Hydrogenation of *cis*-1,4-Polyisoprene Catalyzed by Ru(CH=CH(Ph))Cl(CO)(PCy$_3$)$_2$

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ABSTRACT: Hydrogenation is a useful method which has been used to improve oxidative and thermal degradation resistance of diene-based polymers. The quantitative hydrogenation of *cis*-1,4-polyisoprene which leads to an alternating ethylene–propylene copolymer was studied in the present investigation. To examine the influence of key factors on the reaction, such as catalyst concentration, polymer concentration, hydrogen pressure, and temperature, a detailed study of the hydrogenation of *cis*-1,4-polyisoprene catalyzed by the Ru complex, Ru(CH=CH(Ph))Cl(CO)-(PCy$_3$)$_2$ was carried out by monitoring the amount of hydrogen consumed. Infrared and ^{1}H-NMR spectroscopic measurements confirmed the final degree of hydrogenation. The hydrogenation of *cis*-1,4-polyisoprene followed pseudo-first-order kinetics in double-bond concentration up to high conversions of double bond, under all sets of conditions studied. The kinetic results suggested a first-order behavior with respect to total catalyst concentration as well as with respect to hydrogen pressure. The apparent activation energy for the hydrogenation process, obtained from an Arrhenius plot, was 51.1 kJ mol^{-1} over the temperature range of 130 to 180°C. Mechanistic aspects of the catalytic process are discussed. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 91: 3259–3273, 2004

Key words: rubber; polyisoprene; hydrogenation; ruthenium complex; kinetics; organometallic catalysts

INTRODUCTION

Chemical modification of unsaturated polymers is a process for preparing polymers which are often inaccessible by conventional polymerization. The modification, particularly the hydrogenation of polydienes, has been studied for many years. Hydrogenation of the diene polymers has provided an alternate route to a variety of useful elastomers and thermoplastics with specific structures and properties. The residual double-bond unsaturation present in polydienes is reactive to thermal and oxidative degradation. To overcome this problem, hydrogenation is a very useful method to attain a product with high stability to degradation as compared to the parent polymer. The hydrogenation of polydienes, such as polyacrylonitrile-*co*-butadiene (NBR),[1–9] polybutadiene (PBD),[9–12] and polystyrene-*co*-butadiene (SBR),[13–14] by use of homogeneous catalysts has been the subject of much research.

Generally, hydrogenated diene polymers are derived from processes by using expensive transition metal compounds, such as rhodium complexes as catalysts. Ruthenium complex catalysts, although considerably cheaper than the rhodium complex catalysts, are known to be excellent catalysts for hydrogenation of diene unsaturation; however, the activity of the ruthenium complexes are often not as high as rhodium catalysts for double-bond hydrogenation in the backbone of the polymer and lead to unfavorable crosslinking reaction for certain copolymers. One of the easiest ruthenium complexes to prepare is RuCl$_2$(PPh$_3$)$_3$, and it is an efficient catalyst for hydrogenation of polybutadiene.[11] Kinetic studies of PBD and NBR hydrogenation have been carried out by using RuCl(CO)(OCOPh)(PPh$_3$)$_2$ as catalyst under an atmosphere of hydrogen pressure and mild temperature.[9] It is evident that the hydrogenation of *cis*-1,4-PBD could not achieve greater than 70% conversion under this condition because the Ru complex also catalyzed the isomerization of *trans*-1,4 C=C isomer. Only 40% reduction of C=C in NBR was achieved by using this ruthenium catalyst. Again, isomerization is partly the cause of incomplete hydrogenation. Rempel and coworkers discovered a number of Ru complexes for the facile hydrogenation of NBR copolymers.[5–6] The best catalysts were of the form Ru(X)Cl(CO)L_2, where X = H or β-styryl [CH=CH(Ph)], and L is a bulky phosphine such as tricyclohexyl- or triisopropyl-phosphine. These complexes show excellent activity and are easy to handle prior to reaction as they are
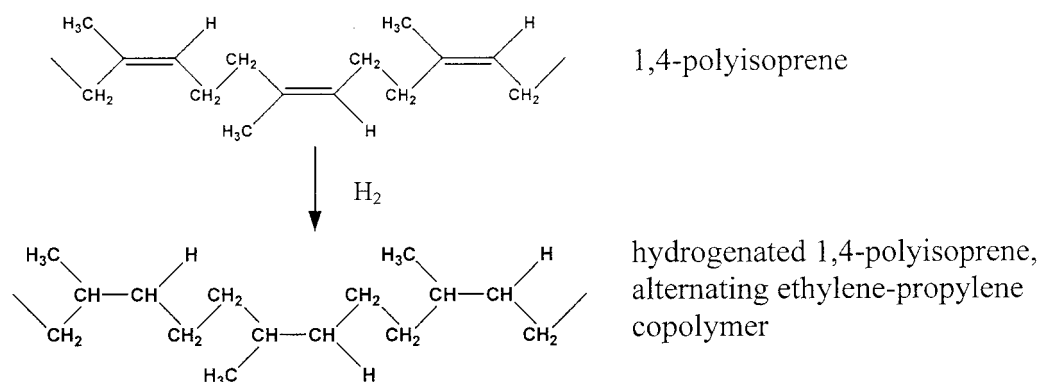
Scheme 1. Hydrogenation of *cis*-1,4-polyisoprene to hydrogenated *cis*-1,4-polyisoprene.

air stable catalysts when in the solid state. The kinetics of NBR hydrogenation showed first-order dependence on [C=C], [Ru], and hydrogen pressure and an inverse dependence on [CN].

Polyisoprene is a diene polymer, which is a polymer made from a monomer containing two carbon–carbon double bonds. Similar to most diene polymers, it has carbon–carbon double bonds in its backbone chain. Hydrogenation of polyisoprene presents a rather difficult case for polydiene hydrogenation. The isopropenyl groups, which constitute the rubber macromolecules, are analogous to trisubstituted olefin derivatives and as a result of steric constraints the addition of hydrogen is expected to be slower than for di- or monosubstituted ethylenes. Quantitative hydrogenation of *cis*-1,4-polyisoprene (CPIP) leads to an alternating ethylene–propylene copolymer (Scheme 1). Hydrogenation of polyisoprene with noncatalytic reagents such as diimide has been investigated.[15–17] This approach, however, leads to chain scission and incorporation of hydrazide fragments in the hydrogenated polyisoprene, which is very undesirable. Previously, heterogeneous catalytic hydrogenation of natural rubber and synthetic isoprene rubber was investigated.[18] Hydrogenation of natural rubber and synthetic *cis*-1,4-polyisoprene has been carried out in the presence of a large amount of nickel catalyst under high pressure and temperature. Singha et al. studied the homogeneous hydrogenation of natural rubber.[19] It was found that hydrogenated natural rubber could be obtained by using RhCl(PPh$_3$)$_3$ at high-catalyst concentration and that the hydrogenation of natural rubber followed first-order kinetics in residual double bonds. OsHCl-(CO)(O$_2$)(PCy$_3$)$_2$ has been recently discovered to be an excellent homogeneous catalyst for hydrogenation of CPIP.[20] Kinetic studies showed that the reaction was first order with respect to catalyst concentration and carbon–carbon double-bond concentration and second-order with respect to hydrogen pressure.

The objective of this work was to investigate the efficiency of the reaction involved in the quantitative hydrogenation of CPIP in the presence of soluble Ru(CH=CH(Ph))Cl(CO)(PCy$_3$)$_2$ catalyst as well as to gain insight into the nature of the hydrogenation mechanism. The effect of catalyst level, concentration of polymer, hydrogen pressure, and temperature was studied. In this article, the kinetics and mechanism for CPIP hydrogenation by Ru(CH=CH(Ph))Cl(CO)-(PCy$_3$)$_2$ are presented and discussed.

EXPERIMENTAL

Materials

Commercial high molecular weight *cis*-1,4-polyisoprene (97% of *cis*) was purchased from Aldrich Chemical Co. (Milwaukee, WI). Reagent grade chlorobenzene (MCB), toluene, and xylene were purchased from Fisher Scientific Ltd. (Fairlawn, NJ). All solvents were used without further purification. The hydrogen gas used, with purity of 99.99%, was supplied by Praxair Inc. (Kitchener, ON, Canada). Ru(CH=CH) (Ph)Cl-(CO)(PCy$_3$)$_2$,[5] RuCl(PhCO$_2$)(CO)(PPh$_3$)$_2$,[9] Ru(CH=CH)-(Ph)Cl(CO)(PPr$^i_3$)$_2$,[21] and RuCl$_2$(PPh$_3$)$_3$[22] were prepared according to the procedures outlined in the literature. RuCl$_2$(CHC$_6$H$_5$)(PCy$_3$)$_2$ was purchased from Strem Chemicals (Newbury, MA). *P*-toluene sulfonic acid (*p*-TsOH), 3-chloropropionic acid, and succinic acid were obtained from Aldrich Chemical Co.

Hydrogenation reactions

Hydrogenation reactions were carried out in a 300-mL Parr pressure reactor. In a typical experiment, a specific amount of the polymer was weighed and dissolved in 130 mL of solvent. The solution was transferred into the reactor. In a glovebox, the ruthenium complex catalyst was dissolved in the 20 mL of solvent and transferred into the catalyst addition device. Then, the reactor and the catalyst addition device were connected. The autoclave was purged with hydrogen gas. Subsequently, the reactor was pressurized to 32 bar before being heated up
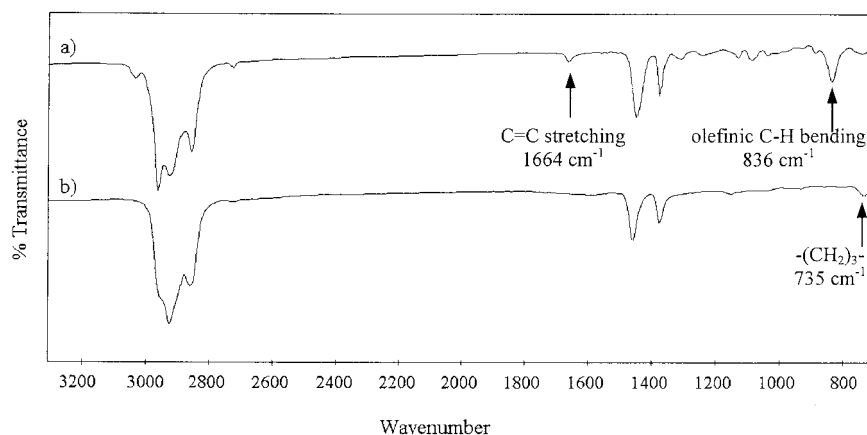
Figure 1 FTIR spectra of (a) CPIP, (b) HCPIP (97% hydrogenation), [Ru] = 200 μM; [C=C] = 260 mM; P_{H_2} = 39.3 bar; T = 160°C.

to the required reaction temperature. When thermal equilibrium was reached in the reactor (vapor/liquid), the catalyst solution was added by pressurized hydrogen gas and the hydrogen pressure was adjusted to the required reaction pressure. During hydrogenation, the mixture was stirred at a constant speed of 600 rpm. This reaction was maintained at the desired temperature and pressure for a given time. After hydrogenation, hydrogenated rubber was precipitated in ethanol and finally dried under vacuum at room temperature for subsequent analysis.

Kinetic studies

Kinetics of the hydrogenation of *cis*-1,4-polyisoprene rubber catalyzed by the Ru(CH=CH(Ph))Cl(CO)-(PCy$_3$)$_2$ complex catalyst precursor were studied by measuring the amount of hydrogen consumed as a function of time by using a gas uptake apparatus developed by Mohammadi and Rempel.[23] The hydrogenation apparatus was maintained at constant temperature ± 1°C and pressure ± 0.02 bar throughout the reaction. Typically, 150 mL of polymer solution was prepared and charged into the reactor. Catalyst was weighed into a small glass bucket, which was placed in a port in the reactor head. The reactor was then assembled. The solution was deoxygenated by partially evacuating and purging with hydrogen gas for a number of cycles. The reactor was pressurized and then stirred at 1200 rpm. Once the thermal equilibrium (vapor/liquid) of the system was established, catalyst was discharged into the polymer solution by using an overpressure of hydrogen. After the gas consumption subsided, the reactor was cooled. After cooling, the product was removed, precipitated in ethanol, and then dried under vacuum.

Characterization

The final degree of olefin conversion was quantified by infrared spectroscopic and NMR spectroscopic

analysis. NMR spectra were recorded on 3% w/v solutions of the rubber in CDCl$_3$ by using an Avance 300 MHz spectrometer (Bruker). Fourier transform infrared (FTIR) spectra of the rubber samples were run as cast films on sodium chloride disk. Spectra of products were collected on a Bio-Rad FTS 3000X spectrometer.

The molecular weight of CPIP and hydrogenated CPIP were determined by gel permeation chromatography. Waters GPC system fitted with a Water Ultrastyragel 10^4 Å column was operated at 30°C, with THF as the carrier solvent. Samples of 0.2% solution in THF were prepared. The system detectors were a multiangle laser light scattering (MALLS) (Wyatt Dawn DSP-F) operating at 630 nm and a Waters DR 401 differential refractive index detector (DRI). Wyatt Astra software was used for data analysis.

The relative viscosity of polyisoprene and the hydrogenated products (0.12500 ± 0.00015 g of polymer/25 mL of toluene) were also measured by means of Ubbelohde capillary viscometer in toluene at 35°C. Samples were filtrated through a coarse, sintered-glass filter to remove insoluble gel before being introduced into the viscometer.

RESULTS AND DISCUSSION

Hydrogenation catalyzed by various Ru(II) complexes

The FTIR spectra of CPIP and the hydrogenated *cis*-1,4-polyisoprene (HCPIP) are shown in Figure 1. The disappearance of the bands at 1664 and 836 cm^{-1} due to C=C stretching and olefinic C—H bending are indicative of quantitative hydrogenation of CPIP. A peak appears at 735 cm^{-1} because of the presence of —(CH$_2$)$_3$— groups during the hydrogenation process. The final degree of hydrogenation of hydrogenated polymer was determined by ^{1}H-NMR. A typical ^{1}H-NMR spectrum of CPIP (a) together with the spectrum
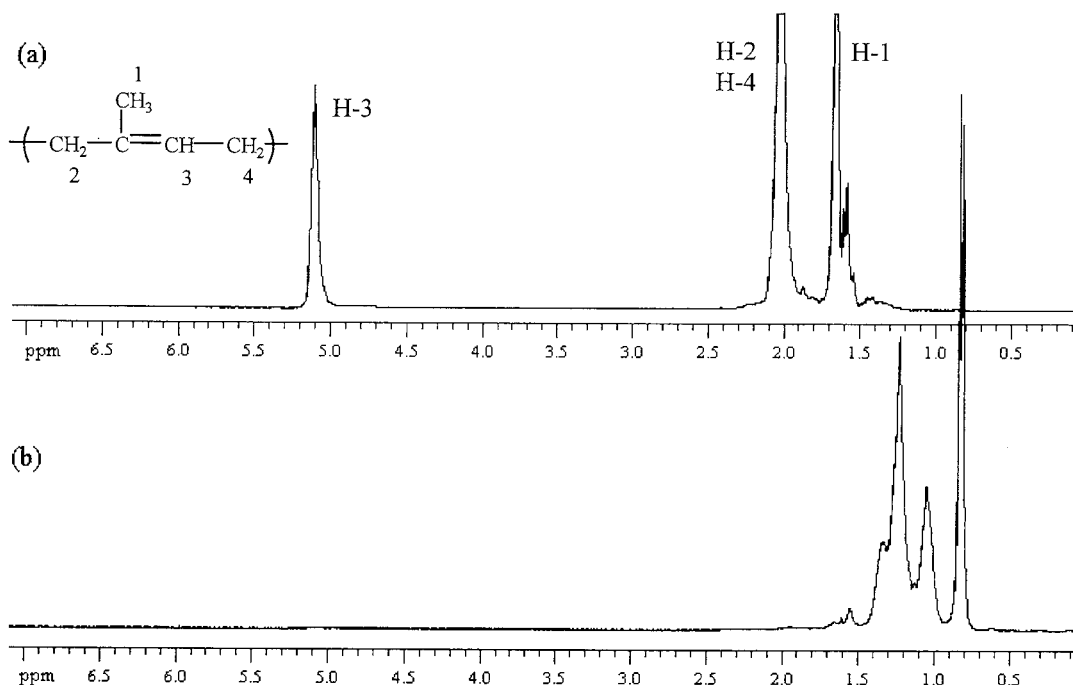
Figure 2 ^{1}H-NMR spectra of (a) CPIP, (b) HCPIP (97% hydrogenation), [Ru] = 200 μM; [C=C] = 260 mM; P_{H_2} = 39.3 bar; $T = 160°C$.

of the hydrogenated CPIP product (b) is shown in Figure 2. The hydrogenation led to the reduction in the peaks of isoprene units at 1.7, 2.2, and 5.2 ppm, which are assigned to —CH$_3$, —CH$_2$—, and =CH groups, respectively, and the emergence of new peaks at 0.8 and 1.1–1.3 ppm, attributed to the propylene–ethylene block of the hydrogenated product. ^{13}C-NMR spectrum of hydrogenated CPIP confirms that the polymer product is strictly an alternating copolymer of ethylene–propylene (Fig. 3). The peak areas at 135.4 and 125.2 ppm decrease, which indicates the reduction of olefinic carbon, and four new peaks appear at 37.8, 33.1, 24.8, and 20.0 ppm, which are attributed to C$_\alpha$, —CH—, C$_\beta$, and —CH$_3$ carbons, respectively.

The results for the catalytic hydrogenation of CPIP by use of various Ru(II) complexes in the batch reactor are summarized in Table I. It is seen that Ru(CH= CH(Ph))Cl(CO)(PCy$_3$)$_2$, Ru(CH=CH(Ph))Cl(CO)-(PPr$^i_3$)$_2$, RuCl(CO)H(PPh$_3$)$_3$, and RuCl(CO)(PhCO$_2$)-(PPh$_3$)$_2$ had similar activity (86–93% olefin conversion after 5 h) with respect to the catalytic hydrogenation of CPIP. One of the easiest ruthenium complexes to prepare is RuCl$_2$(PPh$_3$)$_3$, which has been found to be an efficient catalyst for hydrogenation of polybutadiene under mild conditions.[11] However, for cis-1,4-polyisoprene, RuCl$_2$(PPh$_3$)$_3$ was not active toward the hydrogenation (only 25% olefin conversion was attained after 5 h of reaction). The hydrogenation of CPIP using π-C$_3$H$_5$Ru(CO)$_3$Cl as catalyst was examined; however, it was only possible to achieve 48% hydrogenation after 5 h of reaction, and furthermore, this catalyst system led

to degradation of the polymer chain and isomerization. 1,2-Polyisoprene was produced during the reduction process; its IR spectrum shows a characteristic peak at 968 cm^{-1}. Recently, RuCl$_2$(CHC$_6$H$_5$)(PCy$_3$)$_2$ has been discovered to be an olefin metathesis catalyst with high activity and stability.[24] Unlike for the case of olefin metathesis, the hydrogenation of CPIP with RuCl$_2$-(CHC$_6$H$_5$)(PCy$_3$)$_2$ was found to be less effective; only 63% hydrogenation could be achieved after 5 h.

Based on these initial experimental results, Ru-Cl(CO)(styryl)(PCy$_3$)$_2$ was chosen as the preferred Ru catalyst for a kinetic investigation of CPIP hydrogenation in chlorobenzene as it exhibited the highest activity among the Ru complexes screened in this investigation.

Kinetics of CPIP hydrogenation using Ru(CH=CH(Ph))Cl(CO)(PCy$_3$)$_2$

A kinetic study of CPIP hydrogenation in the presence of the homogeneous catalyst Ru(CH=CH(Ph))Cl-(CO)(PCy$_3$)$_2$ was carried out by using a computer-controlled gas uptake apparatus to investigate the rate dependence of reaction variables, such as polymer concentration, catalyst concentration, temperature, and hydrogen pressure. A representative hydrogen uptake profile corresponding to the olefin consumption with respect to time is shown in Figure 4. All of the CPIP hydrogenation experiments are first order with respect to olefin concentration according to eq. (1) (where k' is the pseudo-first-order rate constant)
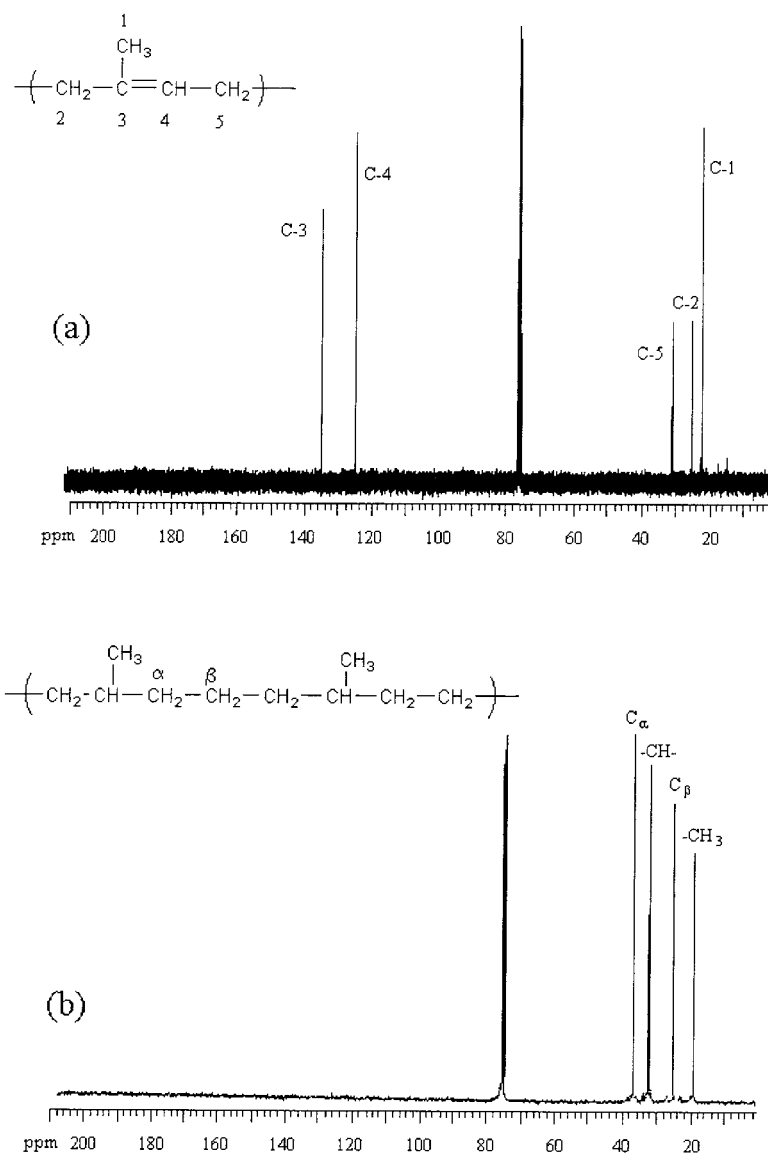
Figure 3 ^{13}C-NMR spectra of (a) CPIP, (b) HCPIP (97% hydrogenation), [Ru] = 200 μM; [C=C] = 260 mM; P_{H_2} = 39.3 bar; T = 160°C.

$$\frac{-d[H_2]}{dt} = \frac{-d[C=C]}{dt} = k'[C=C] \qquad (1)$$

First-order rate constants were calculated from the slope of the linear ln(1 − *x*) versus time plots as shown in Figure 4 (where *x* is the conversion).

2^3 Factorial design experiments

To determine the significance of joint factor interactions, which influence the hydrogenation rate, a two-level factorial design was employed. Three principal factors, which are considered to have a main effect on the experimental rate constant (*k'*), are concentration of polymer, concentration of catalyst, and hydrogen pressure. For each variable, a low and high level was

selected for the ranges of concentration to be examined. The ranges of polymer concentration, catalyst concentration, and hydrogen pressure were 130–520 mM, 100–200 μM, and 39.3–66.1 bar, respectively. In Table II, the results for factorial design experiments are provided. An analysis of variance (ANOVA) of the rate constants is tabulated in Table III. If the *P* is less than 0.05, the observed response is regarded as being significant. In this design, two significant effects on reaction rate are the concentration of ruthenium and hydrogen pressure. In contrast, the existence of two- and three-factor interaction effects is not significant. From these results, univariate experiments were formulated and performed. The influence of each factor on the hydrogenation reaction (i.e., polymer concentration, catalyst concentration, hydrogen pressure,

TABLE I
The Results of Hydrogenation of CPIP Using Ru Complexes in Batch Reactor

Catalyst	[Catalyst] (μM)	Cocatalyst	Solvent	% Hydrogenation
Ru(CH=CH(Ph))Cl(CO)(PCy$_3$)$_2$	80	None	Toluene	90.1
Ru(CH=CH(Ph))Cl(CO)(PPr$_3^i$)$_2$	80	None	Toluene	85.6
RuCl(CO)H(PPh$_3$)$_3$	80	None	Toluene	87.6
RuCl(CO)(PhCO$_2$)(PPh$_3$)$_2$	80	None	Toluene	89.0
Ru(CH=CH(Ph))Cl(CO)(PCy$_3$)$_2$	80	None	MCB	93.0
Ru(CH=CH)(Ph))Cl(CO)(PPr$_3^i$)$_2$	80	None	MCB	90.2
RuCl$_2$(PPh$_3$)$_3$	80	PPh$_3$	MCB	24.8
π-C$_3$H$_5$Ru(CO)$_3$Cl	240	None	MCB	48.0
RuCl$_2$(CHC$_6$H$_5$)(PCy$_3$)$_2$	80	None	MCB	62.7

Conditions: T = 160°C; P_{H_2} = 39.3 bar; [C=C] = 260 mM; reaction time = 5 h.
[C=C] is defined as the weight of *cis*-1,4-polyisoprene divided by molecular weight of repeating unit.

and temperature) was also explored. The results of univariate experiments are provided in Table IV and will be subsequently discussed.

Effect of the ruthenium concentration

The dependence of the initial hydrogenation rate on catalyst concentration was studied over the range of 20 to 250 μM at 160°C in chlorobenzene. The concentration of initial C=C unsaturation was 260 mM under 39.3 bar hydrogen pressure. The conversion profiles at a variety of catalyst concentrations [Fig. 5(a)] indicate that above the 40 μM catalyst concentration the system displays the expected first-order behavior with respect to olefin concentration. The reaction rate is linearly proportional to the total concentration of catalyst as shown in Figure 5(b). This is consistent with the investigations of Martin et al.[5] for NBR hydrogenation catalyzed by Ru(CH=CH(Ph))Cl(CO)-(PCy$_3$)$_2$ and Charmondusit et al.[20] for CPIP hydroge-

nation catalyzed by OsHCl(CO)(O$_2$)(PCy$_3$)$_2$. The first-order response of k' dependence on the total ruthenium concentration confirmed that the active complex is a mononuclear species.

Effect of hydrogen pressure

Martin et al. has previously suggested the estimation of accurate values of hydrogen pressure in the reactor.[5] The partial pressure of chlorobenzene was approximated based on the Harlacher–Braun correlation, assuming that the polymer and hydrogen pressure did not significantly affect the vapor pressure.[25] The actual vapor pressure of the polymer solution, measured by using the gas uptake apparatus in the absence of hydrogen at 160°C, was 0.204 MPa.

A series of experiments in which the hydrogen pressure was varied over the range of 5.7 to 66.1 bar was carried out. The initial concentration of polymer and catalyst was kept at 260 mM and 200 μM, respectively,

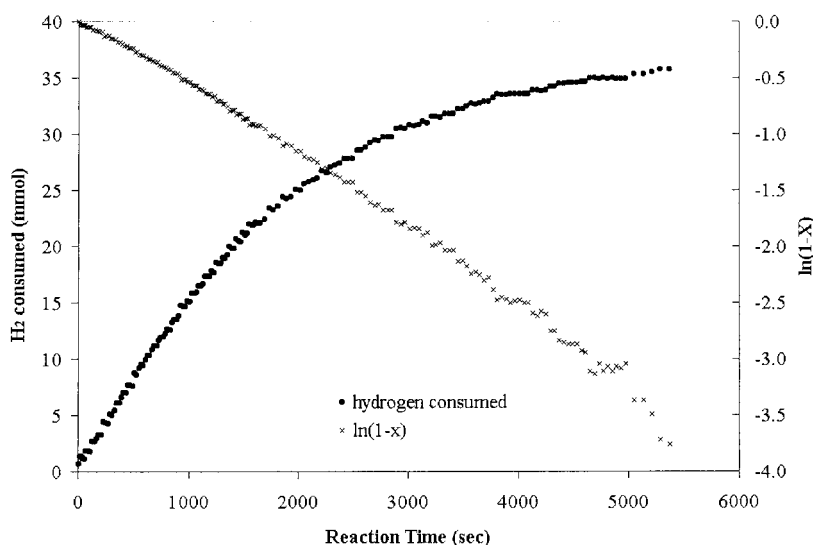**Figure 4** Hydrogen consumption plot for CPIP hydrogenation, [Ru] = 200 μM; [C=C] = 260 mM; P_{H_2} = 39.3 bar; T = 160°C.

TABLE II
2^3 Factorial Design Data for CPIP Hydrogenation

Expt.	[Ru] (μM)	[C=C] (mM)	P_{H_2}[a] (bar)	$k' \times 10^4$ (s^{-1})	Relative viscosity
1	200	130	39.3	6.04	—
2	200	130	39.3	6.09	—
3	100	130	39.3	4.05	5.40
4	100	130	39.3	3.48	—
5	200	130	66.1	9.32	4.19
6	200	130	66.1	11.13	—
7	100	130	66.1	6.13	6.08
8	100	130	66.1	8.56	—
9	200	520	39.3	7.67	3.10
10	200	520	39.3	5.04	—
11	100	520	39.3	4.04	—
12	100	520	39.3	4.12	—
13	200	520	66.1	7.91	7.61
14	200	520	66.1	12.50	—
15	100	520	66.1	8.70	—
16	100	520	66.1	5.64	—

Conditions: T = 160°C; solvent was chlorobenzene.
[a] Partial pressure of H_2.

at 160°C in chlorobenzene. The conversion versus time plots for different hydrogen pressures as shown in Figure 6(a) indicate that the expected first-order behavior with respect to olefin is observed, above 5.71 bar hydrogen pressure. Figure 6(b) illustrates the first-order rate dependence to hydrogen pressure over the experimental range. This first-order behavior implied that a single mechanistic pathway is probably involved in the reaction of the polymer with hydrogen. Otherwise, it might be expected that the relative contribution of these reactions would change as the hydrogen pressure changed. These results are in agreement with those for NBR hydrogenation in the presence of the Ru(CH=CH(Ph))Cl(CO)(PCy$_3$)$_2$ catalyst system,[5] whereas the hydrogenation of NBR[7] and CPIP[20] using the osmium complex, OsHCl(CO)(O$_2$)-(PCy$_3$)$_2$, was known to shift from second order to zero order with an increase in hydrogen pressure.

TABLE IV
Summary of Kinetic Data from the Study of CPIP Hydrogenation Catalyzed by Ru(CH=CH(Ph))Cl(CO(PCy$_3$)$_2$

| Expt.	[Ru] (μM)	[C=C]$_0$ (mM)	P_{H_2}[a] (bar)	Temp. (°C)	$k' \times 10^4$ (s^{-1})	Relative viscosity
1	20	260	39.3	160	1.05	—
2	40	260	39.3	160	2.35	—
3	80	260	39.3	160	3.13	—
4	100	260	39.3	160	4.13	5.28
5	130	260	39.3	160	4.81	—
6	170	260	39.3	160	5.05	5.66
7	200	260	39.3	160	6.17	5.10
8	250	260	39.3	160	7.95	—
9	200	260	5.7	160	0.43	—
10	200	260	12.4	160	0.98	—
11	200	260	19.1	160	1.87	4.11
12	200	260	25.9	160	2.78	5.31
13	200	260	32.6	160	4.98	4.84
14	200	260	66.1	160	9.69	3.23
15	200	260	66.1	160	10.20	2.41
16	200	130	39.3	160	5.96	—
17	200	130	39.3	160	6.04	—
18	200	520	39.3	160	7.67	3.10
19	200	520	39.3	160	5.04	—
20	200	130	66.1	160	9.28	4.19
21	200	130	66.1	160	11.13	—
22	200	520	66.1	160	12.50	—
23	200	520	66.1	160	9.91	7.61
24	100	130	39.3	160	4.05	5.40
25	100	130	39.3	160	3.48	—
26	100	520	39.3	160	4.04	—
27	100	520	39.3	160	4.12	—
28	200	260	39.3	130	1.76	—
29	200	260	39.3	140	3.39	2.98
30	200	260	39.3	150	4.09	3.82
31	200	260	39.3	170	8.33	—
32	200	260	39.3	180	10.47	—
33	200	130	39.3	130	1.82	—
34	200	130	39.3	140	3.25	4.30
35	200	130	39.3	150	3.46	3.23
36	200	130	39.3	160	6.09	—
37	200	130	39.3	170	7.99	2.44
38	200	130	39.3	180	9.40	4.41

Solvent = chlorobenzene.
[a] Partial pressure of H_2.

TABLE III
Analysis of Variance (ANOVA) of 2^3 Factorial Experiments for Rate Constant (k')

Source	Sum of squares	DF	Mean square	F	P[a]
[Ru]	3.02E−07	1	3.02E−07	17.643	0.0030
[C=C]	9.12E−09	1	9.12E−09	0.533	0.4862
P_{H_2}	6.54E−07	1	6.54E−07	38.241	0.0003
[Ru] * [C=C]	9.92E−10	1	9.92E−10	0.058	0.8158
[Ru] * P_{H_2}	8.46E−09	1	8.46E−09	0.495	0.5019
[C=C] * P_{H_2}	1.22E−09	1	1.22E−09	0.072	0.7958
[Ru] * [C=C] * P_{H_2}	1.16E−09	1	1.16E−09	0.068	0.8015
Error	1.37E−07	8	1.71E−08		
Total	9.15E−06	16			
Corrected total	1.11E−06	15			

[a] If $P > 0.05$, then the variable is not significant.
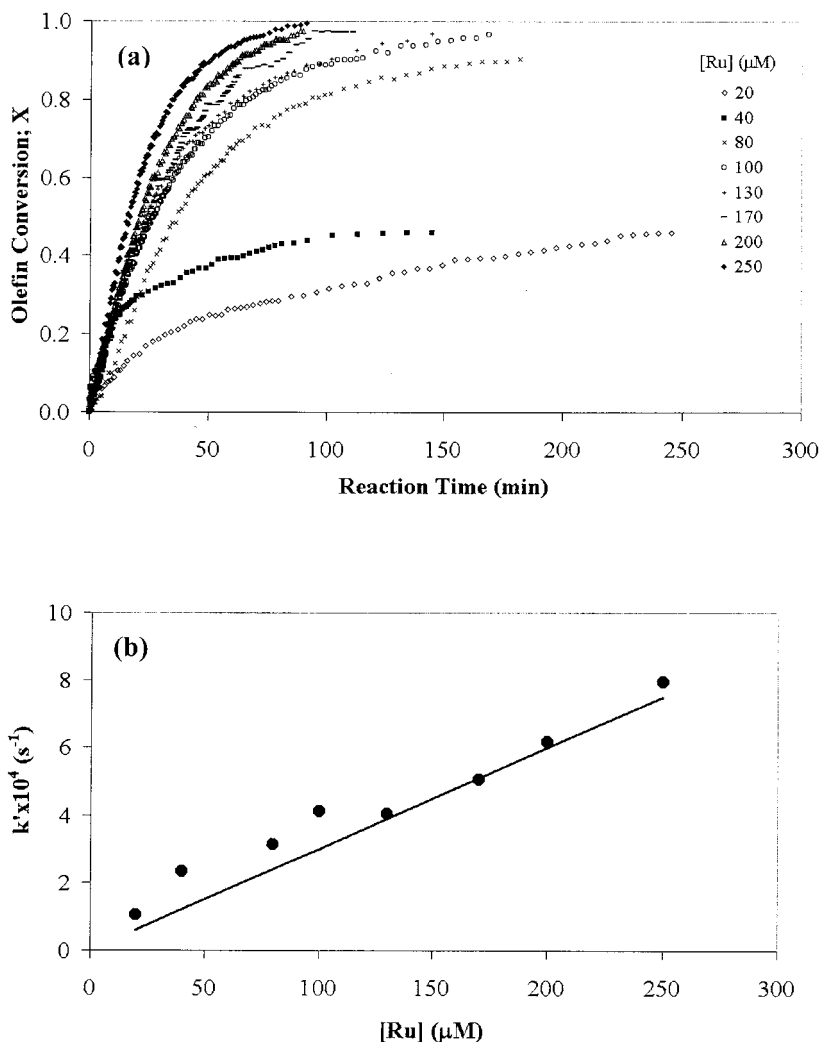
Figure 5 (a) Effect of [Ru] on CPIP conversion profiles, (b) effect of [Ru] on rate constant (●) experimental data, (—) model. [C=C] = 260 mM; P_{H_2} = 39.3 bar; T = 160°C.

Effect of polymer concentration

As mentioned above, the conversion profile for hydrogenation of CPIP is pseudo-first-order with respect to [C=C] and is independent of the amount of olefin charged to the reactor. This behavior was observed at all sets of carbon–carbon double-bond concentrations and reaction conditions employed as shown by the results obtained for the factorial design experiments and univariate studies. The plot of initial reaction rate versus polymer concentration in Figure 7 clearly shows that the reaction rate constants remain relatively unchanged over the range of polymer concentration studied (130–520 mM) at 160°C in chlorobenzene. This behavior is similar to the CPIP hydrogenation catalyzed by OsHCl-(CO)(O₂)(PCy₃)₂.[20] For NBR hydrogenation catalyzed by Ru(CH=CH(Ph))Cl(CO)(PCy₃)₂[5] and OsHCl(CO)(O₂)(PCy₃)₂,[7] the rate constants show an inverse dependence on nitrile concentration due to

competitive complexation of nitrile to the active catalyst site. Consequently, the NBR hydrogenation activity decreased as the amount of polymer concentration increases.

Effect of temperature

Two sets of experiments were carried out over the temperature range of 130 to 180°C, where hydrogen pressure (39.3 bar) and total ruthenium concentration (260 μM) remained constant. The first set investigated the effect of varying temperature by using polymer concentration of 260 mM, whereas a concentration of carbon–carbon double bond of 130 mM was used in the second set. The experimental observations are listed in Table IV and the corresponding Arrhenius plot is shown in Figure 8(a).

Linear responses for both sets of experiments are observed, from which an apparent activation energy
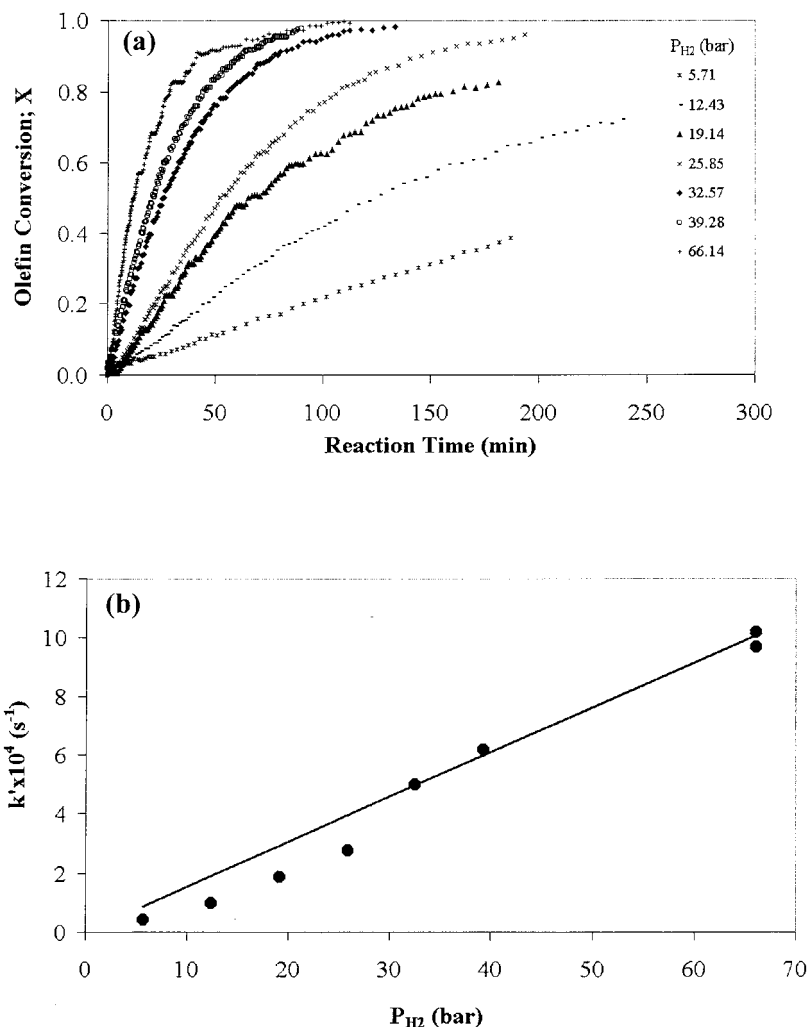
Figure 6 (a) Effect of P_{H_2} on CPIP conversion profiles, (b) effect of P_{H_2} on rate constant ($\bullet$) experimental data, (—) model. [C=C] = 260 mM; [Ru] = 200 μM; T = 160°C.

is estimated to be 51.1 kJ/mol over the temperature range of 130 to 180°C. The rates of hydrogenation for this ruthenium catalyst are very much slower than
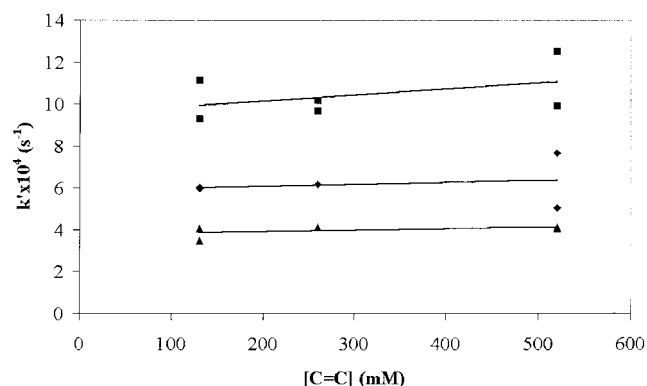

Figure 7 Effect of [C=C] on rate constant for CPIP hydrogenation, T = 160°C. ($\blacklozenge$) P_{H_2} = 39 bar; [Ru] = 200 μM, ($\blacksquare$) P_{H_2} = 66 bar; [Ru] = 200 μM, ($\blacktriangle$) P_{H_2} = 39 bar; [Ru] = 100 μM.

the rate of CPIP hydrogenation in toluene catalyzed by $OsHCl(CO)(O_2)(PCy_3)_2$ for which the activation energy was 109.3 kJ/mol over the temperature range of 115 to 140°C.[20] However, the apparent activation energy of 51.1 kJ/mol is still indicative that the experiments were carried out under chemical control without mass transfer limitation. Furthermore, these experiments also confirmed that the rate constant is independent of polymer concentration. Based on the corresponding Eyring equation [eq. (2)], the apparent activation enthalpy and entropy estimated are 47.6 kJ/mol and -197.2 J/mol K, respectively, as shown in Figure 8(b)

$$k = \frac{k_B T}{h} e^{(-\Delta H^+/RT)} e^{(\Delta S^+/R)} \qquad (2)$$

where k_B is the Boltzmann's constant = 0.381×10^{-23} J K^{-1}, and h is the Plank constant = 6.626×10^{-34} J s.
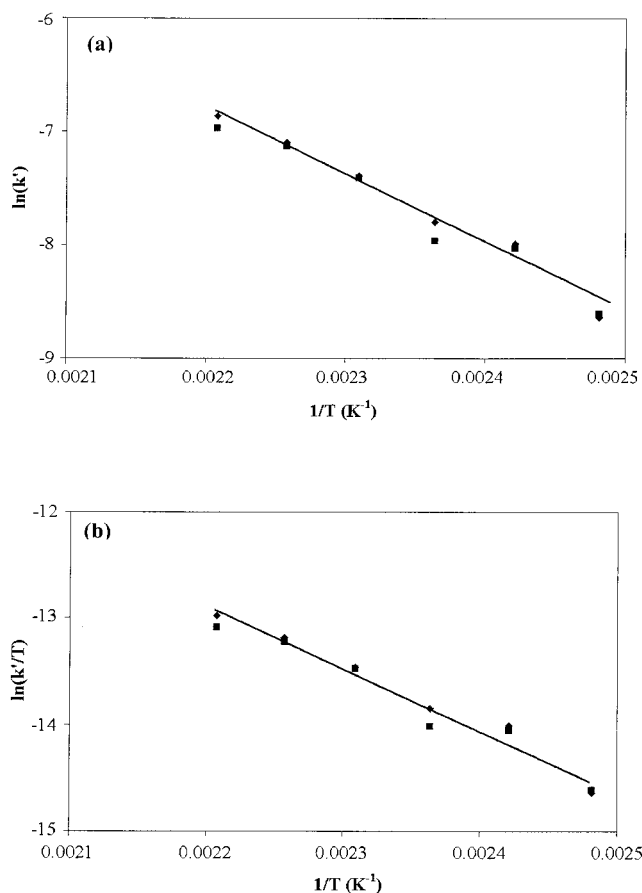
Figure 8 (a) Arrhenius plot, (b) Eyring plot for CPIP hydrogenation, [Ru] = 200 μM; T = 160°C; P_{H_2} = 39.3 bar. (■) [C=C] = 130 mM, (♦) [C=C] = 260 mM.

Effect of adding PCy$_3$

The dependence of the initial hydrogenation rate on the addition of tricyclohexylphosphine was investigated to understand the function of PCy$_3$ ligand in the catalytic mechanism. The values of the experimental rate constant along with the concentration of added PCy$_3$ are presented in Table V. It is evident that adding tricyclohexylphosphine retards the potential activity of the ruthenium complexes for hydrogenation. It may be due to the competitive coordination of PCy$_3$

with the active catalyst species or the inhibition of phosphine dissociation.[5]

Effect of solvent

The hydrogenation of CPIP was also carried out by using various solvents at 160°C and 39.3 bar P_{H_2} in the presence of 200 μM [Ru], and 260 mM [C=C]. Ketone solvents such as acetone and methyl ethyl ketone were not employed as the solvent for CPIP hydrogenation, because polyisoprene does not dissolve in these polar solvents. Table V summarizes the results of CPIP hydrogenation catalyzed by Ru(II) complex in various solvents. The rate of hydrogenation of CPIP increases in the order: chlorobenzene > toluene > xylene. The use of chlorinated solvent results in a faster reaction rate than in any of the other solvents investigated. Therefore, it seems that the more polar the solvent, the higher the rate of reduction. This may be due to the solvent interaction with the polymer in promoting active site availability and the nature of solvated ruthenium hydride. These results of solvent effect are similar to those previously reported by Charmondusit et al. for CPIP hydrogenation catalyzed by OsHCl-(CO)(O$_2$)(PCy$_3$)$_2$.[20]

Effect of polymer purification

To study the effect of polymer purity on hydrogenation, CPIP was purified by dissolving in chlorobenzene and then reprecipitating with ethanol. The polymer was dried under vacuum for a week to remove the trapped solvent. To ensure that no more solvent was left in the sample, the mass of polymer was periodically recorded. The sample was re-dissolved again in chlorobenzene and hydrogenated under the base condition (P_{H_2} = 39.3 bar, T = 160°C, [Ru] = 200 μM, [C=C] = 260 mM, chlorobenzene). The pseudo-first-order reaction rate constant of purified CPIP (6.55 $\times$ 10^{-4} s^{-1}) was insignificantly higher than that of unpurified CPIP (6.10 $\times$ 10^{-4} s^{-1}) at base conditions. The slight increase in rate constant may be due to trace polymer contaminants such as chain transfer agents,

TABLE V
Effect of Solvent and PCy$_3$ Addition on the Hydrogenation of CPIP

Solvent	Mole equivalents of added PCy$_3$[a]	$k' \times 10^4$ (s^{-1})	% Hydrogenation	Reaction time (h)
Xylene	0	3.66	86.1	1.8
Toluene	0	5.01	86.0	1.5
Chlorobenzene	0	6.10	97.7	2.0
Chlorobenzene	1	0.11	77.4	3.0
Chlorobenzene	6	0.03	20.0	3.4

Conditions: P_{H_2} = 3.93 bar; T = 160°C; [Ru] = 200 μM; [C=C] = 260 mM. Solvent = chlorobenzene.
[a] 1 equivalent = 200 μM.
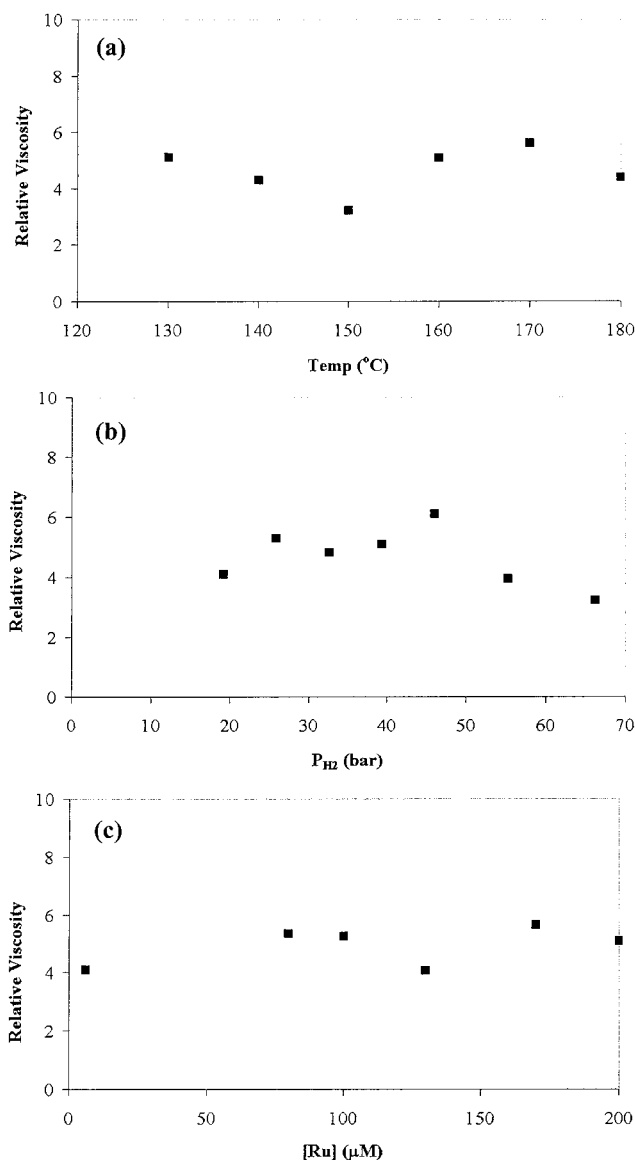
Figure 9 (a) Relative viscosity of HCPIP versus temperature, [C≡C] = 260 mM; [Ru] = 260 μM; P_{H_2} = 39.3 bar. (b) Relative viscosity of HCPIP versus pressure, [C≡C] = 260 mM; [Ru] = 260 μM; T = 160°C. (c) Relative viscosity of HCPIP versus ruthenium concentration, [C≡C] = 260 mM; P_{H_2} = 39.3 bar; T = 160°C.

which are likely removed by solvent extraction and coagulation.

Polymer chain length properties

IR and NMR spectroscopy were used to determine the degree of hydrogenation. However, these techniques lack the sensitivity required to detect the presence of side reactions such as crosslinking and chain scission. Therefore, the relative viscosity (η_{rel}) measurement of a dilute polymer solution with pure toluene was undertaken to investigate the effect of side reactions on the CPIP hydrogenation by using Ru(CH≡CH-(Ph))Cl(CO)(PCy$_3$)$_2$.

The η_{rel} measurement of some hydrogenated CPIP products is also presented in Table IV. Figure 9(a–c) illustrates the effect of catalyst concentration, C≡C concentration, and hydrogen pressure on the relative viscosity of hydrogenated CPIP. It can be seen that relative viscosity of CPIP ($\eta_{rel} \sim 9$) is higher than that of hydrogenated CPIP ($\eta_{rel} \sim 2$–6). The reduction of HCPIP relative viscosity indicates that chain scission occurred during the catalytic hydrogenation of CPIP. The random viscosity shows that the reaction conditions employed have an insignificant effect on the product properties. These results are different from those observed for the hydrogenation of CPIP using OsHCl(CO)(O$_2$)(PCy$_3$)$_2$ at 130°C and 6.9–69 bar P_{H_2} in which no degradation and/or crosslinking occurred during the hydrogenation process.[20] This may be due to the fact that the hydrogenation catalyzed by ruthenium-based catalysts was performed at higher temperature and higher pressure.

Molecular weight reduction was also confirmed by the results from gel permeation chromatography. Table VI shows the decrease in polymer chain length during hydrogenation. Number-average molecular weight (M_n = 150,000–450,000) and weight-average molecular weight (M_w = 250,000–650,000) of hydrogenated CPIP is substantially lower than for the parent polymer (M_n = 9,570,000 and M_w = 1,270,000). Furthermore, polydispersity was somewhat altered during the hydrogenation

TABLE VI
Summary of GPC Molecular Weight Data for CPIP and Hydrogenated CPIP

| Polymer | Condition | | | | M_n | M_w | Polydispersity |
	[C≡C] (mM)	Temp. (°C)	P_{H_2} (bar)	[Ru] (μM)			
CPIP	—	—	—	—	956,800	1,274,000	1.33
CPIP[a]	260	160	39.3	—	284,600	443,600	1.56
HCPIP	260	160	39.3	200	441,000	616,500	1.40
HCPIP	130	160	39.3	200	447,400	658,200	1.47
HCPIP	130	160	66.1	200	331,700	536,200	1.62
HCPIP	520	160	25.9	200	152,900	257,300	1.68
HCPIP	260	150	39.3	200	372,600	557,900	1.50
HCPIP	260	130	39.3	200	307,200	470,400	1.53

[a] CPIP reaction was carried out under this condition for 24 h.
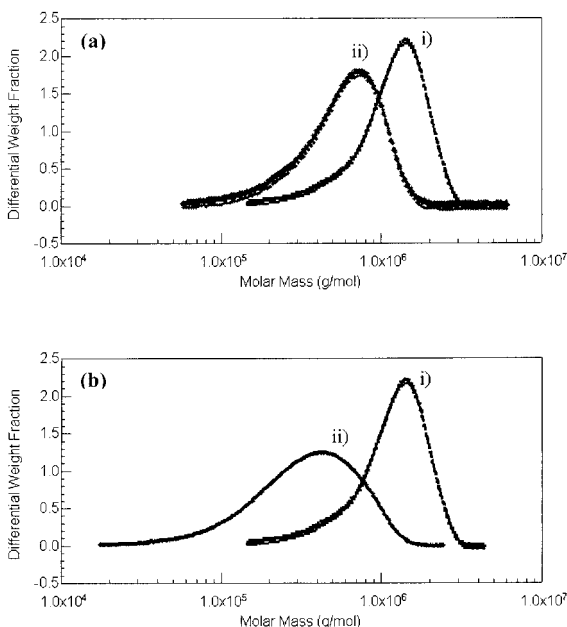
Figure 10 (a) Gel permeation chromatograms of (i) CPIP and (ii) HCPIP (97% hydrogenation). [Ru] = 200 μM; [C=C] = 260 mM; P_{H_2} = 39.3 bar; T = 160°C. (b) Gel permeation chromatograms of (i) CPIP and (ii) CPIP reaction without Ru catalyst. [C=C] = 260 mM; P_{H_2} = 39.3 bar; T = 160°C for 24 h.

reaction [Fig. 10(a)]. One can also notice that treatment of CPIP under the standard hydrogenation conditions without the ruthenium complex for 24 h results in a decrease in molecular weight of CPIP (M_n = 285,000 and M_w = 444,000) compared to the molecular weight of the starting polymer [Fig. 10(b) and Table VI]. This suggests that the high temperature and pressure used during the reaction caused main molecular chain scission of the polymer.

Reaction mechanism

There are two possible paths for the reaction mechanism of hydrogenation of CPIP in the presence of Ru(CH=CH(Ph))Cl(CO)(PCy$_3$)$_2$: the unsaturate path and the hydride path. The probable mechanisms are proposed on the basis of results from the kinetic studies (Table IV). The experimental results showed that the reaction rate was first order with respect to both ruthenium concentration and hydrogen pressure and zero order with respect to C=C concentration. Scheme 2 represents the catalytic mechanism of these two paths. It seems that the first step of both paths is the rapid hydrogenation of Ru(CH=CH(Ph))Cl-(CO)(PCy$_3$)$_2$ to form the active catalytic species (A_0) and styrene.[5-6]

The mechanism in Scheme 2 suggests that the unsaturate path (step $A_0 \rightarrow B \rightarrow D$), which has the C=C group coordination to A_0 first, is followed by hydrog-
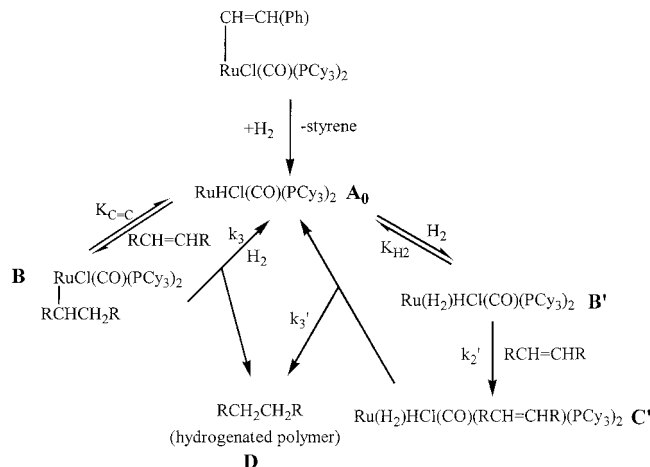
Scheme 2. Proposed mechanism of CPIP hydrogenation using Ru(CH=CH(Ph))Cl(CO)(PCy$_3$)$_2$.

enolysis of the Ru–alkyl complex, then elimination of the hydrogenated product, and regeneration of A_0. It is assumed that the reaction of the alkyl complex with hydrogen is the rate-limiting step,

$$\text{rate} = \frac{-d[\text{C=C}]}{dt} = k'[\text{C=C}] = k_3[\text{B}][\text{H}_2] \quad (3)$$

The total ruthenium concentration may be defined by

$$[\text{Ru}]_T = [A_0] + [B] \quad (4)$$

The equilibrium constants $K_{\text{C=C}}$ shown in Scheme 2 are defined by

$$K_{\text{C=C}} = \frac{[B]}{[A_0][\text{C=C}]} \quad (5)$$

Equation (6) is derived when eqs. (4) and (5) are rearranged and substituted into eq. (3) with substitution for the terms [A_0] and [B] [i.e., RuCl(CO)(PCy$_3$)$_2$, RuCl(CO)(RCHCH$_2$R)(PCy$_3$)$_2$, respectively],

$$k' = \frac{k_3 K_{\text{C=C}} K_H P_{H_2}[\text{Ru}]_T}{1 + K_{\text{C=C}}[\text{C=C}]} \quad (6)$$

TABLE VII
Analysis of Variance Results for
Dependence Variable k_1 and k_1'

Source	DF	Sum of squares	Mean square
Regression	1	4.05E−06	4.05E−06
Residual	14	7.26E−08	5.19E−09
Uncorrected total	15	4.12E−06	
(Corrected total)	14	1.32E−06	

TABLE VIII
Model Parameter Estimates

Parameter	Estimate	Asymptotic std. error	Asymptotic 95% confidence interval	
			Lower	Upper
k_1, k_1'	0.076	0.003	0.070	0.082

It is reasonable to assume that $K_{C=C}$ is relatively small, because the bulky phosphine ligands make coordination of C=C with the metal difficult. If $K_{C=C}$ is small, then the model simplifies to

$$k' = k_1 P_{H_2}[Ru]_T \qquad (7)$$

where k_1 is a lumped constant containing the limiting reaction rate, k_3, equilibrium constant, $K_{C=C}$, and the Henry's law constant for the solubility of hydrogen in chlorobenzene, K_H.

For the hydride path, (steps $A_0 \rightarrow B' \rightarrow C' \rightarrow D$) in Scheme 2 represent the alternative mechanism. The coordination of H_2 to A_0 was suggested to be the initial step in the catalytic cycle because of the absence of a deuterium isotope effect.[5] The next step of the reaction path involved a complexation of B' with olefin followed by rapid elimination of products and reformation of A_0. The hydrogenolysis likely involves η_2 coordinated H_2 interacting with Ru–alkyl species, which would be formed by insertion of olefin into Ru—H

bond. An absence of the isotope effect would imply that the coordination of C=C is the likely rate determining step,

$$\text{rate} = \frac{-d[\text{C}=\text{C}]}{dt} = k'[\text{C}=\text{C}] = k_2'[B'][\text{C}=\text{C}] \qquad (8)$$

The total concentration of ruthenium is given by

$$[Ru]_T = [A_0] + [B'] \qquad (9)$$

Assuming that equilibria of A_0 and hydrogen are rapidly established, this relationship can be expressed by

$$K_{H_2} = \frac{[B']}{[A_0][H_2]} \qquad (10)$$

Equation (11) is derived when eqs. (9) and (10) are rearranged and substituted into eq. (8) and substituted the term $[A_0]$ and $[B']$ [i.e., RuCl(CO)(PCy$_3$)$_2$, RuCl(CO)(H$_2$)(PCy$_3$)$_2$, respectively],

$$k' = \frac{k_2' K_{H_2}[H_2][Ru]_T}{1 + K_{H_2}[H_2]} \qquad (11)$$

The parameter $K_{H_2}[H_2]$ is negligible over the range of reaction investigated, due to the first-order behavior dependence on hydrogen pressure. Then, the model was reduced to the form
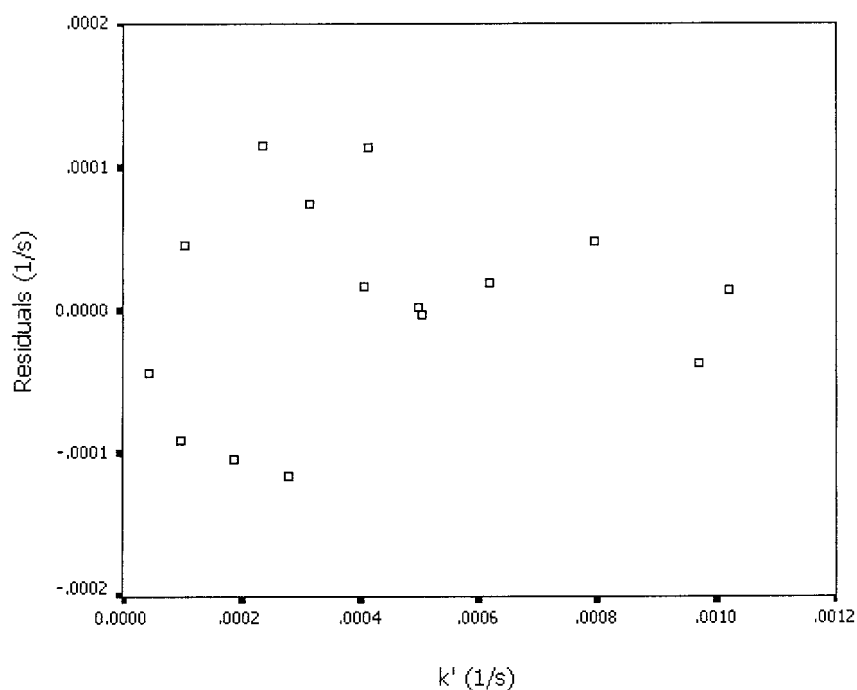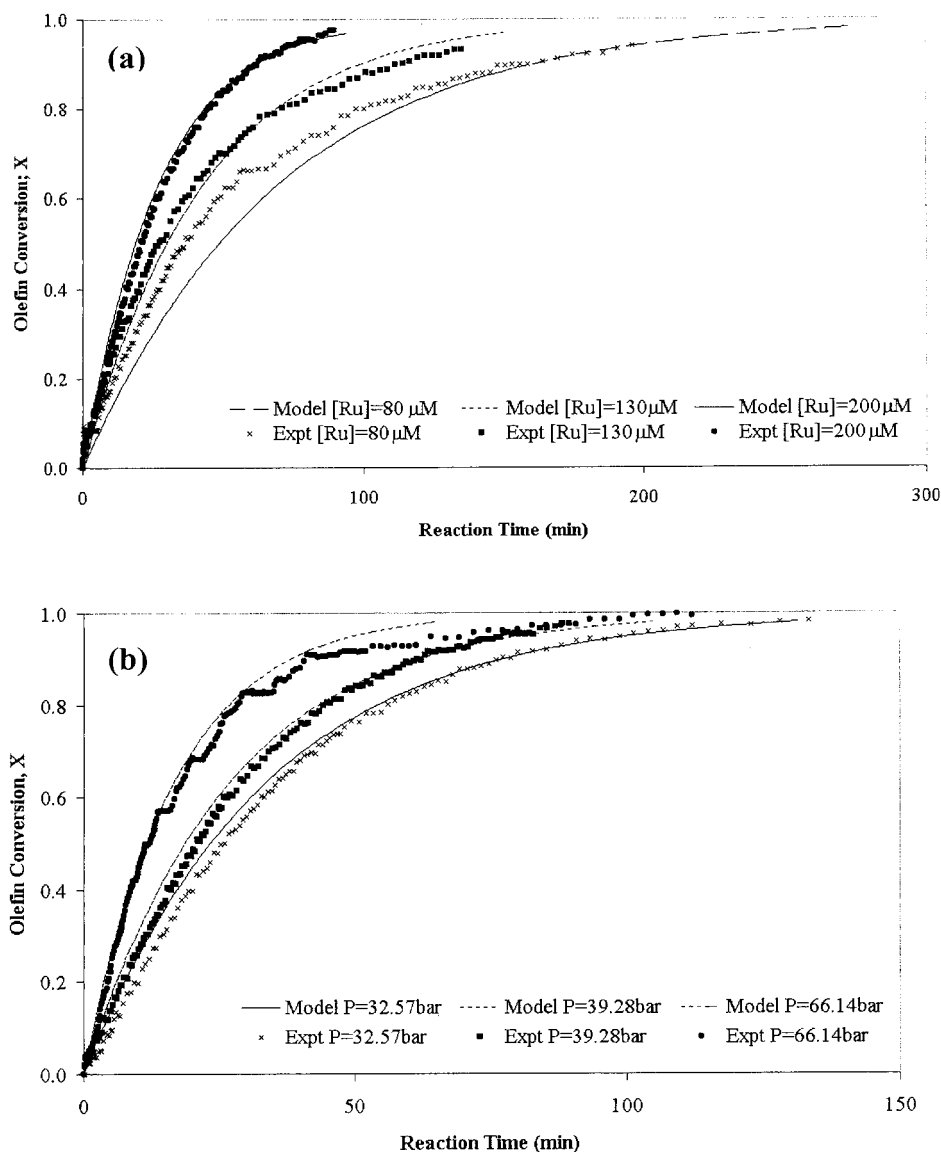

Figure 11 Residual plot of ($k_{\text{actual}}' - k_{\text{model}}'$) versus k'.

Figure 12   (a) Conversion profile of CPIP hydrogenation at various with Ru concentrations, [C≡C] = 260 mM; P_{H_2} = 39.3 bar; T = 160°C. (b) Conversion profile of CPIP hydrogenation at various hydrogen pressure, [C≡C] = 260 mM; [Ru] = 200 μM; T = 160°C.

$$k' = k'_2 K_{H_2} K_H P_{H_2} [Ru]_T \qquad (12)$$

$$k' = k'_1 P_{H_2} [Ru]_T \qquad (13)$$

where k'_1 is a lumped constant containing the limiting reaction rate, k'_2, is the equilibrium constant, K_{H_2}, and the Henry's law constant for the solubility of hydrogen in chlorobenzene, K_H.

The analysis of variance results table (Table VII) displayed that the derived rate expression complied with the observed kinetic data over the range of process conditions studied. A very low value for the mean sum of squares of residue confirms the consistency of the observed hydrogenation kinetics with eqs. (7) and (13). The reaction parameters estimated along with the

95% confidence interval are provided in Table VIII. The residual plot shown in Figure 11 illustrates the random distribution of residual value dependence on the measured rate constant with a few outliners. The straight line of rate constant provided in Figures 5(b) and 6(b) show actual model predictions relative to the experimental data. Actual model predictions of olefin conversion profile relative to the data from gas uptake are plotted in Figure 12(a, b).

Recently, Yi et al. proposed monohydride mechanism for the alkene hydrogenation in the presence of RuHCl(CO)(PCy$_3$)$_2$.[26] An olefin induced dissociation of tricyclohexylphosphine from the ruthenium-hydride followed by H$_2$ addition and reductive elimination of alkane product. However, the rate expression

of this proposed mechanistic pathway does not fit with the kinetic data of CPIP hydrogenation.

CONCLUSION

$Ru(CH=CH(Ph))Cl(CO)(PCy_3)_2$ functions as an efficient catalyst system for hydrogenation of *cis*-1,4-polyisoprene in chlorobenzene. The kinetics of CPIP hydrogenation was studied by monitoring the hydrogen consumption by using a computer-controlled gas uptake apparatus. The process exhibited a first-order dependence on concentration of Ru, carbon double bond, and hydrogen pressure. The activation energy was determined as 51.1 kJ/mol. The proposed mechanism and the derived rate expression are consistent with the observed kinetic data. The high coordinating power of solvent increases the degree of hydrogenation and reaction rate. The main polymer chain length and molecular weight were decreased during the hydrogenation because of the reaction condition (i.e., temperature) used in the catalytic process.

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