.00695	4	0.00174	[Os]
3	-	+	-	0.00334	0.00645	0.00330	0.00259	4	0.00065	[H$_2$]
4	+	+	-	0.00508	0.00730	0.00365	0.00106	4	0.00026	[Os] [H$_2$]
5	-	-	+	0.00227	0.00156	0.00172	-0.00134	4	-0.00033	[C=C]
6	+	-	+	0.00418	0.00174	0.00087	0.00036	4	0.00009	[Os][C=C]
7	-	+	+	0.00314	0.00191	0.00019	-0.00084	4	-0.00021	[H$_2$][C=C]
8	+	+	+	0.00461	0.00147	-0.00045	-0.00063	4	-0.00016	[Os][H$_2$][C=C]

[Os] is concentration of catalyst (µM) : (-) 40 , (+) 80

[H$_2$] is hydrogen pressure (bar) : (-)13.8 , (+) 27.6

[C=C] is concentration of double bond (mM) : (-)260 , (+) 530

Table 2.4 The Calculated Effects and Standard Errors for 2^3 Factorial Experiment

Effect	Estimate ± standard error
Average	0.00361 ± 1.61E-09
Main effect	
Concentration of catalyst, *[Os]*	0.00174 ± 8.03E-05
Pressure, *[H$_2$]*	0.00065 ± 8.03E-05
Concentration of double bond, *[C=C]*	-0.00033 ± 8.03E-05
Two-factor interaction	
[Os] × *[H$_2$]*	0.00026 ± 8.03E-05
[Os] × *[C=C]*	0.00009 ± 8.03E-05
[H$_2$] × *[C=C]*	-0.00021 ± 8.03E-05
Three-factor interaction	
[Os] × *[H$_2$]* × *[C=C]*	-0.00016 ± 8.03E-05

Table 2.5 Kinetic Results of Univariate Experiments

Expt.	[Os] (mM)	[C=C] (mM)	P_{H_2} (bar)	Temp (^{o}C)	k' x 10^3 (s^{-1})
1	0.0215	260.39	13.8	130	0.86
2	0.0499	260.29	13.8	130	2.91
3	0.0699	260.19	13.8	130	3.98
4	0.0997	259.51	13.8	130	5.37
5	0.1200	260.29	13.8	130	6.74
6	0.0218	260.19	20.7	130	1.67
7	0.0302	260.49	20.7	130	2.44
8	0.0497	259.70	20.7	130	3.02
9	0.0697	260.09	20.7	130	4.14
10	0.0700	260.19	20.7	130	4.20
11	0.1000	260.39	20.7	130	5.89
12	0.1199	259.80	20.7	130	7.25
13	0.0297	260.29	34.5	130	2.35
14	0.0300	260.09	34.5	130	2.28
15	0.0497	260.19	34.5	130	3.51
16	0.0496	260.29	34.5	130	3.28
17	0.0703	260.00	34.5	130	4.95
18	0.0703	259.90	34.5	130	4.36
19	0.0999	260.29	34.5	130	6.15
20	0.1199	260.29	34.5	130	7.13
21	0.1499	260.09	34.5	130	8.88
22	0.0708	260.09	3.45	130	0.91
23	0.0699	259.51	3.59	130	1.16
24	0.0700	259.51	5.38	130	2.09
25	0.0700	259.70	6.90	130	3.68
26	0.0699	260.19	6.90	130	3.55
27	0.0699	260.29	48.3	130	5.07
28	0.0703	259.90	69.0	130	5.16

Table 2.5 Continued

Expt.	[Os] (mM)	[C=C] (mM)	P_{H_2} (bar)	Temp (°C)	k' x 10^3 (s^{-1})
29	0.0700	64.19	20.7	130	4.09
30	0.0703	95.99	20.7	130	4.06
31	0.0703	129.02	20.7	130	4.01
32	0.0700	194.02	20.7	130	4.02
33	0.0698	393.92	20.7	130	4.06
34	0.0703	530.78	20.7	130	3.93
35	0.0699	260.29	20.7	115	1.15
36	0.0697	260.00	20.7	120	1.73
37	0.0698	260.19	20.7	125	2.73
38	0.0700	260.19	20.7	135	5.90
39	0.0702	259.51	20.7	140	8.95

given in Table 2.5. Plots of hydrogenation rate constant versus concentration of catalyst are fairly linear for each pressure as shown in Figure 2.7. It can be concluded from this plot that the reaction is first order with respect to the concentration of catalyst. This agrees very well with the observations by Parent et al [8]. for acrylonitrile-butadiene hydrogenation using $OsHCl(CO)(O_2)(PCy_3)_2$. A first order response of k' to concentration of $OsHCl(CO)(O_2)(PCy_3)_2$ suggests that the active complex is a mononuclear species.

b) Effect of Hydrogen Pressure

In this series of experiments, the hydrogen pressure was varied over the range of 3.45 to 69 bar at 130°C in toluene. The concentration of catalyst and polymer were kept constant at 70 μM and 260 mM, respectively. The results of these experiments are presented in Table 2.5 and Figure 2.8. The results shown in Figure 2.8 suggest that a second order dependence on hydrogen pressure are likely observed below 13.8 bar. Above this, the influence of hydrogen pressure continued to decline with increasing pressure with essentially no difference observed between 43.8 to 69 bar. The
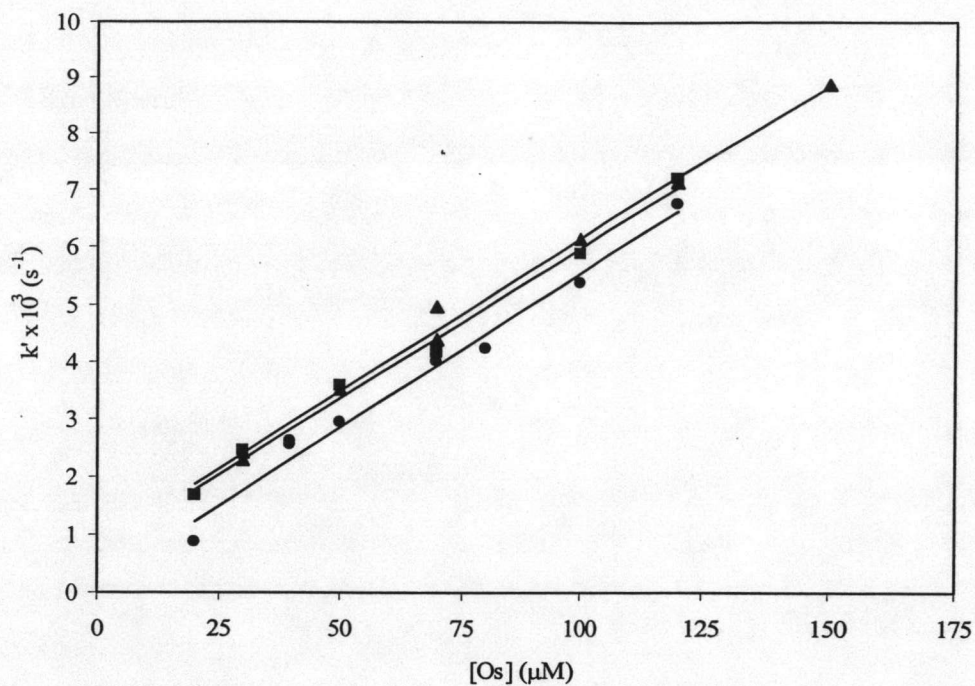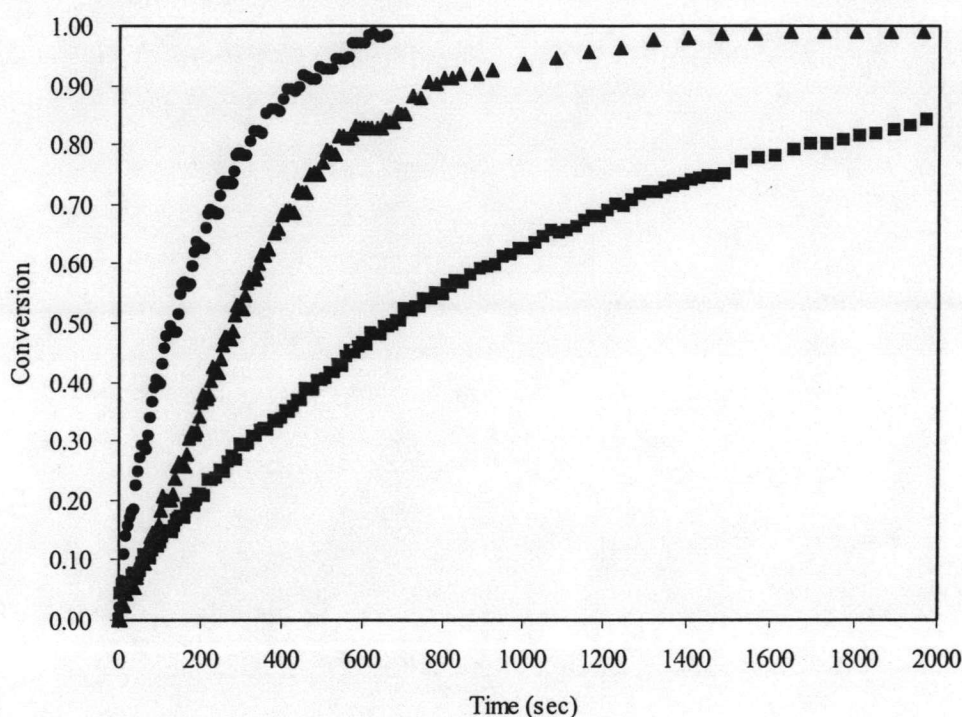
Figure 2.7 Effect of catalyst concentration on the hydrogenation rate at various pressures. [C=C] = 260 mM; T = 130 °C; (•) 13.8 bar, (■) 20.7 bar, (▲) 34.5 bar.
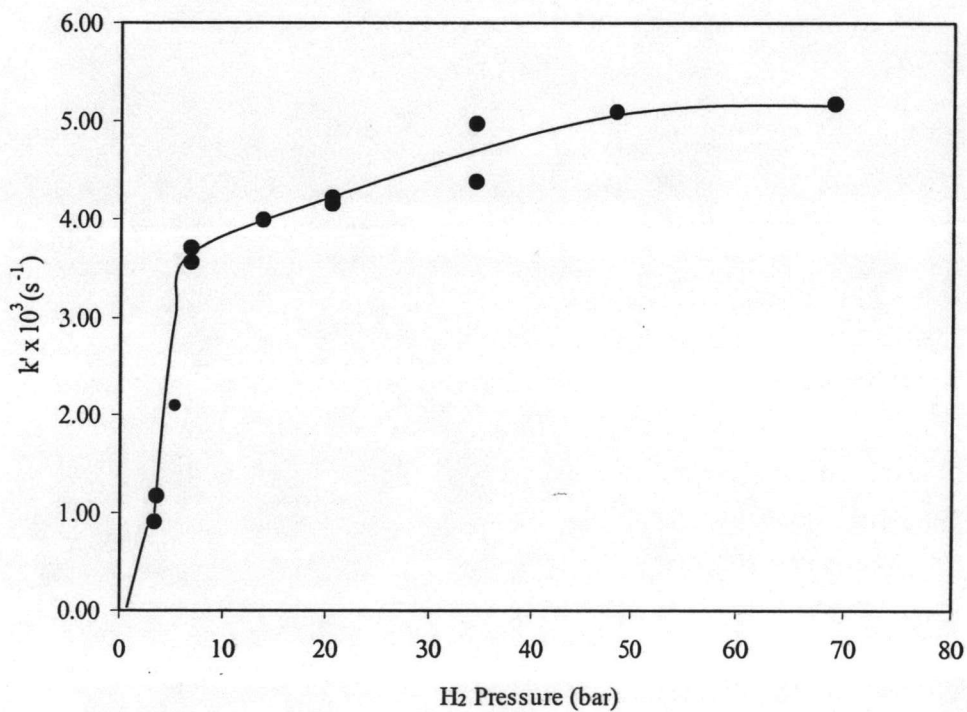
Figure 2.8 Effect of hydrogen pressure on the hydrogenation rate. [Os] = 70 μM; [C=C] = 260 mM; T = 130 °C.

hydrogenation rate tends to a zero order dependence at higher hydrogen pressure. This shift in [H₂] order is accompanied by changes in the influence of [C=C]. With increase in pressure, the conversion versus time plots became increasingly linear as shown in Figure 2.9. Only at elevated conversions did high-pressure profiles revert to first-order kinetics. A shift from second order to zero order with respect to hydrogen pressure was observed on hydrogenation of acrylonitrile-butadiene copolymers using $OsHCl(CO)(O_2)(PCy_3)_2$, whereas, the hydrogenation of styrene-butadiene copolymers using $OsHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ was zero order with respect to hydrogen pressure [8].

Figure 2.9 Cis-1,4-poly(isoprene) conversion profile at various pressures. [Os] = 70 μM; [C=C] = 260 mM; T = 130 °C; (■) 3.45 bar, (▲) 6.9 bar, (●) 69 bar.

c) Effect of Polymer concentration

A series of hydrogenation experiments in toluene with catalyst concentration of 70 μM, hydrogen pressure of 20.7 bar, reaction temperature of 130°C and concentration of carbon-carbon double bond over the range of 260 to 530 mM, was carried out to investigate the effect of carbon-carbon double bond concentration on the hydrogenation rate constant. The results of these experiments are summarized in Table 2.5. As

d) Effect of Reaction Temperature

Experiments were carried out from 115 to 140°C with concentration of catalyst of 70 µM, concentration of carbon-carbon double bond of 260 mM, and at hydrogen pressure of 20.7 bar. The results of the hydrogenation are presented in Table 2.5. An Arrhenius plot of the data is illustrated in Figure 2.11. The activation energy calculated from least squares regression analysis (R^2 = 0.999) of ln (k') versus 1/T was 109.32 kJ/mol. This estimation indicates that the experiments were carried out without mass transfer limitation. For hydrogenation of acrylonitrile-co-butadiene polymer using OsHCl $(CO)(O_2)(PCy_3)_2$ as catalyst, an activation energy value of 96 kJ/mol was reported by Parent et al. [8].
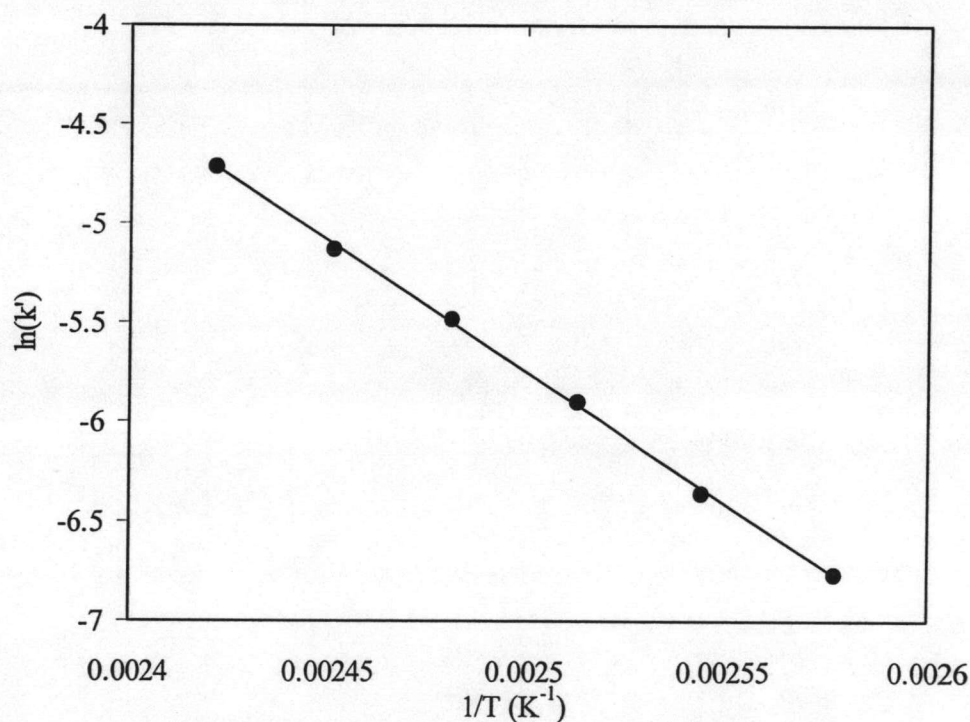
Figure 2.11 Arrhenius plot for the hydrogenation of cis-1,4-poly(isoprene).

[Os] = 70 µM; P_{H_2} = 20.7 bar; [C=C] = 260 mM; T = 115-140 °C.

e) Effect of Solvent

A series of experiments were undertaken using different solvents for cis-1,4-poly (isoprene) hydrogenation at the base condition ($[Os] = 70$ μM, $P_{H_2} = 20.7$ bar, $[C=C] = 260$ mM, and $T = 130°C$). Acetone and MEK were not used as solvent since the OsHCl $(CO)(O_2)(PCy_3)_2$ catalyst has been reported to be inactive in ketone solvents [8]. The effects of solvent type on hydrogenation rate are summarized in Table 2.6. It was found that the rate constant decreased with the nature of solvent in this order: tetrahydrofuran> chlorobenzene> toluene> xylene.

The coordinating power of the solvent is of importance and it should have sufficient coordinating power to produce phosphine ligand dissociation, providing solvation of the metal complex. Table 2.6 shows that the hydrogenation rate was found to increase in solvents, which may coordinate with Os complex catalyst. It has been proposed that a strong coordinating solvent can promote the dissociation of phosphine ligand and the formation of an active 14-electron osmium trihydride species [33].

Table 2.6 Effect of Solvent on the Hydrogenation of Cis-1,4-Poly(isoprene)

Solvent	k' x 10^3 (s^{-1})	Final hydrogenation degree (%)
Toluene	4.14	97.68 (~15 min)
Xylene	1.14	95.89 (~1 h)
Tetrahydrofuran	7.92	98.32 (~5 min)
Chlorobenzene	4.66	97.94 (~15 min)

$[Os] = 70$ μM, $P_{H_2} = 20.7$ bar, $[C=C] = 260$ mM , $T = 130 °C$

f) Effect of Cis-Trans Isomer Structure

Hydrogenation of trans-1,4-poly(isoprene) in toluene as a solvent was carried out using $OsHCl(CO)(O_2)(PCy_3)_2$ at a temperature of $130°C$ with 70 μM of catalyst concentration, 260 mM of C=C concentration, and 20.7 bar of hydrogen pressure. The data presented in Figure 2.12 show a kinetic dependence on the isomer structure of the olefin in poly(isoprene). The trans-1,4-poly(isoprene) conversion profile plotted is first

order with respect to olefin. Trans-1,4-poly(isoprene) were hydrogenated slower than cis-1,4-poly(isoprene), with a pseudo first order rate constant k' = 0.00298 s^{-1} compared with 0.00414 s^{-1} for cis-1,4-poly(isoprene) at indical conditions. This correlates with the ease of olefin coordination to the metal center. Parent et. al observed reaction rate for isomers of heptene decreased in the order 1-heptene > cis-2-heptene > trans-2-heptene using OsHCl(CO)(O$_2$)(PCy$_3$)$_2$ as a catalyst [8].
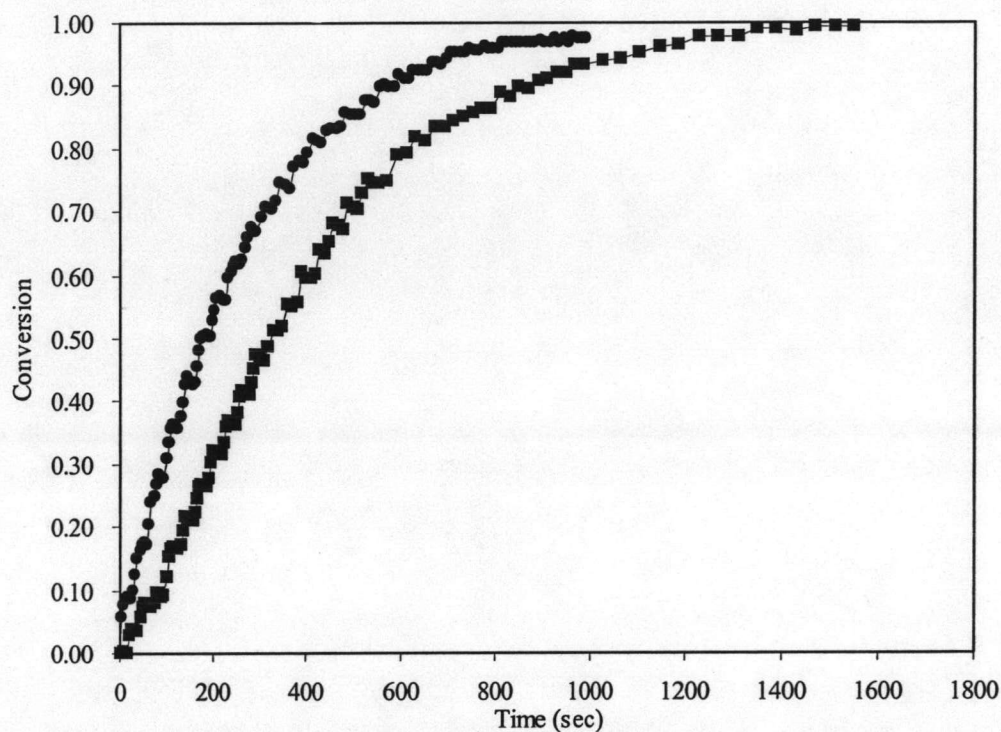
Figure 2.12 Hydrogenation of poly(isoprene) isomers. [Os] = 70 μM, P$_{H_2}$ = 20.7 bar, [C=C] = 260 mM , at 130 °C; (•) cis-1,4-poly(isoprene), ( ) trans-1,4-poly (isoprene).

2.3.5 Relative Viscosity of Hydrogenated Cis-1,4-Poly(isoprene)

In order to investigate the presence of side reactions, such as degradation and crosslinking during the chemical modification processes, the modified polymer product was examined. Dilute solution viscometry has been employed to follow the change of the physical properties of polymer by monitoring the shifts in molecular weight that result from crosslinking. The method has the drawback of an ambiguous relationship of viscosity (η) to molecular weight, especially for copolymers with composition or

structure diversity. Nevertheless, the space occupied by a macromolecule in solution is related to its molecular weight and evident in the value of the solution viscosity. Therefore, the viscosity of a dilute cis-1,4-poly(isoprene) solution relative to pure solvent (η_{rel}) provides a simple and effective means of measuring the consequences of crosslinking. Over the range of conditions explored in this work, ([Os] = 30-150 μM, [C=C] = 260-530 mM, P_{H_2} = 6.9-69 bar at 130°C), it was found that the relative viscosity of hydrogenated cis-1,4-poly(isoprene) (6.5-6.8) was higher than that of cis-1,4-poly (isoprene) (4.48). The increase of relative viscosity suggests that no degradation occurred during catalytic hydrogenation reaction.

Figure 2.13a, b, and c illustrate the effect of catalyst concentration, carbon-carbon double bond concentration, and hydrogen pressure on the relative viscosity of hydrogenated cis-1,4-poly(isoprene) (HCPI), respectively. This also shows results for OsHCl(CO)(O$_2$)(PCy$_3$)$_2$ on cis-1,4-poly(isoprene) hydrogenation, as compared with the results of hydrogenation of acrylonitrile-butadiene copolymers [31]. The relative viscosity of hydrogenated cis-1,4-poly(isoprene) is constant with increasing concentration of catalyst, carbon-carbon double bond concentration and hydrogen pressure. The selectivity of HNBR (hydrogenated acrylonitrile-butadiene copolymers) is compromised by increased amounts of catalyst, concentration of polymer, and hydrogen pressure.

The relative viscosity provides some indication of crosslinking produced over the time taken to complete the hydrogenation process. For the HNBR system, the hydrogenation reaction was affected by crosslinking which involves residual C=C reactivity and possibly the influence of CN group. The cis-1,4-poly(isoprene) contains pendant methyl group in the polymer structure and very little of residual C=C remains after in the hydrogenation reaction. The constant relative viscosity of hydrogenated cis-1,4-poly(isoprene) indicates that no significant crosslinking tookplace during the hydrogenation process.

2.3.6 Reaction Mechanism and Rate Law

The catalytic chemistry of the OsHCl(CO)(O$_2$)(PCy$_3$)$_2$ has been extensively investigated, resulting in greater understanding of intermediates that bring about the
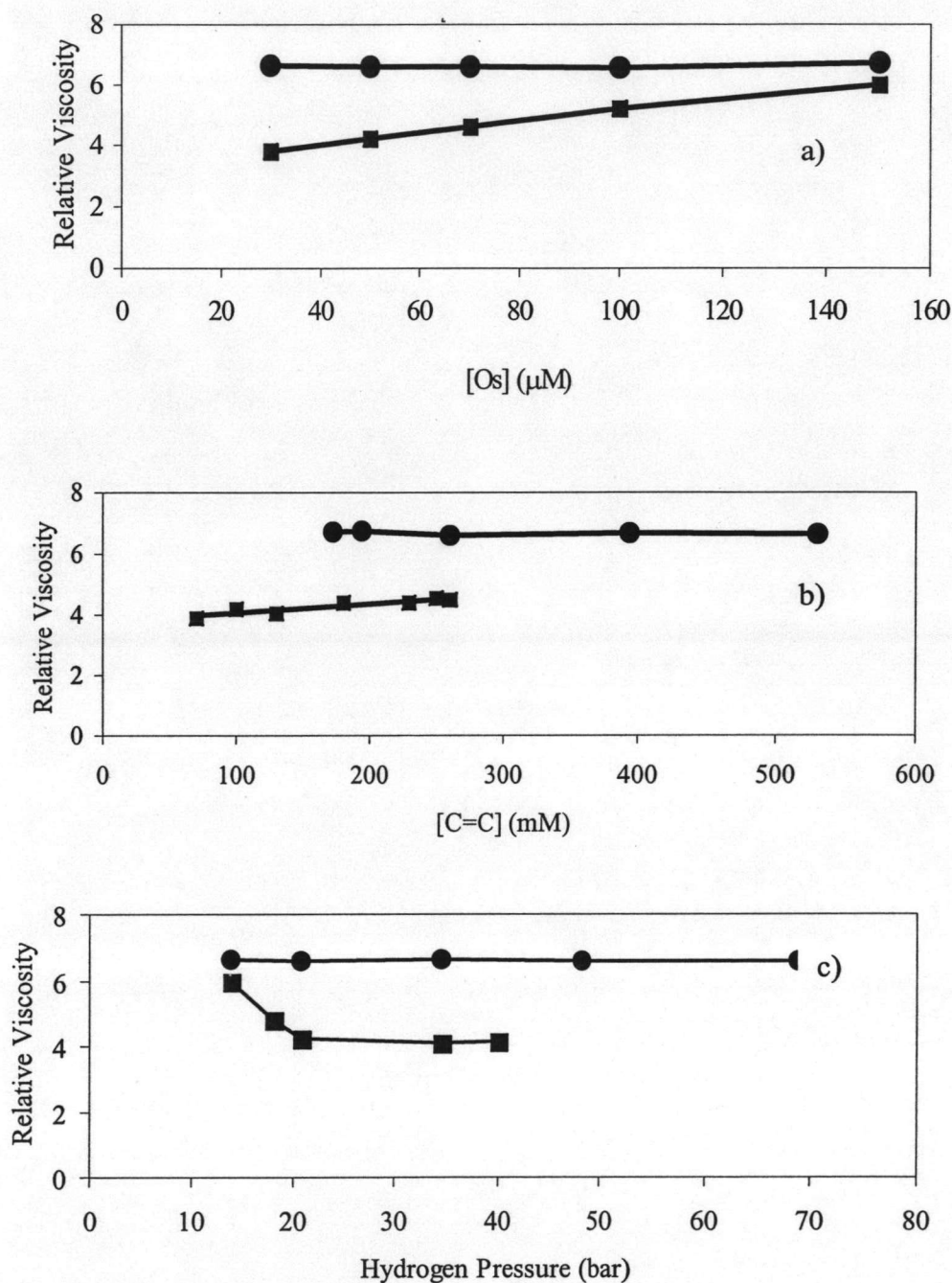
Figure 2.13. a) Selectivity as a function of total metal loading: P_{H_2} = 20.7 bar; [C=C] = 260 mM; T = 130 ^{o}C; [CN] = 172 mM; (●) HCPI, (■) HNBR. b) Selectivity as a function of polymer loading: P_{H_2} = 20.7 bar; T = 130 ^{o}C; (●) HCPI, [Os] = 70 μM, (■) HNBR, [Os] = 80 μM. c) Influence of pressure on selectivity: [C=C] = 260 mM; T = 130 ^{o}C, [CN] = 172 mM; (●) HCPI, [Os] = 70 μM, (■) HNBR, [Os] = 80 μM.

observed kinetic behavior. Figure 2.14 illustrates a catalytic mechanism that is consistent with the kinetic data of Table 2.5 and the previous work of hydrogenation of acrylonitrile-butadiene copolymers using $OsHCl(CO)(O_2)(PCy_3)_2$ [8].
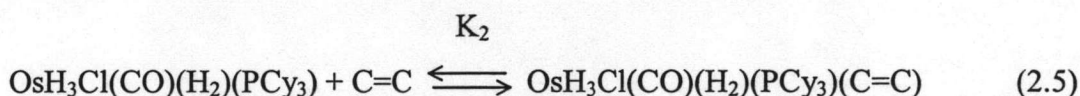
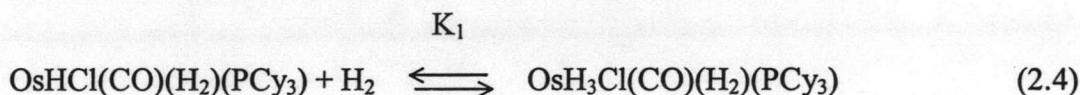The $OsHCl(CO)(O_2)(PCy_3)_2$ oxidatively adds molecular hydrogen to form the trihydrido metal complex $OsHCl(CO)(H_2)(PCy_3)_2$, as shown by eq. (2.2).

$$OsHCl(CO)(O_2)(PCy_3)_2 + H_2 \overset{K_{H_2}}{\longleftrightarrow} OsHCl(CO)(H_2)(PCy_3)_2 + O_2 \qquad (2.2)$$
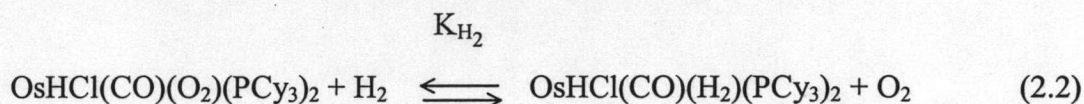
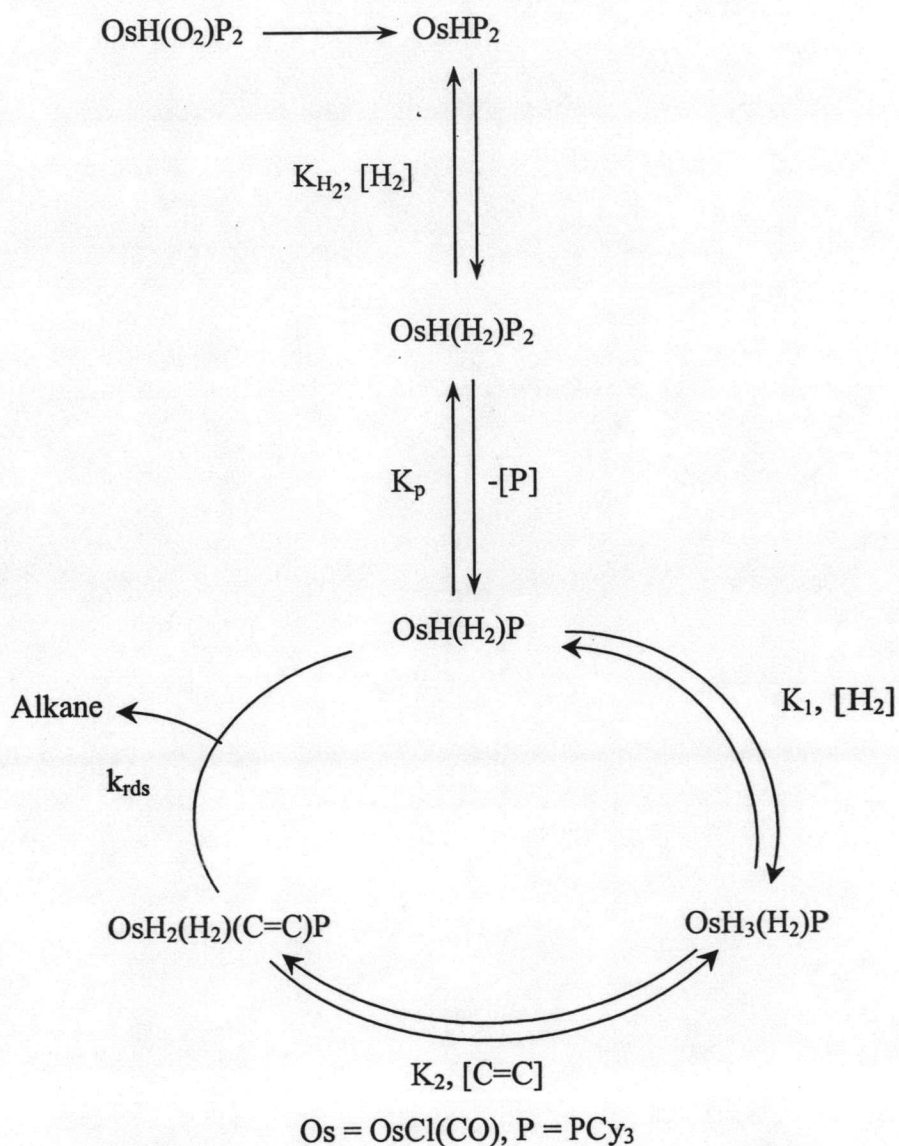The trihydrido complex subsequently dissociates into a monophosphine complex, as shown by eq. (2.3).

$$OsHCl(CO)(H_2)(PCy_3)_2 \overset{K_p}{\longleftrightarrow} OsHCl(CO)(H_2)(PCy_3) + PCy_3 \qquad (2.3)$$
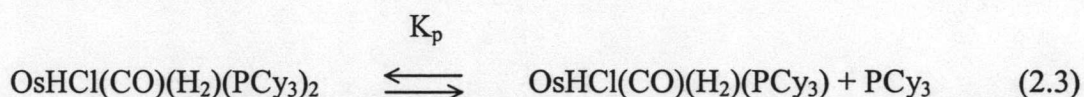
The monophosphine complex oxidatively adds with a second hydrogen molecule to form $OsH_3Cl(CO)(H_2)(PCy_3)$ and then interacts with the carbon-carbon double bonds to form the olefin complex, as shown by eq. (2.4) and (2.5), respectively.

$$OsHCl(CO)(H_2)(PCy_3) + H_2 \overset{K_1}{\longleftrightarrow} OsH_3Cl(CO)(H_2)(PCy_3) \qquad (2.4)$$

$$OsH_3Cl(CO)(H_2)(PCy_3) + C=C \overset{K_2}{\longleftrightarrow} OsH_3Cl(CO)(H_2)(PCy_3)(C=C) \qquad (2.5)$$

Parent et al.[8] proposed that the dihydrogen ligand of $OsHCl(CO)(H_2)(PCy_3)_2$ does not add oxidatively to the metal in such a manner as to permit either the insertion of olefin or the elimination of an alkyl ligand. While the η^2-H_2 ligand may indeed participate in olefin hydrogenation, it is proposed that it cannot do so in the absence of a second molecule of hydrogen. This unconventional assumption is required to account for the second-order behavior observed for NBR hydrogenation. Without it, a mechanism containing a single rate-determining step cannot be derived.

The observed kinetic isotope effect observed by Parent et al. [8] implies cleavage of a bond to hydrogen in the rate-limiting reaction. This could result from the insertion of olefin into an Os-H bond or by a reductive elimination of an osmium-alkyl to yield the saturated product. The proposed mechanism does not discriminate between these possibilities. Rather, it assumes one of these processes is rapid relative to its rate-determining counterpart. Accordingly, olefin hydrogenation could be governed by the rate expression.

$$OsH(O_2)P_2 \longrightarrow OsHP_2$$

$K_{H_2}, [H_2]$

$OsH(H_2)P_2$

$K_p \quad -[P]$

$OsH(H_2)P$

Alkane

k_{rds}

$K_1, [H_2]$

$OsH_2(H_2)(C=C)P$

$OsH_3(H_2)P$

$K_2, [C=C]$

$Os = OsCl(CO), P = PCy_3$

Figure 2.14 Proposed mechanism for cis-1,4-poly(isoprene) hydrogenation by OsHCl(CO)(O$_2$)(PCy$_3$)$_2$.

$$-\frac{d[C=C]}{dt} = k_{rds} [OsH_3Cl(CO)(H_2)(PCy_3)(C=C)] \qquad (2.6)$$

A material balance on the osmium charged to the system is given by eq. (2.7).

$$[Os]_T = [OsH_2Cl(CO)(H_2)(PCy_3)(C=C)] + [OsH_3Cl(CO)(H_2)(PCy_3)] +$$
$$[OsHCl(CO)(H_2)(PCy_3)] + [OsHCl(CO)(H_2)(PCy_3)_2] +$$
$$[OsHCl(CO))(PCy_3)_2] \qquad (2.7)$$

Applying the equilibrium relations defined in Figure 2.14, the concentration of $OsH_3Cl(CO)(H_2)(C=C)(PCy_3)$ may be substituted into eq. (2.6) to provide the resulting rate law, as shown by eq. (2.8).

$$\frac{-d[C=C]}{dt} = \frac{[Os]_T K_{H_2}K_pK_1K_2[C=C][H_2]^2}{[P] + K_{H_2}[P][H_2] + K_{H_2}K_p[H_2] + K_{H_2}K_pK_1[H_2]^2(1+K_2[C=C])} \qquad (2.8)$$

The rate expression derived from the mechanism is consistent with the observed kinetic data. Given this expression, it would be expected that there would be a first order dependence on [Os] and a first order dependence on [C=C] providing that the the term $K_{H_2}K_pK_1[H_2]^2(1+K_2[C=C])$ is small relative to the others in the dominator of eq (2.8). We observe second-order behavior with respect to hydrogen pressure at relatively low pressures (<13.8 bar). Further increase in pressure yielded a diminished influence on the activity until the process was virtually indifferent to hydrogen pressure. A shift to a zero-order is expected at extreme pressure. Most importantly, eq. (2.8) predicts that an increase in H_2 pressure, the term $K_{H_2}K_pK_1[H_2]^2(1+K_2[C=C])$ is the predominant term of eq (2.8), will eventually lead to a zero order dependence on [C=C].

2.4 Conclusions

Cis-1,4-poly(isoprene) can be hydrogenated using $[Ir(COD)py(PCy_3)]PF_6$, $RuCl(CO)(styryl)(PCy_3)_2$, and $OsHCl(CO)(O_2)(PCy_3)_2$. $RhCl(PPh_3)_3$ is an efficient catalyst for hydrogenation of most olefin polymers, but the activity is rather low for hydrogenation of cis-1,4-poly(isoprene). $OsHCl(CO)(O_2)(PCy_3)_2$ has been shown to be the most active catalyst for the hydrogenation of cis-1,4-poly(isoprene) in toluene. Kinetic studies by gas uptake measurement showed that the process was first order with respect to [Os] and [C=C]. A second order to zero order dependence on hydrogen pressure was found. The apparent activation energy was found to be 109.32 kJ/mol. The proposed mechanism and the rate expression for hydrogenation of cis-1,4-poly(isoprene) using $OsHCl(CO)(O_2)$ $(PCy_3)_2$ were consistent with the kinetic data. The viscosity of dilute solutions of fully saturated hydrogenated cis-1,4-poly(isoprene) was measured at 35°C using a Ubellohde viscometer. The relative viscosity of hydrogenated products indicated the crosslinking effect in the polymer structure. Uniform viscosity of hydrogenated cis-1,4-poly(isoprene) suggested that there was possibly no degradation and crosslinking effect over the range of conditions used for the hydrogenation process.