

CHAPTER IV

HYDROGENATION OF NATURAL RUBBER CATALYZED BY



4.1 Introduction

Natural rubber (NR) is one of the most important polymers naturally produced by plants because it is a strategic raw material used in more than 40,000 products, including more than 400 medical devices. The sole commercial source, at present, is natural rubber harvested from Brazilian rubber tree, *Hevea brasiliensis* [54].

Natural rubber contains about 6% non-rubber components such as proteins, lipids and carbohydrates. Rubber hydrocarbon was presumed to be composed of isoprene units of which almost 100% are in the *cis*-configuration with very small amounts of so called abnormal groups such as aldehyde and epoxide [55]. In the poly (isoprene) of natural rubber, there is one double bond for each isoprene unit. These double bonds and the α -methyl groups are reactive groups for vulcanization reactions with sulphur. The double bond can, however, also enter into additional reactions with oxygen or ozone, to degrade the rubber [45]. Chemical modification by catalytic hydrogenation provides a simple reaction to reduce the degree of unsaturation in the natural rubber which provides greater stability against thermal, oxidative, and radiation-induced degradation. Within the general heading of catalytic hydrogenation, there are examples of the use of both heterogeneous and homogeneous catalyst system. The use of heterogeneous catalyst is still prevalent, but many of the new developments in the field of catalytic hydrogenation over the last few years have involved the use of homogeneous catalysis because it provides a better opportunity to realize quantitative hydrogenation [6].

This chapter summarizes the initial studies on hydrogenation of natural rubber using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ in a batch reactor which leads to the understanding of kinetics of natural rubber hydrogenation. The acid-promoted homogeneous hydrogenation of natural rubber has been studied under conditions, which demonstrates the short reaction time required when using a small amount of catalyst.

The range of operating conditions chosen for this investigation was related to that of the hydrogenation of cis-1,4-poly(isoprene) using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$.

4.2 Experimental

4.2.1 Materials

The natural rubber (grade TSR 5L) was obtained from Rubber Research Institute of Thailand. Reagent grade toluene, monochlorobenzene, xylene, tetrahydrofuran, and ethanol were obtained from Scientific Ltd. All solvents were used as received. The acid employed (p-toulene sulfonic acid, 3-chloropropionic acid, succinic acid, glycolic acid, and citric acid) were purchased from Sigma Aldrich. The purity of hydrogen gas obtained from Praxair Inc. was reported to be 99.99%. $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ was prepared by refluxing $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$ with PCy_3 (both from Strem Chemicals) in methoxyethanol according to the procedures of Esteruelas and Werner. [18] The corresponding dioxygen adduct, $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$, was prepared by exposing a suspension of $\text{OsHCl}(\text{CO})(\text{PCy}_3)_2$ in hexane to pure O_2 as detailed by Esteruelas et. al [16].

4.2.2 Hydrogenation Process

a) *Hydrogenation by Batch Reactor*

Hydrogenation reactions were carried out in a 300 mL Parr reactor. 2.65 g of natural rubber 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 the solution for 20 min at 13.8 bar H_2 pressure at room temperature. Where the addition of acid was required, the precise weighing of acid was charged to the polymer solution before being degassed by bubbling hydrogen gas. 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 desired reaction pressure. Hydrogen gas was

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.

4.3 Results and Discussion

The initial studies of natural rubber hydrogenation using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ was carried out in a Parr reactor. The influence of parameters such as solvent type and acidity of acid were investigated. The dilute viscosity of hydrogenated natural rubber product was measured and compared with hydrogenated cis-1,4-poly(isoprene) product. Finally, the hydrogenation of natural rubber using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ in the gas uptake apparatus was investigated to provide a foundation upon which greater understanding may be built in the future.

4.3.1 Hydrogenation of natural rubber using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ in Batch reactor

Hydrogenation of natural rubber using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ in toluene was carried out with catalyst concentration of 80 μM , hydrogen pressure of 27.6 and 41.4 bar, carbon double bond concentration of 260 mM, and at reaction temperature of 140 and 150°C. Typical properties of natural rubber grade TSR 5L used in this work are shown in Table 4.1.

Table 4.1 The Properties of Natural Rubber Grade TSR 5L

Propeties	Test results
Dirt (max, %wt.)	0.04
Ash (max, %wt.)	0.40
Nitrogen (max, %wt.)	0.60
Volatile matter (max, %wt.)	0.80
Initial plasticity (min)	35.0
PRI index (min)	60.0
Colour lovibond scale (individual value, max)	6.00
Mooney viscosity (ML +4, 100°C)	-

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.

4.3 Results and Discussion

The initial studies of natural rubber hydrogenation using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ was carried out in a Parr reactor. The influence of parameters such as solvent type and acidity of acid were investigated. The dilute viscosity of hydrogenated natural rubber product was measured and compared with hydrogenated cis-1,4-poly(isoprene) product. Finally, the hydrogenation of natural rubber using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ in the gas uptake apparatus was investigated to provide a foundation upon which greater understanding may be built in the future.

4.3.1 Hydrogenation of natural rubber using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ in Batch reactor

Hydrogenation of natural rubber using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ in toluene was carried out with catalyst concentration of 80 μM , hydrogen pressure of 27.6 and 41.4 bar, carbon double bond concentration of 260 mM, and at reaction temperature of 140 and 150°C. Typical properties of natural rubber grade TSR 5L used in this work are shown in Table 4.1.

Table 4.1 The Properties of Natural Rubber Grade TSR 5L

Propeties	Test results
Dirt (max, %wt.)	0.04
Ash (max, %wt).	0.40
Nitrogen (max, %wt.)	0.60
Volatile matter (max, %wt.)	0.80
Initial plasticity (min)	35.0
PRI index (min)	60.0
Colour lovibond scale (individual value, max)	6.00
Mooney viscosity (ML +4, 100°C)	-

Natural rubber consists of cis-1,4-poly(isoprene) and would contain 68 g/mol of the repeating unit, $-\text{CH}_2\text{C}(\text{CH}_3)-\text{CH}-\text{CH}_2-$. The typical FT-IR and $^1\text{H-NMR}$ spectra of the hydrogenated natural rubber (HNR) products are shown in Figure 4.1 and 4.2, respectively. The characteristic IR peaks at 1,663 and 843 cm^{-1} due to the C=C stretching and the trisubstituted olefinic C-H bending disappear upon hydrogenation of natural rubber. A very intense peak appears at 735 cm^{-1} , which is attributed to the $-(\text{CH}_2)_3-$ group formed through hydrogenation (Figure 4.1). The major $^1\text{H-NMR}$ peaks of $-\text{CH}_3$, $-\text{CH}_2-$, and $=\text{CH}$ groups of the natural rubber before and after hydrogenation are shown in Figure 4.2. The hydrogenation reaction led to the reduction in the peaks of the isoprene unit of natural rubber at 1.7, 2.2, and 5.2 ppm and the increase in the peaks of the ethylene-propylene block of the hydrogenated product at 0.89 and 1.1-1.3 ppm. The degree of hydrogenation was measured by the reduction of the peak area at 5.2 ppm.

a) Acid-Promoted Hydrogenation of Natural Rubber

In Chapter 2, $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ has been found to be an efficient catalyst for the hydrogenation of cis-1,4-poly(isoprene) in which degradation and crosslinking did not occur in the hydrogenated polymer structure. Therefore, $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ was also applied for the hydrogenation of natural rubber.

Table 4.2 summarizes the initial studies of natural rubber hydrogenation using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ in a batch reactor. The *p*-toluene sulfonic acid was used as acid-promoter for hydrogenation. Little or no hydrogenation was observed under the investigated conditions, when no acid-promoter was present, though the hydrogen pressure and reaction temperature increased. The change of solvent from toluene to monochlorobenzene (MCB) did not increase the catalytic activity of $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$. The addition of *p*-toluene sulfonic acid led to an increase in the catalytic activity of $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ toward hydrogenation of natural rubber. However, higher concentration of *p*-toluene sulfonic acid did not appear to affect the hydrogenation rate (Table 4.2). These results demonstrate the acid-promoted homogeneous hydrogenation of natural rubber.

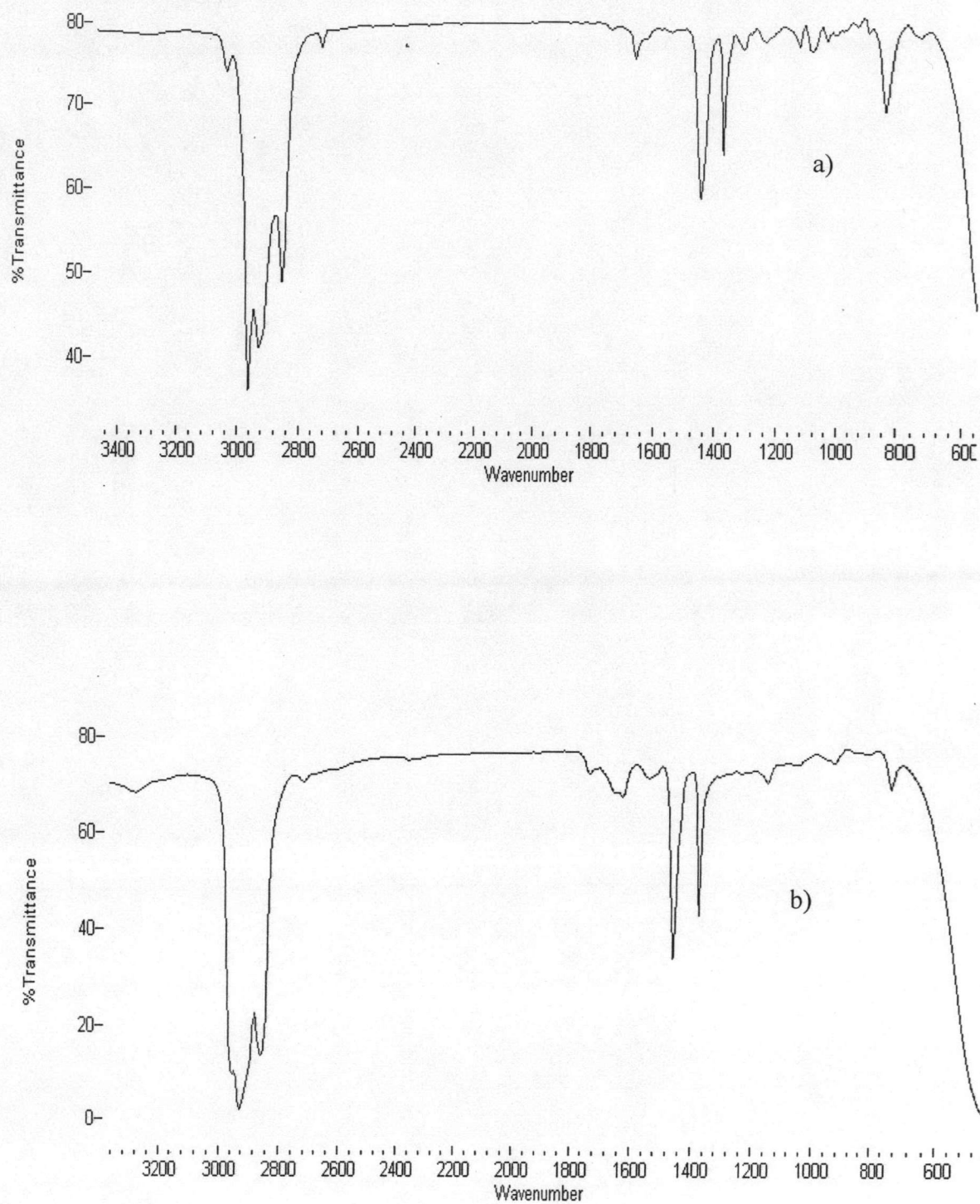


Figure 4.1 FT-IR spectra of: a) natural rubber and b) hydrogenated natural rubber.

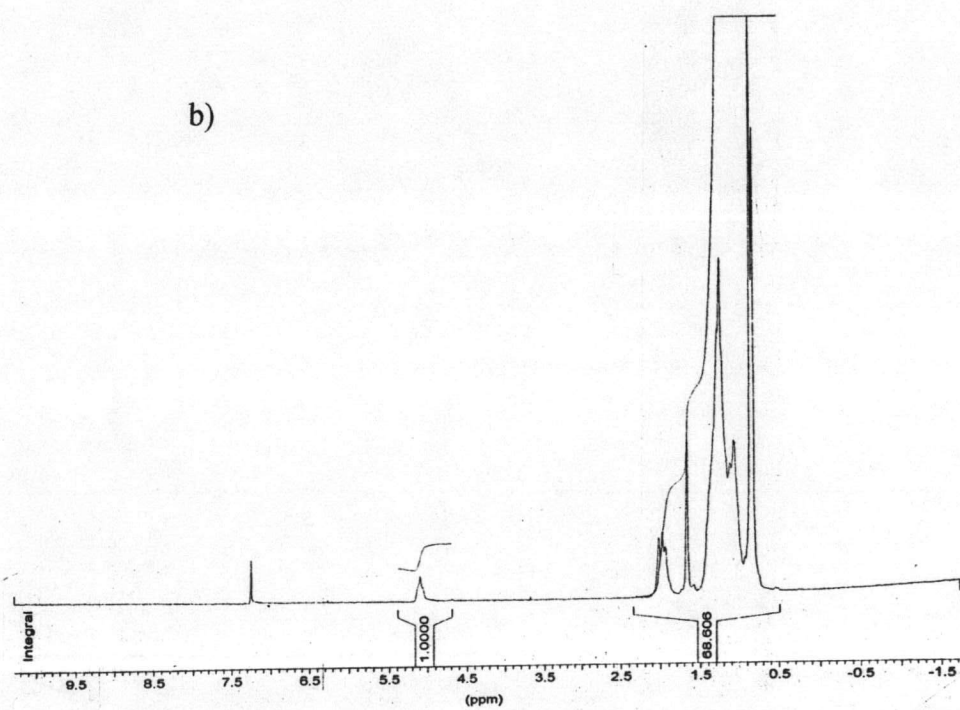
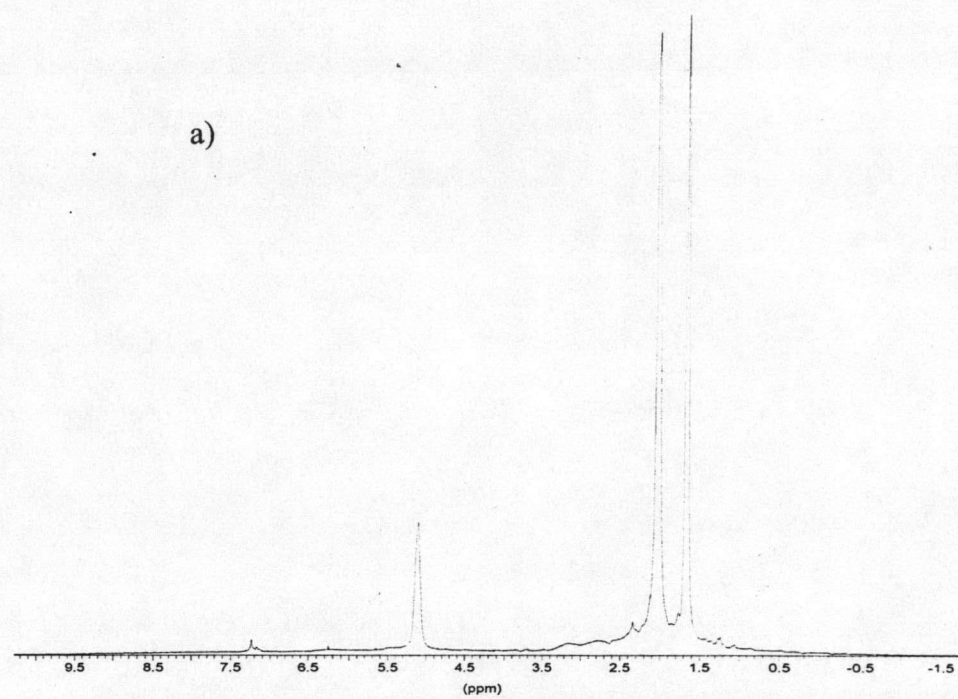


Figure 4.2 ^1H -NMR spectra of: a) natural rubber and b) hydrogenated natural rubber.

Table 4.2 Initial Studies of Natural Rubber Hydrogenation in Parr Reactor

Expt	H ₂ (bar)	Temp (°C)	[Acid]* (%w/v)	Solvent	Result
1	27.6	150	-	Toluene	A little hydrogenation after 6 h
2	41.4	140	-	Toluene	No hydrogenation after 6 h
3	41.4	140	-	MCB	No hydrogenation after 6 h
4	41.4	140	0.06	Toluene	~85% hydrogenation after 3 h
5	41.4	140	0.13	Toluene	~85% hydrogenation after 3 h

p-toluene sulfonic acid; [Os] = 80 μM; [C=C] = 260 mM.

The effect of acid-promoter on hydrogenation can be explained by the dissociation of a phosphine ligand which is one of the most common ways to activate metal-phosphine complexes. For example, metal-phosphine complexes such as RhCl(PPh₃)₃ (hydrogenation), RhH(CO)(PPh₃)₃ (hydroformylation), and (PCy₃)₂(Cl)₂Ru=CHPh (metathesis) have been well-known to generate catalytically active species via an initial dissociation of the phosphine ligand. As a way to increase the catalyst activity, considerable efforts have been directed to develop methods for selectively promoting the dissociation and trapping of phosphine ligands. C. S. Yi et al. [33] reported an acid-induced selective entrapment of the phosphine ligand on the ruthenium-hydride complex RuH(CO)(Cl)(PCy₃)₂. It can be concluded that the increased catalytic activity of OsHCl(CO)(O₂)(PCy₃)₂ by acid might be due to the selective entrapment of the phosphine ligand and the formation of a very active 14-electron osmium-trihydride species. Furthermore, in the presence of the added acid, the impurities in the natural rubber are possibly neutralized.

b) Effect of Acidity

The effect of acidity on the hydrogenation of natural rubber using OsHCl(CO)(O₂)(PCy₃)₂ was investigated by varying the acidity of carboxylic acid. The concentration of catalyst and carboxylic acid were kept constant at 80 μM and 0.06%w/v, respectively.

Table 4.3 The Effect of Acidity on the Natural Rubber Hydrogenation

Expt	Carboxylic acid	K_a	Results
1	3-chloropropionic acid	1.41×10^{-3} (25°C)	93% hydrogenation after 3 h
2	Citric acid	6.40×10^{-4} (18°C)	88% hydrogenation after 4 h
3	Glycolic acid	1.48×10^{-4} (25°C)	87% hydrogenation after 6 h
4	Succinic acid	2.47×10^{-6} (25°C)	77% hydrogenation after 6 h

$[\text{Os}] = 80 \mu\text{M}$; Toluene; $[\text{C}=\text{C}] = 260 \text{ mM}$; $P_{\text{H}_2} = 41.4 \text{ bar}$; $T = 140^\circ\text{C}$;

$[\text{acid}] = 0.06\% \text{ w/v}$.

The acidity of carboxylic acid was considered from the acidity constant (K_a). Table 4.3 shows the results of natural rubber hydrogenation in presence of the small amount of added carboxylic acid. It can be seen that the degree of hydrogenation and rate of hydrogenation increase with increasing the acidity constant of carboxylic acid. This means that the strong acid can produce the selective entrapment of the phosphine ligand more readily than the weak acid. The strong acid could neutralize more effectively the impurities in natural rubber. The 3-chloropropionic acid was found to be an efficient acid-promotor for hydrogenation of natural rubber using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$. 93% hydrogenation was achieved at temperature of 140°C and hydrogen pressure of 41.4 bar in 3 h.

c) Effect of Solvent

The effects of solvent on the hydrogenation of natural rubber are summarized in Table 4.4. A series of different types of solvent were investigated with catalyst concentration of $80 \mu\text{M}$ and 3-chloropropionic acid concentration of $0.06\% \text{ w/v}$.

It was found that the degree of hydrogenation and the reaction rate increase rapidly with increased coordinating power of the solvent. The observed reaction rate varied with the nature of solvent in this order: tetrahydrofuran > toluene \geq chlorobenzene > xylene. 91% hydrogenation of natural rubber in tetrahydrofuran was achieved in 1 h at 140°C and 41.4 bar. Tetrahydrofuran is a fairly strong coordinating solvent, which can promote the dissociation of phosphine ligand and the formation of a

14-electron osmium-trihydride species resulting in increased catalytic activity of $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$. These results are consistent with the hydrogenation of *cis*-1,4-poly(isoprene) using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$.

Table 4.4 The Effect of Solvent on the Hydrogenation of Natural Rubber

Expt	Solvent	Results
1	Toluene	93% hydrogenation after 3 h
2	Chlorobenzene	92% hydrogenation after 4 h
3	Xylene	89% hydrogenation after 4 h
4	Tetrahydrofuran	91% hydrogenation after 1 h

$[\text{Os}] = 80 \mu\text{M}$; [3-chloropropionic acid] = 0.06%w/v; $[\text{C}=\text{C}] = 260 \text{ mM}$;

$P_{\text{H}_2} = 41.4 \text{ bar}$; $T = 140^\circ\text{C}$.

d) Viscosity Measurement

The characterization of hydrogenated natural rubber using IR spectroscopy or $^1\text{H-NMR}$ spectroscopic analysis can be used to determine the degree of hydrogenation. However, these techniques lack the sensitivity required to detect the amount of polymer crosslinks in a manageable hydrogenated natural rubber sample. Therefore, the viscosity measurement of a dilute natural rubber solution relative to pure toluene solvent (η_{rel}) was applied to investigate the effect of crosslinking and degradation reaction on the hydrogenation of natural rubber using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$.

The relative viscosity of hydrogenated natural rubber using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ is summarized in Table 4.5. The hydrogenated natural rubber was prepared in Parr reactor using the base condition ($[\text{Os}] = 80 \mu\text{M}$; [3-chloropropionic acid] = 0.06%w/v; $[\text{C}=\text{C}] = 260 \text{ mM}$; $P_{\text{H}_2} = 41.4 \text{ bar}$; $T = 140^\circ\text{C}$).

It can be seen that the relative viscosity of hydrogenated natural rubber was higher than that of natural rubber. The increase of hydrogenated natural rubber viscosity suggests that no degradation reaction occurred during the catalytic hydrogenation of natural rubber. The constant relative viscosity of hydrogenated natural rubber indicates that there is little possibility of crosslinks in the hydrogenated

natural rubber product during hydrogenation. These results are similar to those of the hydrogenation of cis-1,4-poly(isoprene) catalyzed by OsHCl(CO)(O₂)(PCy₃)₂ and [Ir(COD)py(PCy₃)]PF₆.

Table 4.5. Relative Viscosity Measurement of Natural Rubber Hydrogenation

Rubber	Solvent	Relative viscosity
NR (TSR 5L)	-	7.38
HNR	Toluene	8.64
HNR	Chlorobenzene	8.59
HNR	Tetrahydrofuran	8.75

4.3.2 Hydrogenation of Natural Rubber in Gas Uptake Apparatus

The hydrogenation of natural rubber in the presence of OsHCl(CO)(O₂)(PCy₃)₂ catalyst was investigated in toluene using a gas uptake apparatus. The representative hydrogen consumption plot of the hydrogenation of natural rubber, as shown in Figure 4.3a, suggests that the reaction is apparently first order in the olefinic substrate. The first-order rate constant was obtained from the slope of the linear ln(1-x) versus time plot, as shown in Figure 4.3b, according to equation 4.1 (where x is the conversion of unsaturated double bonds and k' is the pseudo-first-order rate constant).

$$\frac{-d[\text{H}_2]}{dt} = \frac{-d[\text{C}=\text{C}]}{dt} = k'[\text{C}=\text{C}] \quad (4.1)$$

The hydrogenation rate of natural rubber ($k' = 0.00193 \text{ s}^{-1}$) was observed to be much slower than that of cis-1,4-poly(isoprene) using OsHCl(CO)(O₂)(PCy₃)₂, ($k' = 0.00414 \text{ s}^{-1}$ at the central standard condition). It is possible that the impurities in the natural rubber decrease the catalytic activity of OsHCl(CO)(O₂)(PCy₃)₂. Some of the natural rubber hydrogenation experiments by gas uptake are summarized in Table 4.6. The conversion profiles of these experiments are shown in Figure 4.4. As the temperature was decreased to 130°C, the rate constant decreased ($k' = 0.00042 \text{ s}^{-1}$) and the 93% hydrogenation was reached at 5,000 sec.

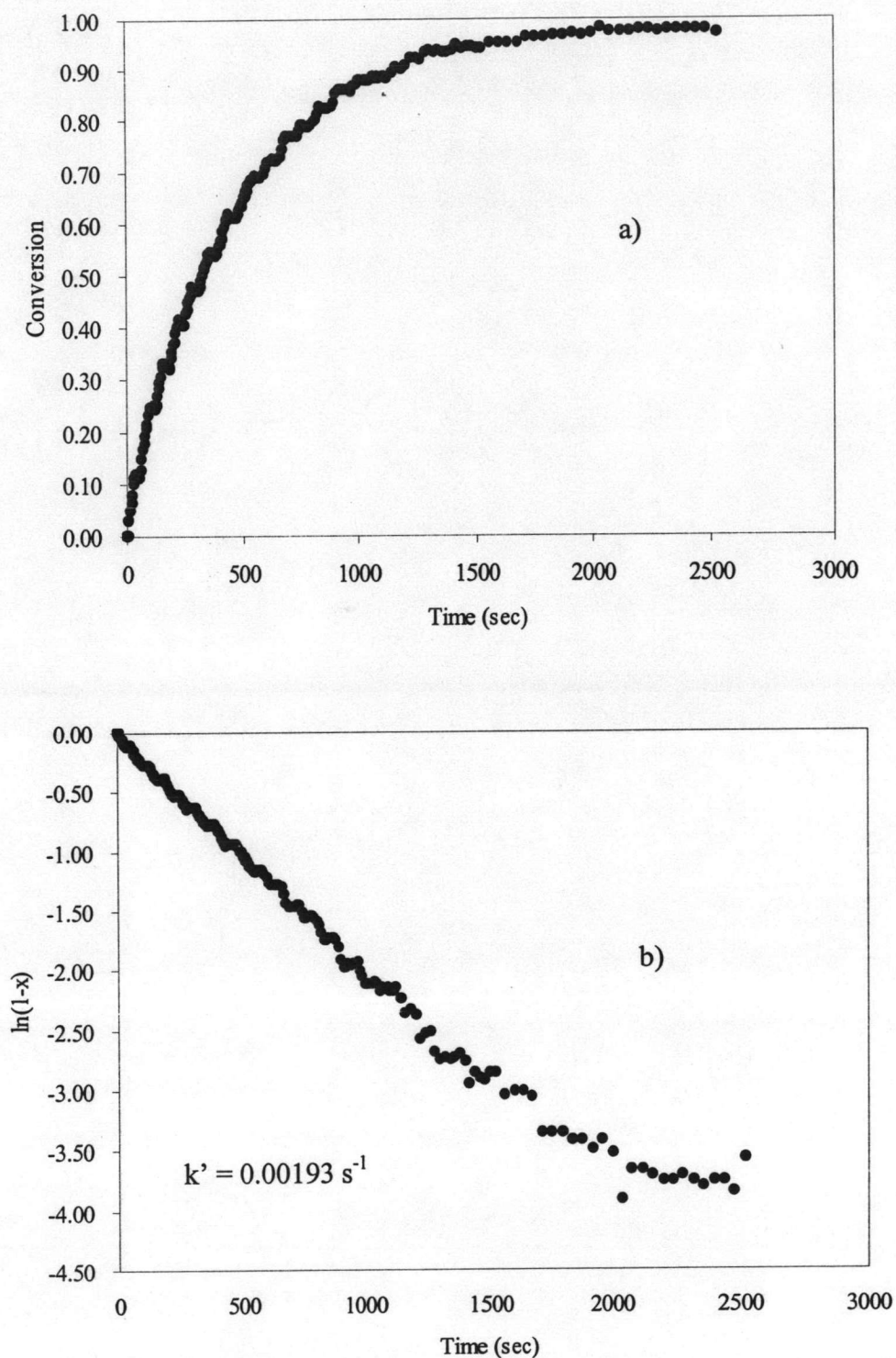


Figure 4.3 a) Conversion versus time profile; $[\text{Os}] = 80 \mu\text{M}$; $P_{\text{H}_2} = 41.4 \text{ bar}$; $[\text{C}=\text{C}] = 260 \text{ mM}$; $T = 140 \text{ }^\circ\text{C}$; $[\text{3-chloropropionic acid}] = 0.06\% \text{w/v}$. b) Ln plot of the x versus time data.

Table 4.6 Hydrogenation of Natural Rubber by Gas uptake Apparatus

Expt	Condition	k' (s^{-1})
1	[Os] = 80 μ M; P_{H_2} = 41.4 bar; [C=C] = 260 mM; T = 140 $^{\circ}$ C; [3-chloropropionic acid] = 0.06%w/v.	0.00193
2	[Os] = 80 μ M; P_{H_2} = 41.4 bar; [C=C] = 260 mM; T = 130 $^{\circ}$ C; [3-chloropropionic acid] = 0.06%w/v.	0.00042
3	[Os] = 80 μ M; P_{H_2} = 41.4 bar; [C=C] = 260 mM; T = 140 $^{\circ}$ C; [3-chloropropionic acid] = 0.13%w/v.	0.00202

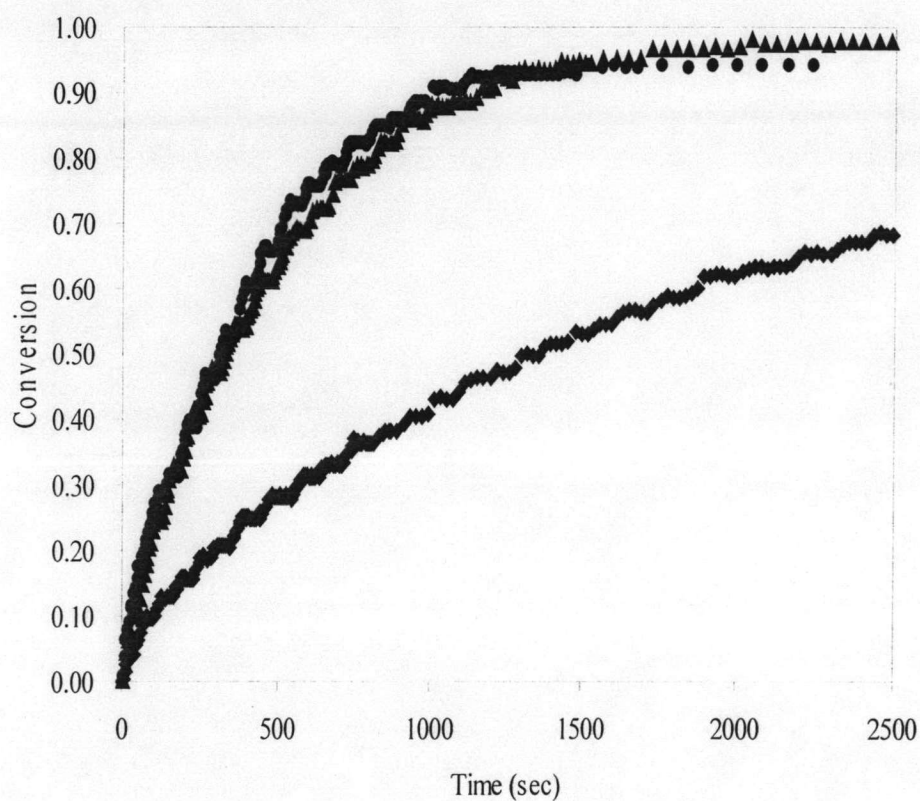


Figure 4.4 Hydrogenation of natural rubber by gas uptake apparatus. [Os] = 80 μ M; P_{H_2} = 41.4 bar; [C=C] = 260 mM; (▲) Expt 1, (■) Expt 2, (●) Expt 3.

4.4 Conclusions

Natural rubber can be quantitatively hydrogenated using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ in the presence of acid. An acid-induced selective entrapment of the phosphine ligand from $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ was found to give a substantial rate increase toward the hydrogenation of natural rubber. Strong acidity of acid and the high coordinating power of solvent increase the degree of hydrogenation and reaction rate. Uniform viscosity of hydrogenated natural rubber suggested that there was possibly no degradation and crosslinking over the range of hydrogenation conditions. The hydrogenation of natural rubber using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ by gas uptake measurement showed that the reaction was first-order with respect to the carbon-carbon double bond concentration therein.