

CHAPTER III

HYDROGENATION OF CIS-1,4-POLY(ISOPRENE) CATALYZED BY [Ir(COD)py(PCy₃)]PF₆

3.1 Introduction

Hydrogenation of polymers has become an important way to meet the increased demand for functional polymers in the industrial world. Hydrogenation improves the weather, heat and oil resistance as well as the miscibility with other polymers. Ni or Pd catalysts can be used for hydrogenation of a functional group of a polymer. But the high steric hindrance, extension of polymer, contact with catalyst and poor diffusion of hydrogen give lower reaction rates in polymers than for similar functional groups in lower molecular compounds. Therefore, catalysts developed for the hydrogenation of polymers must be customized to meet these more stringent conditions. Homogeneous and heterogeneous reaction systems have been commercialized, but problems exist for both. For homogeneous systems, separation of the catalyst from the product remains the problem while complete hydrogenation is difficult in heterogeneous systems [54].

Homogeneous catalytic systems are inherently simpler chemically and kinetically than heterogeneous systems and are much more amenable to detailed study. Heterogeneous systems remain the major synthetic tool for the organic chemist employing catalytic hydrogenation, but an increasing number of researchers are turning to homogeneous systems for more selective and controlled hydrogenations. Industrially important catalytic hydrogenations employ homogeneous systems extensively, but the increasing list of patent applications involving homogeneous systems indicates that they will become increasingly important.

Early catalytic hydrogenation of poly(isoprene) procedures involved reaction at high temperatures and pressures using platinum or nickel catalysts, resulting in considerable degradation or other side reactions. The noncatalytic technique uses a hydrogenation reagent, such as a diimide generated in situ from *p*-toluenesulfonylhydrazide (TSH). The reaction of poly(isoprene) with TSH at 140°C could only produce a low level of hydrogenation (< 40% conversion) despite using a large amount of TSH [46]. In addition, the polymer was partially depolymerized and cyclized. Poly

(isoprene) in form of natural rubber could be quantitatively hydrogenated to the alternating copolymer of ethylene-propylene using a homogeneous $\text{RhCl}(\text{PPh}_3)_3$ catalyst. Using $\text{RhCl}(\text{PPh}_3)_3$ as catalyst in benzene as solvent and at 65°C and 1 atm H_2 pressure, only 23 mol% hydrogenation of natural rubber was reported [47]. Singha et al. [7] studied the hydrogenation of natural rubber using $\text{RhCl}(\text{PPh}_3)_3$ at higher condition. At 40 kg/cm^2 of H_2 pressure and 100°C for 22 hr, 88 mol% hydrogenation of natural rubber in toluene as solvent was achieved.

Many homogeneous hydrogenation catalysts share one shortcoming-hindered olefins, which are not reduced at useful rates. Normally, homogeneous hydrogenation solution contains either coordinating solvents or dissociated ligands which compete with the olefin for catalytically active metal sites, preventing hydrogenation of most hindered olefins. An exception is the Crabtree's catalyst, $[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$, which was treated with hydrogen in a non-coordinating solvent. It differs from all other known hydrogenation catalysts is that its activity is unaffected by the presence of oxygen without reducing ketone carbonyl groups, carbon halogen bonds or cyclopropanes. The Crabtree's catalyst was found to be an efficient catalyst for hydrogenation of polymer, for example; polybutadiene and acrylonitrile-butadiene copolymers. L. R. Gilliom [37] reported the bulk hydrogenation of polybutadiene using the Crabtree's catalyst under moderate conditions in the absence of added solvent. They observed the interesting phenomenon: when the polymer was fabricated as a full-density pellet, the hydrogenation produced a marked reaction front. The polymer was hydrogenated from the outside in. The Crabtree's catalyst application in the hydrogenation of acrylonitrile-butadiene copolymers was studied by J. Hu [32]. In non-coordinating solvents like chlorobenzene, the Crabtree's catalyst was an efficient catalyst precursor for the selective hydrogenation of olefin resident within acrylonitrile-butadiene copolymers.

The results presented in this chapter are concerned with the application of the $[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$ catalyst for the hydrogenation of cis,1,4-poly(isoprene). The effects of process parameters on the hydrogenation rate, concentration of catalyst, polymer concentration, hydrogen pressure, and temperature were investigated. The kinetics of the reaction and a proposed mechanism for cis-1,4-poly(isoprene) hydrogenation by $[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$ are reported.

3.2 Experimental

3.2.1 Materials

The high molecular weight cis-1,4-poly(isoprene) with 97% of cis isomer was provided from Bayer Inc. The Crabtree's catalyst $[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$ was purchased from Strem Chemical. Chlorobenzene, tetrahydrofuran, dichloromethane, ethanol and chloromethane were obtained from Fisher Scientific Ltd. All solvents were used as received. The reaction gas obtained from Praxair Inc. was oxygen-free hydrogen with a purity of 99.99%.

3.2.2 Hydrogenation Process

The hydrogenation of cis-1,4-poly(isoprene) was carried out in the presence of $[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$ in chlorobenzene under various reaction conditions. 1.67-5.10 g of cis-1,4-poly(isoprene) was dissolved in 150 mL of organic solvent in the dark and vigorously degassed in the autoclave before the addition of catalyst. The hydrogenation apparatus, as described in section 2.2.3, was maintained at constant temperature $\pm 1^\circ\text{C}$ and pressure ± 0.02 bar throughout the hydrogenation. The standard reaction procedure is identical to that mentioned in section 2.2.3. Each experiment was allowed to proceed until gas consumption ceased, after which the reactor was quickly cooled and the product isolated by precipitation with ethanol, followed by drying under vacuum.

3.2.3 Characterization and Viscosity Measurement

The final degree of olefin conversion measured by gas uptake was confirmed by infrared spectroscopy and $^1\text{H-NMR}$ spectroscopic analysis. $^1\text{H-NMR}$ 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.

The viscosity of dilute polymer solutions (0.12500 ± 0.00015 g of hydrogenated cis-1,4-poly(isoprene) / 25 mL of toluene) was measured at 35°C by using an Ubbelohde capillary viscometer. Sample filtration through a coarse, sintered-glass filter provided a

means of detecting insoluble gel. The viscosity data (η_{rel}) are reported as the polymer solution viscosity relative to that of toluene solvent at 35°C.

3.2.4 Experimental Design

Of principal interest in the kinetic study is the functional relationship between the rate of reaction and the condition under which it is carried out. The rate of cis-1,4-poly(isoprene) hydrogenation is known to be influenced by factors such as the concentration of catalyst [Ir], olefin substrate [C=C], and hydrogen pressure [H₂] as well as the reaction temperature. Experimental conditions were assigned according to a central composite structure [50], composed of a two-level factorial design and a series of univariate experiments. The first component consisted of a 2³ factorial design of the principal factors of interest ([Ir], [C=C], and [H₂]). This established the significance of joint factor interactions in which two or more factors act in combination to influence the hydrogenation activity. The univariate or “one-at-a-time” experiments in [Ir], [Polym], and [H₂], and temperature examined the influence of each factor acting alone. By varying a single factor in isolation, these studies defined the functional relationship between the catalyst activity and the process factor in greater detail. The selection of an appropriate range for each factor considered the catalyst weighing precision, the polymer solution viscosity, and the reaction rate that the apparatus could control and monitor effectively.

3.3 Results and Discussion

3.3.1 Characterization of Hydrogenated Cis-1,4-Poly(isoprene)

Hydrogenation of cis-1,4-poly(isoprene) in chlorobenzene was carried out using [Ir(COD)py(PCy₃)]PF₆ over the concentration range of 30 to 150 μM with a temperature and hydrogen pressure range of 120 to 140°C and 13.8 to 55.2 bar, respectively. Hydrogenation could be achieved to a level of more than 90% hydrogenation. The hydrogenated product is an alternating ethylene-propylene copolymer, which is difficult to prepare by conventional polymerization and demonstrates superior resistance to degradation by heat, oxygen and ozone.

The final hydrogenation degree of hydrogenated cis-1,4-poly(isoprene) was characterized by FTIR and ¹H-NMR analysis. Figure 3.1 shows typical FTIR spectra of

the cis-1,4-poly(isoprene) and hydrogenated cis-1,4-poly(isoprene). The absorption bands corresponding to the methylene ($-\text{CH}_2-$), C=C stretching and olefinic C-H bending are located at 1449, 1664, and 836 cm^{-1} , respectively. The characteristic signals of unsaturation, i. e., 1664 and 836 cm^{-1} , disappeared in hydrogenated cis-1,4-poly(isoprene). While an intense signal appears at 1449 cm^{-1} , which is attributed to methylene groups formed through hydrogenation.

The $^1\text{H-NMR}$ spectra of cis-1,4-poly(isoprene) and hydrogenated cis-1,4-poly(isoprene) are shown in Figure 3.2. As can be observed, there is an important reduction of the olefinic protons signal at 5.12 ppm, which confirmed that the cis-1,4-poly(isoprene) was hydrogenated. The aliphatic proton signals observed in the range of 0.8-1.2 ppm, attributed to saturated $-\text{CH}_3$ and $-\text{CH}_2-$ group, show a strong increment due to the chemical transformation of double bonds when saturated.

3.3.2 Kinetics of Cis-1,4-Poly(isoprene) hydrogenation using $[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$

Kinetics of cis-1,4-poly(isoprene) hydrogenation in the presence of the selective homogeneous hydrogenation catalyst $[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$ has been studied in chlorobenzene using a gas uptake apparatus. The rate of reaction in the entire system, based on a second-order reaction mechanism, could be expressed as:

$$\frac{-d[\text{C}=\text{C}]}{dt} = k[\text{C}=\text{C}][\text{H}_2] \quad (3.1)$$

where k is the rate constant, and $[\text{C}=\text{C}]$ and $[\text{H}_2]$ are the concentration of unsaturated double bonds and dissolved hydrogen in the chlorobenzene solvent, respectively. The hydrogenation reaction was investigated under constant H_2 pressure. Therefore, $[\text{H}_2]$ was assumed to be in equilibrium with the gaseous pressure and remained constant during the reaction. Consequently, the reaction could be viewed as a pseudo-first-order reaction:

$$\frac{-d[\text{C}=\text{C}]}{dt} = k'[\text{C}=\text{C}] \quad (3.2)$$

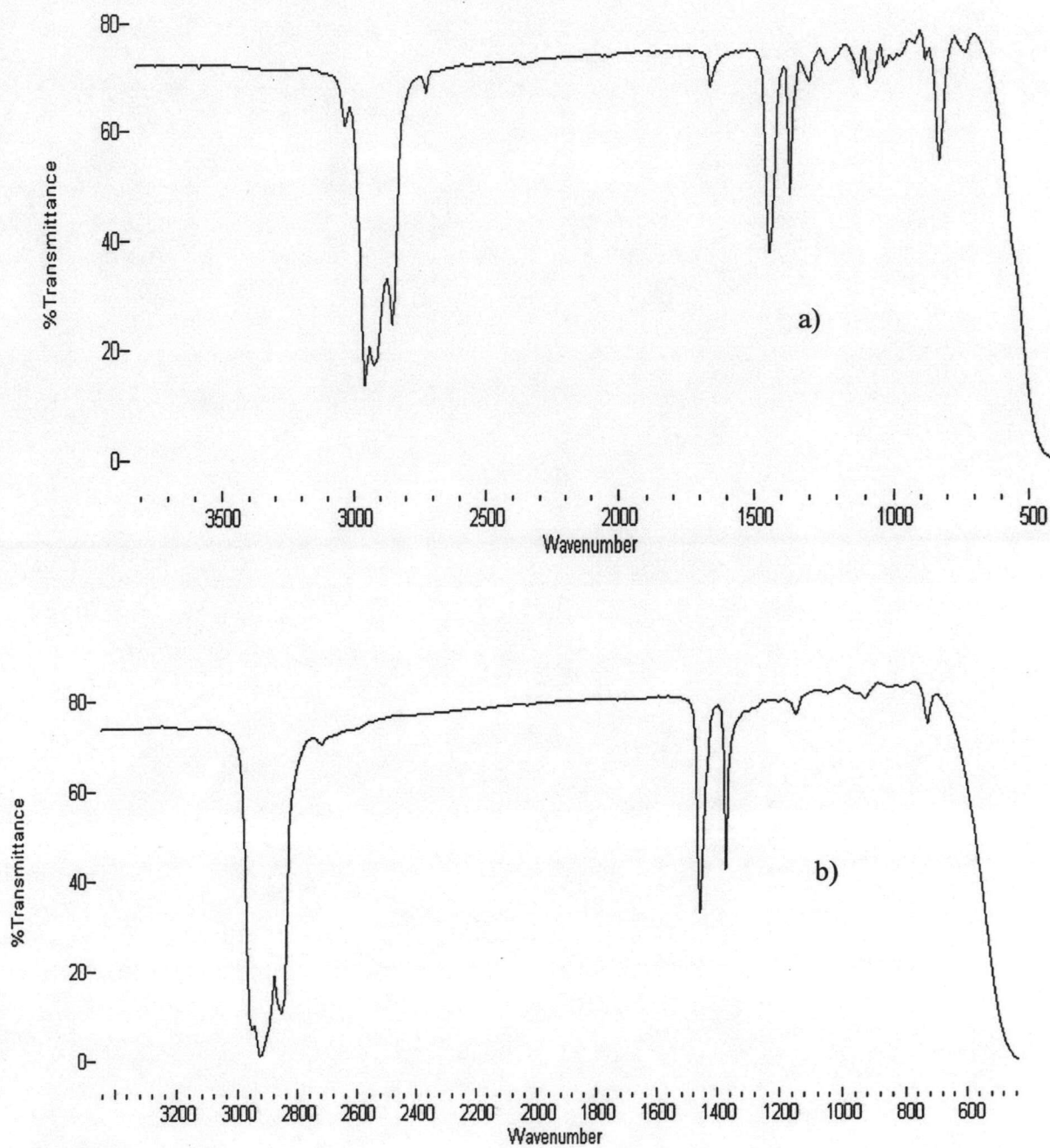


Figure 3.1 Infrared spectra of: a) cis-1,4-poly(isoprene) and b) hydrogenated cis-1,4-poly(isoprene).

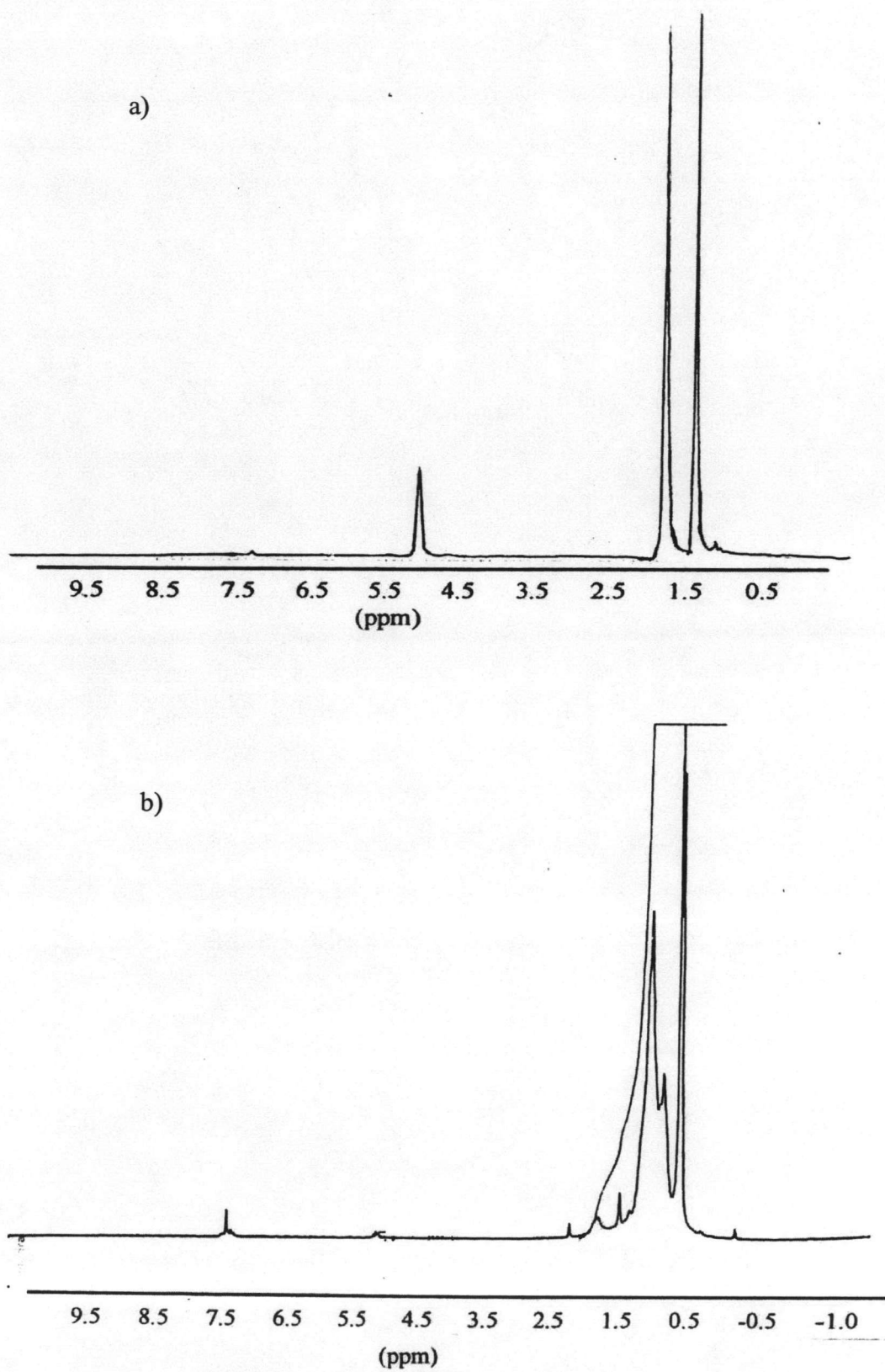


Figure 3.2 $^1\text{H-NMR}$ spectra of: a) cis-1,4-poly(isoprene) and b) hydrogenated cis-1,4-poly(isoprene).

where k' is the pseudo-first-order rate constant. Figure 3.3a represents the plot of conversion with time for the hydrogenation reaction. The hydrogen consumption plot indicates that the reaction is apparently first-order in the olefinic substrate, according to Eq 3.1.

After integration of Eq (3.2), this equation is further expressed in terms of the conversion of unsaturated double bonds (extent of hydrogenation), x

$$\ln(1-x) = k't \quad (3.3)$$

where t is the reaction time. Figure 3.3b shows a linear plot of $\ln(1-x)$ versus time, from which the slope provides the value of k' .

3.3.3 Experimental Design

A two-level factorial design was applied to determine the significance of interactions between factors, which influence the hydrogenation rate and act within the iridium reaction mechanism. The three quantitative variables are the concentration of catalyst and polymer, and the hydrogen pressure. The response for each variable is the rate constant. For each variable, a lower level and higher level was chosen in the range to be studied. The catalyst concentration, polymer concentration, and hydrogen pressure ranged from 80 to 100 μM , 246 to 500 mM, and 20.7 to 34.5 bar, respectively. The two level design can be conveniently coded by minus “-” and plus “+” signs. The results of the factorial experiment are summarized in Table 3.1. A Yates’s algorithm was applied to calculate the various effects. The Yates calculation for the hydrogenation of cis-1,4-polyisoprene and the results of factorial design analysis are shown in Table 3.2 and 3.3, respectively. The estimation considered with their standard errors suggests that the main effect of hydrogen pressure requires interpretation, while the apparent effects remaining could be generated by the noise. There is no evidence that the main effect of hydrogen pressure interacts with any other variable, therefore, the main effect of hydrogen pressure could be individually interpreted. The other two- and three-factor interactions do not appear to be highly significant.

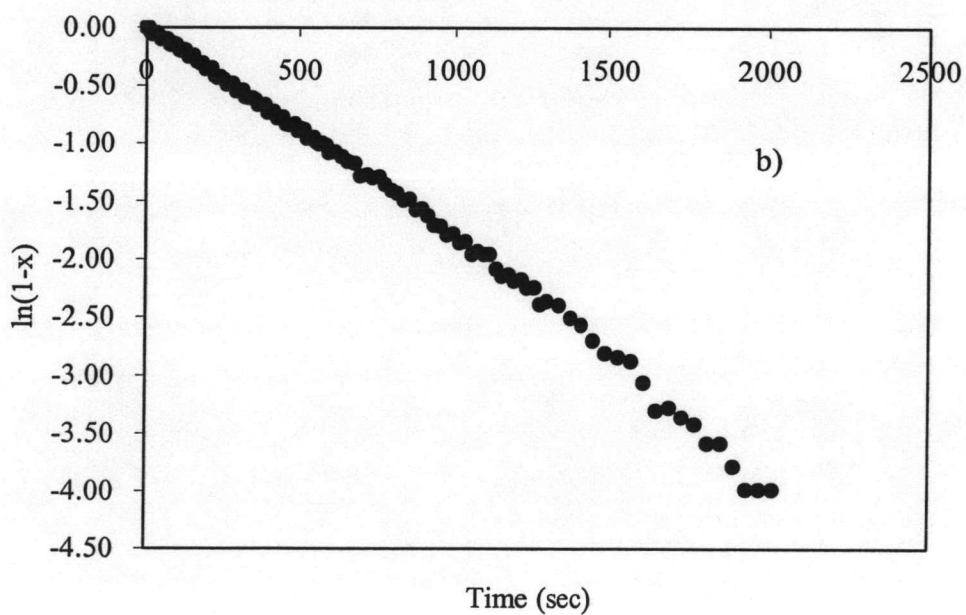
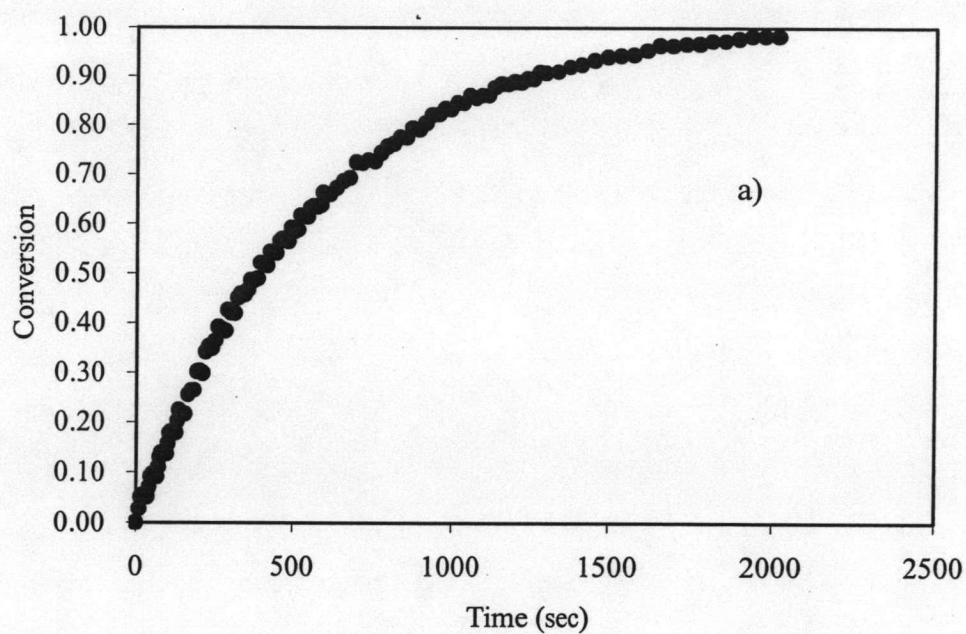


Figure 3.3 a) Conversion profile of hydrogenation of cis-1,4-poly(isoprene). b) A plot of $\ln(1-x)$ versus time. $[\text{Ir}] = 90 \mu\text{M}$; $P_{\text{H}_2} = 27.6 \text{ bar}$; $[\text{C}=\text{C}] = 246 \text{ mM}$; $T = 130 \text{ }^\circ\text{C}$.

3.3.4 Univariate Kinetic Experiment

Although, the results of the two-level factorial design are unable to explore fully a wide region in the factor space, they can indicate major trends and help to determine a promising direction for further experimentation. The univariate components of the central composite design augment the factorial study by exploring how each factor influences the hydrogenation rate in isolation. The experimental factors are varied one at a time, with the remaining factors held constant. This method provides an estimation of the effect of a single variable at selected fixed conditions of the other variables.

a) Effect of Catalyst Concentration

The effect of catalyst concentration on hydrogenation rate was investigated by varying catalyst concentrations from 30 to 150 μM . The concentration of C=C was kept constant at 246 mM, 27.6 bar, and 130°C in chlorobenzene. The results of these experiments are presented in Table 3.4. A plot of initial rate constant versus catalyst concentration is shown in Figure 3.4. The results suggest that a first-order dependence on catalyst concentration occurs below $\sim 100 \mu\text{M}$. Above this, the rate constant tends to a zero-order dependence on catalyst concentration. This shift in [Ir] order is accompanied by changes in the influence of [C=C]. With increase in concentration of catalyst, the conversion versus time plots became increasingly linear as shown in Figure 3.5. Only at elevated conversions did high-concentration of catalyst profiles revert to first-order kinetics.

A well-known side reaction, the dimerization or trimerization of the coordinatively unsaturated catalytically active species to inactive complexes, might be employed to interpret this phenomena [53]. Compared to the hydrogenation of cis-1,4-poly(isoprene) using Os system which showed a first order dependence on the catalyst precursor loading, indicating that the concentration of the active complex is linear proportional to the precursor loading. This means a mononuclear active species.

Table 3.1 Result from 2^3 Factorial Design for Cis-1,4-Poly(isoprene) Hydrogenation,
 $T = 130\text{ }^\circ\text{C}$

Expt	[Ir] (mM)	[C=C] (mM)	P_{H_2} (bar)	Temp ($^\circ\text{C}$)	$k \times 10^3$ (s^{-1})
1	0.0796	246.08	20.7	130	1.26
2	0.0798	246.88	20.7	130	1.28
3	0.0997	246.37	20.7	130	1.41
4	0.0994	246.15	20.7	130	1.37
5	0.0801	246.57	34.5	130	2.41
6	0.0799	246.45	34.5	130	2.30
7	0.0996	245.88	34.5	130	2.68
8	0.0994	246.08	34.5	130	2.55
9	0.0801	500.19	20.7	130	0.89
10	0.0800	500.04	20.7	130	0.91
11	0.1004	500.49	20.7	130	1.35
12	0.0994	500.39	20.7	130	1.42
13	0.0797	500.58	34.5	130	2.04
14	0.0798	500.19	34.5	130	2.16
15	0.1001	500.49	34.5	130	2.20
16	0.1003	500.29	34.5	130	2.35

Table 3.2 Yates's Algorithm Calculation of the 2^3 Factorial Experiments

Test	Design			Algorithm							
	Matrix			k' averg	1	2	3	Divisor	Estimate	Identification	
	Variables	[Ir]	[H ₂]								[C=C]
1	-	-	-	0.00127	0.00266	0.00763	0.01340	8	0.00168	Average	
2	+	-	-	0.00139	0.00497	0.00577	0.00113	4	0.00028	[Ir]	
3	-	+	-	0.00236	0.00229	0.00038	0.00351	4	0.00088	[H ₂]	
4	+	+	-	0.00262	0.00349	0.00075	0.00134	4	0.00034	[Ir] [H ₂]	
5	-	-	+	0.00090	0.00012	0.00231	-0.00186	4	-0.00047	[C=C]	
6	+	-	+	0.00139	0.00026	0.00120	0.00037	4	-0.00009	[Ir][C=C]	
7	-	+	+	0.00210	0.00049	0.00014	-0.00111	4	-0.00028	[H ₂][C=C]	
8	+	+	+	0.00228	0.00018	-0.00031	-0.00045	4	-0.00011	[Ir][H ₂][C=C]	

[Ir] is concentration of catalyst (μM) : (-) 80 , (+) 100

[H₂] is hydrogen pressure (bar) : (-) 20.7 , (+) 34.5

[C=C] is concentration of carbon-carbon double bond (mM) : (-) 246 , (+) 500

Table 3.3 The Calculated Effects and Standard Errors for 2^3 Factorial Experiment

Effect	Estimate \pm standard error
Average	0.00168 \pm 2.86E-10
Main effect	
Concentration of catalyst, [Ir]	0.00028 \pm 3.38E-05
Pressure, [H ₂]	0.00088 \pm 3.38E-05
Concentration of C=C, [C=C]	-0.00047 \pm 3.38E-05
Two-factor interaction	
[Ir] \times [H ₂]	0.00034 \pm 3.38E-05
[Ir] \times [C=C]	0.00009 \pm 3.38E-05
[H ₂] \times [C=C]	-0.00028 \pm 3.38E-05
Three-factor interaction	
[Ir] \times [H ₂] \times [C=C]	-0.00011 \pm 3.38E-05

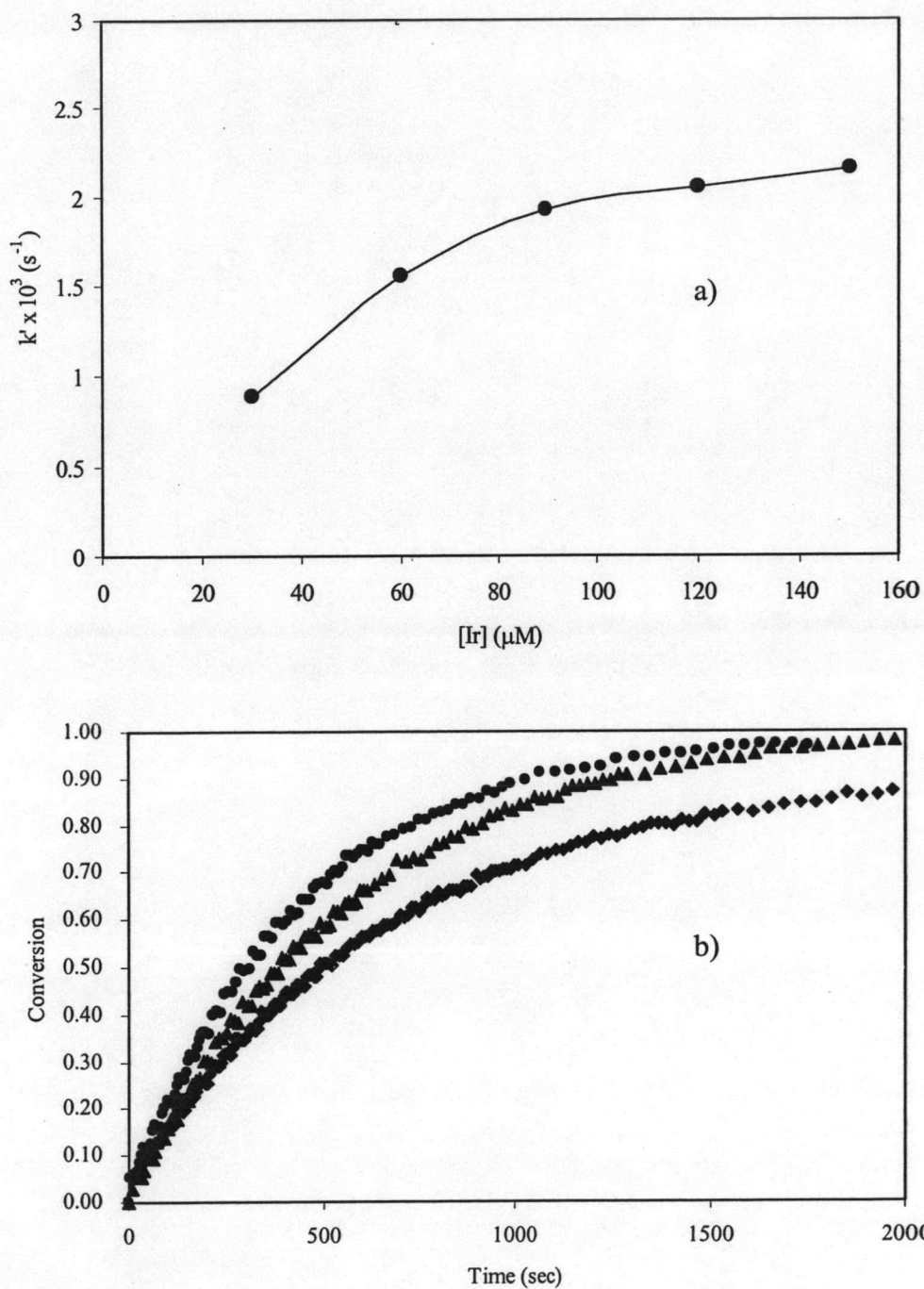


Figure 3.4 a) Effect of catalyst concentration on the hydrogenation rate. $P_{\text{H}_2} = 27.6 \text{ bar}$; $[\text{C}=\text{C}] = 246 \text{ mM}$; $T = 130^\circ\text{C}$ and b) Cis-1,4-poly(isoprene) conversion profile at various $[\text{Ir}]$. $P_{\text{H}_2} = 27.6 \text{ bar}$; $[\text{C}=\text{C}] = 260 \text{ mM}$; $T = 130^\circ\text{C}$; (\blacksquare) $30 \mu\text{M}$, (\blacktriangle) $90 \mu\text{M}$, (\bullet) $150 \mu\text{M}$.

Table 3.4 Kinetic Results of Univariate Experiments

Expt	[Ir] (μM)	[C=C] (mM)	P_{H_2} (bar)	Temp ($^{\circ}\text{C}$)	$k' \times 10^3$ (s^{-1})
1	0.0304	246.08	27.6	130	0.89
2	0.0600	246.47	27.6	130	1.55
3	0.0900	246.27	27.6	130	1.92
4	0.1203	246.57	27.6	130	2.05
5	0.1503	246.47	27.6	130	2.15
6	0.0900	246.37	13.8	130	0.84
7	0.0898	246.57	41.4	130	3.04
8	0.0901	246.27	55.2	130	4.12
9	0.0902	163.72	27.6	130	2.08
10	0.0901	330.00	27.6	130	2.12
11	0.0898	415.09	27.6	130	1.87
12	0.0900	500.78	27.6	130	1.95
13	0.0898	246.66	27.6	120	1.14
14	0.0898	246.37	27.6	125	1.71
15	0.0899	246.27	27.6	135	2.96
16	0.0899	246.37	27.6	140	3.80

b) Effect of Hydrogen Pressure

The effect of hydrogen pressure on the initial hydrogenation rate was varied over the range of 13.8 to 55.2 bar ($[\text{Ir}] = 90 \mu\text{M}$, $P_{\text{H}_2} = 27.6 \text{ bar}$, $[\text{C}=\text{C}] = 246 \text{ mM}$, $T = 130^\circ\text{C}$). The results of these experiments are summarized in Table 3.4. A plot of initial rate constant versus hydrogen pressure is fairly linear as shown in Figure 3.6. It demonstrates that the rate of hydrogenation is first-order with respect to the hydrogen pressure. The first order rate dependence implies that primarily a single reaction pathway is probably involved in the reaction of the unsaturation in polymer with hydrogen. If more than one process were involved, the relative contribution of each pathway should change with varying hydrogen pressure, and thus the dependence might deviate from first order behavior. Such a hydrogen pressure dependence has been found for a number of other catalyst systems. Hydrogenation of *cis*-1,4-poly(isoprene) using the osmium system demonstrates a second to zero order dependence as the hydrogen pressure was increased (section 2.3). The first order rate dependence on hydrogen pressure was observed consistently for hydrogenation of acrylonitrile-butadiene copolymers using the iridium system [32].

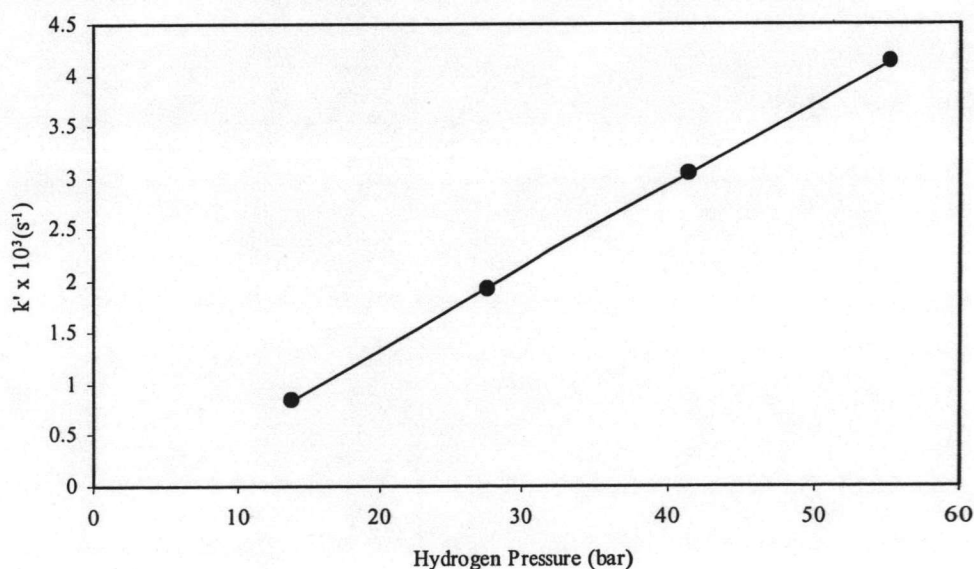


Figure 3.5 Effect of hydrogen pressure on the hydrogenation rate. $[\text{Ir}] = 90 \mu\text{M}$; $[\text{C}=\text{C}] = 246 \text{ mM}$; $T = 130^\circ\text{C}$.

c) Effect of [C=C] Concentration

Experiments at initial C=C concentrations ranging from 163 to 500 mM in chlorobenzene were performed to determine the effect of C=C concentration on the reaction rate. Experiments were performed at the base conditions of the other variables: catalyst concentration of 90 μM , hydrogen pressure of 27.6 bar, and reaction temperature of 130°C. Figure 3.6 shows that the hydrogenation activity was essentially unaffected by the amount of cis-1,4-poly(isoprene). The conversion profiles for hydrogenation that are first-order with respect to [C=C] are, by definition, independent of the amount of olefin charged to the reactor. This agrees with the observations of cis-1,4-poly(isoprene) and styrene-butadiene-styrene copolymers hydrogenation using the osmium system in which the C=C concentration has no effect on the hydrogenation rate [8]. For the hydrogenation of acrylonitrile-butadiene copolymers, the activity of osmium and iridium system were affected by the rubber loading. The corresponding increase in the concentration of nitrile inhibits the catalytic activity of the catalysts.

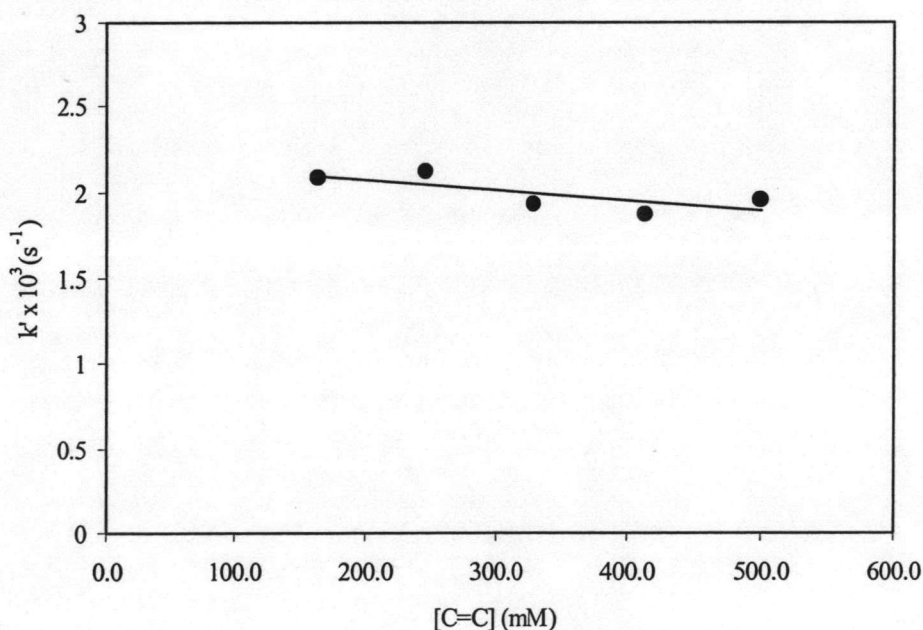


Figure 3.6 Effect of C=C concentration on the hydrogenation rate. [Ir] = 90 μM ; P_{H_2} = 27.6 bar; $T = 130^\circ\text{C}$.

d) Effect of Temperature

A series of experiments were carried out over the range of 120 to 140°C, where the catalyst concentration (90 μM), C=C concentration (246 mM), and hydrogen pressure (27.6 bar) remained constant. The effect of temperature on the rate constant can be represented by an Arrhenius plot. Figure 3.7 shows the Arrhenius plot, which is linear ($R^2 = 0.9789$), over the temperature range of 120 to 140 °C. The slope of $\ln(k')$ versus $1/T$ provided an apparent activation energy of 79.8 kJ/mole. This provides further evidence that the kinetic data were acquired without mass transfer limitation and the diffusion of the reactant is not a rate-determining factor under these conditions. Hydrogenation at higher temperature exhibited a faster reaction rate and led to a higher efficiency. The apparent activation energy of cis-1,4-poly(isoprene) hydrogenation using Crabtree's catalyst are lower than the hydrogenation of cis-1,4-poly(isoprene) hydrogenation using the osmium system, but higher than the hydrogenation of acrylonitrile-butadiene copolymers using Crabtree's catalyst for which the reported value of the apparent activation energy was 68.6 kJ/mol [32].

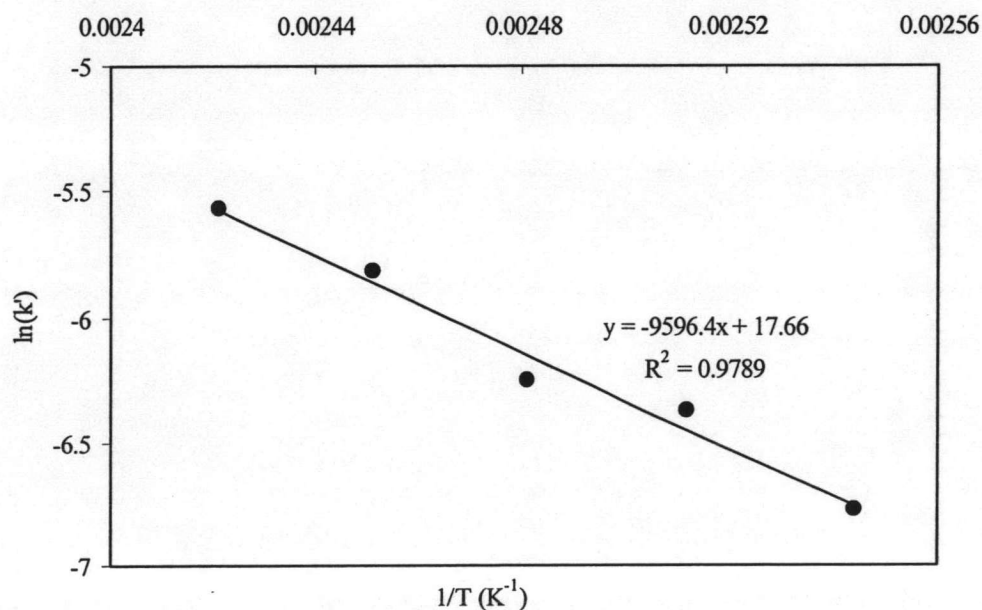


Figure 3.7 Arrhenius plot for the hydrogenation of cis-1,4-poly(isoprene). $[\text{Ir}] = 90 \mu\text{M}$; $[\text{C}=\text{C}] = 246 \text{ mM}$; $P_{\text{H}_2} = 27.6 \text{ bar}$.

e) Effect of Solvent

Several solvents other than chlorobenzene were investigated for cis-1,4-poly(isoprene) hydrogenation using Crabtree's catalyst at base conditions ($[\text{Ir}] = 90 \mu\text{M}$, $P_{\text{H}_2} = 27.6 \text{ bar}$, $[\text{C}=\text{C}] = 246 \text{ mM}$, $T = 130^\circ\text{C}$). In each case, reactions were run at equivalent hydrogen partial pressure. The reactor was charged with the same initial pressure of hydrogen at 25°C (27.6 bar) as in the chlorobenzene experiments and allowed to heat up to 130°C without releasing any gas. Since the differences in solvent partial pressure at 25°C were negligible compared to the partial pressure of hydrogen, the same partial pressure of hydrogen was obtained with each solvent. The effect of solvent on the hydrogenation activity is summarized in Table 3.5. It seems that chlorinated solvents are viable solvents for catalytic hydrogenation with this cationic iridium catalyst. Toluene, hexane and xylene were not used as solvents since they could not completely dissolve the cationic iridium catalyst. Crabtree et al. [22] reported that non-coordinating solvents were disappointing and only catalytically inactive precipitates were formed under hydrogen. The strong coordinating solvent (tetrahydrofuran) was found to be an efficient solvent for the hydrogenation of cis-1,4-poly(isoprene) using the osmium system (section 2.3.4), but it was not a good solvent for the hydrogenation of cis-1,4-poly(isoprene) using the Crabtree's catalyst. Thus, higher activity of Crabtree's catalyst is obtained in non-coordinating solvents. This is consistent with the hydrogenation of acrylonitrile-butadiene copolymers using Crabtree's catalyst [32].

Table 3.5. Effect of Solvent on the Hydrogenation of Cis-1,4-Poly(isoprene)

Solvent	$k' \times 10^3 \text{ (s}^{-1}\text{)}$	Final hydrogenation degree (%)
Chlorobenzene	1.92	98.14 (~35 min)
Tetrahydrofuran	0.80	75.82 (~1 h)
Dichloromethane	2.16	96.60 (~30 min)
Dichlorobenzene	1.73	97.06 (~40 min)
Trichlorobenzene	2.21	97.35 (~30 min)

$[\text{Ir}] = 80 \mu\text{M}$, $P_{\text{H}_2} = 27.6 \text{ bar}$, $[\text{C}=\text{C}] = 246 \text{ mM}$, $T = 130^\circ\text{C}$.

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

One of the major problems associated with the modification of polymers are side reactions such as, chain degradation and crosslinking, which often accompany the desirable modification reaction. These side reactions result in a change in the chain length properties of the parent macromolecules. Estimating the degradation and crosslinking of a sample is complicated by their limited appearance in a manageable sample. The sensitivity of spectroscopic techniques is insufficient to detect the small number of crosslinks which can result in an undesirable viscosity. Therefore, the degree of polymer crosslinking must be inferred indirectly from molecular weight measurements. Dilute solution viscosity has been used to monitor the shifts in molecular weight that are created by crosslinking. The method has the drawback of an ambiguous relationship of viscosity (η) to molecular weight, especially for copolymers with composition or structural dispersity. 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.

The effect of catalyst concentration, polymer concentration, and hydrogen pressure on the relative viscosity of hydrogenated cis-1,4-poly(isoprene) are shown in Figure 3.8. The results show that the relative viscosity of hydrogenated cis-1,4-poly(isoprene) was unaffected by these factors. The relative viscosity of hydrogenated cis-1,4-poly(isoprene) is in the range of 6.8-7.3, as compared with the relative viscosity of cis-1,4-poly(isoprene) (4.48). It was found that the relative viscosity of hydrogenated cis-1,4-poly(isoprene) was higher than that of cis-1,4-poly(isoprene). The increase of the relative viscosity suggests that no degradation occurred during the catalytic hydrogenation reaction. Since relative viscosity of hydrogenated cis-1,4-poly(isoprene) remained constant, it can be concluded that small amount of residual C=C remains after the hydrogenation reaction and also possibly crosslinking did not affect the hydrogenation process. A similar observation was also made for the selectivity of cis-1,4-poly(isoprene) hydrogenation using the osmium system and NBR hydrogenation using the iridium system [32].

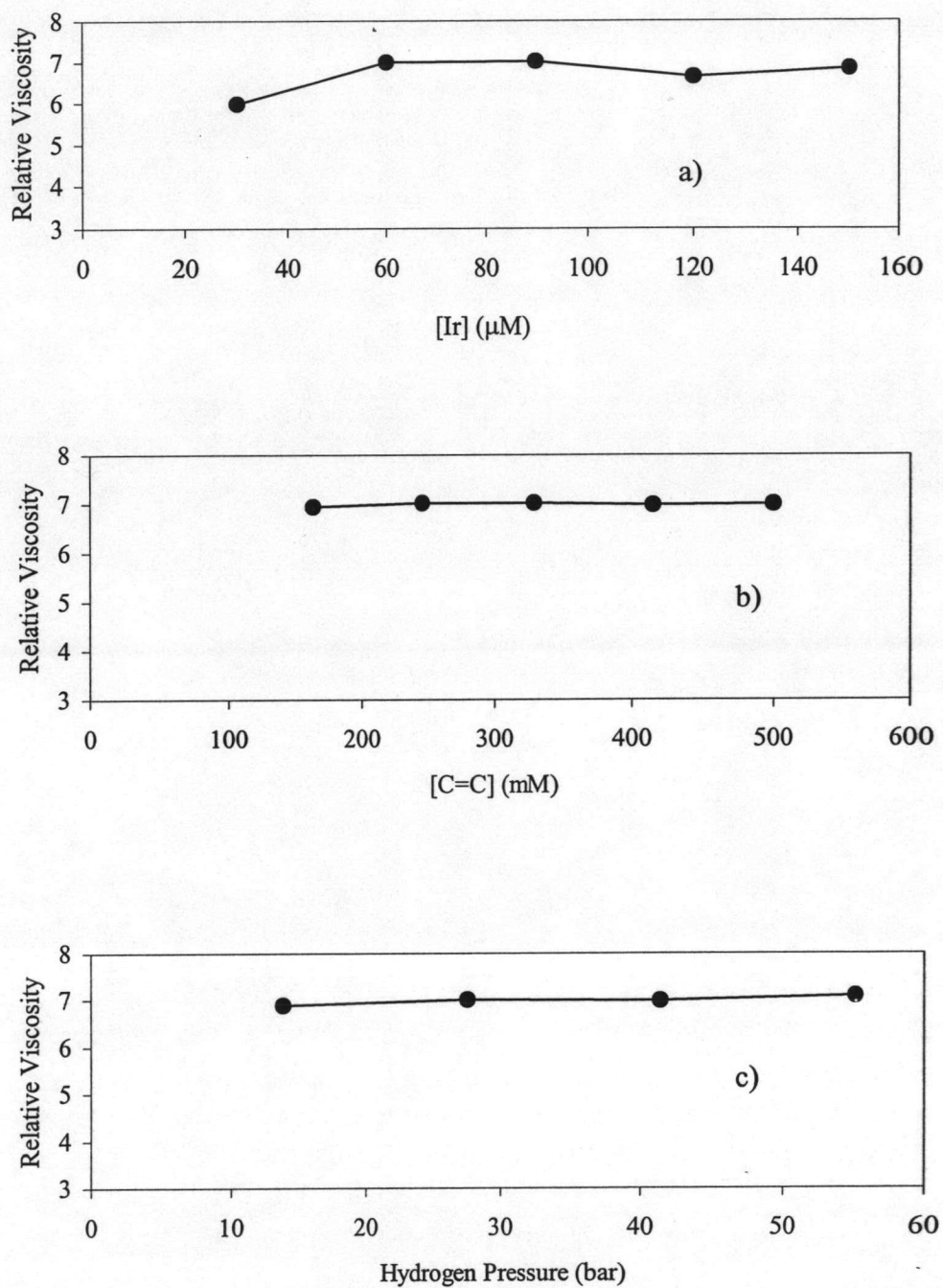


Figure 3.8 a) Selectivity as a function of total metal loading. $P_{\text{H}_2} = 27.6$ bar; $[\text{C}=\text{C}] = 246$ mM; $T = 130$ °C. b) Selectivity as a function of polymer loading. $[\text{Ir}] = 90$ μM ; $P_{\text{H}_2} = 27.6$ bar; $T = 130$ °C. c) Influence of pressure on selectivity. $[\text{Ir}] = 90$ μM ; $[\text{C}=\text{C}] = 246$ mM; $T = 130$ °C.

3.3.6 Reaction Mechanism and Rate Law

Previous studies of Crabtree's catalyst and its analogues have described most of the pathways involved in the catalytic pathway for hydrogenation of olefins. Complexes within its use in cis-1,4-poly(isoprene) hydrogenation are extremely active. Thus, the catalytic pathway must be developed from inferences drawn from the kinetic data, arguments regarding coordination numbers, and electron counting schemes. Figure 3.9 illustrates a catalytic mechanism that is consistent with the kinetic data of Table 3.4, the 16-18 electron rule, and previous reported work [32]. The mechanism implies that the active catalytic species is a two ligand cation, which is formed rapidly from the catalyst precursor after the COD ligand being hydrogenated to COE or COA and removed. Then this species reacts with H₂ molecule to generate the hydride catalyst. The substrate double bond coordinate to the hydride catalyst. Hydride transfer to the pi-olefin complex occurs next to form an alkyl complex. The alkyl complex is cleaved by hydrogen to form hydrogenated polymer and to regenerate the cationic active species.

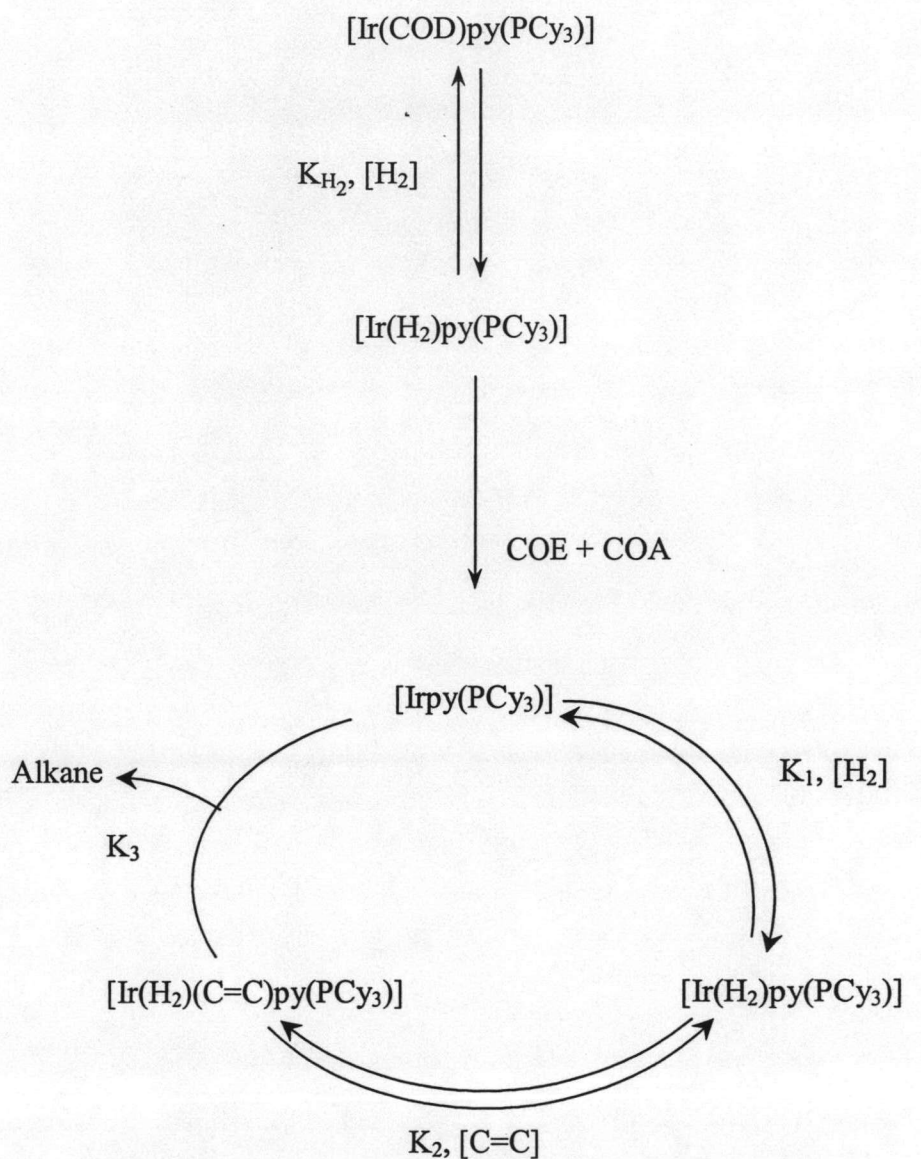
According to the proposed mechanism, the hydrogenation of olefin by iridium is provided by the following rate expression:

$$\frac{-d[\text{C}=\text{C}]}{dt} = K_3[\text{Ir}(\text{H}_2)(\text{C}=\text{C})(\text{py})(\text{PCy}_3)] \quad (3.4)$$

Applying a steady state assumption to each of the equilibrium leading to the formation of $[\text{Ir}(\text{H}_2)(\text{C}=\text{C})(\text{py})(\text{PCy}_3)]$ provides a means of relating the concentration of every species to the rate determining step.

$$[\text{Ir}(\text{H}_2)(\text{py})(\text{PCy}_3)] = \frac{1}{K_2 [\text{C}=\text{C}]} [\text{Ir}(\text{H}_2)(\text{C}=\text{C})(\text{py})(\text{PCy}_3)] \quad (3.5)$$

The formation of alkyl species from the double bond and the hydride species is considered to occur in one reversible step, although the formation of a pi-olefin complexes likely occurs first, followed by hydride transfer to form the alkyl complex. Writing the reaction as to separate equilibrium steps gives no further kinetic formation, since it only includes one more unknown species concentration and unknown equilibrium constant in the rate expression. The overall equilibrium constant K_2 is thus used for simplicity.



COD = Cyclooctadiene; COE = Cyclooctene; COA = Cyclooctane

Figure 3.9 Proposed mechanism for cis-1,4-poly(isoprene) hydrogenation by $[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$.

$$[\text{Ir}(\text{py})(\text{PCy}_3)] = \frac{1}{K_1 K_2 [\text{C}=\text{C}] [\text{H}_2]} [\text{Ir}(\text{H}_2)(\text{C}=\text{C})(\text{py})(\text{PCy}_3)] \quad (3.6)$$

A mass balance on the total amount of Ir charged to the system is as follows:

$$[\text{Ir}]_{\text{T}} = [\text{Ir}(\text{H}_2)(\text{Alk})(\text{py})(\text{PCy}_3)] + [\text{Ir}(\text{H}_2)(\text{py})(\text{PCy}_3)] + [\text{Ir}(\text{py})(\text{PCy}_3)] + 0 \quad (3.7)$$

Yield the concentration of the active center as a function of the total amount of Ir charged to the system.

$$[\text{Ir}(\text{H}_2)(\text{Alk})(\text{py})(\text{PCy}_3)] = \frac{[\text{Ir}]_T K_1 K_2 [\text{C}=\text{C}] [\text{H}_2]}{1 + K_1 K_2 [\text{H}_2][\text{C}=\text{C}] + K_1 [\text{H}_2]} \quad (3.8)$$

Due to the removal of (COE) or (COA) pushing the reaction in the direction of the generation of active species, the formation of the active metal fragment is rapid, the concentration of the dihydro-(COD) Ir complex in solution will be zero. Applying the equilibrium relations defined in Figure 3.9, the concentration of $[\text{Ir}(\text{H}_2)(\text{C}=\text{C})(\text{py})(\text{PCy}_3)]$ in eq. 3.4 is substituted by eq. 3.8 to provide the resulting rate law as follows:

$$-\frac{d[\text{C}=\text{C}]}{dt} = K_3 [\text{Ir}(\text{H}_2)(\text{C}=\text{C})(\text{py})(\text{PCy}_3)] = \frac{[\text{Ir}]_T K_1 K_2 [\text{C}=\text{C}] [\text{H}_2]}{1 + K_1 K_2 [\text{H}_2][\text{C}=\text{C}] + K_1 [\text{H}_2]} \quad (3.9)$$

The function form of this rate expression is consistent with the behavior of the iridium system observed throughout the kinetic investigations. The rate expression would suggest that there would be a first order dependence on $[\text{H}_2]$ and $[\text{C}=\text{C}]$, as K_1 and K_2 are negligible for the range of the reaction conditions and substrate concentration used in this study. The reaction was found to have a first order response of k' to $[\text{Ir}]$ at low concentration of catalyst and shift to zero order at higher concentration of catalyst.

3.4 Conclusions

In monochlorobenzene, $[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$ is an efficient catalyst precursor for the hydrogenation of cis-1,4-poly(isoprene). A first order dependence on hydrogen pressure and carbon double bond concentration were observed. The reaction rate was first order to zero order with respect to concentration of catalyst, implying that the active complex is mononuclear. The apparent activation energy was found to be 79.8 kJ/mol. The proposed mechanism and the rate expression for hydrogenation of cis-1,4-poly(isoprene) using $[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$ were consistent with the kinetic data. The relative viscosity of hydrogenated product indicated that there was probably no degradation and crosslinking in the polymer structure.