

# Hydrogenation of Natural Rubber Latex in the Presence of $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$

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**ABSTRACT:** Hydrogenation is an important method of chemical modification, which improves the physical, chemical, and thermal properties of diene elastomers. Natural rubber latex (NRL) can be quantitatively hydrogenated to provide a strictly alternating ethylene-propylene copolymer using a homogeneous osmium catalyst  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ . A detailed kinetic investigation was carried out by monitoring the amount of hydrogen consumption during the reaction using a gas-uptake apparatus. The kinetic results of NRL hydrogenation indicated that this system had a second-order dependence of the hydrogenation rate on hydrogen pressure and then decreased toward a zero-order dependence for hydrogen pressures above 13.8 bar. The hydroge-

nation was also observed to be first-order with respect to catalyst concentration and inverse first-order on rubber concentration due to impurities present in the rubber latex. Additions of a controlled amount of acid demonstrated a beneficial effect on the hydrogenation rate of NRL. The temperature dependence of the hydrogenation rate was investigated and an apparent activation energy (over the range of 120–160°C) was calculated as 57.6 kJ/mol. Mechanistic aspects of this catalytic process are discussed on the basis of kinetic results. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 640–655, 2006

**Key words:** rubber; catalysis; kinetics (polym)

## INTRODUCTION

Natural rubber latex is produced from rubber trees of which the dominant species is *Hevea Brasiliensis*. Natural rubber latex (NRL) contains a rubber part, a non-rubber part, and water. NRL is known chemically as polyisoprene.<sup>1</sup> The rubber chain possibly has oligopeptide and fatty acid ester at the unidentified initiating and chain-end respectively.<sup>2</sup> The high resilience, tear resistance, excellent dynamic properties, and fatigue resistance are main advantages of natural rubber believed to result from proteins in the rubber structure.<sup>3</sup> Because of the unsaturation of carbon-carbon double bonds within the isoprene backbone, natural rubber is subject to degradation when exposed to sunlight, ozone, and oxygen. Chemical modification of natural rubber has been an active field of research because of the technological importance of the modified products. Hydrogenation is one of the important methods for improving and changing the properties of unsaturated elastomers toward greater stability

against thermal, oxidative, and radiation-induced degradation.<sup>4</sup>

Most hydrogenation reactions employ solutions of rubber as the reaction media.<sup>5,6</sup> However, natural rubber and certain synthetic elastomers are available in the form of aqueous latex or emulsion, thus it would be advantageous to hydrogenate the elastomer in the latex phase. There are three possible ways to hydrogenate elastomers in latex form: hydrogenation of latex via a catalytic method using a cosolvent, using a water soluble catalyst, or by a noncatalytic process.<sup>6</sup> There are many reports of hydrogenation of synthetic polydiene polymers in latex form, such as acrylonitrile-butadiene copolymer (NBR),<sup>7,8</sup> acrylonitrile-butadiene-styrene copolymer,<sup>9</sup> and styrene-butadiene copolymer (SBR).<sup>10</sup> These reports focus on processes catalyzed by a transition metal complex in the presence of cosolvent. In addition, a noncatalytic process technique, using diimide generated from the reaction between hydrazine hydrate and hydrogen peroxide, has also been found to efficiently hydrogenate a NBR<sup>11–14</sup> and a SBR.<sup>15</sup> However, a high level of gel occurred in these reactions.<sup>16</sup> Singha et al.<sup>17</sup> reported the hydrogenation of NBR in the presence of a water soluble catalyst,  $\text{RhCl}(\text{DPM})_3$ , (DPM, diphenyl phosphino benzene *m*-sulfonate). It was found that hydrogenation of NBR up to 60% at 75°C under 1 atm of hydrogen was achieved in 12 h. Diimide generated in situ from *p*-toluenesulfonyl hydrazide has also been

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used for hydrogenation of a diene polymer,<sup>18</sup> however, side reactions such as *cis*–*trans* isomerization, depolymerization, and cyclization<sup>5,7,19</sup> were found. For hydrogenation of NRL, Wideman<sup>16</sup> patented a process based on hydrazine hydrate and air at 100°C, which resulted in a low level of hydrogenation (<25% conversion).

The objective of the present work was to study the kinetics of NRL hydrogenation catalyzed by OsHCl(CO)(O<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub>. The effect of catalyst concentration ([Os]), rubber concentration based on C=C concentration ([C=C]), hydrogen pressure (P<sub>H<sub>2</sub></sub>), *p*-toluenesulfonic acid concentration ([*p*-TSA]), and reaction temperature were studied using a two-level factorial design and univariate kinetic experiments. The results obtained were used to propose a catalytic mechanism. The effects of impurities present in the NRL system on the hydrogenation rate and the thermal properties of hydrogenated natural rubber latex (HNRL) were also investigated.

## EXPERIMENTAL

### Materials

Osmium (III) chloride trihydrate (OsCl<sub>3</sub>·3H<sub>2</sub>O) and tricyclohexylphosphine (PCy<sub>3</sub>) were obtained from Strem Chemicals (Newburyport, MA). Oxygen-free hydrogen gas (99.99%) for hydrogenation experiments was supplied by Praxair Inc. (Kitchener, ON, Canada). Solvents (reagent grade monochlorobenzene) from Fischer Scientific Ltd. (Fair Lawn, NJ), toluene, xylene, hexane, and 2-methoxyethanol from EM Science (Darmstadt, Germany) and tetrahydrofuran (THF) from Caledon Laboratories Ltd. (Georgetown, ON, Canada) were used as received. Succinic acid, stearic acid, 3-chloropropionic acid, and *p*-TSA were purchased from Aldrich Chemical Company, Inc. (Milwaukee, WI). Ammonium hydroxide and hydroxylamine were purchased from Fischer Scientific Ltd. (Fair Lawn). Hexadecylacrylamide was prepared from the reaction of acryloyl chloride, and hexadecylamine from Aldrich Chemical Company, Inc. (Milwaukee). NRL with high ammonia content was provided by Thai Rubber and Latex Co. Ltd. (Bangkok, Thailand). High Molecular weight *cis*-1,4-polyisoprene with 97% *cis* configuration (Natsyn) was obtained from Bayer, Inc. (Sania, Canada). [Ir(COD)py(PCy<sub>3</sub>)]PF<sub>6</sub> was obtained from Strem Chemicals (Newburyport).

### Catalyst preparation

RhCl(PPh<sub>3</sub>)<sub>3</sub><sup>20</sup> and RuCl(CO)(styryl)(PCy<sub>3</sub>)<sub>2</sub><sup>21</sup> were prepared according to literature methods. OsHCl(CO)(O<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub> used as a catalytic precursor for NRL hydrogenation was prepared by refluxing OsCl<sub>3</sub>·3H<sub>2</sub>O with PCy<sub>3</sub> in 2-methoxyethanol under a

nitrogen atmosphere to generate the active catalytic species, OsHCl(CO)(PCy<sub>3</sub>)<sub>2</sub>, according to the procedure of Esteruelas and Werner.<sup>22</sup> OsHCl(CO)(O<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub> was prepared by exposing a hexane suspension of the active species to pure oxygen gas as given by Esteruelas et al.<sup>23</sup> The catalytic complex was washed with cold hexane and then dried under vacuum. Found for OsHCl(CO)(PCy<sub>3</sub>)<sub>2</sub>: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ -33.06 (br.), <sup>31</sup>P{<sup>1</sup>H}NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 37.5 (s). OsHCl(CO)(O<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub>: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ -2.99 (t), <sup>31</sup>P{<sup>1</sup>H}NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 16.63 (s).

### Hydrogenation in batch reactor

Hydrogenation reactions were carried out in a 300 mL Parr pressure reactor. In a typical experiment, a specific amount of latex was weighed and mixed with in 150 mL of solvent. The catalyst was weighed and loaded in to a catalyst addition device. The latex/solvent mixture was transferred into the reactor. The autoclave was purged with hydrogen gas and then pressurized with hydrogen to 24.6 bar prior to heating to the desired reaction temperature. When thermal equilibrium was reached in the reactor, the catalyst was added by applying pressurized hydrogen gas to the catalyst addition device and the hydrogen pressure was adjusted to the desired reaction pressure. During hydrogenation, the mixture was stirred at a constant speed of 600 rpm. The reaction mixture was maintained at the desired temperature and pressure for a given reaction time. After hydrogenation, hydrogenated rubber was precipitated in ethanol and dried under vacuum at room temperature.

### Kinetic study of NRL hydrogenation

Kinetic data were obtained from hydrogen consumption profiles obtained using a gas uptake apparatus developed by Mohammadi and Rempel.<sup>24</sup> This equipment can maintain isothermal (±1°C) and isobaric (±0.02 bar) conditions throughout the hydrogenation process. The NRL mixtures were prepared by dissolving the desired amount of NRL in 150 mL of monochlorobenzene. Catalyst was weighed into a small glass bucket and placed in a port of the reactor head. For experiments performed with added acid, the desired amount of acid was added to the latex/solvent mixture. The rubber latex mixture was degassed by charging with hydrogen gas at 13.8 bar followed by evacuation three times. Hydrogen gas was then passed through the reactor for 20 min while stirring the mixture at 1200 rpm. The reactor was then heated to the desired temperature and the pressure adjusted to the reaction pressure. Once liquid/vapor equilibrium at the desired conditions was established, the catalyst was released by using an overpressure of hydrogen. The amount of hydrogen consumed by the

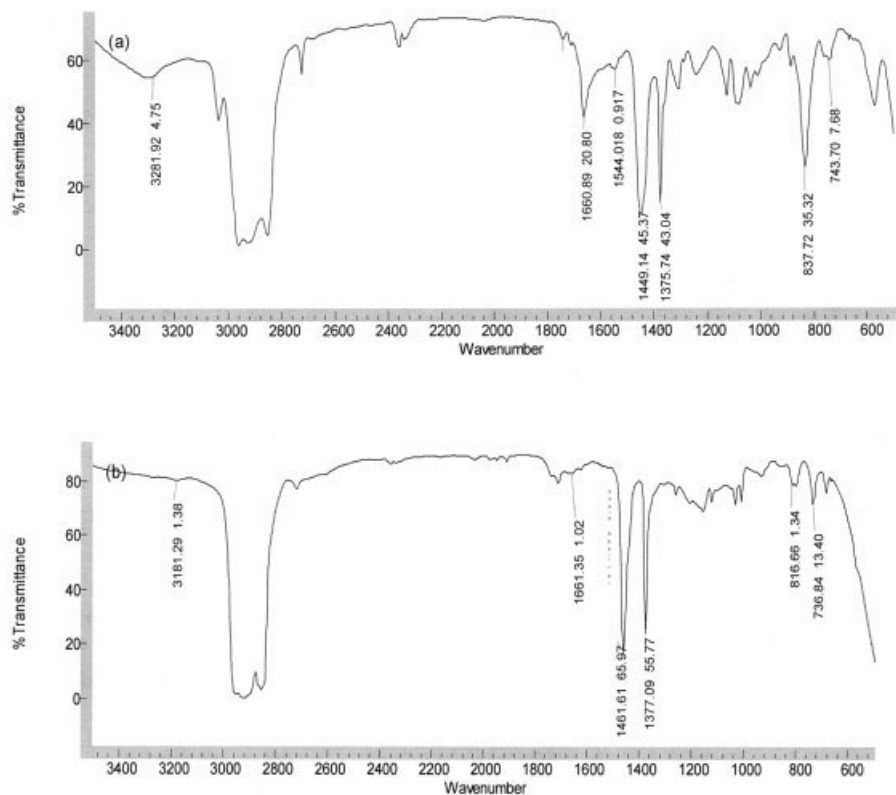


Figure 1 FTIR spectra of (a) NRL and (b) HNRL.

reaction as a function of time and the solution temperature were recorded over the course of the reaction. Each experiment proceeded until no further uptake was recorded, after which the reactor was cooled and the hydrogenated product was isolated by precipitation with ethanol and then dried in vacuum.

### Characterization

The structure of hydrogenated NRL and the exact final conversion provided by the hydrogen consumption profile were confirmed by FTIR and  $^1\text{H}$  NMR spectroscopy. The samples were prepared by casting a film on NaCl plates for FTIR scan obtained on a BIO-RAD Merlin FTS 3000X spectrometer.  $^1\text{H}$  NMR spectra of samples dissolved in  $\text{CDCl}_3$  were obtained using a Bruker 300 MHz spectrometer. The relative viscosity of solutions of hydrogenated natural rubber was also investigated;  $0.125000 \pm 0.00015$  g of HNRL samples were dissolved in 25 mL of toluene at  $35^\circ\text{C}$  and then transferred to an Ubbelohde capillary viscometer through a coarse, sintered-glass filter to separate the insoluble gel in the rubber solution. The relative viscosity data ( $\eta_{\text{rel}}$ ) was reported as the viscosity relative to pure solvent.

Differential scanning calorimetry (DSC) of the sample was carried out on a TA Instrument DSC Model 2920. The instrument signal was derived from the

temperature difference between sample and the reference. The rubber samples were cooled to  $-100^\circ\text{C}$  with liquid nitrogen and then heated at a constant rate of  $20\text{--}25^\circ\text{C}/\text{min}$ . The glass transition temperature ( $T_g$ ) was calculated from the midpoint of the base-line shift of DSC thermogram.

Thermogravimetric analysis (TGA) of the sample was performed on a Perkin-Elmer Pyris Diamond TG/DTA. The temperature was raised under a nitrogen atmosphere from room temperature to  $700^\circ\text{C}$  at a constant heating rate of  $10^\circ\text{C}/\text{min}$ . The flow rate of nitrogen gas was 50 mL/min. The initial decomposition temperature ( $T_{\text{id}}$ ) and the temperature at the maximum of mass loss rate ( $T_{\text{max}}$ ) were evaluated.

## RESULTS AND DISCUSSION

### Hydrogenation catalyzed by various catalysts

The FTIR spectrum for the starting NRL and for the HNRL are shown in Figures 1(a) and 1(b) respectively. The most apparent change in the FTIR spectra are the reduction in the band at 1660 and  $837\text{ cm}^{-1}$  due to  $\text{C}=\text{C}$  stretching and olefinic bending. The augmentation in the band at  $735\text{ cm}^{-1}$  attributed to the  $-(\text{CH}_2)-$  species increases, as the extent of hydrogenation of  $\text{C}=\text{C}$  increases. FTIR spectra indicated that the transmittance at  $3280\text{ cm}^{-1}$  and  $1544\text{ cm}^{-1}$ , which

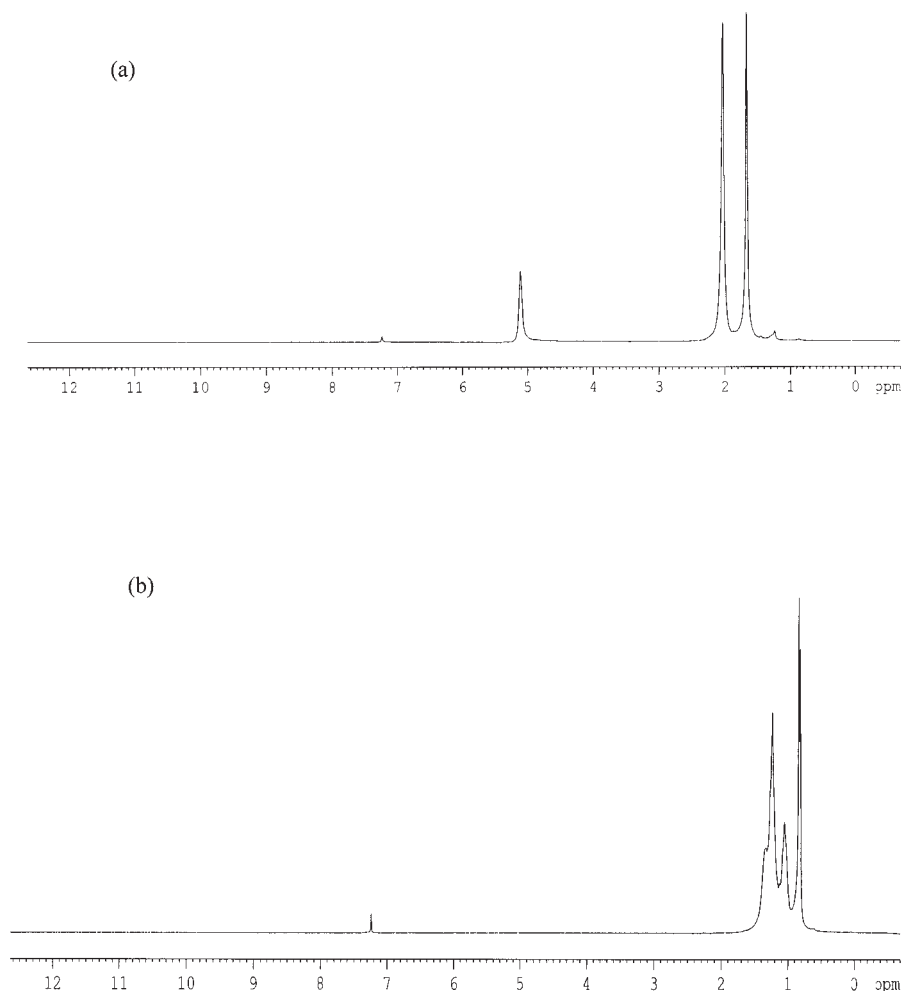


Figure 2  $^1\text{H}$  NMR spectra of (a) NRL and (b) HNRL.

represents N—H stretching and N—C=O amide II vibration (an impurity in NRL),<sup>25</sup> remained unchanged. The final degree of hydrogenation was determined by  $^1\text{H}$  NMR. A comparison between the  $^1\text{H}$  NMR spectrum of NRL and HNRL is shown in Figures 2 (a) and 2(b) respectively. The hydrogenation led to the reduction in the intensity of the peaks at 1.67, 2.03, and 5.14 ppm, which are assigned to  $-\text{CH}_3$ ,  $-\text{CH}_2$ , and olefinic protons, respectively, and the appearance of new peaks at 0.8 and 1.2 attributed to saturated  $-\text{CH}_2$  and  $-\text{CH}_3$  of the hydrogenation product. Confirmation was obtained from  $^{13}\text{C}$  NMR spectrum as shown in Figures 3(a) and 3(b). The polymer product is a strictly alternating copolymer of ethylene propylene. The peak areas at 135.4 and 125.2 ppm decrease with an increase in the reduction of the olefinic carbons and four new peaks appear at 37.8, 33.1, 24.8, and 20.0 ppm, whose areas attributed to  $\text{C}\alpha$ ,  $-\text{CH}$ ,  $\text{C}\beta$  and  $-\text{CH}_3$  carbons, respectively.

The catalytic hydrogenation data for NRL using various catalysts with and without acid at the same reaction conditions, from the batch reactor, are sum-

marized in Table I. All of the catalysts investigated are known to be active for hydrogenation of diene polymers.  $\text{RuCl}(\text{CO})(\text{styryl})(\text{PCy}_3)_2$ ,  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ , and  $[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$  were also found to be active for hydrogenation of NRL at  $150^\circ\text{C}$  in monochlorobenzene with acid addition. In the present study,  $\text{RhCl}(\text{PPh}_3)_3$  was not very effective as a catalyst for the hydrogenation of NRL, although Singha et al.,<sup>4</sup> reported that 80% hydrogenation of natural rubber was obtained in 22 h. In the present study, it is quite probable that  $\text{RhCl}(\text{PPh}_3)_3$  forms an inactive complex species with an impurity in the latex. These results are consistent with those of Charmondusit et al.,<sup>26</sup> who studied hydrogenation of polyisoprene,  $\text{OsHCl}(\text{O}_2)(\text{PCy}_3)_2$  was found to be the best catalyst for hydrogenation of NRL. The rate of hydrogenation was faster than that with  $\text{RuCl}(\text{CO})(\text{styryl})(\text{PCy}_3)_2$  and  $[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$  with acid and without acid. In the examples with added acid,  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  was capable of providing a hydrogenation level of  $>90\%$  of  $\text{C}=\text{C}$  bonds of NRL in 4 h. It is obvious that addition of acid played a key

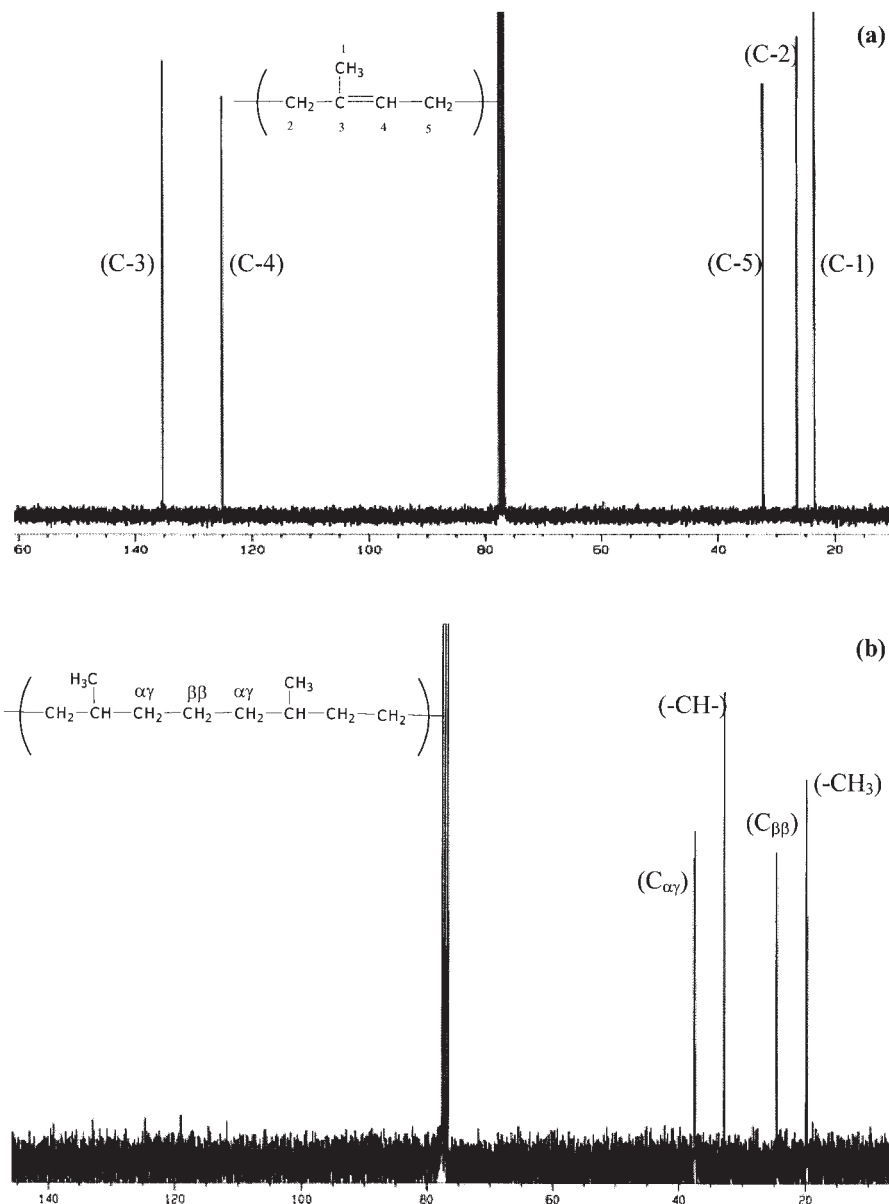


Figure 3  $^{13}\text{C}$  NMR spectra of (a) NRL and (b) HNRL.

role in enhancing the hydrogenation of NRL. The effect of acid will be discussed in more detail.

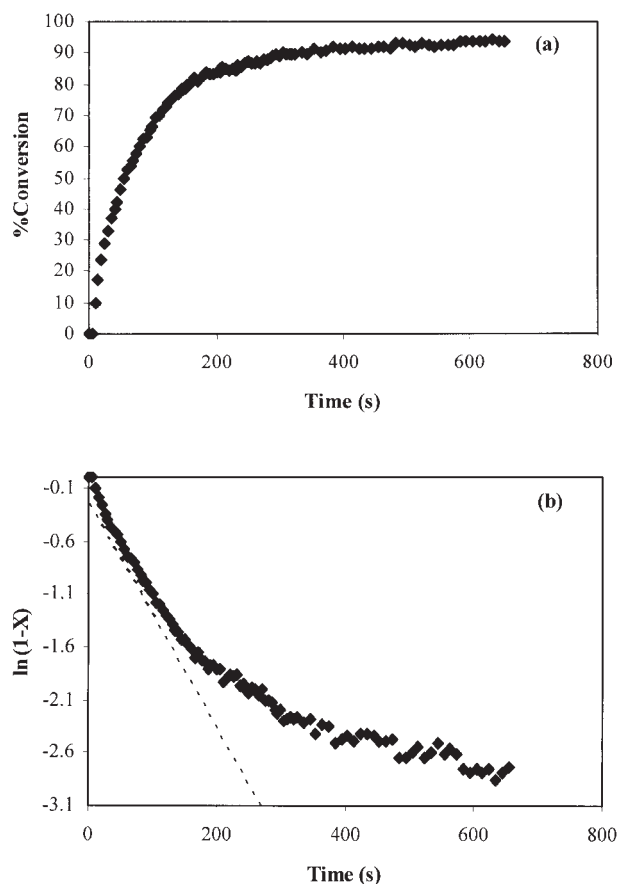
#### Kinetics of NRL hydrogenation in the presence of $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$

For all the kinetic studies of NRL hydrogenation,  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  functioned as an effective catalyst precursor. The computer control gas uptake apparatus was used to investigate the rate dependence of reaction variables, such as polymer concentration, catalyst concentration, acid concentration, temperature, and hydrogen pressure. A representative hydrogen uptake profile corresponding to the olefin consumption with respect to time is shown in Figure 4. The

TABLE I  
Results of NRL Hydrogenation Catalyzed by Various Catalysts

Expt.	Catalyst type	[p-TSH] (mM)	Time (h)	% Conversion
1	$\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$	—	6	25.5
2	$\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$	7	3	95.8
3	$[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$	—	6	16.3
4	$[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$	7	3	67.5
5	$\text{RuCl}(\text{CO})(\text{styryl})(\text{PCy}_3)_2$	—	6	13.5
6	$\text{RuCl}(\text{CO})(\text{styryl})(\text{PCy}_3)_2$	7	3	59.4
7	$\text{RhCl}(\text{PPh}_3)_3$	—	6	5.2
8	$\text{RhCl}(\text{PPh}_3)_3$	7	3	10.0

Condition: [catalyst], 145  $\mu\text{M}$ ;  $\text{P}_{\text{H}_2}$ , 27.6 bar;  $[\text{C}=\text{C}]$ , 180 mM;  $T$ , 150°C in monochlorobenzene.



**Figure 4** (a) Olefin conversion profile of NRL hydrogenation obtained from gas-uptake apparatus and (b)  $\ln(1-x)$  vs. time plot (— model from linear regression).  $[\text{Os}] = 140 \mu\text{M}$ ;  $\text{C}=\text{C} = 150 \text{ mM}$ ;  $P_{\text{H}_2} = 27.6 \text{ bar}$ ;  $[p\text{-TSA}] = 9 \text{ mM}$ ;  $T = 150 \text{ }^\circ\text{C}$  in monochlorobenzene.

hydrogen consumption plot exhibits an apparent first-order dependence for hydrogenation of  $\text{C}=\text{C}$  concentration over the first 75% of the reaction. The first-order rate equation as shown in eq. (1), where  $k'$  is a pseudo first-order rate constant representing the hydrogenation process.

$$-\frac{d[\text{H}_2]}{dt} = -\frac{d[\text{C}=\text{C}]}{dt} = k'[\text{C}=\text{C}] \quad (1)$$

Although the  $\ln(1-x)$  vs. time plot deviates from linearity in the latter stage of reaction,  $k'$  can still be calculated with a fair degrees of confidence. Impurities in the NRL were believed to cause a reduction in catalytic activity as the degree of hydrogenation increased and therefore the  $\ln(1-x)$  versus time plot data deviates from the linear model.

### Two-level factorial design

To determine the significance of joint factor interactions, a two level factorial design was used.<sup>27</sup> Four

principal factors, which were considered to have an effect on the NRL hydrogenation rate, are concentration of rubber as present in terms of carbon-carbon double bond concentration, concentration of  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ , hydrogen pressure, and concentration of  $p\text{-TSA}$ . When a two-level factorial design was applied to calculate the effect of a parameter in the experiment, the level of the factor may be arbitrarily called "low (-)" and "high (+)". The range of rubber concentration, catalyst concentration, hydrogen pressure, and  $p\text{-TSA}$  concentration were 150–300 mM, 120–170  $\mu\text{M}$ , 20.7–41.4 bar, and 6–12 mM in monochlorobenzene, respectively. The reaction temperature was kept constant at 150 $^\circ\text{C}$ . In Table II, the results for factorial design experiments are presented. Yate's algorithm was applied to investigate the main effects and interaction effects on the rate constant derived from the experiment.<sup>28</sup> Tables III and IV represent the results of Yate's algorithm calculation and the calculation of effects and standard error of  $2^4$  factorial experiment. The results in Table III indicated that  $[\text{Os}]$ ,

**TABLE II**  
Results from  $2^4$  Factorial Design Experiment for NRL Hydrogenation

Expt.	$[\text{Os}]$ ( $\mu\text{M}$ )	$P_{\text{H}_2}$ (bar)	$[\text{C}=\text{C}]$ (mM)	$[p\text{-TSA}]$ (mM)	$k' \times (10^3; \text{s}^{-1})$
1	120	20.7	150	6	1.77
2	120	20.7	150	6	1.61
3	170	20.7	150	6	4.89
4	170	20.7	150	6	4.84
5	120	41.4	150	6	1.92
6	120	41.4	150	6	1.78
7	170	41.4	150	6	4.99
8	170	41.4	150	6	5.19
9	120	20.7	300	6	0.22
10	120	20.7	300	6	0.33
11	170	20.7	300	6	2.92
12	170	20.7	300	6	3.05
13	120	41.4	300	6	0.24
14	120	41.4	300	6	0.26
15	170	41.4	300	6	2.91
16	170	41.4	300	6	3.07
17	120	20.7	150	12	6.97
18	120	20.7	150	12	6.83
19	170	20.7	150	12	12.13
20	170	20.7	150	12	11.89
21	120	41.4	150	12	7.83
22	120	41.4	150	12	7.67
23	170	41.4	150	12	12.90
24	170	41.4	150	12	13.09
25	120	20.7	300	12	0.94
26	120	20.7	300	12	1.02
27	170	20.7	300	12	3.32
28	170	20.7	300	12	3.42
29	120	41.4	300	12	1.39
30	120	41.4	300	12	1.37
31	170	41.4	300	12	3.83
32	170	41.4	300	12	3.98

Condition:  $T = 150 \text{ }^\circ\text{C}$  in monochlorobenzene.

TABLE III  
Yate's Algorithm Calculation of the 2<sup>4</sup> Factorial Experiment

Expt.	[Os] ( $\mu\text{M}$ )	P <sub>H<sub>2</sub></sub> (bar)	[C≡C] (mM)	[p-TSA] (mM)	k' average (s <sup>-1</sup> )	1	2	3	4	Divisor	Estimate	Identification
1	-	-	-	-	0.00169	0.00656	0.01349	0.02000	0.06928	16	0.004330	Average
2	+	-	-	-	0.00486	0.00694	0.00650	0.04928	0.02713	8	0.003391	[Os]
3	-	+	-	-	0.00185	0.00326	0.03965	0.01186	0.00312	8	0.000391	PH <sub>2</sub>
4	+	+	-	-	0.00509	0.00324	0.00963	0.01527	0.00035	8	0.000043	[Os] · PH <sub>2</sub>
5	-	-	+	-	0.00027	0.01891	0.00641	0.00036	-0.03702	8	—	[C≡C]
6	+	-	+	-	0.00299	0.02074	0.00545	0.00276	-0.00640	8	0.004627	[Os] · [C≡C]
7	-	+	+	-	0.00025	0.00435	0.01035	0.00009	-0.00131	8	0.000800	PH <sub>2</sub> · [C≡C]
8	+	+	+	-	0.00299	0.00528	0.00492	0.00026	-0.00004	8	0.000164	[Os] · PH <sub>2</sub> · [C≡C]
9	-	-	-	+	0.0069	0.00317	0.00038	-0.00699	0.02929	8	0.000005	[p-TSA]
10	-	-	-	+	0.01201	0.00323	-0.00002	-0.03003	0.00341	8	0.003661	[Os] · [p-TSA]
11	-	+	-	+	0.00775	0.00271	0.00184	-0.00096	0.00240	8	0.000427	PH <sub>2</sub> · [p-TSA]
12	+	+	-	+	0.01299	0.00274	0.00093	-0.00544	0.00017	8	0.000300	[Os] · PH <sub>2</sub> · [p-TSA]
13	-	-	+	+	0.00098	0.00511	0.00006	-0.00040	-0.02303	8	0.000022	[C≡C] · [p-TSA]
14	+	-	+	+	0.00337	0.00524	0.00002	-0.00091	-0.00448	8	0.002879	[Os] · [C≡C] · [p-TSA]
15	-	+	+	+	0.00138	0.00239	0.00013	-0.00004	-0.00051	8	0.000560	PH <sub>2</sub> · [C≡C] · [p-TSA]
16	+	+	+	+	0.0039	0.00252	0.00013	0.00000	0.00004	8	0.000063	[Os] · PH <sub>2</sub> · [C≡C] · [p-TSA]
											0.000005	

**TABLE IV**  
**Calculation of Effects and Standard Errors for 2<sup>4</sup>**  
**Factorial Design Experiment**

Effect	Estimate ± Standard
<b>Average</b>	0.004330 ± 3.54E-05
<b>Main effect</b>	
Catalyst concentration, [Os]	0.003391 ± 1.77E-05
Hydrogen pressure, P <sub>H<sub>2</sub></sub>	0.000391 ± 1.77E-05
Rubber concentration, [C=C]	-0.004627 ± 1.77E-05
<b>Acid concentration, [p-TSA]</b>	0.003661 ± 1.77E-05
<b>Two-factor interaction</b>	
[Os] · P <sub>H<sub>2</sub></sub>	0.000043 ± 1.77E-05
[Os] · [C=C]	-0.000800 ± 1.77E-05
[Os] · [p-TSA]	0.000427 ± 1.77E-05
P <sub>H<sub>2</sub></sub> · [C=C]	-0.000164 ± 1.77E-05
P <sub>H<sub>2</sub></sub> · [p-TSA]	0.000300 ± 1.77E-05
[C=C] · [p-TSA]	-0.002879 ± 1.77E-05
<b>Three-factor interaction</b>	
[Os] · P <sub>H<sub>2</sub></sub> · [C=C]	-0.000005 ± 1.77E-05
[Os] · P <sub>H<sub>2</sub></sub> · [p-TSA]	0.000022 ± 1.77E-05
[Os] · [C=C] · [p-TSA]	-0.000560 ± 1.77E-05
P <sub>H<sub>2</sub></sub> · [C=C] · [p-TSA]	-0.000063 ± 1.77E-05
<b>Four-factor interaction</b>	
[Os] · P <sub>H<sub>2</sub></sub> · [C=C] · [p-TSA]	0.000005 ± 1.77E-05

[C=C], [p-TSA], and the interaction between [C=C] and [p-TSA] had a very strong influence on the hydrogenation rate, whereas the effect of P<sub>H<sub>2</sub></sub> and other interactions were moderate for the system. The [Os], P<sub>H<sub>2</sub></sub>, and [p-TSA] had a positive effect. This implies that the rate of hydrogenation increased with an increase in [Os], P<sub>H<sub>2</sub></sub>, and [p-TSA]. In contrast, [C=C] and interaction between [C=C] and [p-TSA] showed a large negative effect on the hydrogenation rate constant. It can be postulated that the impurities in NRL have an effect on hydrogenation rate. The other binary interactions, [Os]·[C=C], [Os] P<sub>H<sub>2</sub></sub>, [Os] [p-TSA], P<sub>H<sub>2</sub></sub> [C=C], and P<sub>H<sub>2</sub></sub> [p-TSA] also affected the hydrogenation rate, but the three factor and four factor interactions were not highly significant.

### Univariate kinetic experiment

As mentioned above, factorial design is generally used for the experiments involving several factors to study only the main effect and joint effects of factors on the response. The factorial design established the significance of joint factor interaction without determining the functional form. The univariate components augment the factorial study by exploring how each variable influences the hydrogenation rate in isolation. The univariate experiment data are presented in Table V.

### Effect of catalyst concentration

Two sets of experiments were performed to determine the effect of catalyst loading on the rate of hydrogenation. The two sets were carried out under a hydro-

gen pressure of 27.6 bar and 44.1 bar, respectively. The range of [Os] was between 30 and 160 μM, [C=C] = 150 mM, and [p-TSA] = 9 mM at 150°C in monochlorobenzene. The influence of catalyst concentration on the reaction system is illustrated in Figure 5. It can be seen that the reaction rate is linearly proportional to the total catalyst concentration at every hydrogen pressure. It indicated that the active species is linearly proportional to catalyst precursor loading. This observation is consistent with the work of Andriollo et al.<sup>29</sup> It is seen that NRL hydrogenation had a first-order dependence with respect to catalyst concentration. It suggested that this catalyst is a mononuclear active complex. On comparing the present data with that obtained by Charmondusit et al.<sup>26</sup> for hydrogenation of *cis*-1,4-poly isoprene and Parent et al.<sup>30</sup> for hydrogenation of NBR, the dependence on catalyst concentration is the same. The plots of NRL hydrogenation show an intercept on the *x*-axis. This suggests that in the NRL, some portion of the osmium complex reacts with impurities in the NRL and is therefore inactive.

### Effect of rubber concentration

A series of experiments was carried out at varying polymer concentration to examine the effect of rubber concentration. The rubber concentration used ranged from 65 to 400 mM when catalyst concentration (140 μM), reaction temperature (150°C), hydrogen pressure (27.6 bar), and *p*-toulenesulfonic acid (9 mM) were kept constant. The results of these experiments are shown in Figure 6. The results obtained indicated that the reaction rate decreased with an increase in rubber concentration. In contrast, the hydrogenation rate of PIP is constant when the rubber concentration is increased, which is as expected for systems showing a strict first-order behavior.<sup>25</sup> For NBR, a decreasing rate of hydrogenation with an increase in rubber concentration was observed. The nitrile functional group in NBR is known to reversibly coordinate to OsHCl(CO)(O<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub> as the nitrogen lone pair of electrons binds to the metal center.<sup>30</sup> This behavior has also been observed for NBR hydrogenation catalyzed by [Rh(diene)(NBD<sub>2</sub>)]<sup>+</sup>,<sup>31</sup> RhCl(PPh<sub>3</sub>)<sub>3</sub>,<sup>32</sup> RhH-(PPh<sub>3</sub>)<sub>4</sub>,<sup>32</sup> and RuCl(CO)(styryl)(PCy<sub>3</sub>)<sub>2</sub>.<sup>33</sup> The reduction in the NRL hydrogenation rate can be explained by the effect of impurities in the latex. It is generally believed that impurities such as protein in the rubber latex might compete with olefin for metal coordination sites to form inactive complexes. The effect of impurities is reported in a later section of this paper.

### Effect of hydrogen pressure

To investigate the effect of hydrogen pressure, a series of experiments in which the hydrogen pressure was varied over the range 2.1–41.4 bar at 150°C in mono-



TABLE V  
Univariate of Kinetic Data of NRL Hydrogenation Catalyzed by OsHCl(CO)(O<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub>

Expt.	[Os] ( $\mu$ M)	[C=C] (mM)	P <sub>H<sub>2</sub></sub> (bar)	Temp. (°C)	[ <i>p</i> -TSH] (mM)	%Hydrogenation in 10 min	$k' \times$ (10 <sup>3</sup> s <sup>-1</sup> )	$\eta_{rel}$
33	30	150	27.6	150	9	20.0	0.35	6.32
34	60	150	27.6	150	9	57.8	2.84	6.48
35	80	150	27.6	150	9	70.8 (7.8 min)	4.09	7.63
36	100	150	27.6	150	9	85.5	5.46	8.77
37	140	150	27.6	150	9	95.8 (8 min)	8.59	8.95
38	160	150	27.6	150	9	97.0	9.75	8.99
39	30	150	41.4	150	9	35.4	0.88	—
40	60	150	41.4	150	9	56.9	3.13	—
41	80	150	41.4	150	9	73.9	4.66	—
42	100	150	41.4	150	9	88.8	5.95	—
43	140	150	41.4	150	9	96.4 (8.9 min)	8.67	—
44	160	150	41.4	150	9	98.2	10.45	—
45	140	150	2.1	150	9	68.5	1.99	7.11
46	140	150	3.4	150	9	70.9	3.49	7.78
47	140	150	5.2	150	9	80.5	6.77	8.74
48	140	150	6.9	150	9	88.9	7.51	8.86
49	140	150	13.8	150	9	91.2	8.35	8.90
50	140	150	27.6	150	9	96.5	8.61	8.96
51	140	150	27.6	150	9	95.8	8.60	8.96
52	140	150	27.6	150	9	96.9	8.61	—
53	140	150	27.6	150	9	96.8 (8.5 min)	8.60	—
54	140	150	41.4	150	9	97.6	8.65	9.00
55	140	150	41.4	150	9	97.7	8.70	—
56	140	65	27.6	150	9	99.1 (7 min)	14.50	5.25
57	140	100	27.6	150	9	98.8 (8.3 min)	12.50	6.41
58	140	150	27.6	150	9	95.4 (9.2 min)	8.60	8.95
59	140	150	27.6	150	9	95.5 (8.9 min)	8.60	—
60	140	150	27.6	150	9	96.0	8.61	—
61	140	200	27.6	150	9	77.8	4.06	7.65
62	140	250	27.6	150	9	40.3	1.25	6.48
63	140	400	27.6	150	9	15.4	0.58	6.32
64	140	150	27.6	150	0.0	4.4	0.10	4.80
65	140	150	27.6	150	0.4	10.5	0.25	5.10
66	140	150	27.6	150	2.1	14.7	0.30	5.20
67	140	150	27.6	150	6.0	40.0	1.42	6.48
68	140	150	27.6	150	9.0	97.3 (7.8 min)	8.62	8.96
69	140	150	27.6	150	9.0	95.5	8.60	—
70	140	150	27.6	150	9.0	96.8	8.61	—
71	140	150	27.6	150	11.8	97.7	9.94	5.46
72	140	150	27.6	150	19.8	86.6	6.05	4.82
73	140	150	27.6	150	27.7	85.3	5.49	4.76
74	140	150	27.6	120	9	54.0	2.12	—
75	140	150	27.6	130	9	73.0	3.78	—
76	140	150	27.6	140	9	84.8	6.21	—
77	140	150	27.6	150	9	95.5	8.65	—
78	140	150	27.6	160	9	99.2	10.7	—

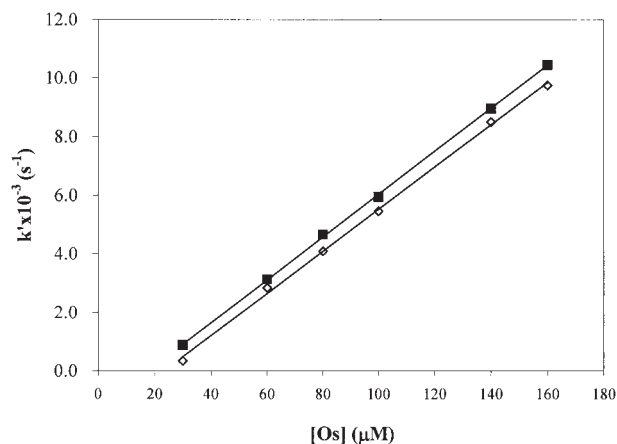
Solvent, monochlorobenzenes relative viscosity of NRL, 455 NR in toluene ( $\eta_{rel}$ ), 7.52.

chlorobenzene was carried out. The concentration of catalyst and rubber were kept constant at 140  $\mu$ M and 150 mM, respectively. The results shown in Figure 7 suggest that the rate of NRL hydrogenation may be second-order to first-order with respect to the hydrogen pressure from 2.1 to 6.9 bar and then shifts to a zero-order dependence at a pressure higher than 13.8 bar. These results are in agreement with those for NBR<sup>30</sup> and PIP<sup>26</sup> hydrogenation in the presence of the OsHCl(CO)(O<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub> catalyst system, whereas NBR hydrogenation using the rhodium complex, Rh-

Cl(PPh<sub>3</sub>)<sub>3</sub>, is found to shift from a first-order to zero-order behavior with increasing hydrogen pressure.<sup>32</sup> In the case of NBR hydrogenation in the presence of the ruthenium complex, RuCl(CO)(styryl)(PCy<sub>3</sub>)<sub>2</sub>, a strict first-order behavior is maintained irrespective of the hydrogen pressure used.<sup>33</sup>

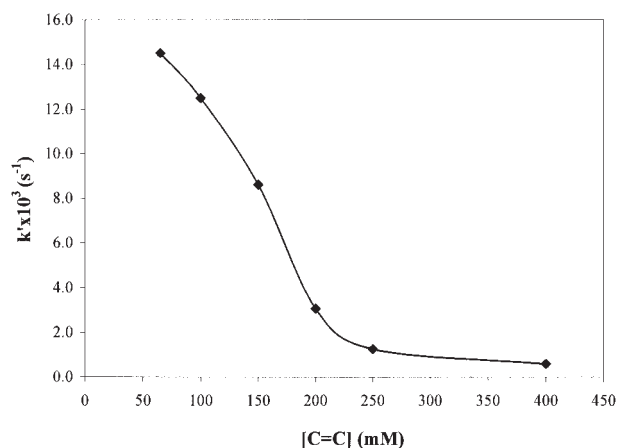
#### Effect of acid addition

Guo and Rempel<sup>34</sup> established that carboxylic acid enhanced the catalytic activity of RuCl(CO)(styryl)(PCy<sub>3</sub>)<sub>2</sub>

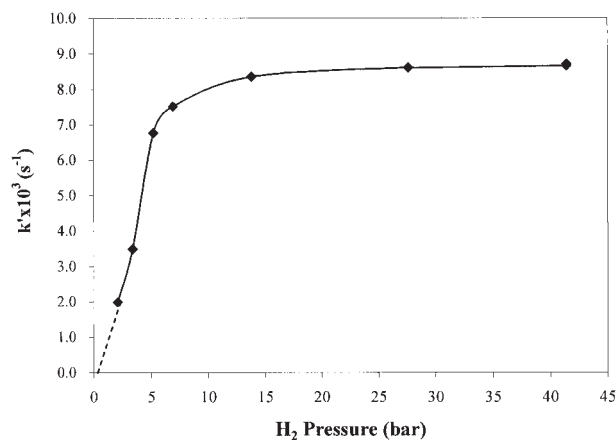


**Figure 5** Effect of catalyst concentration on NRL hydrogenation.  $[C=C] = 150$  mM;  $P_{H_2} = 27.6$  bar;  $[p\text{-TSA}] = 9$  mM;  $T = 150^\circ\text{C}$  in monochlorobenzene;  $P_{H_2} = 27.6$  ( $\diamond$ ) and  $41.4$  ( $\blacksquare$ ) bar.

in the hydrogenation of NBR emulsions. It was suggested that carboxylic acids were very effective in preventing the poisoning of the catalyst. Yi et al.<sup>35</sup> also found that the addition of acid increased the catalytic activity due to the selective entrapment of the dissociated phosphine ligand and the formation of a 14-electron ruthenium-mono species in alkene hydrogenation by  $\text{RuHCl}(\text{CO})(\text{PCy}_3)_2$ . The effect of the acid type was also studied. In this investigation, experiments were carried out at a catalyst concentration of  $140 \mu\text{M}$ , rubber concentration of  $150$  mM, acid concentration of  $9$  mM, hydrogen pressure of  $27.6$  bar, and temperature of  $150^\circ\text{C}$  in monochlorobenzene. Table VI shows the effect of the acid type. It was found that *p*-TSA addition led to the highest hydrogenation rate. It is believed that the strong acid increases the hydrogenation rate more than the weaker acids do.



**Figure 6** Effect of rubber concentration on NRL hydrogenation.  $[\text{Os}] = 140 \mu\text{M}$ ;  $P_{H_2} = 27.6$  bar;  $[p\text{-TSA}] = 9$  mM;  $T = 150^\circ\text{C}$  in monochlorobenzene.



**Figure 7** Effect of hydrogen pressure on NRL hydrogenation.  $[\text{Os}] = 140 \mu\text{M}$ ;  $[C=C] = 150$  mM;  $[p\text{-TSA}] = 9$  mM;  $T = 150^\circ\text{C}$  in monochlorobenzene.

Also, *p*-TSA is noncoordinating with respect to the osmium complex. The strong acid likely reacts with impurities in the NRL more efficiently than the weaker acid; therefore, the rate of hydrogenation was increased. From Figure 8, it is seen that the rate of hydrogenation increased with increasing acid concentration from  $0.03$  to  $9$  mM, then diminished, and leveled off at acid concentrations above  $9.5$  mM.

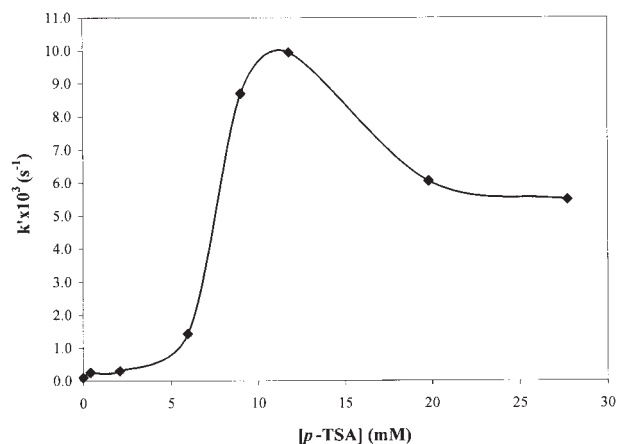
For NRL hydrogenation, it is possible that the acid neutralized the impurity in the NRL and prevented the poisoning of the catalyst. Consequently, the hydrogenation rate was increased. The hydrogenation rate slowly increased over the range of  $0.02$ – $6$  mM. It seems that NRL needs some portion of acid to react with some main impurities in the system, such as ammonia or perhaps the protein. Over the range of  $6.0$ – $9$  mM added acid, the hydrogenation rate was drastically increased. However, at above  $9.5$  mM added acid, the hydrogenation rate decreased. It is quite likely that at higher acid concentration, free excess *p*-TSA that does not interact with any further impurities could reduce the hydrogenation rate. There are two possible ways to explain this result. The first maybe due to the fact that *p*-TSA easily dissociates to  $\text{SO}_4^{2-}$ , which may decrease the efficiency of the cata-

**TABLE VI**  
Effect of Acid Types on NRL Hydrogenation Rate

Expt.	Acid type	$k' \times (10^3 \text{ s}^{-1})$
79	<i>p</i> -TSA	8.69
80	3-CPA <sup>a</sup>	7.89
81	Citric acid	6.77
82	Succinic acid	6.02
83	Stearic acid	1.57

Condition:  $[\text{Os}]$ ,  $140 \mu\text{M}$ ;  $P_{H_2}$ ,  $27.6$  bar;  $[C=C]$ ,  $150$  mM;  $[\text{Acid}]$ ,  $9$  mM;  $T$ ,  $150^\circ\text{C}$  in monochlorobenzene.

<sup>a</sup> 3-chloropropionic acid.



**Figure 8** Effect of acid concentration on NRL hydrogenation.  $[\text{Os}] = 140 \mu\text{M}$ ;  $[\text{C}=\text{C}] = 150 \text{ mM}$ ;  $P_{\text{H}_2} = 27.6 \text{ bar}$ ;  $T = 150^\circ\text{C}$  in monochlorobenzene.

lyst by forming an inactive catalyst species. The other reason may possibly result from the residual *p*-TSA after neutralization of the impurity in NRL that may be involved in side reactions such as polymerization, isomerization, or crosslinking reaction. Consequently, at acid concentrations above 9.5 mM, the hydrogenation rate may decrease. All side reactions may be competitive with the hydrogenation reaction. Moreover, the dried hydrogenated product at high acid level was observed to form gel when dissolved in toluene. This implies that crosslinking reactions occurred during the reaction when the added acid concentration was at a high level.

To gain more insight into the effect of added acid on the hydrogenation of NRL, *cis*-1,4-polyisoprene and hexylamine were used. These results are presented in Table VII. It was found that the addition of the acid decreased the hydrogenation rate. It is possible that the formation between the complex and  $\text{SO}_4^{2-}$  resulting from the dissociation of *p*-TSA and other side reactions occurred. Furthermore in the case of *cis*-1,4-polyisoprene, the addition of hexylamine and acid resulted in a higher hydrogenation rate compared to a reaction in which only hexylamine was added. Thus, it definitely appears that the role of the added acid in the

**TABLE VII**  
Effect of Acid Addition on Hydrogenation Rate of Synthetic *cis*-1,4-Polyisoprene (PIP)

Expt.	[ <i>p</i> -TSA] (mM)	[Hexylamine] (mM)	$k' \times (10^3 \text{ s}^{-1})$
84	—	—	7.05
85	—	1.28	0.97
86	9	—	2.85
87	9	1.28	3.74

Condition:  $[\text{Os}]$ , 140  $\mu\text{M}$ ;  $P_{\text{H}_2}$ , 27.6 bar;  $[\text{C}=\text{C}]$ , 150 mM;  $T$ , 150  $^\circ\text{C}$  in monochlorobenzene

**TABLE VIII**  
Effect of Nitrogen Content on NRL Hydrogenation Rate

Expt.	Rubber type	Nitrogen content (%)	$k' \times (10^2 \text{ s}^{-1})$
88	NRL	0.20	0.86
89	DPNRL	0.02	1.23

Condition:  $[\text{Os}]$ , 140  $\mu\text{M}$ ;  $P_{\text{H}_2}$ , 27.6 bar;  $[\text{C}=\text{C}]$ , 150 mM;  $[\textit{p}$ -TSA], 9 mM;  $T$ , 150  $^\circ\text{C}$  in monochlorobenzene.

NRL, natural rubber latex; and DPNRL, deproteinized natural rubber latex.

NRL hydrogenation was to neutralize impurities in the rubber.

### Effect of impurity

As mentioned before, the effect of impurities was suspected to reduce the hydrogenation rate. To confirm these ideas, the hydrogenation of deproteinized NRL was examined. The deproteinized rubber was prepared according to the literature method.<sup>36</sup> The experiments were carried out at a catalyst concentration of 140  $\mu\text{M}$ , rubber concentration of 150 mM, *p*-TSA concentration of 9 mM, a hydrogen pressure of 27.6 bar, and a temperature of 150 $^\circ\text{C}$ . Table VIII shows the effect of the impurity. The rate constant measured for the hydrogenation of deproteinized NRL has an appreciably higher rate constant than that of virgin NRL. It was established that the protein content in rubber caused a decrease in activity of the  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  catalyst. It is possible that the nitrogen group in protein can coordinate with active species in catalyst in much the same way as the  $-\text{CN}$  group in NBR as reported in previous work.<sup>30</sup> To clarify this idea for the effect of the impurity, an experiment was set up using *cis*-1,4-polyisoprene (CPIP) as an analogue of NRL in terms of rubber microstructure. Hexylamine and hexadecylamide, which have a nitrogen functional group similar to those in proteins, were added in the CPIP hydrogenation to test if the effect would be similar to the protein effect on hydrogenation rate of NRL. The effect of high ammonia content in latex was also investigated to see if it had an influence on hydrogenation rate. Table IX shows the effect of nitrogen-con-

**TABLE IX**  
Effect of Impurity on Hydrogenation Rate of Synthetic *cis*-1,4-Polyisoprene

Expt.	Substance	$k' \times (10^3 \text{ s}^{-1})$
90	—	7.03
91	hexylamine	0.98
92	hexadecylamide	1.24
93	ammonium hydroxide	1.02

Condition:  $[\text{Os}]$ , 140  $\mu\text{M}$ ;  $P_{\text{H}_2}$ , 27.6 bar;  $[\text{C}=\text{C}]$ , 150 mM; [impurity], 1.28 mM,  $T$ , 150  $^\circ\text{C}$  in monochlorobenzene.

TABLE X  
Effect of Dry Rubber Content on NRL  
Hydrogenation Rate

Expt.	DRC (%)	$k' \times (10^3 \text{ s}^{-1})$
94	60	8.63
95	50	6.16
96	40	4.62
97	30	3.06

Condition: [Os], 140  $\mu\text{M}$ ;  $P_{\text{H}_2}$ , 27.6 bar; [C=C], 150 mM; [*p*-TSH], 9 mM; *T*, 150 °C in monochlorobenzene.

taining additives in the rubber. The reaction conditions were [C=C] = 150 mM, [Os] = 40  $\mu\text{M}$ ,  $P_{\text{H}_2}$  = 27.6 bar, and *T* = 150°C in monochlorobenzene. It was found that all compounds with nitrogen functional groups reduced the rate constants for hydrogenation of CPIP. Hexylamine and ammonia have an amine group, which is an electron donating species and can coordinate easily with osmium. For hexadecylamide, the lone pair of electrons of the nitrogen atom can be delocalized between nitrogen and —C=O; therefore, hexadecylamide does not easily form a complex with osmium. However, the effect seen from the hexadecylamide is in line with that of hexylamine and ammonia.

#### Effect of water content in NRL

High ammonia NRL contains 40% water by weight. The rubber particles disperse in water to form an emulsion. Water present in the latex may also possibly reduce the hydrogenation rate of NRL when using the osmium catalyst. Experiments were carried out in which various amounts of water were present in the NRL in terms of percent dry rubber content (DRC) at the base condition ([Os] = 140  $\mu\text{M}$ ,  $P_{\text{H}_2}$  = 29.6 bar, [C=C] = 150 mM, [*p*-TSA] = 9 mM, and *T* = 150°C). Percent DRC means a percent of dry rubber content in the NRL. The range of DRC in this study was between 30 and 60% by weight, corresponding to 70–40% water by weight, respectively. The effect of water content within the NRL on the hydrogenation rate is summarized in Table X. It was found that the rate constant decreased when the amount of water was increased (decrease percent DRC). There are explanations for this. The first idea is that the addition of water may produce more impurities in the system by promoting the release of some protein part in the rubber particles. The more soluble protein part may form a complex with the catalyst. The second idea is based on the premise that the water may act as an impurity in this system to hinder the formation of the catalytic active species. To gain more insight about the effect of water on the NRL system, *cis*-1,4-polyisoprene was used as a model. The condition employed for this investigation are [Os] = 140  $\mu\text{M}$ ,  $P_{\text{H}_2}$  = 29.6 bar, [C=C] = 150 mM,

TABLE XI  
Effect of Dry Rubber Content on Hydrogenation Rate of  
Synthetic 4-Polyisoprene

Expt.	DRC (%)	$k' \times (10^3 \text{ s}^{-1})$
98	—	7.04
99	60	5.00
100	50	5.98
101	40	4.49
102	30	3.79

Condition: [Os], 140  $\mu\text{M}$ ;  $P_{\text{H}_2}$ , 27.6 bar; [C=C], 150 mM; [*p*-TSH], 9 mM; *T*, 150 °C in monochlorobenzene.

and *T* = 150°C. Table XI shows that a lower rate constant was found at 30% DRC. These results suggest that water acted as an inhibitor to hydrogenation in this system.

#### Effect of temperature

A series of experiments were carried out over the temperature range of 120–160°C, with catalyst concentration of 140  $\mu\text{M}$ , natural latex rubber concentration of 150 mM, *p*-TSA concentration of 9 mM, and hydrogen pressure of 27.6 bar. An Arrhenius plot of the acquired data is illustrated in Figure 9. The  $\ln k'$  vs.  $1/T$  plot was linear and yielded a correlation coefficient ( $R^2$ ) of 0.98 and a random distribution of residuals. An apparent activation energy of 57.69 kJ/mol was obtained, which suggests that the experiments occurred under chemical reaction control and that mass transfer limitation of the reaction is not a rate determining step under these conditions.

#### Solvent effect

Several solvents other than chlorobenzene were investigated for NRL hydrogenation at a catalyst concen-

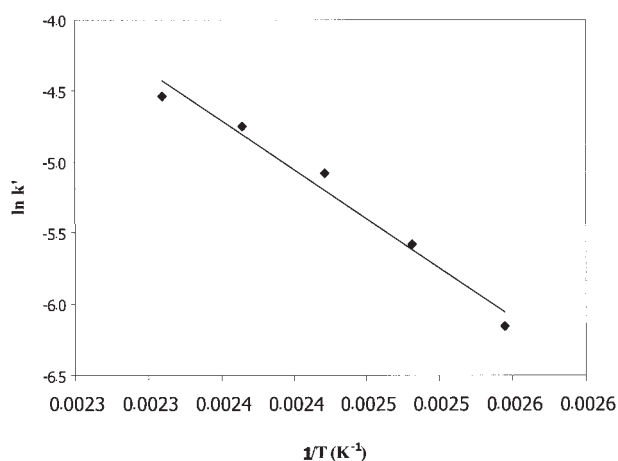


Figure 9 Arrhenius plot for NRL hydrogenation. [Os] = 140  $\mu\text{M}$ ; [C=C] = 150 mM;  $P_{\text{H}_2}$  = 27.6 bar; [*p*-TSA] 9 mM in monochlorobenzene.

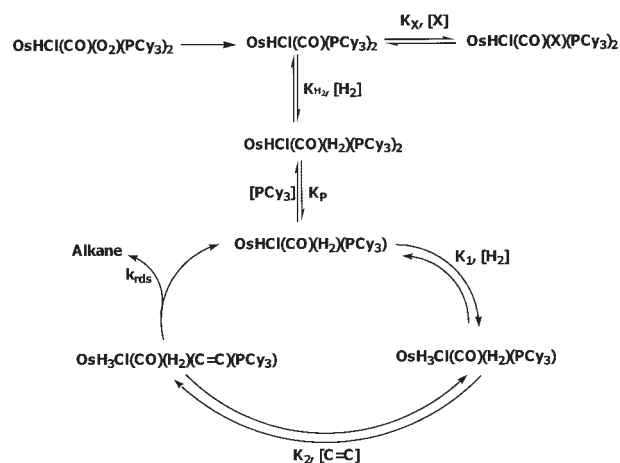
tration of 140  $\mu\text{M}$ , natural rubber from latex concentration of 150  $\text{mM}$ , *p*-TSA concentration of 9  $\text{mM}$ , hydrogen pressure of 27.6 bar, and 150°C. When NRL was added to organic solvents, then the rubber particles swelled and an increase in viscosity resulted. The water soluble impurities were believed to be dispersed in the matrix between the rubber particles. Solvents are believed to reduce the interphase between the hydrophobic (organic phase) and hydrophilic (aqueous phase) zone in the rubber particle. The rubber can move to the organic phase so that the hydrogenation reaction can take place. Table XII lists the pseudo first-order rate constant for NRL hydrogenation at the base condition. Since the solubility of hydrogen in each solvent was not known, the solvent effect contains several factors: the difference in hydrogen solubility, the homogeneity between solvent and latex rubber, and the actual effect of the solvent on the reaction parameters. Thus, few useful conclusions can be drawn from the solvent dependence. However, from the data, it seems that the solvent that has stronger polarity provides a better rate and higher conversion. The hydrogenation rate was higher in a solvent that has sufficient coordinating power to replace the tricyclohexylphosphine ligand in the catalytic cycle of the hydrogenation process. However, it should not be too strong to cause the displacement of alkenes. Solvents in the ketone series, such as methyl ethyl ketone (MEK) and butanone, were not tried because  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  is not an active hydrogenation catalyst in these solvents.<sup>30</sup> MEK is also a poor solvent for NRL and PIP.

The solvent experiments showed that the rate of reaction increased with increasing coordinating power of the solvents in the following order: THF > chlorobenzene > toluene > benzene > *p*-xylene. The higher the polarity of the solvent, the superior is the solubility of NRL, since NRL contains water and has polar groups. Low polarity solvents only swelled the rubber particle. The compatibility between particle in solvent is one of the reasons that the hydrogenation rate decreases when the polarity of the solvent decreases. In this case, the strong polarity such as provided by THF may break rubber particle to dissolve C=C in solution. When the rubber can be dissolved in solution, the rubber can more easily react with the catalyst in solution so as to provide a higher hydrogenation rate.

TABLE XII  
Effect of Solvent on NRL Hydrogenation Rate

Expt.	Solvent	$k' \times (10^2 \text{ s}^{-1})$
103	Tetrahydrofuran	1.49
104	Monochlorobenzene	0.85
105	Toluene	0.74
106	Xylene	0.16

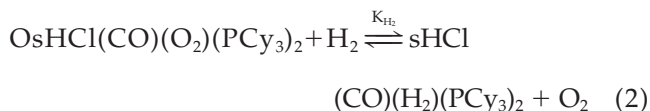
Condition: [Os], 140  $\mu\text{M}$ ; [C=C], 150  $\text{mM}$ ;  $P_{\text{H}_2}$ , 27.6 bar; [*p*-TSH], 9  $\text{mM}$ ; *T*, 150 °C.



Scheme 1 Proposed catalytic mechanism for NRL hydrogenation in presence of  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ .

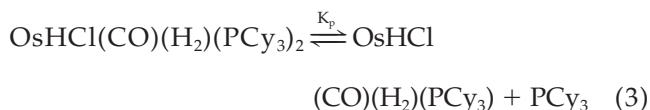
### Reaction mechanism

The catalytic cycle of diene polymer hydrogenation (PIP<sup>26</sup> and NBR<sup>30</sup> hydrogenation) in the presence of  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  has been proposed in previous works. From the kinetic data, the catalytic cycle for  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  catalyzed hydrogenation of NRL is shown in Scheme 1.

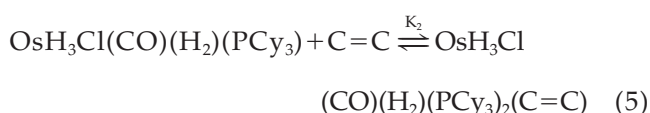
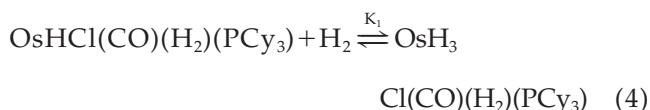


The  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  oxidatively adds molecular hydrogen to form the trihydrido metal complex  $\text{OsHCl}(\text{CO})(\text{H}_2)(\text{PCy}_3)_2$ , as shown by eq. (2).

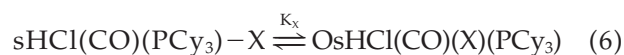
The trihydrido complex subsequently dissociates into a monophosphine complex, as shown by eq. (3).



The monophosphine complex oxidatively adds a second hydrogen molecule to form  $\text{OsH}_3\text{Cl}(\text{CO})(\text{H}_2)(\text{PCy}_3)$  and then interacts with the carbon-carbon double bonds to form the olefin complex, as shown by eqs. (4) and (5), respectively.



The behavior of impurity and water (X) in NRL on hydrogenation was similar to that seen for the nitrile functional group in NBR hydrogenation which can decrease the catalytic activity for the NBR hydrogenation at lower hydrogen pressure. It is possible that impurities in NRL might coordinate with active species of catalyst to reduce the hydrogenation activity as shown in eq. (6)



where X represents an impurity.

Parent et al.<sup>32</sup> proposed that the dihydrogen ligand of  $\text{OsHCl}(\text{CO})(\text{H}_2)(\text{PCy}_3)_2$  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  $\eta^2\text{-H}_2$  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 at lower pressure. Without it, a mechanism containing a single rate-determining step cannot be derived.

The observed kinetic isotope effect observed by Parent et al.<sup>32</sup> 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.

$$\frac{-d[\text{C}=\text{C}]}{dt} = k_{\text{rds}}[\text{OsH}_3\text{Cl}(\text{CO})(\text{H}_2)(\text{PCy}_3)(\text{C}=\text{C})] \quad (7)$$

A material balance on the osmium charged to the system is given by eq. (8).

$$\begin{aligned} [\text{Os}]_{\text{T}} = & \text{OsH}_3\text{Cl}(\text{CO})(\text{H}_2)(\text{PCy}_3)(\text{C}=\text{C}) \\ & + [\text{OsH}_3\text{Cl}(\text{CO})(\text{H}_2)(\text{PCy}_3)] + [\text{OsHCl}(\text{CO})(\text{H}_2) \\ & (\text{PCy}_3)] + [\text{OsHCl}(\text{CO})(\text{H}_2)(\text{PCy}_3)_2] \\ & + [\text{OsHCl}(\text{CO})(\text{PCy}_3)_2] \\ & + [\text{OsHCl}(\text{CO})(\text{X})(\text{PCy}_3)_2] \quad (8) \end{aligned}$$

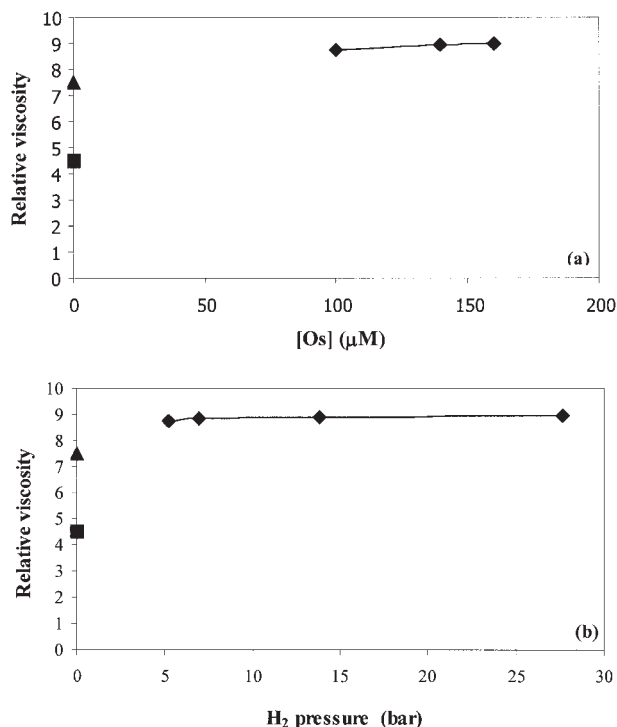
Applying the equilibrium relations defined in Scheme 1, the concentration of  $\text{OsH}_3\text{Cl}(\text{CO})(\text{H}_2)(\text{C}=\text{C})(\text{PCy}_3)$  may be substituted into eq. (7) to provide the resulting rate law, as shown by eq. (9).

$$\begin{aligned} \frac{-d[\text{C}=\text{C}]}{dt} &= \frac{[\text{Os}]_{\text{T}} K_{\text{H}_2} K_{\text{p}} K_1 K_2 [\text{C}=\text{C}] [\text{H}_2]^2}{[\text{PCy}_3] + K_{\text{H}_2} [\text{PCy}_3] [\text{H}_2] + K_{\text{X}} [\text{PCy}_3] [\text{X}] \\ &+ K_{\text{H}_2} K_{\text{p}} [\text{H}_2] + K_{\text{H}_2} K_{\text{p}} K_1 [\text{H}_2]^2 (1 + K_2 [\text{C}=\text{C}])} \quad (9) \end{aligned}$$

The rate expression derived from the mechanism is consistent with the observed kinetic data. The rate law equation for NRL hydrogenation indicates that the reaction exhibits a first-order dependence on catalyst concentration and showed an inverse behavior with respect to rubber concentration because of impurities present in the NRL and the amount of water in the system. At a hydrogen pressure lower than 6.9 bar, the second-order response of  $k'$  to hydrogen pressure was observed. The reaction rate however becomes zero-order in hydrogen when the hydrogen pressure is more than 13.9 bar.

### Relative viscosity of hydrogenated NRL

To investigate side reactions such as degradation and crosslinking during the hydrogenation reactions, dilute solution viscometry can be used to monitor the shifts of molecular weight that is related to morphology and microstructure of the polymer chains. Nevertheless, the absolute value of molecular weight of the HNRL by gel permeation chromatography technique is not yet available, as the specific refractive index increment of hydrogenated natural rubber has not been determined. Therefore, the viscosity of a dilute NRL and HNRL solution relative to the pure solvent ( $\eta_{\text{rel}}$ ) provides a simple and effective means of measuring the consequences of crosslinking and degradation of samples. The hydrogenated natural rubber samples used in the measurement of relative viscosity were produced from reactions carried out in the gas uptake apparatus described in the section for the kinetic study. Over the range of conditions  $[\text{Os}] = 30\text{--}160 \mu\text{M}$ ,  $P_{\text{H}_2} = 2.1\text{--}41.4 \text{ bar}$ ,  $[\text{C}=\text{C}] = 65\text{--}400 \text{ mM}$ ,  $[p\text{-TSA}] = 6\text{--}12 \text{ mM}$  at  $150^\circ\text{C}$ , the results obtained are shown in Table V. Figures 10(a) and 10(b) illustrates the effect of  $[\text{Os}]$  and  $P_{\text{H}_2}$  and temperature at high conversion (84.81–99.21% hydrogenation), respectively. It was found that it was difficult to determine the relative viscosity of NRL because of gel formation. The samples prepared for the latex had a high gel content, especially in the case where high acid concentration was used and low percent hydrogenation (<40%) was achieved. In the case of high acid concentration, crosslinking reaction by the residual acid after removing the impurity in the NRL was believed to be the main factor for gel formation. It is possible that residual acid can protonate radical formation to cause a crosslinking reaction in the system. In the case of low



**Figure 10** (a) Relative viscosity of HNRL as a function of total catalyst concentration (85.5–97.02% hydrogenation). [C=C] = 150 mM;  $P_{H_2}$  = 27.6 bar; [p-TSA] = 9 mM;  $T$  = 150°C. (b) Relative viscosity of HNRL as a function of hydrogen pressure (88.9–97.7% hydrogenation). [Os] = 140 μM; [C=C] = 150 mM; [p-TSA] = 9mM;  $T$  = 150°C. Relative viscosity of NRL (■) is 4.5 and relative viscosity of solid NR (▲) is 7.52.

percent hydrogenation, the residual double bond was inferred as the reason for the crosslinking reaction and gel formation. The relative viscosity of hydrogenated natural rubber varied over a wide range of 4.76–8.99 depending on the reaction condition, degree of hydrogenation, and gel formation. The actual concentration of natural rubber from latex and natural rubber from latex hydrogenated in each solvent was not known in the case where gel formation occurred. Thus, few useful conclusions can be drawn from the relative viscosity measurement. However, from the data, it seems that at high conversion and no gel formation, hydrogenated NRL has a higher relative viscosity than NRL ( $\eta_{rel}$  of rubber latex = 4.5) and natural rubber ( $\eta_{rel}$  of rubber = 7.5) at the same concentration. The relative viscosity results did not change significantly with an increase in [Os] and  $P_{H_2}$ , which is consistent with results obtained for hydrogenated *cis*-1,4-polyisoprene.<sup>25</sup>

### Thermal properties of hydrogenated NRL

Thermal analysis is used to investigate the physical properties of substrates as a function of temperature. These experiments are carried out using a differential

scanning calorimeter (DSC) and TGA apparatus to find the glass transition temperature ( $T_g$ ) and decomposition temperature, respectively. The results of decomposition temperature and  $T_g$  of HNR are shown in Table XIII.

Thermogravimetric analyses of NR, HNR, PIP, and an ethylene-propylene copolymer (EPDM) were conducted under a nitrogen atmosphere. The initial decomposition temperature ( $T_{id}$ ) was determined from the intersection of two tangents at the onset of the decomposition temperature. The maximum decomposition temperature ( $T_{max}$ ) of each sample was obtained from the peak maxima of the derivative of TG curves. The results in Table XIII show that both  $T_{id}$  and  $T_{max}$  of HNR samples increased with an increase in the reduction of carbon-carbon double bond in NR. Therefore, the hydrogenation can improve the thermal stability of NR. On comparison with standard EPDM, it was found that  $T_{id}$  and  $T_{max}$  of the completely hydrogenated NR were close to those of EPDM. It can be concluded that the structure of HNR provides a facile entry and alternative method to alternating ethylene-propylene copolymers.

$T_g$  is the transition related to the motion in the amorphous section of polymer. It is determined from the mid point of the base line shift of the DSC thermogram. The DSC thermogram of the hydrogenated sample indicated the one stop step base line shift. This implies that the HNRL sample has a single glass transition temperature. EPDM having higher  $T_g$  infers that EPDM has a higher degree of crystallinity within the polymer structure than HNRL. It can be concluded that the hydrogenation does not affect appreciably the glass transition temperature of NRL. HNRL still has a high rubbery property. This is in accord with the results reported by Singha et al.<sup>4</sup>

## CONCLUSIONS

OsHCICO(O<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub> functions as an effective catalyst system for hydrogenation of NRL in chlorobenzene.

**TABLE XIII**  
Glass Transition Temperature and Decomposition Temperature of Rubber Samples

Rubber	Hydrogenation (%)	$T_g$ (°C)	$T_{id}$ (°C)	$T_{max}$ (°C)
EPDM <sup>a</sup>	—	-48.4	452.7	470.7
PIP	—	-58.9	359.2	384.1
NRI	—	-64.03	357.2	380.9
HNRL	32.4	-63.2	369.5	395.5
	50.4	-63.1	390.4	421.3
	78.1	-62.9	421.5	450.2
	99.5	-61.8	448.5	469.2

Ethylene-propylene copolymer (EPDM) has ethylene/propylene ratio of as 70/30 and 11.5% diene content.

The kinetics of NRL were studied by monitoring hydrogen consumption using a computer gas uptake apparatus. The process showed a first-order dependence on concentration of osmium, implying that the active complex is mononuclear. Impurities, which increase with rubber at higher rubber concentration, reduce the catalytic activity. The hydrogenation showed an inverse order dependence on rubber concentration. A second-order to zero-order dependence on hydrogen pressure was found as with PIP. The hydrogenation rate was dependent on reaction temperature and an apparent activation energy for this process was 56.79 kJ/mol. The presence of a sulfonic acid in the hydrogenation process helped to prevent the poisoning of the osmium catalyst by impurities present in the emulsion system. The hydrogenation provides a method to improve the thermal stability of natural rubber without affecting its glass transition temperature.

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## References

- Brydson, J. A. *Rubber Materials and Their Compounds*; Elsevier Applied Science Publishing: New York, 1988.
- Tanaka, Y. *Rubber Chem Technol* 2001, 74, 355.
- Morton, M. *Rubber Technology*; Van Nostrand Reinhold Company: New York, 1973.
- Singha, N. K.; De, P. P.; Sivaram, S. *J Appl Polym Sci* 1997, 66, 1674.
- Schulz, D. N.; Tuner, S. R.; Golub, M. A. *Rubber Chem Technol* 1982, 55, 809.
- Singha, N. K.; Bhattacharee, S.; Sivaram, S. *Rubber Chem Technol* 1998, 70, 309.
- Kubo, Y.; Ohura, K. (to Nippon Zeon Co. Ltd.). U.S. Pat. 5,272,202 (1993).
- Rempel, G. L.; Guo, X. (to Polysar Rubber Corp.). U.S. Pat. 5,208,296 (1993).
- Murrer, B. A.; Jenkins, J. A. (to Johnson Matthey & Co. Ltd.). GB Pat. 2,070,023 (1982).
- Krause, R. L. (to Dow Chem Co.). U.S. Pat. 3,898,208 (1975).
- Parker, D. K.; Robert, R. F. *Rubber Chem Technol* 1992, 65, 245.
- Parker, D. K.; Ruthenvurg, D. M. (to The Goodyear Tire & Rubber Co./Olin Corp.). U.S. Pat. 5,424,356 (1995).
- Parker, D. K.; Purdon J. R. (to The Goodyear Tire & Rubber Co.). U.S. Pat. 5,039,737 (1991).
- Xie, H. Q.; Li, X. D.; Guo, J. S. *J Appl Polym Sci* 2003, 90, 1026.
- He, Y.; Daniels, E. S.; Klein, A.; El-Asser, M. S. *J Appl Polym Sci* 1997, 64, 2047.
- Wideman, L. G. (to The Goodyear Tire & Rubber Co.). U.S. Pat. 4,452,950 (1984).
- Singha, N. K.; Talwar, S. S.; Saviram, S. *Rubber Chem Technol* 1995, 68, 281.
- Mango, L. A.; Lenz, R. W. *Makromol Chem* 1973, 13, 163.
- Nang, T. D.; Katabe, Y.; Minoura Y. *Polymer* 1976, 17, 117.
- Osborn, J. A.; Jadine, J. A.; Wilkinson, G. *J Chem Soc A* 1966, 1711.
- Werner, H.; Esteruelas, M. A.; Otto, H. *Organometallics* 1986, 5, 2295.
- Esteruelas, M. A.; Werner, H. *Organometallic Chem* 1986, 303, 221.
- Esteruelas, M. A.; Sola, E.; Oro, L. A.; Meyer, U.; Werner, H. *Angew Chem Int Ed Eng* 1988, 27, 1563.
- Mohammaddi, N. A.; Rempel, G. L. *Comput Chem Eng* 1987, 11, 27.
- Lu, F. J.; Hus, S. L. *Rubber Chem Technol* 1987, 60, 647.
- Charmondusit, K.; Prasassarakich, P.; McManus, N. T.; Rempel, G. L. *J Appl Polym Sci* 2003, 89, 142.
- Montgomery, D. C. *Design and Analysis of Experiments*; John Wiley and Sons: New York, 2001.
- Mason, R. L.; Gunst, R. F.; Hess, L. H.; *Statistical Design and Analysis of Experiments*; John Wiley and Sons: New York, 1989.
- Andriollo, M.; Esteruelas, M.A.; Meyer, U.; Oro, L. A.; Sanchez-Delgado, R. A.; Sola, E.; Valero, C.; Werner, H. *J Am Chem Soc* 1989, 111, 7431.
- Parent, J. S.; McManus, N. T.; Rempel, G. L. *Ind Eng Chem Res* 1998, 37, 4253.
- Mao, T. F.; Rempel, G. L. *J Mol Catal A* 1998, 135, 121.
- Parent, J. S.; McManus, N. T.; Rempel, G. L. *Ind Eng Chem Res* 1996, 35, 4417.
- Martin, P.; McManus, N. T.; Rempel, G. L. *J Mol Catal A* 1997, 126, 115.
- Guo, X.; Rempel, G. L. *J Appl Polym Sci* 1997, 65, 667.
- Yi, C. S.; Lee, D. W.; He, Z. *Organometallics* 2000, 19, 2909.
- Tangpakdee, J.; Tanaka, Y. *J Nat Rubber Res* 1997, 12, 112.